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Pnictogen modified Ge-Ga-Se(Te)-based glasses for optoelectronic devices

by

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Abstract

Chalcogenide glasses compose convenient and cost-effective functional media for modern photonics. Due to easy reproducibility and shaping supplemented with an excellent IR transparency, especially in the case of Se- and Te-based glasses they could be employed for many optical (passive and active fibers, lenses, etc) and semiconductive applications. It allows usage of these materials for numerous fields such as civil, military, and medical sectors. Seeking new modifications, a number of amorphous and glass-ceramic systems has been synthesized to optimize and characterize their thermodynamic, mechanical, electrical, and optical properties.

Primarily the novel chalcogenide glassy alloys, based on pnictogen (bismuth, antimony, phosphorus)-modified Ga-Ge-Se-Te system, were comprehensively investigated towards possible thermoelectric applications. Materials have been studied with respect to amorphous and crystalline phases for as-prepared alloys as well as structural variety induced by further thermal treatment. Structural research has been performed implementing Raman spectroscopy, XRD, Neutron Scattering and SEM/TEM facilities. It has been noted that the highest at.% of Bi added without crystallization was realized under P addition. Thermal treatment – in each studied system – causes mainly formation of Ga₂Se₃, Bi₂Se_xTe_{3-x} and Te phases.

Apart from that, regarding applicatory context, the electrical resistivity has been measured in parallel with additional annealing. Gathered results for Bi₅Ga₅Ge₁₈Se₃₆Te₃₆ glass demonstrate a decrease of resistivity in the range of $10^5 \rightarrow 10^3$ [Ω ·m] as a results of heat treatment. For synthesized alloys, DSC data has been measured in order to investigate the crystallization kinetics. Thermodynamic characteristics have been analyzed by means of the Fraser-Suzuki fitting model, harnessing also Johnson-Mehl-Avrami estimations as an applicability test for fitting. Concurrently, activation energy of crystallization processes has been determined for each system. Moreover, it was shown that up to 5 at.% of Bi₅Ga₅Ge₁₈Se₃₆Te₃₆ system occurs to be amorphous by volume with some initial traces of Ga₂Se₃ crystallites/seeds (100nm) and Bi₂Se_{1.5}Te_{1.5} (5nm) partially-ordered nanoscale inclusions, which were identified with TEM. In addition, IR light attenuation effect was observed (minimal loss >10dB/mm). Small changes in Bi concentration allowed to fabricate ~milimeter thick glass fully transparent (~55%) or opaque (~0%) in ~3 – 16 µm region. In conclusion, we have been successful in fabricating the narrow-bandgap semiconductor medium with an extremely high attenuation coefficient in a wide Vis-IR region of the spectra.

Secondary subject was elaboration and synthesis of novel chalcogenide glass systems for optical fibers as convenient hosts for RE-doping pursuing applications such as: Fiber Evanescent Wave Spectroscopy or remote sources of light. The following modifications have been studied:

- Co-substitution As \rightarrow Sb, Se \rightarrow Te to the Ga₅Ge₂₀As₁₀Se₆₅ matrix
- Substitution As \rightarrow Sb to the Ga-modified As₂Se₃ matrix
- Substitution As \rightarrow Ga to the Te₂₀As₂₂Sb₈Se₅₀ matrix

High attention has been paid to the glass purity as it is essential for fiber applications to generate the lowest attenuation level possible. Thus different purification methods have been employed to improve optical properties. As-received amorphous matrices has been manufactured into optical fibers and characterized in terms of optical attenuation in n-IR and m-IR range. In general description, statically purified glasses presented the lowest attenuation level from 1dB/m to 12dB/m. Whereas, considering specific case of Ga, Sb-modified As₂Se₃ glasses obtained through optimized dynamic distillation protocol, the lowest attenuation measured reached 0.2dB/m.

Streszczenie

Szkła chalkogenkowe wykorzystywane są jako materiały dla nowoczesnej fotoniki ze względu na relatywnie niskie koszty wytwarzania. Stosunkowo łatwo osiągalna w procesie produkcji wysoka powtarzalność właściwości szkieł, a także łatwość ich kształtowania oraz wysoka transmisja, zwłaszcza w przypadku szkieł opartych na Se i Te, powodują, że mogą być one stosowane jako urządzenia optyczne (pasywne i aktywne włókna oraz soczewki), a także jako elementy urządzeń półprzewodnikowych. Materiały oparte o chalkogenki znajdują powszechnie zastosowanie zarówno w obszarze cywilnym, np. medycznym, jak i w obszarze militarnym. W trakcie niniejszych badań w celu dalszej optymalizacji właściwości termodynamicznych, mechanicznych, elektrycznych oraz optycznych aktualnych szkieł wytworzono szereg nowych modyfikacji tych materiałów, przeprowadzono także szczegółową charakteryzację uzyskanych materiałów szklanych i szklano-ceramicznych.

Pierwszym zagadnieniem badawczym analizowanym w pracy jest możliwość wykorzystania materiałów opartych na stopach z układu Ga-Ge-Se-Te modyfikowanych pniktogenami (azotowcami), takimi jak bizmut, antymon czy fosfor, w celu zastosowania ich w urządzeniach termoelektrycznych. Badania właściwości materiałów otrzymanych bezpośrednio po syntezie prowadzono zarówno dla fazy szklistej, jak i dla faz krystalicznych, sprawdzano także skutki krystalizacji wymuszonej zastosowaniem dodatkowej obróbki cieplnej. Badania strukturalne zostały wykonane w oparciu o dyfrakcję rentgenowską, dyfrakcję neutronową, mikroskopię elektronową oraz spektroskopię ramanowską. Wykazano, że aby uniknąć krystalizacji, badany system może być modyfikowany w największym stopniu poprzez wprowadzenie bizmutu (do 7% at.) przy nieznacznym podstawieniu tego pierwiastka fosforem (3% at.). Dla każdego z systemów obróbka cieplna powoduje głównie powstawanie faz Ga₂Se₃, Bi₂Se_xTe_{3-x} oraz fazy czystego telluru. Dodatkowo, dla potrzeb aplikacji, zbadano rezystywność tak uzyskanego kompozytu w zależności od zastosowanego czasu jego wyżarzania.

W wyniku wyżarzania zaobserwowano spadek rezystywności kompozytu Bi₅Ga₅Ge₁₈Se₃₆Te₃₆ na poziomie $10^5 \rightarrow 10^3$ [Ω ·m]. Dane termodynamiczne uzyskane metodą różnicowej kalorymetrii skaningowej posłużyły do określenia kinetyki procesu krystalizacji. Krzywe kalorymetryczne analizowano wykorzystując przy dopasowaniu model Fraser-Suzuki z uprzednim testem stosowalności metodą Johnoson-Mehl-Avrami. Wyznaczono również energie aktywacji poszczególnych procesów krystalizacji. Korzystając z transmisyjnej mikroskopii elektronowej wykazano, że przy zawartości 5% at. bizmutu w badanym materiale system Bi₅Ga₅Ge₁₈Se₃₆Te₃₆ pozostaje amorficzny w całej objętości. Ujawniono także obecność śladowych ilości nanokrystalitów Ga₂Se₃ (o rozmiarach rzędu 100 nm) oraz Bi₂Se_{1.5}Te_{1.5} (5 nm). Analizując inne właściwości wytworzonego materiału zaobserwowano wysoką tłumienność w podczerwieni (minimalne straty poniżej 10 dB/mm). Na podstawie uzyskanych wyników stwierdzono, że subtelna zmiana koncentracji bizmutu może prowadzić (dla szkła o grubości 1,8 mm) do niemal pełnej transparencji (na poziomie 55%), lub znikomej (~0%) w zakresie widmowym od 3 µm do 16 µm. W wyniku prowadzonych badań uzyskano półprzewodnik o wąskiej energetycznej przerwie wzbronionej oraz o bardzo wysokim współczynniku strat optycznych w szerokim zakresie spektralnym Vis-IR.

Kolejnym, ważnym celem było opracowanie i wytworzenie nowych systemów szkieł chalkogenkowych do produkcji włókien optycznych (z możliwością dodatkowego domieszkowania lantanowcami), zarówno dla sensorów działających w oparciu o zjawisko fali zanikającej (z ang. *Fiber Evanescent Wave Spectroscopy*), jak i dla zdalnych źródeł światła.

W wyniku zastosowanych modyfikacji wytworzono następujące szkła:

- Podwójne podstawienie: As \rightarrow Sb oraz Se \rightarrow Te w matrycy Ga₅Ge₂₀As₁₀Se₆₅
- Podstawienie: As \rightarrow Sb w matrycy As₂Se₃ modyfikowanej Ga
- Podstawienie As \rightarrow Ga w matrycy Te₂₀As₂₂Sb₈Se₅₀

Zwrócono szczególną uwagę na czystość szkieł (związaną z czystością całego procesu technologicznego), gdyż jest to podstawowy parametr charakteryzujący włókna optyczne, warunkujący uzyskanie możliwie najniższego poziomu strat optycznych. W celu poprawienia właściwości optycznych zastosowano różne techniki puryfikacji szkła. Z otrzymanych matryc szklanych wytworzono następnie włókna optyczne, które scharakteryzowano pod kątem tłumienności sygnału w zakresie spektralnym bliskiej i średniej podczerwieni. Typowo, włókna optyczne uzyskane poprzez statyczne puryfikowanie szkła wykazywały tłumienność sygnału na poziomie od 1 dB/m do 12 dB/m. W wybranych przypadkach, dodatkowo optymalizując metodę dynamicznej destylacji szkła (Ga,Sb)As₂Se₃, uzyskano minimalną tłumienność 0,2 dB/m.

Extended French Abstract (Résumé)

Introduction

Les verres de chalcogénure (ChG) sont des matériaux incontournables, fonctionnels, faciles d'utilisation et économique pour la photonique moderne. En effet leur synthèse est bien maîtrisée et reproductible, leur mise en forme aisée grâce à leur état vitreux, et surtout, d'un point de vue fonctionnel, ils présentent une large transparence dans le moyen infrarouge. Cette dernière propriété est surtout vraie pour les verres à base de sélénium (Se) et/ou tellure (Te). Ces verres sont ainsi à la base du développement de systèmes optiques (guides planaires, fibres optiques) utilisés pour le filtrage spatial, les capteurs chimiques et biologiques, ou encore pour les systèmes de stockage à base de matériaux à changement de phase ou encore pour la thermoélectricité.

Aujourd'hui, les applications en photonique sont de plus en plus riches et variées et nécessitent le développement de compositions de verre de plus en plus complexes faisant intervenir de plus en plus d'éléments. Ce constat est conforme à ce que nous avons observé pour les verres d'oxydes dont les compositions couramment produites à l'échelle industrielle peuvent contenir plus d'une dizaine d'éléments. Les cahiers des charges se complexifient pour faire face à des contraintes nouvelles par exemple en termes de viscosité à haute température ou de coefficient de dilatation thermique.

Sans atteindre ce niveau de sophistication, il est maintenant très courant d'avoir recours à 3 ou plus constituants dans la composition d'un verre de chalcogénure. Ceci est devenu indispensable pour améliorer simultanément des propriétés divers, mécanique, électronique, optique, magnétique, etc... Concomitamment ceci complique énormément la compréhension de leur comportement et propriétés. Ces compostions peuvent ponctuellement être encore enrichies. Ainsi, quelques éléments chimiques comme le bismuth Bi ou le Gallium Ga modifient le comportement de verre à base de germanium Ge induisant des phénomènes de cristallisation localement de la matrice amorphe ou créant des inclusions partiellement ordonnées à l'échelle nanométrique. Par ailleurs, l'introduction d'éléments tels que le gallium (Ga) ou l'indium (In) permet ensuite un dopage avec des terres rares. Généralement ces éléments nuisent à la vitrification de la matrice, par conséquent, des additifs tels que l'antimoine (Sb) sont utilisés pour limiter ces processus de dévitrification parasite.

Le projet de cette thèse est d'explorer de nouvelles compositions vitreuses dans lesquelles de nombreux éléments interviennent de façon à optimiser les propriétés des verres en vue d'applications en optique d'une part et en thermoélectricité d'autre part.

Concernant la thermoélectricité les enjeux consistent à produire des matériaux présentant simultanément une conductivité électronique élevée et une conductivité thermique basse. Différentes stratégies ont déjà été explorées en ce sens par le passé (verres, vitrocéramiques, matériaux composites ...). Nous nous proposons ici de regarder l'influence du dopage de verre de séléniures par du bismuth (Bi), élément favorisant la nucléation, et du phosphore (P), permettant de maitriser la croissance cristalline dans la matrice.

Pour les applications en photonique, les verres à base de sélénium occupent une place de choix car il présente une stabilité face à la cristallisation qui permet de facilement créer des objets complexes. L'objectif est ici d'explorer les avantages / inconvénients liés à l'introduction d'éléments lourds tels que l'antimoine (Sb) et le Tellure (Te) qui apportent une plus large transparence vers l'infrarouge lointain mais au détriment de la stabilité des matériaux.

Plan du manuscript

Le manuscrit est organisé en 3 chapitres.

Le chapitre 1 détaille les modes de préparations et rappelle les fondements théoriques qui gouverne notre recherche en sciences de la matière. Nous proposons une revue générale des applications des verres de chalcogénures et des différents modes de préparation et de mise en forme de ces systèmes vitreux atypiques. Il s'agit d'un état de l'art sur le potentiel de ces verres en partiuclier pour l'optique infrarouge.

Le chapitre 2 regroupent, d'abord les bases théoriques qui guident le travail en thermoélectricité, et plus généralement les applications en tant que matériaux semiconducteurs. Nous décrivons ensuite les résultats obtenus sur les séléniures de germanium dopés par le bismuth et/ou le phosphore, en particulier :

- Caractérisation des phases obtenues, polycrystalline ou vitro-céramiques à partir des systèmes Bi_xGa₅(Ge_{0.2}Se_{0.8})_{50-(x+5)/2}(Ge_{0.2}Te_{0.8})_{50-(x+5)/2}, Bi_xGa₅Ge₂₀Sb_{10-x}Se₄₅Te₂₀, et Bi_xGa₅Ge₂₀P_{10-x}Se₄₅Te₂₀, études par diffraction des RX, microscopie électroniques (MEB et TEM), diffusion Raman;
- Préparation et Caractérisation des systèmes Bi_xSb_{10-x}Ga₅Ge₂₀Se₄₅Te₂₀ Une étude approfondie des propriétés thermodynamiques de ces matériaux a été mise en oeuvre. Un model spécifique a été développé pour rendre compte des pics exothermiques obtenus par DSC.

 Une étude des conséquences de la substitution du Phosphore par du Bismuth propriétés mécaniques de surfaces par nano-indentation permettant d'obtenir des informations sur les déformations élastiques et sur les propriétés structurales de surface.

Le chapitre 3 quant à lui est consacré aux applications en photoniques. Après un état de l'art sur le développement de fibres optiques pour la spectroscopie par ondes évanescentes, nous exposerons les résultats expérimentaux relatifs aux développements de nouvelles compositions de verres pour fabriquer des fibres optiques innovantes. Certaines compositions sont particulièrement étudiées en vue d'y introduire des terres rares pour créer des sources fibrées fonctionnant dans l'infrarouge. Ce chapitre est lui-même regroupe trois familles de matériaux :

- synthèse et caractérisation de verres au selenium à base de germanium et/ou d'arsenic tels que les systèmes Ga₅Ge₂₀As₁₀Se₆₅, TAS-235 (Te₂₀As₃₀Se₅₀) ou encore As₂Se₃ modifiés par l'introduction de Ga and Sb pour augmenter la solubilité des terres rares tout en stabilisant les matrices vitreuse pour éviter les phénomènes de cristallisation.
- optimisation des propriétés de transparence optique en développant différents modes de purifications des matrices vitreuses, en particulier par distillation.
- La fabrication de fibres optiques simple indice de diamètres variant de 125 à 350 μm, et leurs caractérisations optiques, en particulier les courbes d'atténuations de ces fibres.

Chapitre 1. Les verres de chalcogénures, propriétés et applications

Les verres de chalcogénures sont des matériaux obtenus à partir d'un ou plusieurs chalcogènes, soufre, selenium ou tellure, auxquels sont associés le plus souvent des éléments des colonnes proches des colonnes III à V telles que le germanium, l'arsenic ou l'antimoine. Ils sont régulièrement étudiés depuis les années 60 pour leur propriétés semi-conductrices et surtout pour leur capacité à transmettre la lumière dans le moyen infrarouge. En effet ces verres présentent une très large fenêtre de transmission dépendant de leur compositions (Figure 1), sont souvent opaques dans le visible, sont caractérisés par des indices optiques élevés, des propriétés non-linéaires importantes et sont le plus souvent stables même en atmosphère humide. Les principales applications de ces verres consistent en la fabrication de pièces d'optique pour l'infrarouge proche et moyen, au-delà de 2 microns, sous forme de lentilles ou de fibres optiques [1-3].

Ces verres sont essentiellement covalents, plus que les verres d'oxydes, et leurs propriétés, en particulier les propriétés mécaniques, sont fortement impactées par la nature des polyèdres de coordination (<CN>) et les énergies de liaisons. La connaissance avancée des différents modèles structuraux en cours permet d'anticiper les arrangements structuraux dans des matrices vitreuses plus complexes.



Figure 1. Les éléments à la base de la synthèse des verres de chalcogénures (gauche) ainsi que leur large fenêtre de transmission en fonction de leurs compositions et par comparaison à celles d'autres verres classiques (droite).

Ces verres sont classiquement synthétiser par fusion-trempe. Cette méthode permet de préparer des échantillons de dimensions variables, de haute pureté, de formes différentes et les traitements thermiques à suivre en vue de l'obtention de vitro-céramiques. La Figure 2 présentent les 4 étapes successives de la méthode classique de préparation. Il est parfois nécessaire de mettre en œuvre des procédés plus sophistiqués pour obtenir des verres de haute pureté. Ils intègrent des phases de distillation (Figure 3), voire de distillation dite dynamique. Ces méthodes sophistiquées deviennent indispensables dans la perspective d'obtenir des fibres optiques fonctionnant dans l'infrarouge.



Figure 2. Schema général de préparation par fusion/trempe.

Bien que la méthode générale de fusion-trempe soit incontournable, elle n'est pas exempte d'inconvénient. Ainsi des défauts d'homogénéité peuvent apparaître lors de la synthèse de préformes, et lorsque des micro-cristaux apparaissent dans la matrice vitreuse, souhaités ou subits, montrant des phénomènes de nucléation / croissance concentriques.



Figure 3. Processus de synthèse plus sophistiqué intégrant deux phases de distillation supplémentaires.

Outre les phases de synthèses, un travail important de caractérisations structurales a été mené sur les échantillons préparés par diffraction des RX, spectrosocpie Raman, Microscopie Electronique à Balayage, par Transmission. Au-delà de ces techniques classiques, des cartographies de nano-indentation ont permis de caractériser par différentiation mécanique des séparations de phases à l'échelle sub-micronique.

Un gros travail d'analyse thermique a également été mené par DSC pour caractériser les matériaux étudiés. Les simulations ont été réalisées grâce au logiciel Gaussian par la méthode Fraser-Suzuki. Le modèle de Johnson-Mehl-Avrami a été mis en œuvre pour l'étude des phénomènes nucléation/croissance.

Le chapitre est également l'occasion de répertorier et de décrire les techniques spectroscopiques mises en œuvre pour étudier les propriétés optiques des matériaux synthétisés. Il s'agit de caractériser les matériaux soi sous forme de massif, mais également sous forme de fibres optiques en évaluant les courbes d'atténuation par la méthode du « cut-back ».

C'est l'occasion également de rappeler les principes généraux de la spectroscopie par onde évanescente, ou Fiber Evanescent Wave Spectrocopy (FEWS). Il s'agit simplement d'ATR (Attenuated Total Reflection) en utilisant une fibre optique comme support de propagation en lieu et place d'un « plateau », comme c'est le plus souvent le cas. Les interactions lumières-matière sont ainsi plus denses, la sensibilité meilleure et le signal optique infrarouge est naturellement déporté de la source vers l'échantillon grâce à la nature même de la fibre optique.

Enfin la dernière partie du chapitre est consacrée aux caractérisations structurales et physiques des matériaux préparés. Il s'agit bien sûr de diffraction des RX, essentiellement pour vérifier la nature vitreuse ou partiellement cristallisée des échantillons préparés. Les propriétés mécaniques sont évaluées par indentation pour mesurer les différents modules élastiques. L'analyse thermique est bien sur fondamentale en chimie des verres pour obtenir les températures caractéristiques des matériaux produits (température de transition vitreuse, température de cristallisation, de fusion). Les mesures de viscosité, en fonction de la température permettent quant à elles de mieux appréhender le comportement des verres au moment de les mettre en forme pour créer des objets fonctionnels en optique, comme en thermoélectricité. Enfin, s'agissant de thermoélectricité, des mesures de conductivités électriques ont également été réalisées.

Chapitre 2. Systèmes Ge-Ga-Se-Te enrichi en bismuth Bi et Phosphore P pour des applications en thermoélectricité ou en tant que matériaux semi-conducteurs.

Les céramiques à base de chalcogénures ont largement été étudiées au cours des dernières années pour des applications en thermoélectricité et ont montré tout leur intérêt en particulier dans le domaine des basses températures. Nous proposons ici de développer une autre approche consistant à préparer des vitro-céramiques à partir de verres de chalcogénures. Pour atteindre cet objectif, le projet consiste à introduire du Bismuth et/ou Phosphore et de suivre la céramisation par traitement thermique de ces matrices. Ces éléments sont en effet réputés pour favoriser et catalyser une fine cristallisation. Pour ceci, nous partirons des matrices vitreuses présentant le potentiel le plus grand pour ces applications. Il s'agit de verres comprenant jusqu'à 6 éléments comme le montre le schéma de principe de la Figure 4 qui permet de rationaliser le travail effectuer suivant les 3 stratégies ci-après:

- $Bi_xGa_5(Ge_{0.2}Se_{0.8})_{50-(x+5)/2}(Ge_{0.2}Te_{0.8})_{50-(x+5)/2}$
- Bi_xSb_{10-x}Ga₅Ge₂₀Se₄₅Te₂₀
- $Bi_xP_{10-x}Ga_5Ge_{20}Se_{45}Te_{20}$



Figure 4. Schéma de principe relatif au développement de céramiques et vitro-céramiques pour la thermoélectricité. (Le Bi-doped SGT système a été étudié B. Srinivasan et al. [4], les autres stratégies sont l'objet de cette thèse).

Les compositions des verres de chalcogènures sont de plus en plus riches ce qui permet d'affiner les propriétés physiques de ces matériaux (électronique, optique), mais génère simultanément de grandes complexités structurales et des liens structures/propriétés de plus en plus difficile à comprendre. Il est ainsi de plus en plus difficile de définir des modèles qui permettent de prédire ou d'anticiper l'évolution des propriétés, positives ou non, des compositions envisagées. Dans ce contexte, il devient pertinent de chercher à raisonner à l'échelle nanométrique et à regarder les conséquences de ces nanostructurations sur les propriétés physiques (optique, électronique, thermique, mécanique...). Ainsi des éléments comme Bi, Sb, Ga modifient très localement la structure de la matrice vitreuse ce qui suffit à influencer les propriétés électroniques et l'ordre local par des apparitions de nano-inclusions ou des phénomènes de cristallisations [4-7]. Il devient alors particulièrement pertinent de regarder les phénomènes de percolation de volume entre les différentes phases, cristallisées ou amorphes. C'est pourquoi un gros travail a été mené en thermoélectricité pour essayer de déterminer les énergies d'activation des phases cristallisées dans le système Bi-Te-Se. De telles restructurations se produisent à des températures supérieures à la T_g, température de transition vitreuse, où l'on observe l'apparition de micro-cristaux à partir de T_g+100°.

Il existe de nombreuses applications potentielles pour des matériaux thermoélectriques fonctionnant à basse température. Ainsi l'industrie automobile développe des solutions pour convertir l'énergie thermique provenant du frottement du système de freinage, des batteries ou du système d'échappement du moteur. Des prototypes à grande échelle ont été construits avec succès en utilisant Bi₂Te₃, mais l'efficacité globale du système reste faible en raison des limites liées à la température de fonctionnement de Bi₂Te₃ ne peuvent pas fonctionner pendant une période prolongée au-delà de 525 K. Une autre application potentielle importante justifiant le développement de matériaux thermoélectrique « basse température » réside dans la récupération et la conversion de l'énergie thermique perdue provenant de panneaux solaires. Il existe deux solutions pour s'attaquer à ce problème. Pour que les systèmes thermoélectriques à semi-conducteurs soient compétitifs, il faudrait atteindre une valeur de moyenne pour le facteur de mérite de ZT ~ 4. Une alternative consiste à exploiter des sources de chaleur plus élevées (~ 1200K) permettant de se contenter d'un facteur de mérite plus facile à atteindre ($ZT \sim 2$) pour le module thermoélectrique [8]. Aujourd'hui, les valeurs ZT rapportées pour les poly-cristaux Bi_2Te_3 frittés par exemple par Splash Plasma Sintering SPS, atteignent 0,54 – 0,74 [9]. Des méthodes de dépots chimique de couche mince ont montré qu'il était possible d'atteindre ZT ~ 1 pour Bi_{0.5}Sb_{1.5}Te₃ (type p) et à 0,9 pour Bi₂Te_{2.85}Se_{0.15} (type n) à 300K. Des progrès très récents, cherchant à structurer le matériau à l'échelle nanométrique par voie sol-gel pour Bi₂Te₃₋ _xSe_x et Bi_xSb_{2-x}Te₃, suivis d'un traitement de pressage à chaud, ont conduit à un ZT ~ 1,15 [10] en moyenne avec une valeur maximum de ~ 1,77 [11].

Au-delà de ces applications en thermoélectricité, il est de façon générale intéressant de développer des matériaux hybrides, à la fois pour des applications en optique et en électronique, ce que nous avons appelé « semi-conductive application ».

• Système Bi_xGa₅(Ge_{0.2}Se_{0.8})_{50-(x+5)/2}(Ge_{0.2}Te_{0.8})_{50-(x+5)/2}: ratio Te/Se = 1

La stabilité thermique et les phénomènes de recristallisation des verres de compositions $Bi_xGa_5(GeSe_4)_{50-(x+5)/2}(GeTe_4)_{50-(x+5)/2}$ avec x=1 (Bi1), 5 (Bi5), et 10 (Bi10) ont été suivis par DSC, DRX et diffusion Raman.

Les diffractogrammes de la figure 5 montre que Bi1 et Bi5 sont amorphes alors que Bi10 est déjà largement cristallisé.



Figure 5. Diagramme X des trois matériaux préparés comparés à ceux de Bi₂Te₃ et Bi₂Se₃.

Les suivis des recuits de la figure 6 montrent les nombreuses phases, produits de la recristallisation de ces matériaux. Les résultats d'analyse thermique des composés Bi1 et Bi5 (Figure 7) montrent que les composés cristallisés donnant naissance au pic I sont tous à base de Bi : Bi₂Te₃, Bi₂Se₃ or Bi₂SeTe₂. Cette observation est cohérente avec des résultats précédents sur le système Ge-Se-Te-Bi, qui ont montré que les cristallites correspondaient à Bi₂Se₃. Le second pic II n'évolue pas avec le taux de Bi et a été attribué à des phases à base de Ga telles que Ga₂Te₃, Ga₂Se₃, déjà rencontrées lors de la recristallisation des verres des systèmes Ge-Te-Ga, Ga-As-Se and Ga-As-Se-Te.

Le large pic III correspond probablement à la cristallisation du tellure élémentaire et à des phases métastables Ga/Ge-Te. La deuxième famille de cristaux apparait à plus haute temperature, au-delà de 300°C. Ces pics IV, V et VI correspondent à des phases plus stables du système Ge-Te (GeTe, Ge₂Te₃ ou Ge₁₇Te₈₃) et Ge-Se (GeSe, GeSe₂, Ge₄Se₉).



Figure 6. Diffractogramme X pour différents recuits des trois matériaux préparés.



Figure 7. Exemple de reconstruction des pics DSC avec Gaussian (à gauche) et Fraser-Suzuki (droite) de Bi₁Ga₅Ge_{18.8}Se_{37.6}Te_{37.6} (Bi1), Bi₅Ga₅Ge₁₈Se₃₆Te₃₆ (Bi5) et Bi₁₀Ga₅Ge₁₇Se₃₄Te₃₄ (Bi10).

Les spectres Raman montrent clairement sur la Figure 8 que les recuits génèrent l'apparition de cristaux Bi_2Se_3 (~75, ~130, ~175 cm⁻¹) et Bi_2Te_3 (~62, ~104, ~134 cm⁻¹) [12,13]. On y observe également des groupements GeTe₄ et Ge₂Te₃ dans la gamme ~125 – 140 cm⁻¹.



Figure 8. Spectres Raman des échantillons Bil (a), Bi5 (b) et Bil0 (c) étudiés.

Pour les échantillons vitreux de larges bandes apparaissent et signent la présence importante de tétraèdres GeTe₄ pour Bi1 et Bi5. De plus, pour Bi1, et uniquement pour cet échantillon, nous observons la présence de tétraèdres GeSe₄ (pic à 209 cm⁻¹).

Ces travaux structuraux ont été enrichis par des études par diffusion neutronique et des RX à haute énergie. Elles ont confirmé le caractère essentiellement vitreux de Bi1 et Bi5 alors

que Bi10 comprend des phases cristallisées telles que Ga_2Se_3 ou $Bi_2Se_xTe_{3-x}$ (x=0, 0.5, 1, 1.5, 2). L'analyse du FSDP (First Sharp Diffraction Peak) pour Bi1 et Bi5 montre la présence d'une organisation à moyenne distance semblable pour les 2 matériaux avec des domaine de l'ordre de 2.5 nm.

Ces échantillons ont également été caractérisés en optique et par microscopie électronique en transmission (Figure 9) pour à la fois explorer leur potentiel en infrarouge et d'autre part évaluer leur micro-structuration.



Figure 9. Transmission des échantillons vitreux massifs (a) Bi1 et (b) Bi5. Dans l'insert (a) la courbe de Tauc permet d'évaluer le band gap à 0.75 eV. L'insert (b) illustre l'atténuation de cet échantillon évaluée grâce à des échantillons de différentes épaisseurs. (c) image TEM de Bi5.

Pour les faibles dopages en Bi (Bi1) on observe aucune conséquence sur la transmission optique de l'échantillon dans l'infrarouge (Figure 9a). A l'inverse pour les pourcentages plus élevés (Bi5 et Bi10) les matériaux deviennent progressivement opaques. Pour Bi10, ceci s'explique par la présence de large microcristaux ~ 500 nm qui diffusent la lumière dans cette gamme de longueurs d'onde. Par contre aucune signature de tels cristallites pour Bi5 sur les diffractogrammes X ou par microscopie électronique. On observe sur l'image de la figure 9c la présence de nano-inclusions structuralement mieux organisées dont la taille est de l'ordre de 5 nm. Compte tenu de leur dimension réduite, les phénomènes de diffusion Mie ou Rayleigh par ces inclusions ne semblent pas être de nature à expliquer l'opacité de Bi5. L'opacité de Bi5, alors que Bi1 transmet bien dans le moyen IR reste donc inexpliquée et demande des travaux supplémentaires.

En conclusion, nous avons réussi à fabriquer des matériaux semi-conducteurs à bande interdite étroite avec un coefficient d'atténuation extrêmement élevé dans une large région du visible à l'IR. En effet, de faible variation en concentration de Bi permet de modifier radicalement les propriétés des matériaux et ainsi de fabriquer des supports optiques semiconducteurs d'une épaisseur de ~ millimètre d'épaisseur entièrement transparents ou totalement opaques dans une gamme de longueurs d'onde ~ $3 - 16 \mu$ m. Les matériaux présentent un grand potentiel en tant que matrice universelle pour diverses applications IR, telles que le revêtement semi-conducteur de protection IR, les atténuateurs optiques et les capteurs IR.

• Système Bi_xSb_{10-x}Ga₅Ge₂₀Se₄₅Te₂₀: ratio Te/Se = 0.4

Les échantillons $Bi_xGa_5Ge_{20}Sb_{10-x}Se_{45}Te_{20}$ (x = 1,3,5,10 appelés SBix) ont été préparés par fusion trempe à partir d'éléments hautement purifiés.

Ces matériaux vitreux ont essentiellement été étudiés par analyse thermique. Les T_g évoluent peu, mais ils deviennent de plus en instables face à la cristallisation au fur et à mesure que x augmente. En particulier, de nombreuses variétés cristallisées apparaissent pour SBi10 (Figure 10). Ces matériaux demandent à être étudié plus avant, mais ils constituent potentiellement des matrices intéressantes pour développer des vitro-céramiques.



Figure 10. Les diffractogrammes X à haute énergie (a) ne montrent pas de pic de diffraction, ce qui est confirmé par le caractère homogène de la photo MEB (b) de l'échantillon SBi10 pour lequel de léger pic apparaissent (a).

• BixP10-xGa5Ge20Se45Te20, substitution du bismuth par le Phosphore

Les échantillons, $Bi_{10}Ga_5Ge_{20}Se_{45}Te_{20}$ (RP-0), $Bi_7Ga_5Ge_{20}P_3Se_{45}Te_{20}$ (RP-3), $Bi_5Ga_5Ge_{20}P_5Se_{45}Te_{20}$ (RP-5), $Bi_3Ga_5Ge_{20}P_7Se_{45}Te_{20}$ (RP-7), $Bi_1Ga_5Ge_{20}P_9Se_{45}Te_{20}$ (RP-9) and $Ga_5Ge_{20}P_{10}Se_{45}Te_{20}$ (RP-10), ont été préparés classiquement par fusion trempe (Figure 11).

Ces échantillons ont essentiellement été étudiés par analyse thermique. Pour RP-0, 3, 5, la stabilité thermique ΔT croît avec le taux de substitution. Pour RP-7, 9, 10 il n'est même plus possible de détecter de pics de cristallisation sur les courbes d'analyse thermique.



Figure 11. Les diffractogrammes X (b) ne montrent pas de pic de diffraction confirmant le caractère essentiellement amorphe des matériaux. Les images MEB de RP-3 et RP-10 confirme l'homogénéité des échantillons et de l'analyse EDS.

Les énergies d'activation de cristallisation pour les verres contenant à la fois P et Bi sont plus faibles que pour les compositions ne contenant que l'un des 2 éléments. Finalement, la matrice de verre ne contenant que du Phosphore peut être considérée comme un bon candidat pour le fibrage, pour des applications en optique IR.

• Conclusions

Nous avons d'abord montré qu'il était possible de synthétiser des matériaux mixtes contenant à la fois Ga et Bi, alors que les 2 pris séparément ont une tendance naturelle à provoquer la cristallisation de la matrice. Il est alors possible de nucléer Ga₂Se₃ de façon homogène, puis des phases contenant le bismuth qui peuvent être intéressantes pour des applications en thermoélectricité.

Par ailleurs, nous avons montré que la stabilité d'un verre augmente avec l'ajout de phosphore et la cristallisation ne se produit pas lors des balayages de chauffage DSC réguliers (q > 5 K / min) pour les échantillons contenant au moins 7% de phosphore. De plus, les énergies d'activation de cristallisation pour les verres contenant à la fois P et Bi dans leur réseau sont plus petites que pour les compositions avec seulement Bi ou P. On en déduit que le verre ne contenant que P, Ga₅Ge₂₀P₁₀Se₄₅Te₂₀ peut être considéré comme un bon candidat pour le fibrage, qui peut être utilisé dans les applications de l'optique IR, de la photonique et des capteurs.

Chapitre 3. Des verres de chalcogénures et fibres optiques pour la spectroscopie infrarouge

• Généralités / état de l'art

Les premiers résultats relatifs à la spectroscopie par ondes évanescentes dans le moyen infrarouge date du milieu des années 90, très vite suivis de la mise en œuvre de fibres optiques en verres de chalcogénures comme transducteur optique. Les principaux atouts de la fibre optique sont de permettre des mesures in situ, in vivo, en temps réel. Cependant quelques difficultés persistent comme le manque de sélectivité (acquisition d'un spectre sur la totalité de la plage de longueurs d'onde) et un manque de sensibilité pour détecter les faibles concentrations (sous le ppm). Une méthode complémentaire et alternative consiste à développer des fibres optiques dopées par des terres rares qui servent à la fois à déporter le signal, et de sources secondaires, potentiel gain en sensibilité et sélectivité.

De façon générale la transmission des verres de chalcogènures dépend directement de la nature de l'élément formateur (Figure 12).



Figure 12. Principaux systèmes vitreux intéressants pour la spectroscopie infrarouge déportée.

Ainsi les sulfures sont ceux qui transmettent le moins loin dans l'infrarouge car le soufre est le chalcogène le plus léger. Ainsi sous forme de massif la transmission s'arrête dès 10 μ m et pas au-delà de 6 μ m sous forme de fibres optiques. Pour le séléniures, ces transmissions s'étendent jusqu'à 16 μ m sur massif et 12 μ m pour les fibres optiques. Compte tenu de la stabilité thermique de ces compositions, ce sont généralement les verres au sélénium qui sont à la base des applications mentionnées ci-dessus. Les verres au tellure sont donc naturellement ceux qui transmettent le plus loin dans l'infrarouge (plus de 25 μ m pour les massifs, et environ 18 μ m pour les fibres optiques), mais ils sont nettement moins stables et ont tendance à facilement recrystalliser, limitant leur potentiel opérationnel. Ainsi, les séléniures et les mélange Se/Te sont les systèmes les plus intéressants pour des applications dans le moyeninfrarouge.

La fabrication d'une fibre optique passe par l'étirage d'une préforme de verre de chalcogénure. Cette opération a été rendue possible grâce à la tour de fibrage construite au sein de l'équipe Verres et Céramiques de l'Institut des Sciences Chimiques de Rennes développée pour ce type de verres à bas point de fusion. Elle est équipée d'un système de maintien sous atmosphère inerte, d'une descente préforme automatique, d'un contrôleur de diamètre (Figure 13).



Figure 13. Photographie du haut de la tour de fibrage de l'équipe verres et céramiques (Institut des Sciences Chimiques de Rennes, ISCR) et schéma de principe du fibrage d'un barreau de verre.

Le barreau de verre (préforme) est positionné verticalement et son extrémité placée au centre du four annulaire. Ce four est lui-même fixé à un tube de silice purgé en continu par des flux d'hélium et/ou d'argon pour éviter toute contamination par le dioxygène ou la vapeur d'eau ambiante.

Au cours de précédents travaux, il a déjà été montré que les verres As-Se, Ga-Ge-As-Se, et TAS sont de très bons candidats pour produire de telles fibres optiques en particulier pour des applications de capteurs fonctionnant dans le moyen infrarouge. Ces capteurs fonctionnent le plus souvent par absorption des ondes évanescentes se propageant le long de la fibre optique à l'interface entre la fibre et l'échantillon test. Cette technique est appelée FEWS (Figure 14). Ainsi, à chaque réflexion de l'onde se propageant dans la fibre optique, les longueurs d'onde du signal correspondant aux absorptions fondamentales de l'échantillon, dans l'infrarouge, sont absorbées. Il suffit pour cela de positionner la fibre au contact ou en immersion dans l'échantillon. On peut également parler de réflexion totale atténuée ou ATR. La Figure 14 détaille le principe général et illustre l'intérêt de réduire le diamètre de la fibre optique dans la zone de contact pour améliorer la sensibilité.



Figure 14. Trajectoires des rayons lumineux dans la fibre optique montrant la partie « évanescente » de l'onde a). La réduction du diamètre de la fibre augmente le nombre de réflexions et donc la sensibilité du capteur b). Les courbures de la fibres optiques est préjudiciable à la sensibilité c).

Parallèlement aux travaux menés avec ces verres de chalcogénures, il a également été montré que des fibres optiques alternatives obtenues par extrusion de polycristaux AgCl/AgBr pouvaient également être utilisées [14]. Ces fibres présentent pourtant de nombreux désavantages à commencer par leur grande sensibilité à l'humidité ambiante qui nuit à la qualité de leur transparence avec le temps. De plus la méthode de fabrication par extrusion est couteuse, peu reproductible et ne permet que difficilement de diminuer le diamètre en deçà du mm ce qui est préjudiciable à la sensibilité de ces capteurs [15,16]. Surtout, la nature même des matériaux polycristallins est à l'origine de nombreuses pertes optiques au sein de la fibre optique et les atténuations de plusieurs dB/m restent souvent élevées. Par contre les verres de chalcogénure sont assez inertes, même en solution [17,18]. Leur état vitreux les rend faciles à étirer sous forme de fibres optiques jusqu'à des diamètres de 10 µm, sans aucune interface à traverser par la lumière permettant des minima d'atténuation de l'ordre de 0,5 dB/m.

Alternativement à ces fibres fonctionnant comme un transducteur "passif", un enjeu depuis quelques années consiste à développer des fibres optiques transparentes dans l'infrarouge et émettant un signal, toujours dans l'infrarouge, par excitation et émission de terres rares. Les verres de chalcogénures sont là encore incontournables et l'enjeu est de maintenir une faible atténuation de la fibre tout en incorporant une concentration élevée de terres-rares dans le verre. Il a déjà été montré que l'introduction de gallium, voire d'indium, était des facteurs facilitant la dissolution de ces terres rares. Par contre, l'introduction de Ga rend la matrice vitreuse beaucoup plus instable et très sensible aux phénomènes de cristallisation. Alors, l'introduction d'antimoine Sb, joue un rôle positif pour stabiliser le verre du système As-Se [19] et ainsi augmenter la concentration en Ga et donc, potentiellement, en terre rare. Où l'on voit que la formulation d'un verre de chalcogénure peut devenir complexe. De tels développements font l'objet de ces travaux de thèse.

• Introduction de Sb et Te dans la matrice Ga5Ge20As10Se65

Le premier axe de travail a consisté à substituer Sb et Se à As et Te respectivement dans départ une matrice de connue (appelée 2S2G) suivant la formulation Ga₅Ge₂₀Sb_{10-x}As_xSe_{65-y}Te_y. L'objectif est à la fois de chercher à accroitre la fenêtre de transmission de ces verres tout en le stabilisant afin de faciliter leur mise en forme. Globalement, les matériaux préparés contenant du tellure voient leur transmission gagner environ 1 µm dans le moyen IR, et concomitamment, leur band gap optique diminue de 1.5 à 1eV. Par ailleurs leur Tg diminue suite à l'introduction d'As et leur stabilité mesurée à partir de ΔT diminue également avec l'introduction du tellure.

Ces verres ont également été fibrés de façon à évaluer le gain de ces substitutions sur l'atténuation des fibres optiques. Il apparait alors que l'introduction de Te permet d'abaisser les pertes optiques d'environ 10 dB·m⁻¹ à 6 dB·m⁻¹ dans le moyen IR autour de 9 μ m, mais avec comme contrepartie une atténuation bien plus forte dès 4 μ m dans le proche IR. Notons, à l'inverse, que la substitution de Sb par As, au caractère moins métallique, ne permet pas d'abaisser ces pertes dans le proche IR.

• Introduction de Ga et Sb dans une matrice As-Se pour favoriser le dopage par des terres-rares.

Un objectif important du travail réalisé a consisté à évaluer la capacité de ces matrices vitreuse à accueillir des terres rares pour réaliser des fibres optiques dopées servant de sources dans le moyen infrarouge. L'introduction de Ga facilite grandement la solubilité des terres rares et l'introduction d'antimoine Sb génère des volumes libres facilitant eux-même l'incorporation de Ga. L'objectif a donc consisté à préparer des verres stables co-dopés par Ga et Sb. L'étape suivante a consisté à identifier les compositions prometteuses permettant la distillation. En effet, ces étapes de distillation sont indispensables pour obtenir des fibres optiques présentant des atténuations suffisamment faibles qui n'affectent pas les émissions des terre rares.

Malgré leur synthèse aisée et leur stabilité thermodynamique, les verres du système As-Se sont souvent affectés par des bandes d'absorption parasites dans la gamme 8 – 12 μ m. Par ailleurs de nombreux résultats récents portent sur des verres dopés par le terbium Tb³⁺ qui émet à 7.5 μ m [20], particulièrement pertinent comme capteur de gaz [21]. Il s'est donc révélé particulièrement pertinent de travailler à partir de ce type de matrice et de l'enrichir en Ga et Sb pour faciliter l'introduction des terres rares.

La stratégie a d'abord consisté à partir de As₂Se₃ et en introduisant progressivement Ga: Ga_x(As_{0.4}Se_{0.6})_{100-x} avec x = 0, 1, 2, 3, 4, 5. La seconde étape a consisté à introduire l'antimoine Sb, Ga_x(As_{0.4-y}Sb_ySe_{0.6})_{100-x} avec x=2, y=0; x=2, y=0.12; x=5, y=0.12. A partir de distillation classique, il a été possible de préparer et de fibrer un verre Ga₂(As_{0.4}Se_{0.6})₉₈, par contre les compositions à base de Sb n'ont pas pu être fibrées. La figure 15 montre la courbe d'atténuation avec un fond à environ 1.1 dB·m⁻¹ très encourageant malgré les nombreuses bandes d'absorption liées à des impuretés, hydrures et oxydes.



Figure 15. Courbe d'atténuation d'une fibre de verre de composition Ga₂(As_{0.4}Se_{0.6})₉₈.

Pour approfondir, un gros travail a été réalisé pour optimiser les conditions de distillation dite dynamique du verre. Un processus en trois étapes a été mis au point pour piéger les différentes impuretés. Ila cette fois été possible de préparer des fibres optiques avec les compositions quaternaires incluant à la fois Sb et Ga. La figure 16 montre les courbes d'atténuation obtenues pour ces fibres en ajoutant par étape les phases de distillation. Le minimum d'atténuation est nettement abaissé (environ 0.5 dB·m⁻¹) et la quasi-totalité des bandes parasites a disparu à l'exception d'une bande résiduelle As-H.



Figure 16. Courbe d'atténuation d'une fibre de verre de composition Ga₂(As_{0.36}Sb_{0.04}Se_{0.6})₉₈ purifié en trois étapes successives par distillations dynamique.

• Introduction de Ga et Sb dans une matrice TAS-235 pour favoriser le dopage par des terres-rares.

Le verre TAS, Te₂As₃Se₅ est celui le plus couramment mis en œuvre pour effectuer de la spectroscopie par ondes évanescentes. Il est à la fois stable, permet de préparer des fibres optiques, et transmets plus loin dans l'infrarouge que As₂Se₃ du fait de la présence de tellure dans le mélange initial. Il est donc particulièrement intéressant de suivre le comportement de ce verre lorsqu'on y introduit Ga et Sb, toujours comme préliminaire à un dopage terre-rare ultérieur. Ga₂As₂₀Sb₈Se₅₀Te₂₀ and Ga₅As₁₇Sb₈Se₅₀Te₂₀ ont ainsi été préparés avec succès. Le verre Ga5 présente une très forte atténuation dans le moyen IR, due à l'apparition de cristallites (Figure 17), alors que la composition Ga₂As₂₀Sb₈Se₅₀Te₂₀ a pu être fibrée.



Figure 17. Diffractogramme X des verres TAS enrichi en Ga

En effet, omme le montre la Figure 17, des pics de cristallisation apparaissent très rapodement avec l'introduction de gallium. Ces pics sont dus à l'apparition de cristallites de Ga₂Se₃. Leur présence ets bien sûr nuisible à la transparence optique et provi-oque des phénomènes de diffraction. Cependant, la courbe d'atténuation présentée sur la Figure 18 reste encourageante, même si les pertes sont à un niveau nettement supérieur à celles enregistrée sur le TAS originel.



Figure 18. Courbe d'atténuation d'une fibre de verre de composition Ga₂As₂₀Sb₈Se₅₀Te₂₀ purifié en deux étapes successives par distillations statique.

• Conclusion

Les fibres optiques transparentes dans l'infrarouge sont des objets incontournables pour la spectroscopie infrarouge déportée. L'état de l'art est déjà très riche en particulier grâce aux travaux menés au sein de l'équipe verres et céramiques. C'est la raison pour laquelle nous avons ici focalisé notre contribution sur le développement de fibres permettant de « voir » plus loin dans l'infrarouge et surtout qui soient dopées, ou « dopables » à terme pour ouvrir cette technologie à de nouveaux types de systèmes fibrés qui soit à la fois transducteur et source de lumière IR.

Ainsi, tous les systèmes à base de Ge-As-Se (co-) modifiés Te, Sb préparés selon des procédés de distillation statique en 2 étapes ainsi que la matrice ses ont montré intéressant pour la suite avec possibilité de les étirer sous forme de fibres optiques. L'introduction d'aluminium comme piègeur d'oxygène a permi d'abaisser les pertes optiques autour de ~ 5 et 10 dB / m.

Nous avons également montré qu'il est possible de vitrifier la matrice As2Se3 enrichie en Sb et en Ga avec $\sim 0.2 \text{ dB} / \text{m}$ de perte, permettant l'introduction ultérieure de terre rare. Le travail équivalent mené à partir du verre TAS-235 a quant à lui révélé une cristallisation partielle.

Ces résultats ouvrent la voie miantenant à l'introduction effective de terre rare dans ces verres, tout en gardant leur propriété de fibrabilité.

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General Introduction

Chalcogenide glasses (ChG) compose convenient and cost-effective functional media for modern photonics. Due to easy reproducibility and shaping supplemented with an excellent IR transparency, especially in the case of Se- and Te-based ChG, they could be employed as optical waveguides for space telecommunication, chemical, and biological sensors, phasechange memory, thermoelectric (TE) devices, etc. Moreover, a high nonlinearity of ChG gives a chance to create on their basis novel systems of nonlinear and integrated optics — IR optical fiber lasers and amplifiers, high-speed switches, Raman lasers, frequency converters, and supercontinuum generators. Amongst numerous fields of usage such as civil, military, and medical sectors, optical materials constructed on the base of ChG can be divided into passive and active groups.

Nowadays, the-up-to-date developments in chalcogenide photonics require more chemically complex ChG systems. This idea of manufacturing more complex ChG should not wonder, even considering tendencies in such large-scale industry as oxide glass production, when series of modifiers like alkalines or oxides supporting vitrification has been widely employed, that is not only restricted to the shaping of technological properties (i.e. high-temperature viscosity) but also to induce some crucial optimization (i.e. for thermal expansion coefficient).

Using the concept of *more than three constituents in ChG composition* opens wide possibilities to improve medium properties (mechanical, electronic, optical, magnetic, etc.), despite complicating enormously their understanding. In this regard, several chemical elements like Bi and Ga are found to modify Ge-based ChG at the nanoscale by carrier charge reversal, triggering local crystallization of amorphous matrix or creating partially ordered nanoscale inclusions. On the other hand, modification of ChG by Ga or In activators allows successful rare-earth (RE) doping, while restricting notably their glass-forming ability. Therefore, additional additives like Sb have been employed to restrict these devitrification processes.

Another cutting-edge topic is materials for TE applications. Since demand for electric modules will be constantly rising due to the recent trends for the creation of ecofriendlyenvironment, energy harvesting, etc, there are numbers of high-tech or daily-life functions of TE devices. This work has been devoted specifically to the creation of novel low-temperature (operating below 150°C) TE media. The strategy is to combine high electrical conductivity and lower thermal transport, thus the concept for TE glasses or glass-ceramics appeared. To meet demands for sufficient electrical semiconductivity of any type, it has been planned to co-substitute Ga-Ge-Se-Te-based glasses with pnictogens (precisely bismuth, antimony, and phosphorous), to create an interplay of increase in the tendency to crystallize by Bi and Sb dopant and supposedly stabilize amorphousness post-synthesis by P dopant. It was done to check two types of approach: to create promising material in fast process as-synthesized, or to prepare as-synthesized preform in the glassy state and then anneal it nearby T_g in another process.

The equivalent but a separate task was to explore new chemical compositions for ChG optical fibers as RE-doped Fiber Evanescent Wave Spectroscopy (FEWS) sensors, RE-doped remote sources of light, substituting already existing in common – inside Ga₅Ge₂₀As₁₀Se₆₅ system – arsenic with heavier Sb, in pursuance of the efficient and complete static distillation process (see Chapter 3 for more details). Another variable aspect was to substitute Se in the matrix by 20 at.% of Te in order to extend the transmission window further in the IR and perform the static distillation procedure. The goal was to check the transparency (indirectly level of glass impurity) of optical fibers as-drawn from preforms obtained via 2-step static purification processes and initial pre-purification of raw elements.

In this work, most of the studied materials for both types of applications were based on Ge-Ga-Se(Te) glasses modified by Pnictogen atoms (P, As, Sb, Bi).

The dissertation is organized into three chapters:

Chapter 1 provides a sufficient background of the applicatory field of studied materials and recalls the theoretical background paying special attention to the structure of the ChG. The next section deals with synthesis details and describes fundamentals governing the experimental techniques employed.

Chapter 2 conducts briefly through up to date research advances in TE materials. The experimental part demonstrates research results on Bi- and P-modified Ge-Se-based alloys, including:

- characterization of phase multiplicity of complex ChG and glass-ceramics alloys from Bi_xGa₅(Ge_{0.2}Se_{0.8})_{50-(x+5)/2}(Ge_{0.2}Te_{0.8})_{50-(x+5)/2}, Bi_xGa₅Ge₂₀Sb_{10-x}Se₄₅Te₂₀, as well as Bi_xGa₅Ge₂₀P_{10-x}Se₄₅Te₂₀ systems by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman scattering techniques;
- an insightful study of the thermodynamic properties of the aforementioned alloys, proposal of an adequate fitting model for deconvolution of exothermic crystalline peaks gathered with differential scanning calorimetry (DSC) technique.

- preparatory experimentation for the assessment of changes in electrical conductivity and Seebeck coefficient for chosen thermally modified Bi-containing alloy.
- investigation of nanomechanical surface response as a valuable tool to study elastic deformation leading to structural predictions using nanoindentation technique.

Chapter 3 encompasses state-of-the-art in the RE-doped FEWS sensors and an explanation of the physical phenomena on which optical sensors operate. The following part presents experimental results concerning ChG-based single-index fibers, being composed of the following parts:

- synthesis and characterization of multi-component Ge and/or As-based selenium glasses, such as Ga₅Ge₂₀As₁₀Se₆₅, TAS-235 (Te₂₀As₃₀Se₅₀), or As₂Se₃ modified with Ga and Sb to increase the RE solubility and maintain stability of the amorphous state;
- optimization of optical properties employing different purification and distillation processes;
- drawing and characterization of ChG-based single-core fibers of diameters ranging from 125 to 350 µm, as well as attenuation loss examination of the prepared as-drawn waveguides.

Chapter 1. Chalcogenide glass properties and technological features of synthesis and characterization

1.1. Introduction

This chapter contains description of theoretical background for better understanding of the following chapters. It starts from an introduction to chalcogenide glasses (ChG), structural/atomic arrangement in the ChG due to certain modifications, chemical bond approach as a theoretical basis for planning of chemical composition changes demonstrated in several examples. The following part of this chapter will be an explanation of ChG synthesis including its distillation procedures as well as pre-purification of raw elements. In the following section, the theory concerning characterization methods used will be shown in details: transmission and signal attenuation measurements, XRD measurements on polycrystalline and glassy materials, nanohardness testing approach to ChG, thermodynamic properties estimation using the DSC technique, a brief overview of viscometric techniques, and electrical measurements.

1.2. Chalcogenide glasses

ChG based on the chalcogen elements (such as sulfur S, selenium Se, and tellurium Te) alloyed with group IV–V elements (**tathogens** such as Ge, Si, and **pnictogens** such as P, As, Sb, Bi, etc.) belong to the category of optical materials that have been known and extensively studied since the mid-1950s. The ChG typically possess a broad region of infrared (IR) transparency (Figure 1.1), limited visible transparency, low optical attenuation, large refractive index, and high optical nonlinearity, and are generally stable to atmospheric moisture. High interest has been in the usage of the ChG-based optics for IR beyond 2 μ m [1-5].



Figure 1.1. Basic elements used in ChG synthesis (left) and advantage of the ChG systems regarding wide transmission in mid- and far-IR region (right).

The positive role of Ga and Sb on As-Se glasses affecting the RE solubility and glass stability of this system has been already reported by their structure and thermodynamic investigations [1]. Technologically it was proven by obtaining amorphous material taking into account substitution of As with Ga up to 3 at.% [1]. Further investigations lead to an idea of co-doping of As₂Se₃ with Ga and Sb. After significant efforts done with the use of positron annihilation lifetime (PAL) spectroscopy, there was the strong premise that Sb as a much heavier atom and similarly coordinated to As, influences free volumes in the amorphous structure, contracting the inaccessible free volume shell what is partially understood by its densification processes caused by substituting Sb. Structural studies performed by means of PAL spectroscopy have led to the conceptual scheme of the genesis of expected positron trapping sites in parent glassy As₂Se₃ (see Figure 1.2a). The most efficient preferential positron trapping sites are defined by extended free-volume spaces near Se atoms neighboring with AsSe_{3/2} polyhedrons [2,3].



Figure 1.2. Formation of free-volume positron trapping sites in glassy As-Se under subsequent nano-structuring stages: evolving host As₂Se₃ matrix (a), Ga-doped Ga₂(As_{0.40}Se_{0.60})₉₈ (b), Ga-doped and Sb-modified glassy Ga₂(As_{0.28}Sb_{0.12}Se_{0.60})₉₈ (c), and Pr³⁺-doped (500 wppm) glassy Ga₂(As_{0.28}Sb_{0.12}Se_{0.60})₉₈. The inner atomic-accessible free-volume core is white-marked, the outer atomic-inaccessible free-volume shell is blue-light shadowed while the surrounding network composed of different glass-forming polyhedrons is blue-dark shadowed (adopted from [4]).

Because of the strong directionality of covalent bonding in ChG, the Se atoms form lower electron-density spaces known as bond-free solid angles (BFSA) in terms of Kastner [5]. This atomic-inaccessible BFSA contributes to neighboring geometrical free volumes, ensuring effective negative electrical charge due to proximity with electronegative Se atoms linked with more electropositive As. So, the BFSA originated from Se atoms form an outer shell for an inner geometrical hole of the free-volume void, which can be identified in view of its preferential electric state as counterparts of a cation-type vacancy in crystals [6]. Therefore, the most efficient positron trapping sites in As₂Se₃ can be imaged as free-volume voids formed within a network of interlinked corner-shared AsSe_{3/2} pyramids, composed of an atomicaccessible geometrical hole (void core) arrested by surrounding atomic-inaccessible Se-based BFSA (void shell), as it is illustrated in Figure 1.2.

1.3. Structure of amorphous state

1.3.1 Definitions of the glassy state

Not all substances of solid consistency possess the same type of ordering as crystalline matter. There are many solid-state bodies, in which similarly as for liquids exists only local ordering, whereas in contrary to liquids they are not characterized by density fluctuation. Precise differentiation of such a state of solid matter took place until the 20th century, employing the XRD method defining so-called widely expanded "amorphous halo", instead of sharp, well-defined peaks originating from mono- or polycrystalline phases. Also, the fact that the term "amorphous solid body" (formless) and "glass" are not identical. Indeed the glass is an amorphous body, however not every amorphous body is the glass. Thus, it should be convenient to name glasses as amorphous bodies that form due to the cooling of liquids. The glass heated starts to soften and in the end mobile liquid forms. What is important such a process is reversible. On the contrary, heated crystalline body at exact temperature (melting temperature), more or less rapidly turns into a state of mobile liquid depending on congruency or non-congruency respectively. Glass may be defined at last in several equivalent ways [7]:

- **Morphological definition:** The glass which forms from the liquid phase, in contrast to crystals, does not take its structural shape. Such property is a sufficient defining glass.
- **Phenomenological definition:** The glass exhibits isotropy of all properties, while regarding crystals it is enough that exhibits anisotropy one and the only one property.

- Maxwell's definition: The glass behaves like all the substances, which due to cooling turns continuously from the state of the mobile liquid phase (exceeding temperature of vitrification in which, substance reaches viscosity of 10¹³ Pa·s) into a solid phase.
- **Structural definition:** The structure of glass is characterized by a lack of long-range order and as a consequence, such structure does not diffract X-rays specifically.
- Thermodynamic definition: The glass is in the state of a lack of configurational balance (structural-textural), not thermal. Transformation of liquid phase into a glass, despite features describing second-order thermodynamic transition, is not a thermodynamic transition, because it is not a transition from one equilibrium state to another. The glass as a non-equilibrium phase undergoes isothermal relaxation, at first into a metastable state like for super-cooled liquid, and then as a result of crystallization to the stable equilibrium state.

1.3.2. Ordering scale of vitreous structure

To better understand the properties of glass bringing its origin mostly from structural ordering, it is extremely important to know at which scale were done observations of the atomic arrangement concerning utilized research method. Two major types of ordering in glasses should be distinguished:

SRO – short-range order exists at a scale of nearest neighbor arrangements (it can extend below 6 Å) [8] and is determined by efficient atomic packing in clusters or polyhedrons. The packing of these quasi-equivalent clusters gives rise to a distinct medium range order;

MRO – medium-range order which can be defined as an order extending beyond the length scale of nearest and next-nearest neighbor atomic distances or ordering in a scale above the first coordination sphere. MRO can be regarded as given by the structural correlations in the range of approximately 5 to 10 Å [9].

The slightly different opinion about SRO and MRO distances has been defined by authors [10] who described those changes as follows: "While crystals possess long-range order (LRO), in amorphous materials short-range order (SRO) still exists. Although the first and second nearest-neighbor coordination shells are well defined, atoms in the third coordination sphere start to become uncorrelated with those in the first one. In other words, the limit of short- and medium-range order is the first 3–4 interatomic distances. The price to be paid for the loss of LRO is the appearance of fluctuations in angles and distances between the bonds".

1.3.3. Chemical bond approach estimations

The role of microscopic topology in determining the structure and properties of glassforming compounds has been explored theoretically for several years. The concept of an average atomic coordination number was presented by Phillips in constraint-counting arguments explaining the strong glass-forming tendency of certain alloy compositions. A considerable amount of additional theoretical work has been carried out to understand the properties of ChG in general and glassy switching materials in particular. Studies, performed by Fadel [11], on semiconducting ChG in the system Ge-As-Se appear as a sufficient basis for many theoretical and experimental investigations. Moreover, no research yet has been conducted to correlate the experimental data with the chemical bonding expected to exist in complex Ge-As-Se doped with Ga, Sb, and Te. The bond energies for heteronuclear bonds are calculated according to Pauling's relation [12]:

$$D_{(A-B)} = \left[D_{(A-A)}D_{(B-B)}\right]^{1/2} + 30(X_A - X_B)^2$$
(1.1)

Using electronegativities X_A , X_B for constituent elements $X_{As} = 2.18$; $X_{Ge} = 2.01$; $X_{Se} = 2.55$; $X_{Te} = 2.1$; $X_{Sb} = 2.05$; $X_{Ga} = 1.81$, the types of bonds expected to exist within these systems are shown in Table 1.1.

Bond	Bond energy; kJ/mol	Bond	Bond energy; kJ/mol
Se-Ga	223.85 [12]	Se-Se	184.1 [11,12]
Se-Ge	206.69 [11,12]	Ga-Ga	183.32 [12]
Se-Sb	179.46 [12]	Ge-Ge	157.32 [11,12]
Se-As	174.43 [11,12]	Te-Te	138.07 [12]
Ge-Ga	154.38 [12]	As-As	134.3 [11,12]
Ge-As	148.59 [12]	Sb-Sb	126.36 [12]
Ge-Te	148.53 [13]	-	-
Ge-Sb	142.86 [12]	-	-
Te-As	136.04 [12]	_	-
Te-Sb	132.21 [13]	-	-

Corresponding coordination numbers CNR_xR for each of glass constituent are $CN_{Se} = CN_{Te} = 2$; $CN_{Ge} = 4$; $CN_{Sb} = CN_{As} = 3$; $CN_{Ga} = 4$ [12]. On a basis of presented above data specifically Ge, as ChG glass constituent, regarding its tendency to be highly-coordinated (CN = 4), increases mean bond energy of the ChG network (see the respective heteronuclear bond energies in Table 1.1), what has its practical outcome – an increase of glass stability (especially against crystallization when doping the glass with other elements, such as, for instance, Ga or In).

Regarding assumptions made by Tichý and Tichá [12], that for ternary Ge-As-Se system (Se < 55at.%) the radial distribution function gives an estimate of mean coordination number around $\langle CN \rangle = 3.6 - 3.7$. This approach reveals that the standard assumption about coordination of chalcogen atom (i.e. CN_{Se}) is not valid. Some explanations relate to the low selenium concentration in a matrix of the glass. In such a case, in the liquid state, the network has to break apart because there are not sufficient Se atoms to form enough Ge-Se-As bridges, thus mobility of the atoms increases what forces them to arrange in the structure with higher coordination numbers. This theory contradicts significantly Tanaka's approach [14], where Te reaches coordination within the Ge-Sb-Te system mixed in between two-fold and six-fold.

Assuming that all chalcogen atoms (Se and Te) are similarly two-fold coordinated, taking analogy with statements reported by Tichy explained approach could be transposed for more chemically complex glass systems. In this prediction, the maximum number of elements used for the creation of glass is included. Hence, the equation model of the mean coordination number refers to the elemental mixture of six constituents. Such equation should involve a quantitative ratio of chalcogen components (Se, Te) taking into consideration an equal tendency of each chalcogenide constituents to create bonds with Ga and to be 3-fold coordinated:

$$\langle CN \rangle = aCN_{Ge} + bCN_{As} + cCN_{Sb} + dCN_{Ga} + 3d + (f - d)CN_{Chalc}$$
(1.2)

where: 3d means that there are d threefold-coordinated chalcogen atoms and hence (f - d) twofold-coordinated chalcogen atoms ($CN_{Se} = CN_{Te} = 2$). Moreover, the requirement for the qualitative advantage of chalcogen atoms regarding at.% of Ga is fulfilled e > d and f > d.

Another equation emerges with the statement that Te does not create a bond with Ga maintaining six-fold coordination regarding relatively (to Se) lower bond energy of each bond created by Te with common ChG constituents (see Table 1.1)

$$\langle CN \rangle = aCN_{Ge} + bCN_{As} + cCN_{Sb} + dCN_{Ga} + eCN_{Te} + (3d) + (f - d)CN_{Se} \quad (1.3)$$

where: *3d* means there are *d* threefold-coordinated Selenium atoms and hence (f - d) twofoldcoordinated chalcogen atoms ($CN_{Se} = 2$; $2 \le CN_{Te} \le 6$ – condition described by Tanaka [14]).

For clarity, these theoretical models of CN determination in multicomponent glasses need to be thoroughly studied and tested by vibrational spectroscopy, Raman experiments, or other adequate techniques. Mean coordination numbers corresponding to studied Sb, Temodified Ga-Ge-As-Se glasses are listed below (see Table 1.2)

Glass composition	<cn></cn>		
Ga5Ge20As10Se65	2.65		
Ga5Ge20Sb5As5Se65	2.65		
Ga5Ge20As10Se45Te20	$\begin{array}{c} 2.65\text{-}3.45 \\ (2 \leq \text{CN}_{\text{Te}} \leq 6) \end{array}$		
Ga5Ge20Sb5A85Se45Te20	$\begin{array}{c} 2.65\text{-}3.45 \\ 2.66(2 \leq CN_{Te} \leq 6) \end{array}$		

Table 1.2. Mean Coordination numbers *<CN>* of some Ge-based ChG (iso-coordinated element substitution does not influence mean coordination number within this set of materials)

1.3.3.1. Correlation between mean coordination number and hardness of ChG

Changes in glass composition affect severely elastic properties of glasses. Especially, this statement refers to glasses based on chalcogenides. For example, a wide change of structural properties and its derivatives within the A_xSe_{100-x} system can appear due to changes in atomic ratio x from 0 - 60 at.%. Meanwhile, oxide glasses based on silica may vary only at a molecular level allowing for structural modification only at vacancy or stacking faults level (< 1%). As it was explained by Tanaka [14] such differentiation was referred to relatively more covalent ChG and ionicity of hardly modified Si-O-based glasses.

Since the object of this work was to synthesize multi-compositional Ge-Sb-Se-Te-based glasses, the hypothesis arose that when Te is more likely to exist in a glassy matrix as six-fold coordinated such materials should possess bigger hardness and elasticity. However, it has been already reported that Te-modified Ge-Se-Sb-based ChG possess weaker Vickers hardness what undermines such an idea [15]. A rational explanation for such consequence may be maintained by experimentally tested energies of hetero-bonds of ChG constituents with Te which are much

smaller than their analogs with Se (see Table 1.1). Nonetheless, this subject demands more insightful experimental efforts to prove the negative impact of Te on mechanical properties.

Ternary diagrams (Figure 1.3) and superimposed compositional range of synthesized Ge-Se-Sb-based matrices lead to an observation that the structure of such a glass matrix is notably much more strained and floppy comparing to stoichiometric glass manifesting $\langle CN \rangle = 2.4$ per mean-field rigidity theory. This can be even explained by a comparison of the thermodynamic stability of glasses (see Chapter 2).



Figure 1.3. Variation of Vickers hardness kg f/mm² (upper diagram) and fracture toughness $[MPa \cdot m^{/2}]$ (lower diagram) of Ge-Sb-Se compositional range. Lines corresponding to equal average coordination number $\langle CN \rangle$ have been presented [15].

1.4. Glass synthesis

1.4.1. Raw elements and their purification

The synthesis of ChG starts from the collection of appropriate elements from the chemical industry. Optical devices such as fiber waveguides require special attention paid for purity, especially from an optical efficiency point of view or even simple technological possibility to obtain optically permeable material. As-received raw elements are not sufficiently pure (usually 5N or 6N) for high-distance transmission media such as optical fibers. To maintain the quality of raw materials, storage under argon gas protection in the glovebox under extremely safe ambient conditions should be provided (~0ppm of O_2 , ~5ppm of H_2O). Nevertheless, the characterization of the cleanness of the product does not include solid-state impurities (especially oxides or hydrides). Thus, there is a need for the implementation of purification techniques of starting elements with an individual approach for each of substrates.

The quality of the elements utilized for synthesis was as follows:

- selenium Se (5N, UMICORE Electro-Optic Materials)
- tellurium Te (5N, JGI Jean Goldschmidt International SA)
- germanium Ge (5N, Umicore Electro-Optic Materials)
- arsenic As (5N, Umicore Electro-Optic Materials)
- gallium Ga (7N, Alfa Aesar)
- antimony Sb (6N, Alfa Aesar)
- bismuth Bi (5N, Alfa Aesar)
- phosphorus red P (5N, Alfa Aesar)

Additional purification processes were done on Se, Te, and As, excluding Ga, Sb, Bi, which were enough pure, and Ge which is difficult to melt ($T_{m(Ge)} \sim 940^{\circ}C$) and make it volatile what leads to a necessity of purification with an addition of chemical getters such as Al, Mg (5N) for both static and dynamic purification procedures or chalcogenide chlorides (i.e. TeCl₄) during dynamic processes for hydride removal from the structure.

The principles of Se purification are based on the difference between the vapor pressure of Se (~32 Pa at 573K) and SeO₂ (26,7 kPa at 573K) what promotes oxide vaporization. In general, to perform the purification process, the initial charge should be introduced into previously cleaned and dried under vacuum silica ampoule (Figure 1.4). This operation requires inert gas protection in the glovebox. Silica tubes should be evacuated during the purification process up to high vacuum (HV) conditions ($10P^{-6}$ mBar).



Figure 1.4. Arrangement of apparatus for purification of Se (a) and image of aspurified/quenched Se (b).

Purification of Se is performed in a specially narrowed "valve" located over the top of the silica container. Such configuration is made to avoid the dropping of evaporated SeO_2 contaminants (Figure 1.4a). Such a problem does not exist in the case of highly volatile As oxides, therefore As purification setup (roughly similar to Se purification setup) does not require this special narrow tube section.

In turn, Te purification process is practically identical to the dynamic distillation of already prepared ChG alloys, thus the two-chamber silica setup (Figure 1.5a) is involved. The elemental charge within this process requires temperatures around 500°C for proper distillation.



Figure 1.5. System for a dynamic purification of Te (a) and as-purified Te ingot in sealed ampoule (b).

Individually for dynamically-purified glass syntheses – discussed in detail in subchapter 3.5.3 – a special method of the dynamic As purification has been implemented. Special care must be taken to washing/drying protocol for silica glassware, as well as, the combination of impurity removal stages in order not to resublime material into not yet prepared/cleaned section of the setup, hence heating resistive wire and thermal isolation is being used to keep the temperature constant (~ 270°C) in the region of undisturbed arsenic's impurities (oxides) flow (Figure 1.6a).

Sublimation of As occurs at around 470°C. Cardinally, during the process special attention should be directed to maintain an unconstrained flow of sublimating As in the thin transition section between two batches, therefore volume after the transition zone must be thoroughly isolated with refractory wool covering the entrance to the furnace. In the final step, the output batch has to be thermally treated causing a reasonably high-temperature gradient along the batch's axis to resublime and compress arsenic into the desired form (see Figure 1.6c).



Figure 1.6. System for a dynamic purification of As (a) sealing sections (b) final thermal treatment for as-purified As compression (c).

1.4.2. Melting of glasses from non-purified substrates

Synthesis of ChG, especially for fiber technology, requires the melting of the charge in sealed silica glass vacuum ampoules due to the high vapor pressure of chalcogenide melt and oxidation vulnerability under high-temperature conditions. The interior of silica setups has to be etched thoroughly in hydrofluoric acid for technological dust removal (silica, organic molecules, etc.), rinsed sufficiently in distilled water, and dried under vacuum. Classically, high optical quality glasses are obtained through homogenization in the rocking furnace with constant oscillation and amplitude provided by an arm attached to the body of the furnace and electrical engine. The presented basic procedure of glass melting and homogenization was performed for samples synthesized for semiconductive, TE applications, or as the first step for fiber drawing preforms manufacturing (Figure 1.7a). For maintenance of high vacuum conditions, silica setups are connected to the HV system by a special tap/valve connection that enables flexibility of manipulation (i.e. put into the glovebox, sealing, etc.) – see the inserted photo on Figure 1.7.



Figure 1.7. Scheme representing a procedure for basic synthesis without purification of the glass (a) and an exemplary temperature regime for rocking furnace (b).

The dried silica setup is filled with an elemental charge under the protection of argon gas in the glovebox. In the next step filled tube is connected to a cooled by liquid nitrogen trap and a vacuum in the setup exceeds 10⁻⁶ mBar thanks to a conjugated mechanical, rotational pump with turbomolecular HV pump. Later, the silica setup with the charge is sealed and then introduced into the rocking furnace.

Regarding remarkably low stability of the Sb and Ga-containing complex ChG systems, in the final step samples were homogenized at 900°C for 10h. However, in the case of the initial first step of multiple-stage synthesis usually, specimens were homogenized at 700°C for 10h just to sustain mechanical consistency afterward. On the other hand, as an important quenching process also needs to be individually matched to the glass composition. More viscous melts as Ge-containing systems can be quenched at higher temperatures.

As an example reported viscosity of $Ge_{20}Se_{80}$ at 700 °C exceeds nearly 10² Pa·s [16]. It is even beneficial from a structural point of view (better conditions for homogeneous glass transition). Common As₂Se₃ system is less viscous under comparable circumstances (10² Pa·s at 650°C) [17], thus a controlled decrease of quenching temperature may positively influence the preform shape (lack of wetting of the inner surface of silica tube).

1.4.3. Synthesis of glasses by two-step static purification process

In this work, the same glasses were synthesized using a multi-stage two-step purification method as presented in Figure 1.8 and Figure 1.9. Since Ge is not easy substrate to be purified because of high melting temperature, additional chemical and physical purification has to be done during the glass preform preparation process. For the classical TAS glass system (composing by ternary Te-As-Se), chemical purification based on aluminum has been reported as an efficient process [18,19].

Taking into account information derived from Ellingham-Richardson diagrams, Al is one of the highest redox potential element and simultaneously highly-non-corrosive under atmospheric conditions due to the efficient passivation phenomenon. Thus, Al is known to be the best oxygen getter as previously shown in [20]. On that basis, the Al (up to 5N level of purity) had been chosen for purification experiments.



Figure 1.8. The first step in the two-step static purification procedure (regular melt quenching synthesis of glass).

First of all, the initial elemental substrates together with Al getter are introduced and sealed in a thoroughly cleaned silica tube (Figure 1.8). The experimentally chosen quantity of Al is usually around 100 wppm. The glass is prepared by the classical melt quenching method, thus the oxide component of the glass matrix can react efficiently over homogenization time. In the next step, the mixture containing crystalline corundum is transferred to another silica setup equipped with a filtration chamber (Figure 1.9).



Figure 1.9. The second step in the two-step static purification procedure (static distillation step and an exemplary temperature regime implemented for distillation furnace).

The heating regime parameters for the second homogenization procedure performed after static distillation (see Figure 1.10) differs from the basic synthesis. Homogenization temperature is usually significantly higher promoting the melting of every elemental constituent of the glass. On the other hand, the main assumption for initial glass synthesis is to maintain mechanical stability or cohesion of material for further lossless manipulations. The final product of these two stages can be directly used as a preform for single index fiber drawing or precision molding of high optical quality lenses.



Figure 1.10. Indicative thermal treatment regime for Se-Te-As-Ge based ChG preforms for fiber drawing procedure.

1.4.4. Quenching conditions - TTT diagrams

There are two strategies for thermal treatment during the manufacturing of glasses:

- absolute avoidance of nucleation;
- precise steering of nucleation rate and crystal growth when synthesizing glass-ceramic.

To maintain stable temperature regimes for the synthesis of glasses as well as glassceramics, referring also to its size/volume and possible heat gradients changing thermodynamic conditions with a time of process it is essential to recognize information derived from timetemperature-transition (TTT) diagrams (Figure 1.11). TTT diagrams usually are represented with several curves in the function of temperature vs time or log(time).



Log Time

Figure 1.11. Scheme of TTT diagram.

From theory, in terms of thermodynamics, nucleation occurs when the size of a conglomerate of atoms is greater than critical nucleus size r^* , which determines activation barrier ΔG^* (Figure 1.12). Moreover, the theory describes a barrier for an atom to cross the interface separating the nucleus and its vicinity ΔG_m . Thus the rate of nucleation relies on these three components what was described, among the others, by [21].

$$I = K_{\nu}(T)e^{\left[-\frac{(\Delta G^* + \Delta G_m)}{K_B T}\right]} = K_{\nu}(T)e^{\left[-\frac{(\Delta G^*)}{K_B T}\right]}e^{\left[-\frac{(\Delta G_m)}{K_B T}\right]}$$
(1.4)

where: $K_v(T)$ is a pre-exponential factor which is defined by structural parameters of material like a number of atoms per unit volume, number of surface atoms on a nucleus, and quantum parameter of an atomic vibration frequency.

The general conclusion from such theoretical model is that when the *T* decreases, the $\Delta T = T_M - T$ increases, then the activation barrier ΔG^* decreases and the $e^{\left[-\frac{(\Delta G^*)}{K_BT}\right]}$ increases. As *T* decreases below T_M , the nucleation rate *I* increases. By the time, when the T decreases, the $e^{\left[-\frac{(\Delta G_m)}{K_BT}\right]}$ also decreases. Therefore, nucleation is a process which has its maximum due to two contradictive mechanisms [21].



Figure 1.12. Different strategies for the realization of melt-quench technique: approach illustrating high-nucleation rate thermal process a), low-nucleation rate process b), necessary conditions for total vitrification. Prepared based on lectures published by members of Zang Research Group from the Department of Materials Science & Engineering, the University of Utah [22].

In complex material system, alloying elements reach the efficiency of TE materials comparing the doping procedure. In general, alloying increases the power factor, whereas the thermal conductivity falls downwards. The guest grains of the crystalline component in a glassy matrix material acts as a scattering center, which decreases the thermal conductivity and enhances the electrical properties. The heavier guest atoms act as "rattling" atoms generating dynamic disorder, thus scattering phonons and creating a conducting path for the electrons [23,24]. The electronic structure can be either modified by doping mechanisms. Alloying elements can introduce atomic disorder at an atomic site via an induced atomic fluctuation or the strain field effect, which reduces the lattice thermal conductivity [25].

Another type of strategy of thermal conductivity reduction is nanostructuring. By introducing nanoscale heterogeneities and nanodispersions, one can obtain the quantum confinement and the energy-filtering effect. It is a consequence of the fact that when the system size decreases and the length scale is comparable to its electron mean free path or wavelength.

Under such conditions, the density of states increases, eventually increasing the Seebeck coefficient. Inversely, the thermal conductivity lowers due to the scattering of phonons caused by their interaction with nanostructured surfaces or interfaces [26].

In the case of bulk materials, the nanoscale effects can be controlled by decreasing the grain size to nanometer regimes or using nanoparticles. Thus, the occurrence of these interfaces can induce a notable increase in TE figure of merit (ZT), particularly in the case of nanostructured materials. A nanocrystalline sample prepared by ball milling exhibits a ZT value of 1.4 at 127 °C in comparison with a Bi-Sb-Te alloy ingot [27]. Zhou et al. studied the effect of annealing on the TE properties, in relation to the microstructure of the system [28]. However, nanostructuring does not affect the power factor. In some cases, it was reported that long-term annealing can even cause a 50% increase in ZT [28].

1.5. Spectroscopic methods and optical properties

1.5.1. Transmission and absorption measurements

Absorption spectroscopy enables us to figure out which frequencies of incident light are absorbed as they are passing throughout the matter. If absorption of a specific frequency of radiation occurs, it indicates that studied materials structural components have undergone the transition from a basic state of energy E_1 to an excited state of energy E_2 what is represented by equation 1.5 [29].

$$hv = E_2 - E_1 \tag{1.5}$$

When the incident light passes through an infinitely tiny piece of material dz, the intensity of incident light *I* reduce. Internal losses of intensity *dI* are proportional to the thickness dz, what is well prescribed by the following equation [29]:

$$dI = -\alpha I dz \tag{1.6}$$

where: α is the absorption coefficient expressed by units of cm⁻¹, which relies both on absorbing species of matter and the frequency value of incident light. Combining two sides of relation 1.6 reveals intensity *I* as a function of *z*: $\ln(I) = -\alpha z + C$. For a material of thickness 1 the difference between the intensity of incident light I₀ and intensity I_T that penetrates matter at *z* = *l* is given by the formula: $\ln(I_0) - \ln(I_T) = (-\alpha 0 + C) - (-\alpha l + C) = \alpha l$ which in turn can be transformed into well-known Beer-Lamberts law [29].

$$I_T = I_0 e^{-\alpha l} \tag{1.7}$$

Because absorption coefficient α does not depend on the concentration of a measured substance an aspect of concentration of absorbing material *c*, is described by the separate formula:

$$dI = -\sigma I c dz \tag{1.8}$$

Taking into account that c is described as a number of absorbing substructures per volume of material, thus σ is the absorption cross-section and has units of area. Individual absorption measurements employing spectrophotometers usually leads to results in the value of absorbance, which is defined as:

$$A = \log_{10} \frac{I_0}{I_T} = -\log_{10} T \tag{1.9}$$

1.5.1.1. Fresnel losses in the normal incidence condition

Since the reflection of the beam perpendicular to material, at each of its interfaces is not negligible (when refractive index difference between transmitting media is high) Fresnel losses have to be estimated. This can be done using the following formula:

$$R = \left| \frac{n_1 - n_2}{n_1 + n_2} \right|^2 \tag{1.10}$$

where: R is the reflection coefficient; n_1 and n_2 are refractive indices of the two next to each other media.

Moreover, reflection by a glass comes from the front side as well as the backside, and that some of the light "bumps back and forth" a couple of times between the two interfaces. Therefore, combined reflection coefficient R_c was defined as:

$$R_c = \frac{2R}{1+R} \tag{1.11}$$

It is important to note that calculated Fresnel losses for, as an example, Te-based glasses (n > 3), reaches 40% considering air as an ambient $(n \approx 1)$. Thus, it can be stated that the majority of losses come from a reflection in high-index ChG. Scattering and absorption losses are minor effects in this context. This aspect of ChG optics is also highly influenced by the quality of forming/polishing performed on a raw material by its counter surface parallelism and micro-roughness.

1.5.1.2. Absorption cross-section calculations

An absorption cross-section is a probability of an atom/molecule to absorb a photon of a particular wavelength and polarization. Quantitatively, the number dN of photons absorbed, between the points x and x + dx along the path of a beam is the product of the number N of photons penetrating to depth x times the number n of absorbing molecules per unit volume times the absorption cross-section σ :

$$\sigma = \frac{\alpha}{N} \tag{1.12}$$

where: α - absorption coefficient (cm⁻¹); N – atomic number density (cm⁻³).

In turn, the absorption coefficient is defined by the following equation:

$$\alpha = \frac{1}{d} \ln \frac{100}{T} \tag{1.13}$$

where: d – sample thickness (cm); T – transmission (%)

Atomic number density which is equal to the number of atoms per volume in the context of absorbing RE ions within the glassy matrix can be described more specifically as:

$$N = \frac{n}{V} = \frac{\frac{C_{RE} \cdot m}{\mu_{glass}} N_A}{V} = \frac{\frac{C_{RE} \cdot \rho \cdot V}{\mu_{glass}} N_A}{V} = \frac{C_{RE} \cdot \rho \cdot N_A}{\mu_{glass}}$$
(1.14)

where: n - number of atoms in mass (mol); c_{RE} - atomic percent of RE; ρ - density of compound; μ_{glass} - molar mass of glass; $N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$ - Avogadro's number. Finally, the experimentally useful formula for absorption cross-section measurements is defined as:

$$\sigma \left[cm^{-2} \right] = \frac{\alpha \cdot \mu_{glass}}{c_{RE} \cdot \rho \cdot N_A} \tag{1.15}$$

1.5.2. Waveguide optical loss

The attenuation of a waveguide is an important parameter to be measured, especially under the restriction dictated by optoelectronic applications, which is low loss. There are a couple of ways for assessment of optical losses in waveguides ie. Fabry-Perot resonance method, prism coupling, scattering method, and cut-back procedure [30,31]. The last one, which is adequate for fiber drawn optics, was employed in this study. The cut back technique offers high measurement accuracy and resolution however, it is time-consuming and impractical in most situations, since it requires fibers are cut and cleaved as part of the measurement process.

1.5.2.1. Signal attenuation evaluation

The essential property of photonic devices such as fiber, planar waveguides, or optical lenses is its attenuation of the signal passing through the studied device. Internal loss of electromagnetic light propagating in a given medium can be attributed to several phenomena, therein: mainly scattering of electromagnetic wave on separate crystalline phases of material, absorption of the specific wavelength of light by distinct constituents of the structure. The general equation which enables to calculate, relative to the thickness of the irradiated medium, internal loss looks as follows:

$$(Attenuation)\alpha \left[\frac{dB}{m}\right] = \frac{10 \cdot \log_{10} \frac{l}{I_0}}{\Delta l}$$
(1.16)

where: I – input intensity of light, I_0 – output intensity of light, Δl – the distance between the initial dimension of a medium and output lowered dimension of an object

To understand the dB scale, it has to be clarified that when the output power/intensity of light is half of the input, the attenuation loss is $10 \log_{10} 2 \approx 3.01 \, dB$. Likewise, the reduction in signal intensity is by a factor of 10 or 100, the signal attenuation is 10 dB and 20 dB respectively. Also, observed amplification of light can be represented in dB scale (for example 30 dB of amplification means the gain in the output signal is one thousand times more intense than the input signal.

1.5.2.2. Length reduction approach for fiber attenuation study

The so-called cutback method is a reliable technique to measure attenuation within fiber waveguide under two restrictions:

- mounting optical fiber to the spectrometer with alignment setup allowing micrometric precision;
- minimized external influences i.e. lamps emitting in the IR range;
- stable conditions for the operation of the spectrometer unit, its detector, source, etc.

The approach relies on a comparison of the output powers of different waveguide lengths by several cycles of cleaving the fiber with monitoring the signal after each cut. One simple principle has to be provided: each cleaving before the test should be done from the signal output side of a waveguide to fixate a parameter of input cleavage quality as it is shown in Figure 1.13.



Figure 1.13. Scheme demonstrating cut-back method for fiber attenuation test.

Nevertheless, of huge importance is the fact that depending on what is the relative volume reduction of transmitting media x: if it is a long initial cut referring to relation L_1 and L_2 , or small trimming of the fiber, like for L_3 and L_4 (Figure 1.13) different phenomenon is tested. In the first case "long-distance attenuation" is a more representative result reflecting the attenuation coefficient referring to not affected by inherent absorption transmission ranges (regions of low attenuation limit). The second approach is to measure "small-distance attenuation", for two reasons:

- to confirm general attenuation values gathered through long-distance measurements, in other words, to gain information on homogeneity or inhomogeneity of glass imperfections distribution within a volume of optical fiber;
- to describe with higher precision the attenuation values covering regions of intense absorption caused by chemical impurities (i.e. chalcogen-H, As-H, or H₂O bonds).

1.5.2.3. Attenuation measurement uncertainties

The indispensable requirement for a reliable attenuation study is the awareness of the investigator about structural morphology and homogeneity of the examined material. The problem is even much more essential regarding investigations performed on long fiber-shaped material due to technological difficulties for the successful preparation process. Thus, attenuation measurement may be utilized as a tool for quality control of fiber. In general, a good method for credible test of glass homogeneity is to compare a long-range attenuation data α_1 with a small range packet of measurements described here as α_2 (Figure 1.14).



Figure 1.14. The influence of structural imperfections on the attenuation measurements: a) homogeneous in the entire volume of the waveguide; b) inhomogeneities localized in primary cut part of the waveguide; c) inhomogeneities located in secondary cut part

It should be emphasized the situation a) (presented in Figure 1.14) should not affect the reliability of measurement, because changes in attenuation value obtained are stable. However, in case of situations b) and c) an output signal may not be captured precisely due to:

- observation of relatively low value in long-range and high value in short-range (intensity I₀ measured on 1-st cleavage will be significantly lower than intensity I measured on 2-nd cleavage) for situation c)
- reversibly in case of situation b)

The signal which strongly depends on an optical alignment of a waveguide may be falsified because initial optical alignment (see Figure 1.14c,b) has been performed on a qualitatively different volume of material than for second attenuation measurement. For optical fiber applications, photonic devices have to be as homogenous as possible.

1.5.2.4. Angular influence on transmission losses in ChG optical fibers

The intention of such evaluation is more specific than attenuation measurement with an almost similar equation. However, in this case, measured losses are not considered per length of a fiber cut. It is irrelative to length but in relation to an angle registered for a certain value of an obtained loss (Figure 1.15).



Figure 1.15. The schematic diagram of the fiber bending angles and bending loss spectra of the Ge-Sb-Se-based double-index optical fiber. Image courtesy © [32].

In this case, the losses are calculated according to the following equation:

$$Loss_{bend} = -10\log\frac{T_{bend}}{T_0} \ [dB] \tag{1.17}$$

where: T₀ is the transmittance of straight fiber

Such measurement gives fruitful information on the pure engineering (thus less scientific) aspect of ChG optical fiber application.

1.5.3. Refractive index analysis, the critical angle

The guidance of a light passing through the optical fiber is possible due to the occurrence of total internal reflection (TIR) circumstance. Refractive index of transmitting media:

$$n = \frac{c}{v} \tag{1.18}$$

where: c – the speed of light in vacuum $c \approx 3 * 10^8 \left[\frac{m}{s}\right]$; v – the speed of light in that medium.

Additionally, when a ray of light is incident to the interface of two media, the ray undergoes partial reflection and partial refraction as described in Figure 1.16.



Figure 1.16. (a) A ray of incident light on a denser medium $(n_2>n_1)$; (b) A ray incident on a less dense medium $(n_2>n_1)$; (c) For $n_2>n_1$ when the angle of incidence is greater than the critical angle, a ray will undergo total internal reflection [33].

The angles φ_1 , φ_2 , and φ_r represent the angles that the incident ray, refracted ray, and reflected ray create with the plane normal to the boundary of separate media. Angular relations are well defined by Snell's law and the law of reflection:

$$n_1 \sin \varphi_1 = n_2 \sin \varphi_2 \text{ and } \varphi_1 = \varphi_r \tag{1.19}$$

Moreover, an incident ray, a reflected ray, and a refracted ray are situated in the same plane. From Figure 1.16a, since $n_2 > n_1$, according to Snell's law, it has consequences on the angles $\varphi_2 < \varphi_1$ i.e. the ray will bend toward the normal plane (dotted line). From another point of view, if a ray is an incident at the interface of less dense media $n_2 < n_1$, the ray will bend away from the normal plane Figure 1.16b. The angle of incidence, for which the angle of refraction is 90°, is known as the critical angle φ_c [33]. Thus, when:

$$\varphi_1 = \varphi_c = \sin^{-1}\left(\frac{n_2}{n_1}\right)$$
 (1.20)

 $\varphi_2 = 90^\circ$. When the angle of incidence exceeds the critical angle (i.e., when $\varphi_1 > \varphi_c$), there is no refracted ray, which is well known as the total internal reflection (Figure 1.16c). Considering the refractive index as an important parameter in fiber optics, the main characteristic dependencies for such a shape of material should be explained. The corresponding (Figure 1.17) refractive index distribution (in the transverse direction) [33] is given by:

$$n = n_1 \quad for \quad r < R \tag{1.21}$$

$$n = n_2 \quad for \quad r > R$$

Where n_1 and n_2 ($< n_1$) are respectively the refractive indices of core and cladding, *R* is the radius of the core.



Figure 1.17. a) an optical fiber consisting of a cylindrical central core cladded by a material of insignificantly lower refractive index. b) electromagnetic rays colliding on the core-cladding boundary at an angle greater than the critical angle inducing TIR phenomenon [33].

To characterize the optical fiber, the so-called fractional refractive index change Δ has to be defined as [33]:

$$\Delta \equiv \frac{n_1^2 - n_2^2}{2n_2^2} \tag{1.22}$$

If $\Delta \ll 1$ (what is even confirmed for real silica fiber for which n_1 is almost equal to n_2), the previous relation (1.22) can be reduced in the following way [33]:

$$\Delta = \frac{(n_1 + n_2)(n_1 - n_2)}{2n_1^2} \approx \frac{(n_1 - n_2)}{n_1} \approx \frac{(n_1 - n_2)}{n_2}$$
(1.23)

1.5.4. Attenuated total reflectance measurement

Attenuated total reflectance (ATR) sampling techniques depend on directly illuminated by IR light waveguides of a relatively higher refractive index than the ambient matter. Good reflection conditions of such waveguide (literally total internal reflection conditions) fixate the light signal passing through a material.

However, on the surface of the waveguide takes place the evanescent wave field phenomenon which projects orthogonally the ambient matter in intimate contact with the ATR waveguide. Due to such interaction of the evanescent field, some of the energy of initial light can be absorbed, scattered, or effectively reflected from the surrounding substance. The reflected radiation of lower energy (for the ambient substance optical properties) is returned to the waveguide and the detector. The analysis of substances utilizing ATR devices is easy, nevertheless, it is obligatory to be aware of several experimental factors and its influence on recorded spectra. The main factors of an ATR module and an analyte are:

- Refractive indices.
- Angles of incidence of IR wave.
- Critical angles.
- The wavelength of IR beam.
- Depth of evanescent field penetration.
- Number of reflections.
- Contact of sample to the ATR device.

The refractive indices of the crystal and sample govern the basic phenomenon of the ATR sampling technique under the following equation:

$$\theta_c = \sin^{-1} \frac{n_2}{n_1} \tag{1.24}$$

where n_2 is the refractive index of the sample, n_1 is the refractive index of the crystal and θ_c is the critical angle.

One of the useful factors for appropriate ATR measurements is the depth of penetration d_p of the IR wave into the analyzed substance. It is defined as follows [34]:

$$d_p = \frac{\lambda}{2\pi (n_1^2 \sin^2 \theta - n_2^2)^{1/2}}$$
(1.25)

where: λ is the wavelength of light and θ is the angle of incidence of the IR beam relative to a perpendicular from the surface of the crystal.

Typically the parameter of penetration depth varies between $0.5 - 5 \mu m$ depending on experimental values. The evanescent field decays quickly with the progression of the distance between an ATR crystal and a sample. For difference estimation between ATR measurement and transmission measurement it is convenient to use the following equations which enable to calculate effective penetration of IR beam, described also as a volume of evanescent wave [35]:

$$d_{eff \perp} = \frac{n_1^2 n_2 \cos \theta}{(n_1^2 - n_2^2)} \times \frac{\lambda}{\pi \sqrt{n_1^2 \sin^2 \theta - n_2^2}}$$
(1.26)

$$d_{eff\parallel} = \frac{n_1^2 n_2 \cos\theta}{(n_1^2 - n_2^2)} \times \frac{2n_1^2 \sin^2\theta - n_2^2}{(n_1^2 - n_2^2) \sin^2\theta - n_2^2} \times \frac{\lambda}{\pi \sqrt{n_1^2 \sin^2\theta - n_2^2}}$$
(1.27)

Thus, the effective penetration for a not polarized IR beam is the arithmetic average of perpendicular and parallel components [35]:

$$d_e = \frac{d_{eff\perp} + d_{eff\parallel}}{2} \tag{1.28}$$

Amongst the types of ATR devices, a single reflection ATR is ideal for qualitative analysis and also multi-reflection ATR which allows a more subtle investigation of minor components qualitatively and quantitatively. To create such muti-reflection ATR waveguide, it is inherent to increase effective path length by enlarging the number of reflections (N) [35]:

$$EPL = N \times d_e \tag{1.29}$$

Appropriate selection of ATR material characteristics straight to the samples which will be detected is practically important. The choice is performed referring to its control depth, penetration of IR beam, hardness, desired spectral range and corrosion behavior which can be optimized to desired application i.e. Ge-Se-based glasses are corrosion-resistive against aqueous solutions, acidic (1mol/1 HCl or HNO₃), however quite weak against caustic treatment [36,37]. The temperature was expected to affect severely each type of corrosion in ChG [36].

1.5.5. Intra-modal dispersion characteristics of certain ChG representatives

The ChG combines low phonon energy and high optical nonlinearity, therefore optical fibers are suitable not only as sensing devices in the m-IR spectral region but also as m-IR supercontinuum generation (SCG) sources [38] or remote sources of light [39]. Development of bright, broadband m-IR-SCG waveguides will give an advantage in terms of remote, real-

time FEWS devices [40], m-IR endoscopes, borescopes for real-time imaging or IR laser beam transmitting media for surgery [41].

Regarding the major application for which a considerable part of this work is dedicated (the FEWS sensor), dispersion factor of such fiber waveguides should be as low as possible at each wavelength, taking into account the transparency window of ChG-based optical fibers (typically for 2 to 14 μ m considering Te, Se-based glasses, excluding sulfur which is not the object of investigations upholding this study, exhibiting shifted transparency window towards visible region). For fiber sensing in the m-IR, dispersion acts as a phenomenon, which should be taken into consideration when significantly affects a light transmitted through the ChG matrix within meters of fiber regrading limiting attenuation of such media. It has been reported that As₂Se₃ and Ge₁₀As₂₃Se₆₇ reveal nonsignificant dispersion considering a path of transmission as a kilometer (see Figure 1.18).



Figure 1.18. Material dispersion calculated by the fitted/chosen type of Sellmeier model for As-Se and Ge-As-Se glasses. The inset presents a zero-dispersion wavelength range [42].

Further analyzing dispersion characteristics, intensification of dispersion process concerns especially n-IR region, whereas in the m-IR range dispersion falls to minimum values. Dispersion is measured in units of $ps/(nm \cdot km)$ since it expresses the temporal spread (ps) per unit propagation distance (km), per unit pulse spectral width (nm).
Problem with a dispersion of light at certain wavelengths may be effectively resolved by appropriate design of graded-index fiber being appropriately cladded or possessing gradient of dopant concentration as the general dispersion of combined waveguide is the sum of material dispersion D_M and waveguide dispersion D_W .

$$D = D_M + D_W \tag{1.30}$$

The material dispersion parameter is calculated from the standard formula [43]:

$$D_M = -\frac{\lambda}{c} \left(\frac{d^2 n}{d\lambda^2} \right) \tag{1.31}$$

The same physical processes which introduce fiber attenuation also produce a refractive index that varies with wavelength. This intrinsic, or material, dispersion is primarily a property of the glass used in the core, although the dispersion of the cladding will influence the fiber in proportion to the fraction of guided energy that resides outside the core. Material dispersion is particularly important if sources of broad spectral width are used, but narrow-linewidth lasers that are spectrally broadened under modulation also incur penalties from material intra-modal dispersion. For single-mode fibers, material dispersion must always be considered along with waveguide and profile dispersion, however, this subject will not be extensively presented in this work, being the object of interest for photonic engineers instead of materials scientists.

1.6. Structural investigations

1.6.1. XRD study through the FSDP theory

It is not an obvious conclusion that XRD research methods are a powerful tool for studying a structure of amorphous materials. Since poly- or mono-crystalline matter generates, depending on the research approach, unequivocal information about its crystallography, employment of XRD methods to check amorphousness, or additionally characterize material with the use of the First Sharp Diffraction Peak (FSDP) estimations, was slightly omitted. Meanwhile, it turns out that the beginning point of development of this approach reaches the 1970's of the 20th century [44]. Therefore, papers facing this branch of structural analysis can be counted in hundreds.

As an example, two XRD patterns of two Se-based glasses with observed FSDP halos are shown in Figure 1.19.



Figure 1.19. XRD pattern of Ga₂(As_{0,4}Se_{0,6})₉₈ and Ga₅(As_{0,4}Se_{0,6})₉₅ ChG.

Diffraction patterns of amorphous materials are analyzed using FSDP spectral data treatment. Patterns collected by X-Ray irradiation of amorphous solids manifest a narrow prepeak known as the FSDP. FSDP analysis gives the possibility to investigate structural properties of glass such as the formation of clusters [45,46], presence of layered structure [47,48]. Several FSDP parameters are essential to interpret them to characterize non-ordered structure:

$$Q_1 = \left(\frac{4\pi}{\lambda}\right)\sin\theta \tag{1.32}$$

$$R_1 = 2\pi/Q_1 \tag{1.33}$$

$$\Delta Q_1 = (4\pi/\lambda)\sin(FWHM/2) \tag{1.34}$$

$$L_1 = 2\pi / \Delta Q_1 \tag{1.35}$$

where: FSDP's values such as the angle of diffraction 2θ and full width at half maximum (FWHM) of the peak are collected from XRD pattern

- R₁ can be described as a constant characteristic distance corresponding to the size of structural unit which diffracts X-Rays most effectively in FSDP angular range, or to the distance between layers, or density variations in a quasi-periodic amorphous structure;
- L₁ may be expressed as the structural correlation length and it is related to FWHM of the FSDP;

• Q_1 and ΔQ_1 are respectively the magnitudes of scattering vector and its change or in sequence the position and width of the FSDP in the reciprocal space.

LR₁R is as identified as the scale of medium-range order (MRO). On the other hand, R₁ is indicated as the characteristic distance between fundamental structural units which effectively diffracts X-Ray's in the FSDP angular range of diffraction spectra [49], or the size of the stable cluster structure [50,51], or the correlation length over which the quasi-periodic real space density fluctuations are maintained [52]. The main idea for which FSDP analysis can be utilized is an evaluation of the preparation route (particularly quenching) effects, external physical and chemical factors affecting the glassy matrix.

1.6.2. Mechanical study in the nanoscale (the Oliver-Pharr's approach)

ChG due to their relatively strong elastic properties (i.e. Young's modulus (*E*) ~ 18 GPa, nanohardness ~ 2,4 GPa for nearly stoichiometric As-Se) are adequate materials for nanoindentation investigations, mostly regarding the method of manufacturing utilized for the synthesis of these materials (melt quenching technique), which practically eliminates apparent density. The melt quenching process determines the high consistency of material, full amorphousness, and isotropic structure, which may be indicated by the low standard deviation for a set of data. For example, considering Ga-doped As-Se glasses standard deviation of Young's modulus and nanohardness reaches less than 15% regarding partially crystallized glasses (at.% $_{Ga} > 4$), and less than 8% considering homogeneous amorphous Al₂O₃ using the atomic layer deposition technique, allows for data scattering up to 5%, on the other hand, bulk, monocrystalline silicon is grown via Czochralski's process permits to reach standard deviation below 2.5% as reported in [53].

The Oliver-Pharr's method [54] enables measurement of the hardness and Young's modulus which are calculated from indentation load-displacement curve (Figure 1.20) such as:

- the maximum load P_{max} ;
- the maximum displacement h_{max} ;
- the elastic unloading stiffness or "contact stiffness" S = dP/dh can be described as the slope of the upper portion of the unloading curve during the initial stages of unloading).
 The additional important value is the permanent depth of penetration after the unloading

of the indenter h_{f} . A truly registered unloading set of data points has its inherent curvature

connected with strain relaxation. However, to maintain flat punch approximation conditions utilized by Doerner and Nix [55], the contact area remains constant, thus the result is linear.



Figure 1.20. Graphic representation of unloading process a) and scheme of loaddisplacement data described by crucial measurement parameters b)[54].

1.6.3. Analysis of chemical composition by SEM-EDS

Energy-Dispersive X-ray Spectroscopy (EDS) is a qualitative and quantitative technique for microscopic observations that can supply data on the chemical composition of a specimen for elements with an atomic number higher than a material of EDS detectors window.

The physical principle of operation is that an incident electron generated by a cathode of a scanning electron microscope hits the surface of a specimen. As a result electron of material is injected into an inner shell and creates an electron/hole pair in an atomic orbital. Then electron from the outer, higher-energy orbital refills the empty energetic state. Energy dispersive spectrometer measures the energy of emitted X-rays what is shown in Figure 1.21.



Figure 1.21. Diagram presenting principles of X-Ray emission phenomenon a) and exemplary EDS spectrum for Bi, Ga - modified GTS glass.

The possible error in chemical composition measurement exceeds $\pm 1-2\%$. EDS is a powerful tool for an assessment of glass homogeneity. During the purification steps elemental charge losses may take place, therefore a crucial aspect for the manufacturing of preforms is to control the chemical composition of the glasses.

1.7. Physical parameters

1.7.1. Control of ChG thermal stability (DSC technique)

DSC is a thermo-analytical method that operates on a base of difference between the quantity of heat supplied (commonly demonstrated as the number of Watts per gram of analyte (W/g) to elevate the temperature of specimen and reference. The resulting heat flow data is presented as a function of temperature (see Figure 1.22). Phase transitions occurring in an analyzed substance can be divided into [29]:

- the first-order exothermic phase transition of crystallization means that less heat flow is needed from DSC heaters to the specimen for maintenance of equivalent temperatures in the specimen and reference pans;
- the second-order endotherm phase change of glass transition which is depicted either as a minimum or an inflection point of DSC curve depending on chemical composition and thermal history of the glass;
- the first order endothermic phase transition of melting.



Figure 1.22. Typical DSC curve for low T_g *ChG.*

In general, for ChG, it has to be mentioned that thermal effects originating from firstorder phase transitions are much larger than second-order (see Figure 1.22).

From a technological point of view, the temperature of the crystallization onset is a more important parameter than the temperature of the crystallization peak. The reason for that relies on the collapse of optical properties due to a much higher refractive index of crystalline phases than for an amorphous component of the matrix. For instance, refractive index *n* at 1,55 μ m for amorphous Ge₅₀Te₅₀ = 3.88 in combination with *n* for crystalline Ge₅₀Te₅₀ = 6.8 [56], points to the conclusion that a small volume of a crystallized component in an amorphous matrix may cause large scattering losses.

1.7.2. Viscometry

The temperature-dependent viscosity of ChG is one of the most fundamental properties regarding the formation n and synthesis of these materials (Figure 1.23). Analysis of the viscosity curve enables the estimation of a glass transition temperature (T_g). Besides, viscoelastic behavior as a function of temperature and time concerns multiplicity hot-forming processes i.e. low-temperature extrusion, high-temperature fiber drawing. From a more basic point of view, the viscosity-temperature dependencies contents information about connections in the atomic scale and structure-related properties that may be derived.



Figure 1.23. General ChG dependence of viscosity in a function of temperature, showing ranges of commonly used technological operations.

Parallel plate viscometry. Such a technique is utilized for viscosity tests extending in the range of 10^{6} - 10^{9} Pa·s, where the glass behaves similarly to pitch in a room temperature ~ 10^{7} Pa·s. A cylindrical sample of investigated glass is compressed under load at a temperature between two parallel silica plates. Viscosity is calculated from the compression rate through the following equation:

$$\eta = 2\pi \frac{Mgh^5}{30V(\frac{dh}{dt})(2\pi h^5 + V)(1 + \alpha T)}$$
(1.36)

where: η is viscosity (Pa·s), g is gravitational acceleration, M is applied load (g), V is sample volume (cm³), h is the height of specimen (as a function of time), dh/dt is compression rate, α stands for thermal expansion coefficient of the glass.

As one can figure out from Figure 1.24, the parallel plate method serves as a relevant tool for estimation of $log(\eta)$ vs T characteristics only in a region of viscosity lower than 10^9 Pa·s, which allows for a good approximation of results employing, in particular, Vogel-Fulcher-Tamman's exponential model.



Figure 1.24. Compositional dependence of viscosity changes, measured using the parallelplate method. Corresponding T_g 's for each type of 2-step statically purified glass are presented in the upper part of the chart.

1.7.3. Electrical conductivity measurement

"Four-point probes" (Figure 1.25) is an easy method to test sheet electrical resistivity.



Figure 1.25. Four-point probe method scheme.

A current is passed through the outer probes and induces a voltage in the inner voltage probes. The bulk resistivity could be measured using the voltage (V) and current (I) readings from the probe and sample thickness (d) using the empirical formula below [57]:

$$\rho = \frac{\pi}{\ln 2} d \frac{V}{I} = \frac{4.532Vd}{I}$$
(1.37)

The results calculated by the formula above are consistent when the thickness of an object measured is less than half of the probe spacing (t < s/2). Conductivity (σ) is defined as the inverse of resistivity.

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Chapter 2. Pnictogen modified Ge-Ga-Se-Te chalcogenide glasses for thermoelectric and other semiconductive applications

2.1. Introduction

Te- and Se-based glass matrices are suitable for many optical and semiconductive applications combining high IR transparency, excellent thermal processing capability, large optical nonlinearities, unique electrical properties, and good solubility of various dopants [1,2]. The latter allows further enhancement of the intrinsic physical properties of these materials through nanoscale design.

In particular, several chemical elements (Bi, Sb, P, RE elements, Ga) are shown to modify these glasses at a nanoscale, leading to significant changes in their electrical conductivity [3,4], thermo-electric behavior [5,6], phase-change memory effect [7], the potential to host low-dimensional quantum systems [8], unique optical properties [1], and other interesting phenomena. The combination of all these features makes ChG alloys modified at nanoscale a very appealing multifunctional medium for numerous applications, including (nano)optics and (nano)electronics. The progress in such applications depends on our ability to fabricate ordered regions of desired size and concentration in the amorphous matrix of ChG by modifying the technological process of their synthesis or using external influences, such as thermal treatment (crystallization above the glass transition temperature), photo-exposure (laser-induced fluidity, local melting) or others.

Among all dopants, Ga ,Bi, Sb look especially attractive for nanoscale modification. Ga is usually added to a ChG matrix to improve the solubility of RE elements, while Bi and Sb are known to be unique dopants in ChG (which normally are highly insensitive to metal doping and possess *p*-type conductivity) capable of unpinning the Fermi level and thus changing the conduction from *p*- to *n*-type [3,4]. Moreover, Bi-doped chalcogenide polycrystals are capable of strong thermo-electric effect [1,9], whereas Bi-based crystals (Bi₂Te₃ and Bi₂Se₃) have been proven to possess topological insulator properties [8].

These narrow-bandgap (\leq 1eV) materials have vast potential in today's IR devices, including IR sources, detectors, energy harvesting, and power electronics IR astronomy systems, TE applications, etc. Low effectiveness and significant manufacturing costs of widespread semiconductors like HgCdTe, InAs, InSb, PbSnTe are good motivation for further research in this field. One of the promising competitors for the new generation of narrow bandgap media can be material, created on a basis of ChG with subtle modifications at the nanoscale by Bi, Sb, and Ga dopants.

Overall, the use of ChG as a matrix enables them to change their bandgap by simple variation in composition. Technologically such modifications are quite simple due to the generally large glass-forming region determined by chemical composition.

The equipollent object of interest regarding Bi and Sb modified Ge-Te-Se glasses are materials having potential for TE applications. Especially intriguing is the optimization of electrical and thermal transport phenomena maintaining the physical and chemical stability of semiconductors. In this work preliminary data collected on electrical properties will be presented, therefore it is reasonable to provide a short outline of the basics of thermoelectricity.

Materials for energy conversion such as solar and fuel cells serve as good support for the conventional energy sources. However, their relatively low efficiency, poor long-term stability, and high cost still demand research and development. From this branch of energetics, TE is known as an option of the lowest conversion efficiency 5-20% (see Figure 2.1) but enabling to recover heat energy waste into electricity.



Figure 2.1. Bar diagram encloses efficiency domains in% for each technology based on semiconductors [10]; circle graph shows general predictions regarding the contribution of each category of TE materials (gathered in 2016 from Web of Science and SciFinder [11]).

Upon many ChG systems, Ge-based systems in terms of thermoelectricity are known to possess relatively higher thermal stability than As-Se; Te-As-Se. What is true, As-S, Ge-As-S, or in general S-based systems are even more reliable towards thermal stability; however, in terms of TE devices, they are not reported as promising functional media. The applicatory goal was to introduce Bi, Sb or P into matrix up to such content which would not provoke partial or dominant crystallization of the as-prepared preform of chalcogen-based material, leading to

overall amorphousness. Te in this system is known as a chalcogen constituent which, in general, lowers the glass-forming ability of the system (Figure 2.2).



 Figure 2.2. Ternary diagram presenting the previous study on glass-forming ability upon Ge-Te-Se system (black dots indicates fully-vitrified chemical compositions) [2]. Red elliptical areas demonstrate a compositional range of base ChG matrices for further substitution experiments performed. (Extended region of forming ability by melt-quench technique – marked as red dotted line acknowledges that GeTe₄ can be fully vitrified using this method).

The key and global idea staying behind such preference in theoretical compositions of studied ChG matrices is to check the outcome of preparation of such materials under the substitution with Bi, Sb, or P via melt-quench technique. It appears to be of importance to check the effectiveness of exchange of Te atoms by Se into $Bi_2Se_xTe_{3-x}$ Rphases since Bi_2Te_3 compound is most promoted regarding its lowest activation energy needed for nucleation and crystal growth. Pursuing the goal of well-homogeneous, semiconductive glass or glass-ceramic materials encompassing Bi-Se-Te, but rich in selenium which recently has been reported specifically in therms of solvo-thermally prepared thin films [12]. Authors claim that they have obtained thin films of $Bi_2(Se_xTe_{(1-x))3}$ covering the entire compositional range with Se substituting Te. However, most promising results on TE power factor, electrical conductivity, Seebeck coefficient point out that the optimal atomic percentage of Se appears around x = 0.6 - 0.75. Thus, in order to distinguish between the efficiency of Bi-Se-Te phase enrichment with selenium, we have planned two types of matrices having an atomic ratio of Te/Se = 1 and 0.4.

Nonetheless, to obtain effective TE glass-ceramic material, there is a need to maintain as much Te in the matrix as possible. Simultaneously, the substitution of Ge by only Bi leads to the inevitable bulk crystallization of the preform. In other words material or preform, *a posteriori* is not homogenously polycrystalline due to the specificity of the melt-quench process, which eliminates it for further thermal treatment and manufacturing of fine glass-ceramics.

TE figure of merit is the measure of a material efficiency that relies on a couple of factors:

- High thermo-power (absolute value of Seebeck coefficient).
- High electrical conductivity.
- Low thermal conductivity.

However, energy transfer characteristics depend on interrelated material properties. In other words, these parameters have to be optimized (Figure 2.3).

In general, there are two major problems in TE materials design:

First, optimization between:

- carrier concentration,
- electrical conductivity
- Seebeck coefficient.

Second, optimization between thermal conductivity and electrical conductivity.

Absolute thermal conductivity κR_{total} Rof a certain TE material originates from two kinds of energy transport:

- Electrons and holes transporting heat $\kappa_{e.}$
- Thermal phonons in the crystal lattice or amorphous net $\kappa_{latt.}$

The Holy Grail of TE applications (maximizing ZT) can be realized by lowering thermal conductivity and enhancement of electrical conductivity. Whereas the electronic thermal conductivity (which is desired to be minimum) is directly associated (i.e. direct proportionality) to the electrical conductivity (which has to be maximum).

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Figure 2.3. The scheme representing an optimal window for semiconductor-based TE materials design as a compromise between electrical conductivity and Seebeck coefficient regarding charge carrier concentration. The positive outcome of the design is reflected by the power factor ($PF = S^2\sigma$) curve possessing its maximum at $10^{19} - 10^{21}$ cm⁻³carrier concentration characteristic for heavily doped semiconductors. Image Courtesy © [11].

For maintenance of a high Seebeck coefficient, it is preferential to arouse the domination of electrical transport by only one type of conductor (or n-type or p-type charge carriers). Whereas the occurrence of n-type and p-type charge carriers of the same mobility and quantity will weaken the Seebeck effect, decreasing thermo-power of the system.

2.2. Description of studied materials

Supporting an idea of materials possessing novel semiconductive properties or certain advantages as a TE material, Ga-Ge-Se-Te-based matrix has been proposed to be further modified with other **pnictogens** (Bi, As, Sb, P) as a prospect base for obtaining reliable alloys. In contrast to the study performed by Srinivasan et al. [13] of which the object was a synthesis of Te-rich SGT glass modified with Bi what evidently led to the production of nearly pure TE Bi₂Te₃ phase, the basis for this study was to obtain **pnictogen-modified** glass-ceramic material having inside crystallites of Bi₂Te_xSe_{3-x} solid solutions. The hypothesis was that the TE phase,

well distributed in the glassy matrix, could possess more structural defects caused by the formation of chemically and structurally more complex $Bi_2Te_xSe_{3-x}$.

Over the past few years, the concept of TE glasses has gained considerable interest. Telluride glasses, particularly known for their low thermal conductivity [14] and simple meltquench synthesis process, making them ideal candidates. An array of compositions of ChG and glass-ceramics with low thermal conductivity and unusually high electrical conductivity for a glassy phase have been previously reported [15-17]. Though these kinds of semiconducting glasses, especially Cu-doped telluride glasses, exhibit high Seebeck coefficient at room temperatures [18-20], their high degree of structural disorder causes large electron scatterings that results in low mobility and electrical conductivity, which collapses the power factor and overall ZT to values that are insufficient for any relevant large-scale industrial applications.

The novelty of this part should be identified in general conclusions assuming separate sections of structural research like Bi-containing glasses and glass-ceramics from the substitution ranges (Figure 2.4):

- $Bi_xGa_5(Ge_{0.2}Se_{0.8})_{50-(x+5)/2}(Ge_{0.2}Te_{0.8})_{50-(x+5)/2}$
- Bi_xSb_{10-x}Ga₅Ge₂₀Se₄₅Te₂₀
- $Bi_xP_{10-x}Ga_5Ge_{20}Se_{45}Te_{20}$



Figure 2.4. Conceptual schema of developed ChG for low-temperature TE materials (Bi-doped SGT systems were intensely studied by B. Srinivasan et al. [13], other types of alloys modified by pnictogens were investigated in this work).

Complications with the abbreviation of materials systems that were studied within this work, lead to an idea to create some internal rules of nomenclature. In particular, the case is quite simple when certain ChG material possesses two or three elemental constituents and chalcogen appears as one element i.e. when considering As-Se, the particular person has a rough idea of what is all about (all the compounds possessing these two elements in the different atomic ratio).

The materials presented in this chapter are multi-chalcogen-based systems doped with Bi, Sb and P. Studied systems varied also in the ratio between chalcogen constituents creating two distinct ChG systems, therefore it was decided to name matrix of such system with the acronym in two ways:

- GTS-s in which the latter "s" denotes the symmetric atomic ratio between chalcogen constituents;
- GTS should be differentiated by the domination in the molar quantity of certain chalcogen (the last character of the acronym stands as dominant chalcogen in the system) thus, as an example, glass with chemical composition Bi₁Ga₅Ge_{18.8}Se_{37.6}Te_{37.6} will be described in general as Bi, Ga-modified GTS-s, while, in case of Bi₁Ga₅Ge₂₀Sb₉Se₄₅Te₂₀ it will be additionally written as Bi, Ga, Sb-modified GTS system).

Substitution affecting certain chalcogenide systems may be presented in form of chemical formula with variables included (i.e. $Bi_xGa_5(Ge_{0.2}Se_{0.8})_{50-(x+5)/2}(Ge_{0.2}Te_{0.8})_{50-(x+5)/2}$ (y=5, x=1,5,10) alloys) what allows for a more exact description of structural changes during substitution process. Nevertheless, some "written way" to express what has been substituted should be proposed.

The aforementioned example depicts the situation when a glass matrix consisting of Ge, Se, and Te undergo substitution by Bi which will be realized with proportion 1-2-2 respectively, evidently, the atomic ratio of Ga remains the same. Thus, the problem of reduction can be resolved as Bi-doped Ga-containing GTS-s alloys.

2.3. $Bi_xGa_5(Ge_{0.2}Se_{0.8})_{50-(x+5)/2}(Ge_{0.2}Te_{0.8})_{50-(x+5)/2}$ alloys with symmetric chalcogenide ratio Te/Se = 1

2.3.1. Preparation conditions of Bi, Ga-modified GTS-s alloys

The ChG of $Bi_xGa_5(Ge_{0.2}Se_{0.8})_{50-(x+5)/2}(Ge_{0.2}Te_{0.8})_{50-(x+5)/2}$ system with x = 1, 5 and 10 (Table 2.1) were prepared by conventional melt quenching method using high-purity (5 N or more) elements.

The appropriate amount of precursors with total mass ~25 g were vacuum-sealed in silica ampoules of 10mm in diameter. They were heated up to 900 °C with a 2 °C/min heating rate, homogenized at this temperature for 12 h in a rocking furnace, and quenched from 700 °C into the water at room temperature. To relieve the mechanical strains that appeared as a result of rapid quenching, the specimens were additionally annealed at 160 °C for 3 h.

The actual composition of the prepared materials, as checked by EDS, was found to be very close to the desired glasses (Table 2.1). The slightly scattered composition is observed for Bi10 sample due to phase separation in this glass as shown later.

Moreover, attributed to chemical composition densities of synthesized alloys has been listed in Table 2.1 displays gradual increase caused by the substitution of matrix components with heavy Bi, which also indicates lack of closed porosity in as-prepared Bi10 alloy and comparable molar volume of polycrystalline phases existing in as-prepared Bi10 sample to the molar volume of amorphous component for the rest of samples.

Sample	Planned chemical composition	EDS determined chemical composition	Density (g/cm ³)
Bi1	Bi ₁ Ga ₅ Ge _{18.8} Se _{37.6} Te _{37.6}	Bi _{1.1} Ga _{5.2} Ge _{18.6} Se _{37.4} Te _{37.7}	5.083 ± 0.005
Bi5	Bi5Ga5Ge18Se36Te36	Bi5.5Ga5.5Ge18.9Se36.8Te33.3	5.345 ± 0.005
Bi10	$Bi_{10}Ga_5Ge_{17}Se_{34}Te_{34}$	$Bi_{10}Ga_{5.8}Ge_{18.4}Se_{36.9}Te_{28.9}$	5.624 ± 0.005

 Table 2.1. Chemical composition and density of studied samples.

2.3.2. Phase identification of Bi-doped Ga-containing GTS-s alloys

All as-prepared samples were vitreous in nature, except the $Bi_{10}Ga_5Ge_{17}Se_{34}Te_{34}$ (Bi10) composition, which showed the presence of crystalline peaks on XRD patterns (Figure 2.5).



Figure 2.5. XRD spectra of as-prepared investigated samples and theoretical patterns of Bi₂Te₃ and Bi₂Se₃ crystals.

The further refinement of the crystallization peaks was achieved from the XRD analysis of the samples after the heat treatment (Figure 2.6). Samples were annealed at 250, 300 and 400°C for 30 minutes dwelling time.

Structural research has been performed using Bruker D8 Advance operating in Bragg-Brentano's geometry (configuration θ - θ), equipped with Cu anode ($\lambda = 1,5406$ Å). Chosen optics for primary beam was: divergence slit 0.1°, Soller slit 2.5°, for secondary beam: Ni K_β filter, Soller slit 2.5° and antiscattering slit 4,2 mm. Additionally, sample holder was rotated (20 rpm) preventing texture or privileged orientation effects.





Figure 2.6. XRD spectra of the investigated samples after heat treatment at 250 °C, 300 °C and 400 °C as indicated.

XRD spectra of as-prepared and annealed samples for each separate composition are shown in Figure 2.7.

According to PDF database, the phases crystallizing at lower temperatures can be identified as Te, $Bi_2Se_xTe_{3-x}$ (x = 0, 0.5, 1, 1.5, 2) and Ga_2Se_2Te compounds [21-23]. The intensities of the corresponded reflexes in the XRD patterns from Bi-based complexes correlate well with Bi content in the samples (Figure 2.6 and 2.7). The phases crystallizing at higher temperatures can be associated with the crystallization of GeSeTe, GaGeTe, and GeBi₂Te₄ phases.

It is observable from Figure 2.7, that as-prepared materials with lower Bi content Bi1 and Bi5, were initially in a dominant amorphous state, which was also proven by SEM (see Figure 2.8a). As expected, the occurrence of an amorphous phase for all investigated specimens gradually decreases by volume with an increase of annealing temperature (Figure 2.8b,c,d).



Figure 2.7. Summary diffractograms of studied alloys a) Bi₁Ga₅Ge_{18.8}Se_{37.6}Te_{37.6} (Bi1), Bi₅Ga₅Ge₁₈Se₃₆Te₃₆ (Bi5) Bi₁₀Ga₅Ge₁₇Se₃₄Te₃₄ (Bi10)

Supplementary EDS measurements were performed on a fresh cleaves/cracks to detect areas, grains of distinct chemical composition as a trace for phase analysis (Figure 2.8).



Figure 2.8. Microstructure of as-prepared Bi1 (Bi_{1.1}Ga_{5.2}Ge_{18.6}Se_{37.4}Te_{37.7}) sample (a) and asreceived fractures of the Bi1 sample annealed at 400 °C (b),(c) and (d)

As could be seen from SEM image (Figure 2.8d), the $Bi_2Se_xTe_{3-x}$ is the main phase that appears during the annealing. This is a solid solution type of phase determined by partial substitution of Te atoms by Selenium. However, in general, the position of this peak on the XRD (~ 27.8 2 θ) ensures that the considered phase is constantly Te-rich, in which Se may be described as an electronic modifier. More specifically results show that with annealing temperature for Bi5 sample Se interruption into $Bi_2Se_xTe_{3-x}$ increases. Surprisingly chemical content of the richest in elemental Bi molar fraction, sample (Bi10) seems to behave in a reverse manner. This might be an explanation for peak shifts, nonetheless, other diffraction related effects as peak shifts of certain phase due to an increase in an internal mechanical strain of grains cannot be omitted without comment. However, strain-related effects, which may occur in such a combined amorphous-crystalline system, are contributing rather to peak broadening than a shift of its maximum intensity. EDS analysis performed on cleavages of materials Bi1 and Bi5, annealed at 400 °C, in an evident way reveal the manifestation of pure, hexagonal tellurium phases and Bi₂Se_xTe_{3-x} solid solutions (Figure 2.8c,d).

2.3.3. Thermodynamic studies of Bi, Ga-modified GTS-s alloys

The DSC thermograms obtained for investigated Bi1, Bi5, and Bi10 samples measured at 10 K/min heating rate after background and baseline subtraction are shown in Figure 2.9.



Figure 2.9. DSC curves recorded t at 10 K/min heating rate for Bi1, Bi5, and Bi10 samples.

The onset values of glass transition temperature T_g , a peak value of the first crystallization temperature T_c (determined for 10 K/min runs), as well as Dietzel criterion of glass stability are given in Table 2.2.

Chemical composition	T _g (°C)	T _x (°C)	T_x - T_g (°C)
Bi ₁ Ga ₅ Ge _{18.8} Se _{37.6} Te _{37.6}	174	245	71
Bi ₅ Ga ₅ Ge ₁₈ Se ₃₆ Te ₃₆	186	230	44
Bi ₁₀ Ga ₅ Ge ₁₇ Se ₃₄ Te ₃₄	215	Partially crystallized	-

Table 2.2. Thermodynamic parameters of studied Bi, Ga-modified GTS-s alloys.

It is obvious, that glass becomes less stable with Bi addition and finally, Bi-based crystallites appear in Bi10 sample with 10 at.% of Bi (Figure 2.9). Nevertheless, T_g of all the investigated samples is higher than 160 °C, which makes them attractive compositions for applications in many IR instruments.

The DSC curves of Bi1 and Bi5 samples exhibit two families of crystallization exothermic peaks, which correspond to the crystallization regions (Figure 2.9), namely "low-temperature" (~210-300 °C) and "high-temperature" (~320-370 °C). Gaussian or Fraser-Suzuki fits of DSC heating curves measured at 5 K/min (Figure 2.10) both suggest the crystallization of at least five different phases in Bi5 sample (consistent also with the first derivative analysis of DSC curves): three phases in the first and two in the second region.

By the comparison of DSC and XRD analysis, we can argue that peak I (Figure 2.10) is dominated by the crystallization of Bi-based compounds (like Bi₂Te₃, Bi₂Se₃, or Bi₂SeTe₂). Such an assignment is consistent with the reports of other authors investigating crystallization in Ge-Se-Te-Bi system [24], where crystallization of Bi₂Se₃ phase was found in 260-310 °C range depending on the heating rate. The second peak II observed in the first region of DSC curves does not change much with Bi addition (Figure 2.10). Therefore, it can be attributed to the crystallization of Ga-based phases (like Ga₂Te₃, Ga₂Se₃, or mixed), which were identified in crystallized products of Ge-Te-Ga, Ga-As-Se, and Ga-As-Se-Te glasses as well. The broad peak labeled III in the first region of DSC curves, most probably includes crystallization of trigonal Te and various metastable Ga/Ge-Te phases, like GeTe₂.

Second family of crystallization processes occurred in high-temperature region (peaks IV-VI) can be related to crystallization of stable Ge-Te (GeTe, Ge₂Te₃, or Ge₁₇Te₈₃), Ge-Se (GeSe, GeSe₂, Ge₄Se₉) or mixed phases. Despite the crystallization of GeSe₂ phase is reported for Ge-Se-Bi [21] and Ge₂₀Se₅₀Te₃₀[25] glasses in similar temperature range, the crystallization of this phase in pure Ge-Se system usually is observed at higher temperatures (~530 °C).

Although there is a possibility that the existence of Ga-/Bi-based crystallites and the addition of Te can facilitate the crystallization of the GeSe₂ phase, triggering it at lower temperatures, the obtained Raman and XRD data have little support of its formation in present materials after heat treatment.



Figure 2.10. The Gaussian (left column) and Fraser-Suzuki (right column) fittings for DSC curves of Bi₁Ga₅Ge_{18.8}Se_{37.6}Te_{37.6} (Bi1), Bi₅Ga₅Ge₁₈Se₃₆Te₃₆ (Bi5) and Bi₁₀Ga₅Ge₁₇Se₃₄Te₃₄ (Bi10) samples recorded at 5 K/min heating rate.

2.3.4. Activation energy estimation of crystallization in Bi, Ga-modified GTS-s alloys

The DSC study of crystallization kinetics usually analyzed with Johnson-Mehl-Avrami (JMA) nucleation-growth model [26,27]. However, the JMA equation for non-isothermal conditions is valid only if a certain number of criteria are satisfied: the entire nucleation process takes place during the early stages of the transformation, and becomes negligible afterward; the overall crystallization rate is defined only by the temperature and does not depend on the previous thermal history. Fundamental kinetic equations for non-isothermal crystal growth from preexisting nuclei have been developed by Ozawa [28] and a simple method of kinetic analysis of DSC data for these processes has been proposed:

$$\frac{d\alpha}{dt} = Af(\alpha)e^{\left(\frac{-E_a}{RT}\right)}$$
(2.1)

where α is a fraction of crystallized volume

$$\alpha = \frac{1}{\Delta H_c} \int_0^T \phi dT \tag{2.2}$$

Here φ is the specific heat flow measured with DSC (W/g) and ΔH_c is the total enthalpy change associated with the crystallization process; the pre-exponential factor A and activation energy E_a are kinetic parameters that should not depend on the temperature T and α ; and

$$f(\alpha) = m(1 - \alpha) [-\ln(1 - \alpha)]^{1 - \frac{1}{m}}$$
(2.3)

is an algebraic expression of the JMA model. It has been demonstrated that the JMA exponent m is a characteristic parameter linked to crystal-forming morphology. In particular, $m \sim 1$ means predominant surface crystallization, while $m \sim 3$ corresponds to three-dimensional bulk crystallization. A simple test for the applicability of JMA model according to the above-mentioned criteria is proposed by Malek [29]. It is based on the analysis of probe functions:

$$y(\alpha) = \phi e^{\left(-\frac{E_a}{RT}\right)} \tag{2.4}$$

$$z(\alpha) = \phi T^2 \tag{2.5}$$

In the case of non-isothermal crystallization, for JMA equation to be valid the maximum of the $z(\alpha)$ function should occur around $\alpha = 0.63 \pm 0.02$ value.

The activation energies (E_a) calculated using Ozawa's plot (ln q vs 1000/T) are shown on Figures 2.11-2.13 for studied Bi1, Bi5, and Bi10 samples, respectively. An increase in Bi concentration as from 1 to 5 at % leads to a general increase of activation energies of I-III peaks (Figures 2.9, 2.10). This can be explained by the fact that the crystallization of Bi5 sample starts at lower temperatures than that of Bi1, where the viscosity of a supercooled liquid is generally higher.



Figure 2.11. Ozawa's plots for $Bi_1Ga_5Ge_{18.8}Se_{37.6}Te_{37.6}$ (Bi1) sample to determine activation energies (E_a) for the crystallization processes as per Gaussian (solid symbols) and Fraser-Suzuki (open symbols) fits.

The higher viscosity means more constraints for structural rearrangements needed for crystallization to occur. Therefore, if the crystallization of Bi1 glass starts at higher temperatures (Figure 2.9), the lower viscosity of supercooled liquid allows easier structural rearrangements and, consequently, smaller activation energies.



Figure 2.12. Ozawa's plots for $Bi5Ga_5Ge_{18}Se_{36}Te_{36}$ (Bi5) sample to determine activation energies (E_a) for the crystallization processes as per Gaussian (solid symbols) and Fraser-Suzuki (open symbols) fits.

The activation energies for peaks IV-V of Bi10 sample is almost twice smaller than for peaks IV-V of Bi1 and Bi5 samples. The easier crystallization in the "high-temperature" region of Bi10 sample in comparison to Bi1 or Bi5 can be explained by a pre-existence of crystallized Bi- and Ga-based phases, which facilitate seeds formation for the Ge-Te crystallites.



Figure 2.13. Ozawa's plots for $Bi_{10}Ga_5Ge_{17}Se_{34}Te_{34}$ (Bi10) sample to determine activation energies (E_a) for the crystallization processes as per Gaussian (solid symbols) and Frase-Suzuki (open symbols) fits.

Although the obtained Gaussian fitting curves can be used to estimate the activation energies with more or less acceptable accuracy (see Figure 2.11-2.13), they cannot be used for probe $z(\alpha)$ functions at all, because Gaussian curves are symmetric and would give $z(\alpha)$ maximum always at $\alpha \sim 0.5$. Thus, the Fraser-Suzuki function fitting should be employed for these purposes.

On the other hand, it can be seen from Figures 2.9 and 2.10 that peak V dominates each DSC signal in the "high-temperature" crystallization range of all samples. So, it is also possible to use a real shape of DSC signal ϕ to calculate $z(\alpha)$ for peak V. Both approaches have been used to build $z(\alpha)$ functions for peaks V to check the applicability of JMA model at least in the second crystallization region. As seen from Figure 2.14, the maxima for most $z(\alpha)$ functions occur within the range of 0.6 < α < 0.7, which includes the α = 0.63 value.

semiconductive applications



Figure 2.14. Z(α) functions for "high-temperature" crystallization region of Bi1-Bi10 samples to check the applicability of JMA equation. Full symbols correspond to the peak V in Fraser- Suzuki fit, open symbols - experimental data points.

One of the important aspects of the investigated ChG alloys as a medium for the phasechange memory is the crystallization rapidity. In order to quantify it, an "index of crystallization rapidity" (ICR), which defines crystallization rapidity as a determined ratio between the peak height and width, can be calculated [26]:

$$ICR = \ln\left(\frac{MH}{FWHM}\right)$$
 (2.6)

where: MH is the maximum height of the peak (in W g⁻¹) and FWHM (in °C).

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The calculated according to equation 2.6 *ICR* criterion for the most rapid crystallization occurred in the studied materials (peak V) is given in Table 2.3. for a 10 K/min heating rate.

Chemical composition	ICR (peak V)
$Bi_1Ga_5Ge_{18.8}Se_{37.6}Te_{37.6}$	0.124
Bi5Ga5Ge18Se36Te36	0.120
$Bi_{10}Ga_5Ge_{17}Se_{34}Te_{34}$	-0.011

Table 2.3. Index of crystallization rapidity ICR respectively of studied samples.

The obtained ICR is higher than for Se-Te, Ge-Sb-Se, or Bi-containing Ge-Sb-Te alloys, which makes the investigated Bi1 and Bi5 glasses promising materials for phase-change memory applications, even taken into account the crystallization of several phases.

2.3.5. Raman spectroscopy studies of Bi, Ga-modified GTS-s alloys

The Raman spectra of the studied samples are presented in Figure 2.15. The main A1 breathing mode at ~210 cm⁻¹ of corner-shared GeSe_{4/2} tetrahedra in crystalline GeSe₂ is not observed in any of the heat-treated samples. Instead, a feature at ~190 cm⁻¹ is the closest one which can be associated with formation of GeSe₂ crystallites, but it is weak and observed only in Bi5 and Bi10 samples after respective heat treatments. There is, of course, a possibility that the addition of Bi leads to a significant decrease in the intensity of Raman signal from GeSe₂ vibrations as reported in [30], but a reason for such effect in the investigated materials is not clear. Moreover, a small difference between the Raman spectra recorded for Bi1(Bi5) samples after crystallization at 300 (250) °C and 400 °C suggests superior crystallization of the telluride-based phases. The interpretation of the rest features in Raman spectra is not straightforward because of the variety of possible structural units in which vibrational modes strongly overlap. The obtained Raman spectra (Figure 2.15) are dominated by the vibrations from Ga-, Bi- and Ge-based telluride complexes, which for vitreous Bi1 and Bi5 samples are observed as broad bands in the ranges of ~80-110 cm⁻¹, ~120-160 cm⁻¹ and ~180-210 cm⁻¹.

The band at ~80-90 cm⁻¹ is usually observed in a single-crystal α -GeTe and can be attributed to $\Gamma_3(E)$ mode of rhombohedrally deformed rocksalt structure or bending modes of GeTe₄ tetrahedra. The band peaking at ~125-140 cm⁻¹ is characteristic to A1 mode of corner-shared GeTe₄ tetrahedra and lighter Ge₂Te₃ complexes.



Raman shift, cm⁻¹

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Raman shift, cm⁻¹

Figure 2.15. Raman spectra of the investigated Bi1 (a), Bi5 (b) and Bi10 (c) samples before and after heat treatment at different temperatures. Fitting is performed with a minimum number of Gaussians as a guide for the eyes.

The vibrational modes of edge-shared GeTe₄ tetrahedra usually give rise to a band in Raman spectra at ~160 cm⁻¹. Nevertheless, the position of all these peaks can be shifted in the investigated materials because of Te substitution in GeTe₄ tetrahedra with Se, Bi or Ga atoms, forming mixed GeTe_{4-n}(Se/Bi/Ga)_n units. The third family of low-intensity peaks within ~180-210 cm⁻¹ range, most probably, originate from GeSe₄ tetrahedra, where one or two Se glasses because of the low Ga concentration (5 at.%) and their strong overlap with other modes of telluride-based units. The crystalline Bi₂Se₃ usually gives rise to Raman bands at ~75, ~130, and ~175 cm⁻¹, while Bi₂Te₃ Raman active modes lay at ~62, ~104, ~134 cm⁻¹ [26,30]. All of

them can be assumed in the experimental Raman spectra of the heat-treated Bi1, Bi5, and Bi10 samples, but they cannot be unambiguously resolved without appropriate theoretical modeling due to a strong overlap with other modes of Ga- and Ge-based structural units.

2.3.6. Investigation of subtle structural arrangements by means of high-resolution X-Ray diffraction and neutron scattering techniques

The neutron scattering (NS) experiments were performed at Nanoscale-Ordered Materials Diffractometer (NOMAD) at Spallation Neutron Source, Oak Ridge National Laboratory. The bulk samples were measured in 3mm quartz capillaries in an argon atmosphere to reduce scattering from the air [23]. Three independent measurements for each sample's composition were performed to confirm good reproducibility of the results. The total X-ray scattering and Bragg XRD experiments were performed at the beamline 11-ID-B, Advanced Photon Source, Argonne National Laboratory, using synchrotron X-rays with wavelength 0.2127 Å and position-sensitive Perkin Elmer amorphous silicon image plate detector [32]. Measurements were carried out at room temperature using coarsely powdered (with mortar and pestle) samples sealed in Polyimide capillaries. The NS data were normalized with respect to the scattering from the solid Vanadium rod, and the X-ray scattering using PDFgetX2 software package developed by Qiu et al. [33]. Standard corrections for the area detector setup were applied [32]. After correction, the structure factor S(Q), which contains information on the atomic pair correlations in the investigated material, was extracted as described elsewhere [34].

The absence of strong crystalline reflexes in XRD patterns of Bi1 and Bi5 samples (Figure 2.16) testifies their overall glassy nature, while the readable XRD reflexes in Bi10 sample (10 at.% of Bi) show the formation of Ga₂Se₃ and extended Bi₂Se_xTe_{3-x} (x=0, 0.5, 1, 1.5, 2) mixed crystallites. The latter were identified according to PDF database and confirmed by SEM-EDS analysis, showing an increased concentration of Te and Bi chemical elements across the observed crystalline inclusions in Bi10 sample (Figure 2.17). The Ga₂Se₃ and crystallites of Bi₂Se_xTe_{3-x} solid solutions are not the only species, which can be formed in the multinary matrix of the investigated materials. At least five different phases crystallize during heating as shown in the previous subchapters.


Figure 2.16. Synchrotron XRD patterns of studied materials. The inset shows a magnified fragment with readable reflexes of Ga₂Se₃ seeds (pointed by arrows) for Bi1 sample.



Figure 2.17. SEM-EDS micrographs of fresh fracture of Bi10 sample, showing Ga_2Se_3 crystallites embedded into the residual vitreous matrix (a), and presumably $Bi_2Se_xTe_{3-x}$ crystalline inclusions in the form of lamellae-like structure (b).

If not crystalline and partially-ordered inclusions, then the vitreous matrix itself should be examined towards the possible reason for giant light attenuation in Bi5 sample, as shown further (subchapter 2.3.8). Since glassy state is characterized by the absence of LRO in atomic arrangements, the MRO and SRO are to be studied. Information on the MRO can be obtained by FSDP analysis, observed at around ~ 1 Å⁻¹ in S(Q) structure factor of Bi1 and Bi5 glasses determined from both synchrotron X-ray scattering and NS data (Table 2.4, Figure 2.18).

		FSDP					Peak 1			
	Sample	Q	FWHM	Area	L	Q	FWHM	Area		
		(Å-1)	(Å-1)	(a.u.)	(nm)	(Å-1)	(Å-1)	(a.u.)		
NS	Bi1	1.028	0.247	0.057	2.54	2.048	0.409	0.518		
	Bi5	1.023	0.252	0.052	2.49	2.051	0.408	0.441		
	Bi10	1.023	n/a	n/a	n/a	-	-	-		
XRD	Bi1	1.071	0.257	0.035	2.44	2.026	0.415	0.543		
	Bi5	1.051	0.262	0.037	2.40	2.032	0.425	0.605		
	Bi10	1.048	n/a	n/a	n/a	-	_	-		

Table 2.4. The FSDP (pre-peak) and first principal diffraction peak (Peak 1) parameters determined from synchrotron X-ray and neutron scattering data per Gaussians' fit.



Figure 2.18. Neutron scattering (NS) and X-ray scattering results. Structure factors S(Q) as obtained from NS and synchrotron X-ray scattering data for the investigated samples show the overall vitreous nature of Bi1 and Bi5 samples and the number of crystalline reflexes in Bi10 sample. Inserts show the region with the FSDP and first principal structural peak after background subtraction, fitted with Gaussians.

If we assume that FSDP in glass originates from some kind of periodicity in real space, like crystalline Bragg peaks but at the medium range order scale, it is possible to estimate size of such regions using the Scherrer-like equation $L \cong 2\pi / \Delta Q$ [Å], where ΔQ is FWHM of the FSDP. The estimated dimensions of such regions from the FWHM of FSDP measured for Bi1 and Bi5 samples are within the range of 2.4 – 2.5 nm (Table 2.4). They are lower than the

average size of partially-ordered regions (~5 nm in diameter) observed with TEM (Figure 2.19), which interlayer distance ~0.314 nm (determined from electron diffraction pattern presented on Figure 2.20) roughly corresponds to d (h k l)=d (0 1 5) of Bi₂Se_{1.5}Te_{1.5} crystal [35,36].



Figure 2.19. Elemental scanning TEM images. Top-left picture shows STEM HAADF image, top-right picture shows STEM bright field image of ~100 nm crystalline inclusions found in Bi1 sample. The chemical composition mapping of Se, Ga, Te, Ge, and Bi elements across such region (bottom panels) allows us to identify these inclusions as Ga₂Se₃ seeds.

Although the FSDP has more complicated origin than just the size of partially-ordered fragments and cannot be described explicitly by only one structural parameter (degree of density fluctuations, disorder ratio, etc.), the similarity of the FSDP parameters for Bi1 and Bi5 samples suggests that there is no significant structural difference between these two vitreous matrices at the medium range order scale. So, if the opacity of Bi5 sample is caused by atomic arrangement, the short-range order has to be further examined.

semiconductive applications



Figure 2.20. High-resolution TEM image of the typical small partially-ordered region observed in Bi1 and Bi5 samples. The electron diffraction pattern gives interlayer distance ~0.314 nm, which roughly corresponds to $d (h \ k \ l) = d (0 \ 1 \ 5)$ of Bi₂Se_{1.5}Te_{1.5} crystal [35,36].

2.3.7. Nanomechanical properties mapping for Bi, Ga-modified GTS-s alloys

The CSM Instruments nanoindenter equipped with Berkovich-type pyramidal diamond tip (with a radius of ~100 nm) was used to determine the values of nanohardness and reduced elastic modulus (the Young's modulus E). Before the measurements, the nanoindenter was calibrated using a standard sample of fused silica with an elastic modulus of 73 GPa and Poisson's ratio of 0.17. Such calibration allowed reliable load and displacement resolution at the level of 10 nN and 0.1 nm, respectively. The load-displacement curves were recorded simultaneously, using a 20 mN/min loading-unloading rate and 15 s dwell time at maximum load of 10 mN. Data analysis was performed using the Oliver-Pharr method (see Chapter 1). The surface of tested samples (polished before the measurements) was scanned in five randomly selected locations. At least five nanoindentation measurements were performed at each location. Such experimental measuring protocol allows a quite acceptable locality of each

measuring test, eliminating influence of indentation-size effects. The values of nanohardness H and Young's modulus E were statistically averaged. All nanoindenter fingerprints were observed by an optical microscope and additionally characterized by an atomic force microscope (AFM) in non-contact mode, both integrated with CSM UNHT system.

Initially, using the classical Archimedes' Law-based method, it has been established that the increased devitrification ability may be caused by the addition of Bi into Ga-containing (GeSe₄)-(GeTe₄) glasses what leads to a general increase in their density (Table 2.1). The nanohardness H, and Young's modulus E, obtained through nanoindentation measurements (Figure 2.21) follow the same trend while going from Bi1 to Bi5 sample, e.g. both these parameters show a slight increase with Bi content: H increases from 3.02 GPa in Bi1 to 3.25 GPa in Bi5, E increases from 28.73 GPa in Bi1 to 30.43 GPa in Bi5 (Table 2.5).

Sample	Planned chemical formula	H (GPa)	E (GPa)
Bi1	Bi1Ga5Ge18.8Se37.6Te37.6	3.02 ± 0.02	28.73 ± 0.14
Bi5	Bi5Ga5Ge18Se36Te36	3.25 ± 0.02	30.43 ± 0.01
Bi10	Bi ₁₀ Ga ₅ Ge ₁₇ Se ₃₄ Te ₃₄	3.17 ± 0.15 (dark area) 2.26 ± 0.10 (bright area)	28.25 ± 0.84 (dark area) 27.86 ± 1.03 (bright area)

Table 2.5. Nanohardness H and Young's modulus E of studied materials.

The deviations in H and E values for Bi1 and Bi5 were quite small (< 0.5%) for different tested locations, which confirms good macroscopic homogeneity of Bi1 and Bi5 glasses and also an absence of macroscopic voids (like bubbles, etc.) or significant density fluctuations. Results of nanoindentation measurements for Bi10 sample are more scattered, being considerably different for two observed regions arbitrary named as "bright area" and "dark area" (Figure 2.21c). The average nanohardness H=3.17 \pm 0.15 GPa obtained from the imprints in the "dark area" (imprints 4, 5, and 6 in Figure 2.21c), correlates well with the values for Bi1 and Bi5 samples. Therefore, the "dark area" can be identified as the remaining amorphous matrix of Bi10 sample.

Such a matrix has a significant elastic component of the deformation, which can be ascertained from AFM image: depth of the indentation imprint for the "dark region" is ~215 nm (Figure 2.22), while nanoindenter was intruded into the sample for ~500 nm.



Figure 2.21. Nanoindenter fingerprints (a, b, c) and load-displacement curves (d) showing 5 fingerprints for Bi1 sample (a), 5 fingerprints for Bi5 sample (b), and 3 fingerprints in the "dark area" and 3 fingerprints in the "bright area" for Bi10 surface (c).

The average value of nanohardness H= 2.26 ± 0.10 GPa obtained for the imprints in the "bright area" (imprints 1, 2 and 3 in Figure 2.21c) is lower than for the host vitreous matrix and Ga₂Se₃ crystals (H= 3.6 ± 0.7 GPa), but higher than for Bi₂Te₃ (H= 1.6 ± 0.2 GPa) and Bi₂Se₃ (H= 0.9 ± 0.1 GPa) single crystals [37,38]. Therefore, the origin of "bright area" can be guessed as the regions with smashed by polishing Ga₂Se₃ and Bi₂Se_xTe_{3-x} crystallites, similar to those visible on a fresh fracture of Bi10 sample in Figure 2.17.



Figure 2.22. AFM image demonstrates the approximate depth of the indentation.

2.3.8. Optical transmission of studied Bi, Ga-modified GTS-s matrices

The optical properties have been measured with a Bruker Vertex 70 V spectrometer. The optical transmittance window for Bi1 sample extends from \sim 3 µm to \sim 16 µm (Figure 2.23a) without any signature of significant impurities. It is a typical transmission for purified amorphous chalcogenide semiconductors of that kind [39,40]. On the other hand, the Bi5 and Bi10 samples do not transmit electromagnetic radiation within this range (transmission is<1% for ~2mm thick Bi5 sample, see Figure 2.23b). The multiple samples of each composition were used to confirm the reproducibility of the results.



Figure 2.23. Optical transmission spectra of (a) Bi1 and (b) Bi5 glasses. Insert (a) shows the Tauc plot for the Bi1 sample, obtained with PARAV software [43] to estimate optical gap E_{og} . Insert (b) shows the attenuation calculated for Bi5 glass, using various thicknesses samples.

The non-transparency of Bi10 sample can be well explained by prevailing scattering of the light on crystalline inclusions of ~500 nm size and larger (Figure 2.17), while the giant attenuation effect observed in Bi5 sample [40] cannot be attributed solely to this mechanism. The reason is that only partially-ordered regions of about ~5 nm dimensions (like quantum dots) can be observed with TEM in Bi5 sample, which is not enough to cause a significant Mie or Rayleigh scattering for IR light [41,42]. Moreover, similar partially-ordered ~5 nm-sized regions (though more rarely distributed) and even more extended ~100 nm Ga₂Se₃ seeds have been identified in Bi1 sample using TEM scanning elemental analysis (Figure 2.19). The existence of Ga₂Se₃ seeds in Bi1 sample can also explain slight crystalline-like reflexes on top of the overall amorphous synchrotron XRD pattern (see insert to Figure 2.16). The above inclusions, however, do not cause the opacity of Bi1 sample (Figure 2.23a), while Bi5 sample, which on the other hand does not contain the larger ~100 nm seeds, is completely opaque (Figure 2.23b). Initial data on transmission properties of Bi-containing GTS-s alloys gave us basis for further insightful research on high attenuation loss especially focusing on sample Bi5.

While the non-transparency of the Bi10 sample can be well explained by prevailing scattering of the light on crystalline inclusions of \sim 500 nm size and larger (Figure 2.24) the negligible transparency of the Bi5 sample (Figure 2.24b) cannot rely on the same mechanism since no such inclusions were found either with XRD or with electron microscopies.

Only partially ordered regions with estimated dimensions of about ~ 5 nm were observed in this sample with TEM (Figure 2.24b). They are embedded in the vitreous matrix and occur at roughly the same distances from each other. However, scattering from these regions cannot account for the full opacity of ~ 2 mm thick Bi5 glass to the electromagnetic radiation, because their size is too small to cause any significant Mie or Rayleigh scattering in an IR region [40,44].

Moreover, similar partially ordered regions (though more rarely distributed) exist in the Bi1 sample too (Figure 2.24c), which is well transparent in a $\sim 3 - 16 \mu m$ wavelength range (Figure 2.23a) with an optical gap estimated as 0.75 eV (Table 2.6) using a Tauc plot and PARAV software [43]. If not scattering, the absorption and reflection mechanisms are to be considered. If we had a lot of free electrons in the Bi5 sample, then it would behave like a conducting medium (reflecting and absorbing, rather than transmitting), and that would explain the low transmittance of IR radiation.

Table 2.6. Density ρ , molar volume V_m , activation energy of DC conductivity E_{DC} , and estimated optical gap E_g^o for $Bi_xGa_5(Ge_{0.2}Se_{0.8})_{50-(x+5)/2}(Ge_{0.2}Te_{0.8})_{50-(x+5)/2}$ samples.

Sample	Planned Composition	ρ, g/cmP ³	V _m , cmP ³ P/mol	E _{DC} , eV	E_{g}^{o} , eV
Bi1	Bi1Ga5Ge18.8Se37.6Te37.6	5.083±0.005	19.06±0.09	0.46±0.03	0.75±0.05
Bi5	Bi ₅ Ga ₅ Ge ₁₈ Se ₃₆ Te ₃₆	5.345±0.005	18.97±0.09	0.48±0.03	n/a
Bi10	$Bi_{10}Ga_5Ge_{17}Se_{34}Te_{34}$	5.624±0.005	19.02±0.09	n/a	n/a



Figure 2.24. SEM image of Bi10 (a), and TEM images of Bi5 (b) and Bi1 (c) samples. The nanoscale partially ordered regions are circled.

However, the electric properties and activation energies of conductivity are nearly the same for Bi5 and Bi1 samples, being typical for narrow-bandgap semiconductors. Reflection coefficient, measured for powdered samples with attenuated total reflection module of Bruker Vertex 70 spectrometer, is found to be smooth in the whole $1 - 27 \mu m$ wavelengths interval, and its value was even lower for the Bi5 sample, compared to the Bi1 sample (the transparent one). Thus, the mechanism should rely entirely on the absorption within the glass bulk. To characterize the absorption, transmission spectra for Bi5 samples of different thicknesses were measured, and the attenuation coefficient was calculated (insert to Figure 2.23b). It is found to be remarkably high (>10 dB/mm) in a broad IR range, comparable to the value of commercial attenuation effect in the Bi5 sample still needs to be established, it is connected with the presence of Bi and/or randomly oriented partially ordered nanostructured regions. The latter also could be responsible for the observed peak in the attenuation coefficient spectrum near ~4 μm (insert to Figure 2.23b), if considered as quantum dots of ~5 nm dimensions.

In conclusion, the narrow-bandgap semiconductor medium with an extremely high attenuation coefficient in a wide IR region of the spectra was fabricated. Small changes in the Bi concentration allowed us to fabricate ~millimeter thick fully transparent or fully opaque in $\sim 3 - 16 \mu m$ wavelength range semiconducting optical media. The materials show great potential as a universal matrix for various IR applications, such as IR protective semiconducting coating, optical attenuators, and IR sensors.

2.3.9. Electrical properties and preliminary scope for thermoelectric behavior

The electrical conductivity (DC), measured in 200–500 K range using carbon electrodes and a computer-controlled Hioki IM3536 LCR impedance analyzer (4 Hz–8 MHz frequency), changes from a value typical for semiconductors in Bi1 and Bi5 glasses (see Figure 2.25a), to one of the conductors in the Bi10 sample (see Figure 2.25b). The activation energies of DC conductivity, determined as a slope of $ln(\sigma_{DC})$ versus 1000/T dependence for higher temperatures, are listed in Table 2.6 for Bi1 and Bi5 glasses.

As it may be deduced from a preliminary study of Bi5 alloy in terms of Seebeck coefficient vs T, as well as resistivity changes vs T, the Bi5 sample, which has been additionally

annealed in an inert gas atmosphere for 20 hours at 180 °C shows as suspected n-type semiconductivity often reported for Bi-Se-Te crystalline compounds. Measurement has been carried out using self-made apparatus equipped with a thermally-isolated sample compartment keeping a thorough soldering approach of electrical contacts enabling for $\Delta V/K$ and resistivity $[\Omega \cdot m]$ measurements. Despite special care for the creation of good electrical contact, resistivity measurement seems to reflect a need for improvement due to large signal fluctuations in the low-temperature range (see Figure 2.26).



Figure 2.25. DC conductivity for as-synthesized $Bi_xGa_5(Ge_{0.2}Se_{0.8})_{50-(x+5)/2}(Ge_{0.2}Te_{0.8})_{50-(x+5)/2}$



Figure 2.26. Electrical transport properties: (a) Seebeck coefficient, S; (b) Electrical resistivity, σ *of Bi5 alloy - inset photo shows approximate dimensions of a sample.*

Under aforementioned circumstance Bi5 alloy (annealed to induce crystallization) as dominantly by volume amorphous material has large resistivity which directly affects its Seebeck coefficient. According to preliminary status for electrical measurements, giant resistivity measured for as-prepared Bi1 and Bi5 alloys reaching $10^5 \Omega \cdot m$ at room temperature. Significant decrease caused by devitrifying annealing of Bi5 leading to $10^3 \Omega \cdot m$ (measurement with high uncertainty – (see Figure 2.26b) collected with self-designed TE apparatus). Result of the same order of magnitude obtained applying more precise four-point probe device equipped with Keithley source.

Volt-Ampere characteristics presenting the influence of annealing on resistivity measured with the four-point probe method are listed in Table 2.7. Measured values represent only measurements done at the highest possible current applied to the sample as the most relevant records.

Table 2.7. Volt-Ampere measurements collected with the use of four-point probe method for *Bi5 as-prepared and post-annealed.*

	Bi5 as-prepared	Bi5 ann. for 10h	Bi5 ann. for 20h
Current [µA]	0.002	0.1	0.5
Voltage [mV]	60	233	196
Resistivity $[\Omega \cdot m]$	$2.7 \cdot 10^5$	$2.1 \cdot 10^4$	$3.5 \cdot 10^3$

Poor TE properties obtained via the presented approach of free annealing at 180°C indicate that thermal treatment would be provided more radically - at a higher temperature. In addition, ramping up to the selected temperature should not be performed too rapidly. Another way in which the sample would be treated pursuing the goal of TE chalcogenide glass-ceramic could be annealing with the maintenance of inhomogeneous thermal distribution through the block of glass creating directional crystallization. For a more insightful study of the subject, consequently, further experimentation should be provided - concentrated on different annealing methods with constant monitoring of microstructure by SEM and IR microscopy, as well as nanostructure using TEM for better understanding of crystal growth behavior. Of special interest would be an investigation of the volumetric ratio of the crystalline component relatively to the amorphous matrix.

2.3.10. Summary

Research performed on the GTS-alloys (modified with Bi and Ga) with a symmetric atomic ratio of chalcogen components revealed several interesting features. These materials possess complex crystallization behavior what can be deduced from DSC analyses with implemented Frazer-Suzuki mathematical approach, indicating at least five separate crystallization processes caused by heating up to 350°C.

In the foreground, at the low-temperature region, one may observe crystallization peaks originating from semiconductive phases of $Bi_2Se_xTe_{3-x}$ solid solutions. Such information is essential to obtain an appropriate protocol for heat treatment in terms of fostering the formation of these semiconductive crystals. As-prepared, by means of the melt-quench process, alloys conserve their amorphousness while keeping content of Bi below 5 at.%, whereas optical properties of Bi5 sample suggest beginning of at least aggregation or even crystallization processes at nanoscale caused by classical annealing at the temperature below glass-transition temperature T_g of the glassy component.

Noteworthy, that was evidenced by volume, the crystallization like in the case of Bi10 alloy obtained through melt-quench method leads to polycrystalline nature of as-prepared alloy with concentric large, multi-phase grains extending on the whole radius of chalcogenide rod, what seems to exclude such material as technologically-beneficial, regarding its disastrous mechanical properties and inability to get homogeneous, bulk prefabricate.

On the other hand, the as-prepared Bi10 sample exhibited the highest level of Se incorporation (at the expense of Te) into Bi₂Se_xTe_{3-x} phase, reaching a ratio at.%_{Se} / at.%_{Te} \approx 1/3. Furthermore, the post-annealed Bi10 sample reveals disconnection of Se from TE phase, changing the ratio of chalcogens at.%_{Se} / at.%_{Te} \approx 1/5.

A tendency to increase the ability for the substitution of Se by Te is more pronounced for Bi1 and Bi5 samples. Simultaneously, at this stage, it is difficult to predict which kind of phase could be beneficial for certain semiconductor applications.

2.4. $Bi_xSb_{10-x}Ga_5Ge_{20}Se_{45}Te_{20}$ alloys with chalcogenide ratio Te/Se = 0.4

2.4.1. Synthesis, investigation of chemical composition and amorphousness

The Bi_xGa₅Ge₂₀Sb_{10-x}Se₄₅Te₂₀ (x = 1,3,5,10) glasses were prepared by conventional melt quenching technique using high-purity Ga, Bi, Sb, Ge, Se, and Te precursors (5N or more). Alloys were homogenized for 12 h at 900 °C, quenched into room-temperature water from 700 °C and annealed for 3 h at ~30 °C below the glass transition temperature [45].

An overall glassy was confirmed by the absence of crystalline reflexes in their XRD patterns (Figure 2.27a). Nevertheless, some minor reflexes have been noticed in the XRD pattern of Bi₁₀Ga₅Ge₂₀Se₄₅Te₂₀ sample (Figure 2.27a), which could be attributed to the formation of small-size nucleation sites. The homogeneity and actual compositions of the prepared materials Ga₅Ge₂₀Sb₁₀Se₄₅Te₂₀ (SBi0), Bi₁Ga₅Ge₂₀Sb₉Se₄₅Te₂₀ (SBi1), Bi₃Ga₅Ge₂₀Sb₇Se₄₅Te₂₀ (SBi3), Bi₅Ga₅Ge₂₀Sb₅Se₄₅Te₂₀ (SBi5) and Bi₁₀Ga₅Ge₂₀Se₄₅Te₂₀ (SBi10) were verified by SEM-EDS, and X-ray photoelectron spectroscopy (XPS).



*Figure 2.27. High-energy XRD patterns of the studied Bi*_x*Ga*₅*Ge*₂₀*Sb*_{10-x}*Se*₄₅*Te*₂₀ *glasses a); SEM picture of a fresh cleave of as-prepared SBi10 sample b).*

No significant impurities or deviations (more than ± 1 at.%) from nominal compositions have been found, as well as no significant inhomogeneities have been detected through SEM (Figure 2.27b). The high-energy XRD experiment was performed at the beamline 11-ID-B, Advanced Photon Source, Argonne National Laboratory, using X-rays with wavelength 0.2127Å and position-sensitive Perkin Elmer amorphous silicon image plate detector.

2.4.2. Thermodynamic properties of Bi, Sb-doped, Ga-containing GTS alloys

The DSC thermograms of the investigated glasses recorded at different heating rates q = 2, 5, 10, 20, 30 K/min show glass transition (Figure 2.28) and crystallization (Figure 2.29) features in all cases. The onset temperature of the glass transition T_g^{on} , and the peak temperature of the first crystallization process T_x (both values determined for 10 K/min DSC runs) were used to calculate Dietzel criterion of glass stability $\Delta T = T_x - T_g^{on}$ shown in Table 2.8. It is found that T_g value as determined from DSC heating curves does not change significantly with Bi addition ($T_g = 230 \pm 2$ °C for 10 K/min runs), except the noticeable decrease for SBi10 sample ($T_g \sim 220$ °C). The glass stability criterion ΔT is shown to be higher then for Bi_xGa₅(Ge_{0.2}Se_{0.8})_{50-(x+5)/2}(Ge_{0.2}Te_{0.8})_{50-(x+5)/2} glasses (see subchapter 2.3)



Figure 2.28. DSC scans at different heating rates for $Bi_xGa_5Ge_{20}Sb_{10-x}Se_{45}Te_{20}$ alloys, showing the glass transition region.

Sample	Planned chemical formula	ρ, g/cm ³ (±0.005)	T ^{on} , ℃ (±1)	T _x , °C (±1)	ΔT, °C (±2)	E _{Tg} , kJ/mol (±50)	Eg ^o , eV (±0.05)
SBi0	$Ga_5Ge_{20}Sb_{10}Se_{45}Te_{20}$	4.983	231	381	150	310	1.00
SBi1	Bi1Ga5Ge20Sb9Se45Te20	5.043	230	373	143	630	0.85
SBi3	Bi ₃ Ga ₅ Ge ₂₀ Sb ₇ Se ₄₅ Te ₂₀	5.100	228	346	118	510	0.80
SBi5	Bi ₅ Ga ₅ Ge ₂₀ Sb ₅ Se ₄₅ Te ₂₀	5.226	229	303	74	360	0.71
SBi10	Bi10Ga5Ge20Se45Te20	5.441	218	261	43	282	n/a

Table 2.8. Density, thermodynamic parameters, activation energies of viscous flow E_{T_g} and estimated optical gap E_g of the investigated $Bi_xGa_5Ge_{20}Sb_{10-x}Se_{45}Te_{20}$ alloys.



Figure 2.29. DSC scans at different heating rates for $Bi_xGa_5Ge_{20}Sb_{10-x}Se_{45}Te_{20}$ alloys, showing the crystallization region.

The activation energy of viscous flow E_{Tg} , determined using the Ozawa method from the data in Figure 2.29, demonstrates a maximum in composition dependence at ~ 1 - 2 at.% of Bi (Table 2.8). The density of glass measured by the Archimedes' method increases (Table 2.8) and the glass becomes less stable (smaller Δ T values) when Sb is substituted with Bi, the most unstable being the Bi10 composition with 10 at.% of Bi content. For the samples with low Bi content (x < 5 at.%) one family of crystallization peaks is observed, while for SBi5 and SBi10 samples the low-temperature crystallization emerges (Figure 2.29).

Fraser-Suzuki fits of DSC heating curves (Figure 2.30) suggests the crystallization of at least 2 phases for the Bi-free sample (SBi0 composition).



Figure 2.30. Fraser-Suzuki fittings for DSC curves of Ga₅Ge₂₀Sb₁₀Se₄₅Te₂₀ (SBi0), Bi₁Ga₅Ge₂₀Sb₉Se₄₅Te₂₀ (SBi1), Bi₃Ga₅Ge₂₀Sb₇Se₄₅Te₂₀ (SBi3), Bi₅Ga₅Ge₂₀Sb₅Se₄₅Te₂₀ (SBi5) and Bi₁₀Ga₅Ge₂₀Se₄₅Te₂₀ (SBi10) samples recorded at 5 K/min heating rate.

For intermediate Bi concentration samples (SBi1, SBi3, and SBi5 compositions) at least 3 crystallization phases could be identified with Fraser-Suzuki fits (Figure 2.30), while in case of SBi10 sample as many as 5 phases are observed.

It should be noted, however that shape of real crystallization peaks can be more complicated than Fraser-Suzuki form and usually depends on the crystallizing phase [46]. So, the proposed fits should be considered as idealized models with precautions, especially if there are weak shoulders that can be obscured by an asymmetric form of Frazer-Suzuki function.

They are, however, our best estimates (due to the overlapped crystallization processes of unknown nature) to determine the crystallization temperatures and activation energies of crystallization processes (see Figure 2.30).

2.4.3. Summary

The investigated $Bi_xSb_{10-x}Ga_5Ge_{20}Se_{45}Te_{20}$ alloys with chalcogenide ratio Te/Se = 0.4 shown to be suitable for the incorporation of quite high concentration of Bi keeping the glassy state. With Bi addition, the increase in density and decrease in glass transition and glass stability criterion is observed. Nevertheless, the T_g of all investigated samples (including SBi10) is higher than 200°C, which makes these glasses attractive for applications in many IR instruments.

Analysis of the crystallization kinetics reveals only a few crystallization processes which can be described with JMA model, while the majority of them do not pass JMA applicability test (at least per Frazer-Suzuki fits). Glass-ceramics formation by crystallization becomes more rapid in Bi-rich glasses.

The nature of the crystallizing phases in each case requires further relevant investigations using a combination of Raman/IR spectroscopy, SEM, XRD analysis, and such complementary structural probes as XPS and EXAFS. Nevertheless, on the basis of previous studies, we expect that in the low-temperature region the predominant crystallization of Bi-based compounds (like Bi₂Te₃, Bi₂Se₃ or Bi₂SeTe₂) should occur. In the high-temperature range beyond ~320°C, the crystallization processes should rely mostly on the crystallization of stable Ge- and Sb-based chalcogenide phases.

2.5. Substitution of Phosphorus by Bismuth in Ga-containing GTS matrix (chalcogenide ratio Te/Se = 0.4)

2.5.1. Synthesis, investigation of chemical composition and amorphousness

The ChG of $Bi_xGa_5Ge_{20}P_{10-x}Se_{45}Te_{20}$ alloys (Table 2.9) were prepared by conventional melt quenching technique. The appropriate amount of high-purity (5N or more) Ga, Bi, P, Ge, Se, and Te precursors (~20 g in total) were heated up to 900 °C, homogenized for ~10 hours at 800 °C, and quenched into water from 650 °C. To relieve the mechanical strains that appeared during quenching, glasses were annealed at ~30 °C below the glass transition temperature for 3 h. Then, the ingots were cut (and polished when necessary) for the measurements [47].

The overall glassy state of the obtained materials was confirmed by the absence of crystalline reflexes in the XRD patterns of as-prepared samples (Figure 2.31) studied using the X-ray diffractometer PANalytical X'Pert Pro (Cu K α radiation with λ =1.5418 Å).



Figure 2.31. SEM images of representative regions in RP-3 and RP-10 samples with EDS analysis of the composition a). XRD patterns of the investigated glasses b).

The homogeneity and actual compositions of the prepared $Bi_xGa_5Ge_{20}P_{10-x}Se_{45}Te_{20}$ (x=0,1,3,5,7,10) glasses were verified by SEM-EDS technic using FEI Helios NanoLab 650 microscope. No significant deviations (more than ±2 at.%) from nominal compositions have been found, and no significant inhomogeneities have been detected through SEM study (Figure 2.31a).

2.5.2. Thermodynamic properties of P-,Bi-doped Ga-containing GTS alloys

The DSC thermograms of the investigated P-containing ChG recorded at different heating rates q = 2, 5, 10, 15, 20, 30 K/min (Figure 2.32) may be used to estimate the activation energy of viscous flow, E_{Tg} , employing, for example, the Ozawa method [28]. As it is obvious from the obtained results, the thermally annealed samples do not show any strong compositional dependence of E_{Tg} , except for RP-10 sample where E_{Tg} has its maximum (Table 2.9).

The density measured by the Archimedes' method, on the other hand, decreases by ~5-8 % when Sb is substituted with P, and shows a strong dependence on Bi, increasing with Bi content in both families (see Table 2.9).

Table 2.9. Density, thermodynamic parameters, activation energies of viscous flow E_{Tg} and estimated optical gap E_g of the investigated $Bi_xGa_5Ge_{20}P_{10-x}Se_{45}Te_{20}$ alloys. Corresponding values of the same parameters determined for isocompositional $Bi_xGa_5Ge_{20}Sb_{10-x}Se_{45}Te_{20}$ glasses (see subchapter 2.4.2) are given in square brackets for comparison.

Ref.	Planned chemical formula	ρ, g/cm ³ (±0.005)	<i>T_g^{on}</i> , ^o C (±1)	T _x , °C (±1)	Δ <i>T</i> , °C (±2)	$E_{Tg},$ kJ/mol (±50)	Eg, eV (±0.05)
RP-0	$Bi_{10}Ga_5Ge_{20}Se_{45}Te_{20}$	5.441	218	261	43	280	n/a
RP-3	Bi7Ga5Ge20P3Se45Te20	5.212	217	301	84	270	0.69
RP-5	Bi ₅ Ga ₅ Ge ₂₀ P ₅ Se ₄₅ Te ₂₀	5.042 [5.226]	215 [229]	357	142 [74]	280	0.76 [0.71]
RP-7	Bi ₃ Ga ₅ Ge ₂₀ P ₇ Se ₄₅ Te ₂₀	4.858 [5.100]	214 [228]	n/a	n/a [118]	270	0.80 [0.80]
RP-9	Bi ₁ Ga ₅ Ge ₂₀ P ₉ Se ₄₅ Te ₂₀	4.671 [5.043]	213 [230]	n/a	n/a [143]	270	0.91 [0.85]
RP-10	$Ga_5Ge_{20}P_{10}Se_{45}Te_{20}$	4.575 [4.983]	215 [231]	n/a	n/a [150]	400	1.01 [1.00]



Figure 2.32. Non-isothermal (RP-0, RP-3, RP-5) and isothermal (RP-7, RP-9, RP-10) DSC scans for Bi_xGa₅Ge₂₀P_{10-x}Se₄₅Te₂₀ glasses, showing crystallization.

The onset temperature of the glass transition T_g^{on} and the peak temperature of the first crystallization process T_c (determined from 10 K/min DSC runs) were used to calculate Dietzel criterion of glass stability $\Delta T = T_c - T_g^{on}$. The glass stability according to Dietzel criterion generally increases with substitution of Sb or Bi with P, losing its meaning for the glasses with P content more than 5 at.% (x < 5) due to the disappearance of crystallization peaks in DSC heating mode. So, we can conclude, that higher P content in the composition leads to enhanced stability of the glass phase depressing nucleation and crystal growth processes.

On the other hand, the density of glass increases, and the glass becomes less stable (smaller ΔT values) when Sb or P is substituted with Bi (see Table 2.2, 2.8), the most unstable being the RP-0 with 10 at.% of Bi content (it is still a glass, according to XRD, Figure 2.31b).

In the samples with higher Bi content (x > 5), two families of crystallization peaks are observed, which merge into a single broad complex peak in RP-5 glass (Figure 2.32). The RP-7, RP-9, and RP-10 samples do not show considerable crystallization peaks during regular DSC heating scans, but crystallization can be observed using isothermal DSC mode (Figure 2.32).

Fraser-Suzuki fits of non-isothermal and isothermal DSC curves (Figure 2.33) suggest crystallization of at least five phases for RP-0 glass (which may contain Bi-based nuclei and nanocrystallites), three for RP-3, RP-5, RP-7 and RP-9 glasses, and two in RP-10 sample.



Figure 2.33. Fraser-Suzuki fittings for non-isothermal (RP-0, RP-3, RP-5) and isothermal (RP-7, RP-9, RP-10) crystallization DSC curves of Bi_xGa₅Ge₂₀P_{10-x}Se₄₅Te₂₀ glasses.

It should be noted, that shape of real crystallization peaks can be more complicated than Fraser-Suzuki form depending on the nature of the crystallizing phase, but such a fit is considered the best estimate to determine crystallization temperatures and activation energies of overlapped crystallization processes of unknown nature.

2.5.3. Optical transmission of P/Bi substituted GTS alloys

The optical properties of the P-containing ChG are consistent with those of the same family chalcogenides [45,48,49]. The optical transmittance window extends from ~2 to ~16 μ m (Figure 2.34a), showing some absorption bands in ~2 – 4 μ m range caused by the atmospheric contaminations (water vapor and CO₂, on the first hand), weak impurity absorption at ~4.5 μ m due to Se–H vibrations [50], and a broad ~8 – 11 μ m absorption feature of complex origin.



Figure 2.34. Optical transmission (a) and absorption coefficient (b) spectra of studied glasses (*RP-0 sample is not shown due to complete opacity in this region*).

The latter includes contributions from oxygen-containing impurity complexes (P–O, Ge–O) [50,51], as well as possible intrinsic absorption from mixed P-Ga-Ge environment [52]. The apparent longwave shift of multiphonon cut-off is due to a substitution of P by heavier Bi. Optical transmission in the fundamental optical absorption edge region was used to calculate the absorption coefficient (Figure 2.34b) and estimate the optical gap (Table 2.9) using Tauc plot and PARAV program [43]. The obtained data show that substitution of P with Bi in glass composition leads to decrease in optical gap (Table 2.9), as was also observed previously in similar Bi-containing ChG [45]. It is interesting to note, though, that estimated optical gap values of the investigated P-containing ChG are comparable with those of isocompositional Sb-containing ones (Table 2.9, values in square brackets) [45], preserving a general trend on Bi concentration dependence (RP-0 sample being opaque). So, it can be concluded that Sb and P both have a smaller impact on the optical gap, than Bi.

2.5.4. Anti-Arrhenius behavior of P-rich GTS alloys

The estimated activation energies (E_a) of crystallization are presented in Table 2.10 for all resolved peaks. In the case of non-isothermal crystallization, the ln (q) vs $10^3/T_c$ dependences were used, while for isothermal kinetics the activation energies were estimated using ln (t_c) vs $10^3/T_i$ dependences (t_c is the time of the crystallization peak occurring at T_i isothermal temperature) [47]. Although at this point it is not possible to derive strict compositional regularities, because it is not obvious that all numbered peaks in Table 2.10 represent the same crystallizing phases in different samples, some conclusions can still be drawn.

E _a Planned composition	Peak I kJ/mole	Peak II kJ/mole	Peak III kJ/mole	Peak IV kJ/mole	Peak V kJ/mole
BinggarGeogSenaTeog	(± 3)	(±3)	(±3) 300	(± 3)	$\frac{(\pm 3)}{242}$
	271	205	500	220	242
Bi ₇ Ga ₅ Ge ₂₀ P ₃ Se ₄₅ Te ₂₀	87	70	51		
Bi5Ga5Ge20P5Se45Te20	47	47	57		
Bi ₃ Ga ₅ Ge ₂₀ P ₇ Se ₄₅ Te ₂₀	102	112	128		
$Bi_1Ga_5Ge_{20}P_9Se_{45}Te_{20}$	-90	-136	116		
$Ga_5Ge_{20}P_{10}Se_{45}Te_{20}$	142	144			

Table 2.10. The average activation energy of crystallization E_a calculated for the investigated materials using the Ozawa's plots.

First of all, the replacement of Bi with P in composition (compare RP-0 and RP-10 glasses) leads to a decrease in the number of crystallizing phases and a drop in the crystallization activation energy. Glasses having both chemical elements in their structure demonstrate even smaller values of activation energies for crystallization (Table 2.10). Such a trend can be explained by an overall shift of the crystallization process to lower temperatures (as one goes from RP-5 to RP-0 glass), where higher viscosity of supercooled liquid imposes more constraints on structural rearrangements needed for crystallization to occur. A very distinct behavior has been recorded for crystallization activation energies of RP-9 glass (Table 2.10): two (for peaks I and II) out of three appear to be negative (anti-Arrhenius behavior). The negative apparent activation energy of crystallization is an interesting phenomenon observed in some polymer glass-formers, which is associated with the interplay between the free energy of nuclei formation and activation energy for diffusion across the phase boundary [53].

According to the nucleation theory proposed by Turnbull and Fisher [54] and discussed comprehensively by Wunderlich [55], the temperature dependence of the nucleation rate r is given by the followunf eq.:

$$r = r_0 e^{-\left(\frac{E_d}{RT} + \frac{\Delta F}{RT}\right)}$$
(2.7)

where r_0 is the preexponential factor, E_d is the activation energy for diffusion across the phase boundary, and ΔF is the maximum free energy needed for nucleus formation.

The ΔF and E_d exponential terms have opposite effects on the nucleation rate. The value of E_d is considered to be approximately constant [57], whereas ΔF is inversely proportional to the degree of supercooling [53]:

$$\Delta F \sim \frac{1}{\left(T - T_m\right)^2} \tag{2.8}$$

According to expression 2.16, the value of ΔF increases drastically when *T* approaches melting point T_m . In this case, the overall crystallization rate would be determined by the nucleation rate, in which temperature dependence is controlled by the temperature variation of ΔF . As it is evident from (2.8.), ΔF decreases when temperature departs from T_m , that causes ΔF exponential term in equation (2.7.) to increase, which, in turn, gives rise to the crystallization rate in close proximity to T_m [53]. This anti-Arrhenius behavior yields a negative value of the experimental (apparent) activation energy for the phases, in which crystallization temperature is close to the melting point T_m [53]. After ΔF drops below a certain value at further temperature decrease, the E_d exponential term in (2.7) becomes dominant, and then the nucleation rate is controlled by a transport process, which obeys regular Arrhenius temperature dependence.

So, the negative values of apparent activation energies for crystallization observed for peaks I and II of RP-9 glass can be explained by the close proximity of the crystallizing phases to their corresponding melting points, where crystallization rate is determined by the temperature dependence of free energy needed for nucleus formation.

2.5.5. Summary

The stability of ChG increases with P addition in glassy ($Bi_xGa_5Ge_{20}P_{10-x}Se_{45}Te_{20}$), and crystallization does not occur during regular DSC heating scans (q > 5 K/min) in the samples with x < 5. Non-isothermal and isothermal crystallization kinetics analyzed with Frazer-Suzuki fit function reveals negative apparent activation energy for crystallization of two phases in the x = 1 (RP-9) sample. This anti-Arrhenius behavior is explained by a dominant role of free energy of nucleus formation in the crystallization rate if crystallization occurs in proximity to melting points of these phases.

The activation energies of crystallization for the glasses with both P and Bi in their network are smaller than for the edge compositions with only Bi or P. This is consistent with the idea that an increase in E_a can be caused by a shift of the crystallization processes to lower temperatures. Owing to the obtained results, the developed P-containing glass matrix can be also considered as a good candidate for fiber drawing, which can be used in IR optics, photonics, and sensor applications.

2.6. Conclusions

The role of Ga and pnictogen atoms Sb, Bi, and P modification of the Ge-Te-Se matrix was first studied. The major topics embodied in this research being as follows:

- Thermodynamic characterization of synthesized alloys in order to establish the glass stability criteria and investigate the crystallization kinetics.
- Structural analysis of these alloys with respect to XRD, Raman spectroscopy, SEM and TEM methods in order to investigate the amorphous-crystalline nature of the samples as well as to establish the crystalline inclusion (phases).
- Preliminary investigation of electrical properties changes for the chosen as most potent Bi-containing GTS alloy caused with controlled thermal devitrification.

Two-fold effects caused by Ga-addition into Ge-Te-Se matrix.

Apart from described earlier impacts of Ga atoms on the increase of lanthanide solubility in ChG matrices other effects can be described. First of all, considering the pure materials science aspect of desired fully-amorphous material after synthesis Ga may act as "filler" in Ge-Te-Se glass structure in order not to saturate matrix with Bi, which immediately could cause crystallization. Contrariwise, Ga may also support homogeneous crystallization promoting a prior existence of Ga₂Se₃ hexagonal crystallites before exerting heterogeneous crystallization of Bi-containing TE phases. The distribution of such Ga₂Se₃ crystallites is expected to be random in chalcogenide alloys, which in turn may act as "skeleton" for heterogeneous crystallization of Bi-Se-Te phases (occurring at higher temperatures).

Bi, Ga-modified GTS alloys with symmetric chalcogenide ratio Te/Se = 1.

Considering the simplest compositional variation in this study, as of Ga-modified GTS alloys ($Bi_xGa_5(Ge_{0.2}Se_{0.8})_{50-(x+5)/2}(Ge_{0.2}Te_{0.8})_{50-(x+5)/2}$) with the matrix being modified by Bi, specifically sample Bi5 reveals the compositional edge for glass-forming window. Only sample with 10% of Bi ($Bi_{10}Ga_5Ge_{17}Se_{34}Te_{34}$) showed the presence of crystalline inclusions already after quenching. According to the DSC analysis, at least five different crystallization processes can be assumed in these glasses according to Gaussian and Fraser-Suzuki fits, three of which occur in *"low temperature domain"* (~210-300 °C) and the other two in *"high temperature domain"* (~320-370 °C). Activation energies for crystallization in low-temperature domain increase with Bi concentration and with decreasing the crystallization temperatures. Combination of XRD analysis together with Raman spectroscopy, SEM and TEM microscopies

allowed to establish the possible crystallization phases. In a low-temperature domain crystallization of Te, Bi₂Se_nTe_{3-n} (n = 0, 0.5, 1, 1.5, 2) and Ga₂Se₂Te phases is expected, while predominant crystallization of GeSeTe, GaGeTe and GeBi₂Te₄ phases has been assumed at higher (> 300 °C) temperatures. It was shown that as-prepared Bi10 sample exhibited the highest level of Se incorporation (at the expense of Te) into Bi₂Se_xTe_{3-x} phase, reaching a ratio at. $%_{Se}$ / at. $%_{Te} \approx 1/3$. Furthermore, the post-annealed Bi10 sample reveals disconnection of Se from TE phase, changing the ratio of chalcogens at. $%_{Se}$ / at. $%_{Te} \approx 1/5$.

IR light attenuation effect was observed in a Bi5 glass. Small changes in Bi content allowed to fabricate \sim mm thick glass fully transparent or fully opaque in \sim 3-16 µm region.

$Bi_xSb_{10-x}Ga_5Ge_{20}Se_{45}Te_{20}$ alloys with chalcogenide ratio Te/Se = 0.4

The investigated $Bi_xSb_{10-x}Ga_5Ge_{20}Se_{45}Te_{20}$ glasses shown to be suitable for the incorporation of quite high concentration of Bi keeping the glassy state. This matrix was shown to be more stable against crystallization (during Bi addition) in comparison to GTS alloys with symmetric chalcogenide ratio. However, as in all studied systems, with Bi addition, the decrease in glass transition and glass stability criterion is observed. Nevertheless, the T_g of all investigated samples (including SBi10) is higher than 200°C, which makes these glasses attractive for applications in many IR instruments.

DSC analysis of the crystallization kinetics reveals only a few crystallization processes which can be described with JMA model. The glass-ceramics formation by crystallization is shown to become more rapid in Bi-rich glasses.

P (Phospourus) as modifier for Ge-Te-Se-based ChG.

Generally, P-based glasses showed to be the most stable against crystallization during Bi addition. DSC analysis of the crystallization kinetics showed to be similar to the results obtained for $Bi_xSb_{10-x}Ga_5Ge_{20}Se_{45}Te_{20}$ system. Thus, P suppresses low-temperature crystallization between 240 – 300 °C, or even in parallel shifts and merges these two peaks to the high-temperature range at the onset of crystallization at ~ 330 °C into one peak, which is most probably attributed with Bi-Se-Te phase. Whereas remarkably, the most promising results obtained through Bi/P substitution are for RP-3 alloy (containing 7 at.% of Bi in composition), maintaining homogeneous amorphous structure regarding its evident n-IR – m-IR transmittance.

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Chapter 3. Chalcogenide glass matrices for IR fiber sensing applications

3.1. Introduction

As far as we know, the first note describing in detail the conception of biosensors operating on the evanescent wave absorption principle was reported in the U.S. (the patent from 1994 [1]). The construction of such a device was complicated, mainly regarding the necessity to encompass features like durability, multi-tasking, user-friendliness. The key aspect of this apparatus was to maintain an appropriate flow of molecular solution by the construction of special multiple channels causing the turbulent flow of the analyte located in the vicinity of the planar waveguide, maintaining high reproducibility of results and storage of many samples to measure each one separately. Looking further, the earliest scientific reports on ChG fiber evanescent wave sensors are from the late '1990s [2,3]. The main advantage of the detection unit with IR fiber is the possibility to perform *in-situ* and *in-vivo* measurements, which allows monitoring even dynamic processes like chemical or biological reactions. The most recent activity in this field concentrates on the introduction of RE elements into ChG fibers to obtain remote sources of IR light as fiber laser cavities, signal amplifiers specific FEWS sensors, etc.

The transmission window of ChG depends on the chalcogen dominantly present in the vitreous composition. Thus, S-based glasses, the lightest of the three chalcogens, are the ones that transmit the least in the IR, up to $10 - 12 \mu m$ in form of bulk glass (not more than 6 μm for optical fiber). Se-based ChG are good glass formers and possess transmission up to $16 - 18 \mu m$ as a bulk or up to 12 μm as fiber. These glasses are at the origin of the applications mentioned above. The Te-based ChG are of course the ones that potentially transmit in far IR, beyond the transmission windows of the atmosphere. Therefore, in the form of bulk glass, telluride can transmit up to 25 - 30 μm , and about 16 μm as an optical fiber. However, in comparison to Te-based ChG, the Se-based glasses possess better thermodynamic and optical properties. Thus, the Se-based or mixed Se-Te ChG are certainly the best candidates for fiber applications.

The RE doping allows to extend the applicatory field of the ChG [4-6], however, Ga (or In) addition is required in this case which, on the other hand, often provokes devitrification. It was shown that Sb addition in As-Se glass creates an appropriate distribution of free volumes for the homogeneous location of Ga atoms [4]. Thus, one of the objectives of this thesis was to check the RE-doping potential. The first step was to assess the potentiality of matrices co-doped with Ga and Sb reaching a feasible concentration of Ga in host As₂Se₃ maintaining its complete vitrification. The next step was to choose a promising system distilling it by using more effective dynamic processes, subsequently elaborating an appropriate way of distillation for highly-refractory elemental constituents like Sb and Ga in terms of their low vapor pressure.

3.2. ChG fibers – physical principles governing remote sources of light and fundamentals of glass shaping technology

3.2.1. Glasses for active applications – motivation note

The ChG doped with RE ions have been considered as potential materials for mid-IR lasers and fiber-optic amplifiers due to their low multiphonon relaxation compared to oxide glasses. The multiphonon relaxation competes against the desired emission and reduces its efficiency. On the other hand, the ChG have relatively low phonon energy and therefore, can provide enhanced emission of certain fluorescence that are usually quenched in oxide hosts.

Active applications of ChG-based fibers are where the initial light propagating through the fiber is modified by a process other than that due to scattering, absorption, and end face reflection losses associated with the fiber. Examples of these include fiber lasers, amplifiers, bright sources, gratings, and nonlinear effects. RE ions possess characteristic electronic energy levels, which are only slightly influenced by the host matrix due to the screening effect of the d-electrons. When pumped with the appropriate energy, the electrons are excited into upper levels from which they can subsequently decay to lower levels.

3.2.1.1. Physical phenomena affecting ChG-based optical fibers

In order to interpret transmission spectra in terms of optical, physical phenomena behind the shape parameters of data collected should be initially introduced. One may distinguish optical absorption edge consisting – among others – of Urbach edge, weak absorption tail, Rayleigh scattering, and multiphonon edge (see Figure 3.1).

In the vicinity of the optical absorption edge, the absorption spectrum has an absorption coefficient, α , that increases exponentially with increasing photon energy up to α of $\sim 10^4$ cm⁻¹. The absorption spectrum in this energy range is usually labeled as the Urbach tail or the Urbach edge [7-9].

At energies less than the Urbach tail, the absorption spectrum departs from the exponential function of the Urbach edge, having another approximately exponential decrease with decreasing photon energy with a smaller slope, which is labeled as the weak absorption tail (WAT) [7,9]. WAT is related to the MRO in a glass structure and localized energy states in the band gap. The generally weak covalent bonds in ChG are attributed to unsatisfied bonds and network vacancies. This disorder results in a large density of states in the band gap [9] as

an overlap of localized states, which permits absorption of lower energy (longer wavelength) photons [9]. The WAT, therefore, is sensitive to glass purity and thermal history [10]. The losses in this spectral range have been attributed to absorption by impurities and defects comprising bonding departures from usual valence requirements [11,12].



Figure 3.1. Estimation of theoretical minimum loss in ChG fiber; a) and b) represent poor and high-quality glasses, respectively (Image courtesy © J.S. Sanghera et al. [13]).

Another, detrimental contribution to the transmission spectra of ChG optical fibers as well as bulk glasses is Rayleigh scattering. The nature of Rayleigh scattering in a glass is still not clearly described. Its origin among glasses is connected with the possible existence of micro-, submicron crystallites in amorphous state. The universal physical formula examining quantitative and qualitative aspects of this phenomenon does not exist. The reason for this appears as simple. Since each glass structure and microstructure is highly-determined by chemical composition basis and thermal conditions of synthesis, this implies that shape, size, distribution refractive index of crystallites in a volume of the glass varies significantly, and each type of material (even within the same compositional group like silica-based glasses) is peculiar. Nonetheless, there were many attempts to characterize this phenomenon constructing numerous semi-empirical models [14].
3.2.2. Technological aspects of glass fibers fabrication

It is a trivial fact that the glass industry is dictated by the demand for oxide-based glasses. The alloys consisting predominantly of silicon, boron, or phosphorus oxides possess:

- high glass transition temperature (T_g even more than 500 °C);
- good thermomechanical properties and wide process window ($\Delta T = T_x T_g$);
- chemically stability due to SiO₂ content (excluding HF resistance);
- generally weak thermal expansion coefficient;
- Comparing to hard ceramics low fracture toughness K_{IC} (rarely more than 1 MPa/m^{0.5}, ignoring the whole group of glass-ceramic composites which are more crack resistant);
- In the case of P-based glasses relatively low melting point around 1100 °C [15];

Contrary to these advantages, they present a major inconvenience by a reason of their strong covalent bonds and low atomic weight of constituents, which in turn causes high energy of phonon vibration throughout such optical media. Such property leads to a shift of transmission range in the n-IR region into higher energies of light. Obviously beyond transmission window material cannot be used for searching and processing spectroscopic data. Besides, most of the chemical and biological analytes interact with electromagnetic waves in the m-IR spectral region due to their specific fundamental vibration modes.

3.2.3. Principles of the fiber drawing process

Fiber drawing processes were done thanks to self-crafted (by members of the Glass and Ceramics team at the Institute of Chemical Sciences in Rennes) fiber drawing tower equipped with precise inert gas injection valves with simultaneous preform motion and diameter control of processed glass (system shown in Figure 3.2).

In this method, the bulk rod of ChG is located in a vertical position in the ring heating zone. The furnace is tightly fixed in the silica glass tube and continuously purged by He and/or Ar gas to avoid external, ambient contamination by O_2 and H_2O . Routinely, initially before starting of glass rod softening process, the interior of the silica tube is purged in the Ar atmosphere for 2 h maintaining flow rate on the level of 3 l/min. During the drawing process, inert gas has to be changed on He (2 l/min) to increase the solidification speed of as-melted glass. Afterward, the glass is heated up to its softening point. Then the droplet of glass is created under the gravitation force. The resulting ChG fiber is stretched under optimized tension and winded on the take-up spool.



Figure 3.2. General scheme of fiber drawing machine and the photograph of drawing tower Image courtesy © *Glass and Ceramics Team, Institute of Chemical Sciences in Rennes.*

The advantage of such an approach is the latitude of fiber diameter fabrication (from millimeters even up to tens of microns). This dimension can be dictated by matching two process parameters:

- speed of preform descent (V_p) ;
- speed of rotation of take-up spool (V_t) .

Assuming the volume of glass preform is equal to the volume of obtained fiber, appropriate V_p , and V_t values can be estimated referring to equation 3.1.

$$\frac{\pi\varphi_p^2}{4}V_p = \frac{\pi\varphi_f^2}{4}V_t \tag{3.1}$$

where: ϕ_p and ϕ_f are the diameters of preform and fiber.

Typically for compositional comparative study, the final diameter of the fiber is around 350 microns in diameter. In general, the fiber of a bigger diameter is more brittle. Thus, drawing a fiber of 125 μ m in diameter, in some cases was convenient. Typical fiber fabrication parameters are listed in Table 3.1.

Fiber diameter established	350 μm
Velocity of preform V_p	2 mm/min
Velocity of drawing (take-up spool) V _t	0.8 m/min
Purging Ar time	2 h
Purging Ar flow rate	260 l/h
He flow initially	1.5 l/min
He flow during process	1.5 l/min
Heating rate	25 °C/min
Temperature to make a droplet	~500 °C
Temperature of process	~530 °C
Tension	~20 g

 Table 3.1. Exemplary fiber drawing process parameters for Ge-based ChG systems.

In comparison with extrusion method [16], the main disadvantage of extrusion relies on the inability to maintain inert atmosphere and purity of extruder's interior what reflects in much lower purity of such glasses especially regarding humidity-related contaminants.

That is why, for this work, the fiber drawing technique (drawing from the rod) has been chosen as a much cleaner process mainly regarding the lack of contact of a glass preform with working parts of the drawing machine (at least when the preform is partly heated above softening point). Processing cleanliness is essential in ChG optical fibers, due to their high vulnerability to surface crystallization especially considering fiber evanescent wave sensors which are not cladded single-index waveguides. Moreover, optical fibers are also subjected to precise tapering processes – that can be realized exclusively by drawing.

3.2.4. Fiber waveguides for IR photonics

Historically and originally chemical detection by means of ChG optical fiber was proposed by Compton et al. in 1988 [17] through the investigation of butanone. Over the past two decades, many authors have proven the capability of photonic devices for the detection of a wide range of organic molecules. The ChG fiber sensors reveal linear detected signal versus concentration characteristics complying with the linearity of Beer-Lamberts law. This phenomenon explains its utility for the quantitative analysis of organic solutions. In parallel to advancements in the ChG-based fiber sensors, another group of AgCl/AgBr polycrystalline fibers has been also developed. However, such sensors are relatively sensitive to air contamination what destructs IR transparency. Also, the crucial aspect of manufacturing simplicity does not apply to polycrystalline fibers due to difficulties in implementation and the high cost of extrusion methods. Also, the sensitivity of such devices is limited by the relatively longer cross-dimensions of such waveguides (order of 1mm in diameter) [18]. Declared IR signal attenuation for Ag and Tl halide fibers, of which diameter is 1mm, exceeds even less than 1 dB/m, thus they can transmit 50-100W continuously [19].

Up to now, As-Se, $Ga_5Ge_{20}As_{10}Se_{65}$, and TAS-235 glasses have been demonstrated as good candidates for the elaboration of special fibers to be implemented in optical sensors. They are especially suitable for FEWS sensors. This technique uses the evanescent field formed, as a beam propagates by internal reflection, at the interface between the waveguide and the sample to test absorption peaks of the sample at specific wavelengths (Figure 3.3).



Figure 3.3. a)Trajectories of rays in fiber-optic sensors determining penetration depth of evanescent wave b) Increase in fiber sensor sensitivity due to tapering or flattening process. Effects of U-shaping to the sensitivity of sensing zone c).

The interference between the incident and the reflected waves gives rise to the generation of an evanescent field away from the fiber, which is perpendicular to the interface. When an absorbing sample is in contact with the fiber, the evanescent wave could be partially absorbed at specific wavelengths, causing the reflectivity lower than 1. *De facto*, ATR is the fundamental, more universal phenomenon on which FEWS devices sensors operate.

3.2.4.1. Tapered chalcogenide glass fibers for biosensing applications

The process of tapering is a well-known method for an increase in the intensity of the signal coming from the evanescent wave fiber sensor (Figure 3.4). Considering fiber waveguide the number of reflections at the glass/air interface is influenced by the waveguide diameter regarding the following expression:

$$N(\theta, d, L) = L \cdot \frac{\tan(90 - \theta)}{d}$$
(3.2)

where: *L* is the contact length between the fiber and the sample, θ is the incident angle, and *d* is the fiber diameter in the sensing zone.



Figure 3.4. Explanation of an increase in a number of internal reflections within fiber waveguide caused by the decrease of its diameter and exemplary results obtained for chloroform analyte gathered in a region of the significant absorption band at 1050 cm⁻¹ Image Courtesy [©] [18].

There are already two alternative methods for the precise tapering process.

- Etching process in highly acidic solutions i.e. piranha H₂O₂/H₂SO₄
- Changing the ratio between preform feed velocity and drum rotation velocity

These methods allow to locally reduce diameter from around 400 to 100 μ m in the sensing zone – being in contact with the analized substance. In particular, the effect of diameter reduction on signal intensity has been investigated by recording FEWS spectra of chloroform with different fiber diameters (200 to 50 μ m). In that case, the diameter was controlled by immersion of the fiber in the oxidizing solution as a function of time. Results show definite increase in signal intensity when diameter had been reduced (see Figure 3.4b).

Finally, aforementioned results has been proven towards increase detection efficiency of many other substances. The optimal arrangement of FEWS device exhibit the following profile: 400 μ m diameter in the transportation zone between the source of the spectrometer and the sample, 100 μ m in the sensing zone where the sample is in contact with the fiber, and 400 μ m, again, in the transportation zone between the sample and the detector.

3.2.4.2. Optical fibers for active applications

In general, the addition of Sb into As-Se glass creates an appropriate distribution of free volumes for the homogeneous location of Ga atoms [20]. Thus, one of the objectives of this thesis was to check the RE doping potential. The first step was, to assess a potentiality of matrices co-doped with Ga and Sb reaching a feasible concentration of Ga in host As₂Se₃ maintaining its complete vitrification.

The next step was to choose a promising system distilling it by using more effective dynamic processes, subsequently elaborating an appropriate way of distillation for highly-refractory elemental constituents like Sb and Ga in terms of their low vapor pressure. One could conclude from Figure 3.5, in the context of RE-doped chalcogenide matrices, the glass purity issue is of incontestable importance.

Special attention should be paid to the removal of H-impurities bonded with matrix constituents. On the other hand, oxygen remnants in the matrix severely affect attenuation in the m-IR region below 8 μ m, which in turn is the desired region for the detection of lower energy organic bonds as demand for universal fiber evanescent wave sensor.



Figure 3.5. Attenuation spectra for $Ga_2(As_{0.28}Sb_{0.12}Se_{0.60})_{98}$ single-index optical fiber registered by cut-back method. The upper scheme presents recognized absorption peaks originating from technological impurities; on spectra downwards, absorption and emission bands, which were registered in other ChG systems [21,22], are marked.

Despite its high glass-forming ability and good transparency the As-Se-based ChG are strongly affected in the 8 – 12 μ m region by numerous oxygen-related absorption bands and multi-phonon absorption of matrix bond itself. Among the range of accessible RE elements feasible to incorporate them into the ChG, terbium is known as luminescing effectively at 7.5 μ m or more exclusively at 8 μ m. Recent investigation on Tb³⁺ emission bands in Ga-Ge-Sb-Se fiber proved effective luminescence in the far-IR range [23].

It is noteworthy, that such investigations find potential applicatory background, as a hazardous gas sensor [23]. Before, measurement of the luminescence originating from the ${}^{7}F_{4}\rightarrow{}^{7}F_{5}$ transition of Tb³⁺ ions was reported only in two papers. The first observation of this radiative emission was confirmed at 7.5 µm for Ga-Ge-Sb-Se glass doped with 1000 ppm of Tb³⁺ [24]. Moreover, the work of Churbanov et al.[25] proved emission at 4-5 µm region in the ChG based on As-Se and As-S-Se matrices. They fabricated Tb-doped optical fibers presenting 1.5 dB/m optical losses at 6 – 9 µm which implies a low level of impurities. However, the Tb³⁺ emissions from the ${}^{7}F_{4}$ level at 3.1 µm (${}^{7}F_{4}\rightarrow{}^{7}F_{6}$) and at 7.5 µm (${}^{7}F_{4}\rightarrow{}^{7}F_{5}$) were not observed.

According to these reports, there is still a lot of interest in $Ga_5Ge_{20}As_{10}Se_{65}$ glass as an effective host matrix for RE dopants. Therefore the next issue of this thesis was to check general dependencies in this system caused by partial substitution of the chalcogenide component with Te and Sb with As to clarify a direction for further compositional optimization.

Research performed on modifications to $Ga_5Ge_{20}As_{10}Se_{65}$ glass ensured that a 2-step static purification process (including chemical purification using getters) significantly improves the optical purity of glass. Substantial substitution with Te extends the transmission window of single-index fibers above 10 μ m (see Figure 3.6) what has its confirmation [23].



Figure 3.6. Comparative attenuation spectra of modified Ga₅Ge₂₀As₁₀Se₆₅ *single-index fibers synthesized from statically purified precursors. Inset photo ensures the quality of cleaving.*

Another statement can be the only speculation about the initial purity of elemental precursors which may explain small shifts of a transmission window towards shorter wavelength due to substitution of As with Sb what brakes the principles governing shifts of multi-photon cut-off energy which are mostly attributed with changes of the mass of raw elements. For instance, arsenic may be suspected as an H-impurities host. Apart from that, the undoubted affirmative effect of a chemical purification on a glass purity has been estimated to increase minimal attenuation losses nearly three times, when comparing the best matrix with the worst (Figure 3.6).

3.2.4.3. Examples of Pr and Dy-doped Ga5Ge20Sb10S(Se)65 active FEWS sensors

Over many years of research, FEWS devices were considered only as passive, more universal IR sensors covering a wide range of vibration modes regarding constituent bonds of many organic liquids as well as gaseous substances. Such versatility in some cases may be at the expense of detection sensitivity, especially in regions of glass transmission violation, mainly due to absorption by bonds of ChG constituents and lighter atoms of impurities (H, O₂, H₂O). Thus, RE-doping potential for ChG matrices (even if it is small comparing with oxide glasses) creates a possibility to increase the sensibility of FEWS devices in specific spectral regions.

As an active sensor example, the detection of certain characteristic vibration modes of chloroform CHCl₃ was shown (Figure 3.7). The point is that under such circumstances, RE-doped optical fiber has to emit light at the range of wavelength covering the absorption band of the analyzed substance. In this context, 2G2S (Ga₅Ge₂₀Sb₁₀S₆₅) matrix has been proposed as a valuable RE host, being drawn into a single index optical fiber of 350 µm in diameter and additionally tapered [5]. The absorption band of chloroform overlaps with the wide emission of Pr³⁺, due to ³H₅ \rightarrow ³H₄ and ³H₅ \rightarrow ³H₄ transitions (Figure 3.7a). Thus, the broad emission Pr³⁺ ions in the range of 3 to 5 µm (Figure 3.7a) serves as a light source for chloroform detection.

It was also demonstrated that Dy-doped Se-based glasses were preferred candidates for 1.3 μ m fiber amplifiers due to the lower phonon energy of the host glass, and the larger absorption and emission cross sections for Dy [26]. Consequently, the efficiency was expected to be about 90% and the gain coefficient approximately doubles the value for the best Pr-doped sulfide fiber [26]. Modeling has shown that the Dy-doped selenide fiber can tolerate larger losses compared with the Pr-doped sulfide fibers. Therefore, it allows shortening device length, in such a way that a 45 cm length of doped Se-based fiber retains an attenuation of about 10dB/m what results in 40 dB gain at 1.34 μ m.



Figure 3.7. Elaboration of Pr-doped 2G2S active FEWS sensor: a) summary chart of emission intensity as well as the intensity of absorption by analyte; b) relative absorption signal gathered on chloroform sample. Image courtesy © R. Chahal et al. 2016 [5].

Additionally, multimode fibers with losses of about 6 dB/m at 1.3 μ m and less than 3 dB/m at about 6 μ m were obtained [27]. The bare optical fibers were fabricated with losses of about 3 dB/m at 1.3 μ m and below 1 dB/m at 6 μ m (see Figure 3.8).



Figure 3.8. Attenuation of unclad Dy-doped Se-based ChG fiber (*Image courtesy* © *J.S. Sanghera et al. 1999* [13])

Preliminary single-mode fibers have been drawn with minimum losses of about 3 dB/m [27]. Authors explain that transitions become increasingly more efficient in longer wavelength transmitting hosts, such as the ChG due to less multiphonon influence, and IR fluorescence emissions beyond 2 μ m are only seen in ChG (see Figure 3.8).

3.2.5. Mechanical properties of Ge-based ChG as potential matrices for FEWS sensors – a couple of dependencies caused by certain modifications in chemical composition

A great variety of photonic devices were made from ChG such as single-index fiber sensors, micro-structured supercontinuum waveguides, IR lenses for night vision, thermometry. All of these areas of use provoke many kinds of mechanical impact which material should withstand. However, this branch of materials lingers due to its high brittleness, which influences the high standards of a fabrication/manipulation process and a small life span of manufactured products (if not well protected).

In this context, the study of the mechanical properties of ChG seems to be a natural consequence of its delicateness against surface destruction. A detailed overview of the mechanical properties has been presented in Table 3.2.

Glass composition/Ref.	Vickers Hardness kgf/mm ²	K _{IC} MPa m ^{1/2}	E GPa
Ge ₁₀ Se ₉₀ [28] ([29])	72.4 (76)	0.12 (0.21)	12.08
$Ge_{15}Se_{85}[28]$	98.91	0.22	13.80
$Ge_{20}Se_{80}[28]([29])$	130.5 (134)	0.28 (0.27)	14.73
Ge ₂₅ Se ₇₅ [28]	162.1	0.22	16.05
Ge ₃₀ Se ₇₀ [28] ([29])	191.7 (184)	0.20 (0.38)	17.90
Ge _{33.3} Se _{66.6} [29]	165	0.32	-
Ge ₄₀ Se ₆₀ [28] ([29])	222.3 (213)	0.16 (0.19)	22.38

Table 3.2. Overview of basic mechanical properties of certain Ge-Se-based glasses.

A lack of results on mechanical values of ChG might be simply explained by a fact that hardness testing is a destructive method of measurement that stands as a real inconvenience for research performed on expensive and time-consuming materials (from a viewpoint of manufacturing). Nevertheless, such mechanical assessment may be considered as an important parameter for the commercialization of ChG in an industry. The suitability of these glasses for a certain application often relies on their elastic properties. Although the hardness, fracture toughness, and elastic modulus were studied for several composition ranges.

A significant divergence or even contradiction of K_{IC} results (Table 3.2), which has been collected by different research teams emerges. As the connectedness of glass structure increases with an increase of Ge content from 0 to 40 at.% the K_{IC} parameter should follow this trend to rise. Consequently, theoretical calculations of the mean coordination number also show its rise with more addition of Ge. Taking that into account, K_{IC} values collected by Swiler et al. [29] seems to reproduce a more suspected tendency. Whereas, what is interesting, Ga as well as Sb decreases the fracture toughness (K_{IC}) and increases the hardness (HV) of glasses (Table 3.3).

Glass composition/Ref.	Vickers Hardness kgf/mm ²	K _{IC} MPa mP ^{1/2}	E GPa				
G	Ga-modified counterparts						
Ge11.0Ga3.9Se85.1 [29]	85	-	14.1				
Ge _{18.4} Ga _{6.5} Se _{75.1} [29]	153	0.257	17.1				
Ge _{29.5} Ga _{10.4} Se _{60.1} [30]	214	0.169	24.8				
S	b-modified counter	parts					
Ge ₁₀ Sb ₁₀ Se ₈₀ [29]	111	0.18	-				
Ge ₂₀ Sb ₁₀ Se ₇₀ [29]	158	0.22	-				
Ge ₂₅ Sb ₁₀ Se ₆₅ [29]	168	0.21	-				
Ge ₃₀ Sb ₁₀ Se ₆₀ [29]	194	0.24	-				
Complex modification							
Ge ₂₅ Ga ₅ Sb ₁₀ Se ₆₀ [31]	-	-	23.9				

Table 3.3. Overview of basic mechanical properties of Ga/Sb-modified Ge-Se-based glasses

3.3. Glass system selection (choice of chemical composition)

As it was specified the object of this work relates to the group of ChG revealing its promising properties towards near-IR, mid-IR, and far-IR fiber sensors and remote sources of light (liable glass matrices for specific RE doping)

In a general view, as it is presented in the scheme below (Figure 3.9) potential ChG matrices can be divided into five major sorts of materials.



Figure 3.9. Conceptual schema of developed ChG matrices for fiber waveguide technologies.

Taking into account As-containing glasses such as binary As-Se and ternary Te-As-Se, the biggest difference between those two types is the wider glass-forming ability region of Te-containing alloys which shifts to its melting point without crystallization [32,33] (see also DSC data on chemically related glasses [34]). Whereas ΔT of As₂Se₃ reaches ~145°C [34] what restricts its technological capabilities. From another viewpoint, lower energy of multi-phonon absorption by a matrix of TAS-235 glasses enables to extend transparency of drawn fiber waveguide towards higher wavelengths in the m-IR than it is in the case of As₂Se₃.

However, considering *in-situ* and/or *in-vivo* spectroscopic methods of detection, the toxicity of material constituents has to be taken into account, therefore there is a clear need for the development of arsenic-free compositions based on Ge, Sb, La as a non-chalcogen

component. Regarding such restrictions another group of glasses is Te-rich, Ge-based matrices subtly modified by Se up to 8at.% what extends sufficiently their glass-forming region, thus enabling the drawing process [35,36]. The real advantage over the whole bunch of materials is their lowest phonon cut-off energy, allowing detection of the lowest energy modes, i.e. CO₂.

Regarding the vital subject of obtaining highly-efficient remote sources of light in the m-IR region, Ga₅Ge₂₀Sb₁₀Se₆₅-based glasses were reported as relevant host matrices for doping with RE activators, even up to 0.5 mol. % (considering Er) [37] or 0.2 mol. % of Pr [38]. Another immanent advantage of Ge-based systems is their increased thermal stability, as a consequence, allowing higher energy densities for pumping considering the diversity of active and passive photonic applications. Taking into consideration the mechanical properties of fibers, Ge-As-Se-based matrices are significantly weaker in terms of their tensile strength comparing with As-Se or the most mechanically relevant As-S. It is worthy to note that measurements do not correspond with theoretical calculations based on experimentally gathered Young's modulus values (Ge-based alloys are stiffer compounds than As-Se) [39].

Another criterion, for sensing devices, optical fiber amplifiers, or light converters is their thermal stability what can be partially assigned synthesizing the Ge-based Se-rich matrix. For an active source of light to increase the ability for sufficient RE dopant spatial distribution also a significant modifier is Ga and Sb. In case of waveguides operating in the n-IR, m-IR light for longer distances special attention should be paid to S-based Ga-La-S glass which demonstrates, relatively to other ChG-based media, the low value of non-linear refractive index simultaneously revealing the low intensity of two-photon absorption what reflects in a high optical figure of merit (seven-times higher than for Ge₃₀Se₇₀, As₂Se₃, As₂S₃).

3.4. Complex Ge-based chalcogenide glasses for fiber waveguides

With respect to the outstanding robustness, relatively good thermal stability, minimized toxicity broad optical transparency, practical optical nonlinearities induced by the Kerr effect, ChG in the Ge-Sb-Se system exhibit attractive optical properties that make them very useful for several applications and have been studied by various authors [40,41]. Also, the physical and thermal properties of Ge-Se-Sb have been extensively investigated [42,43]. Meanwhile, the Ge-Sb-Te ChG have a broad spectrum of applications as phase-change materials and in the construction of electrically switched memories [44,45]. Besides, optical fibers in the Ga-Ge-Sb-Se-Te system due to significant Ge-content allow obtaining a glass containing even up to

20at.% of Te without lowering greatly glass stability in terms of Dietzel criterion as well as Hruby parameter [23,46]. Therefore, ChG in the Ga-Ge-Sb-Se-Te system needs to be further studied in this direction. Focusing on the other properties of basal Ge-Sb-Se-Te glass system, the part of the glass-forming ability [46,47], structure [48], amorphous-crystallization transformation [49], and crystallization kinetics [44] have been already studied.

3.4.1. Effect of Sb and Te addition to Ga₅Ge₂₀As₁₀Se₆₅ matrix

The role of Sb and Te addition on $Ga_5Ge_{20}As_{10}Se_{65}glass$ was investigated according to the following formula: $Ga_5Ge_{20}Sb_{10-x}As_xSe_{65-y}Te_y$ (Table 3.4).

Composition	Type of synthesis	Type of synthesisSe by Te (at.%)		Comments
Ga5Ge20As10Se65	Without chemical purification	-	$y_{As} = 10$	glass
Ga5Ge20Sb5A85Se65	2-step. stat.	-	$y_{As}=5$	glass
Ga5Ge20Sb5As5Se45Te20	2-step. stat.	$x_{Te}=20$	$y_{As} = 5$	glass
Ga5Ge20As10Se45Te20	2-step. stat.	$x_{Te}=20$	y _{As} =10	glass

Table 3.4. Studied glasses of Ga5Ge20Sb10-xAsxSe65-yTey system.

The optical transmittance spectra of these ChG systems in m-IR and f-IR $(3.2 - 25 \,\mu\text{m})$ are presented in Figures 3.10 and 3.11. All the studied glasses are transparent up to around 18 μm with the transmission saturation value between 65-70 % for a 1.5-2.0 mm thick sample. The farthest IR transparency is observed for the Ga₅Ge₂₀Sb₅As₅Se₄₅Te₂₀ glass.

Taking into account the semiconductive properties of modified $Ga_5Ge_{20}As_{10}Se_{65}$ systems their optical band gaps were calculated which stands as important data for estimation of electron-hole pair binding energy. The least squared fitting performed on Tauc plots gives a rough estimation of optical gaps (listed below in Table 3.5). This data was obtained from transmission spectra measured in the 500 – 2500 nm region. Considering, points of intersection between slope dark lines (indicating multiphonon cut-off) and zero absorption axis, the cut-off wavelength is evaluated (see Table 3.5). To clarify, zero transmission line should not be recognized as an ultimate physical parameter, because glasses still transmit the light at that region (as shown in Figures 3.10 and 3.11).



Figure 3.10. m-IR transmission spectra collected for bulk 2mm thick discs of glasses from $Ga_5Ge_{20}Sb_xAs_{10-x}Se_{65}$ (x=0;5) substitution range. Inset charts present the position of the multi-phonon absorption edge.

The estimated from Vis-n-IR transmission data optical band gap energies are listed in Table 3.5. In general, the substitution of Se by Te leads to a decrease in optical bandgap from $\sim 1 \text{ eV}$ to $\sim 1.6 \text{ eV}$. In the case of Ga₅Ge₂₀As₁₀Se₆₅ glass, the substitution of 5 at.% of As by Sb causes a decrease in the optical bandgap of about 0.05 eV. However, both mixed Te-modified Ga₅Ge₂₀As₁₀(As₅Sb₅)Se₆₅ show a reverse trend – an increase of optical bandgap due to the same substitution (5 at.% of As by Sb) of about 0.02 eV.



Figure 3.11. m-IR transmission spectra collected for bulk 2mm thick discs of glasses from $Ga_5Ge_{20}Sb_xAs_{10-x}Se_{45}Te_{20}$ (x=0; 5) substitution range. Inset charts present the position of the multi-phonon cut-off.

It might be the evidence of the competitive mechanism between glass constituents, especially juxtaposing m-IR transmission results showing the multiphonon cut-off position for each glass system. On the other hand, the IR edge (multiphonon cut-off) is also red-shifted under Te addition (Table 3.5).

For $Ga_5Ge_{20}As_{10}Se_{65}$ system substitution of 5at.% As by Sb causes subtle shrinkage of m-IR bulk transmission window (Table 3.5). Contradictory, for Te-modified $Ga_5Ge_{20}As_{10}Se_{65}$ systems, the substitution of 5at.% As by Sb induces a slight red-shift (Table 3.5).

Table 3.5. The estimated optical band gap and multiphonon cut-off for studied Ge-Se and Ge-Se-Te-based glasses.

Glass composition	Optical bandgap, E _{op.} (eV)	Multiphonon cut-off (intersection point with zero transmission axis) (µm)
Ga5Ge20As10Se65	1.62 ± 0.05	17.47
Ga5Ge20As5Sb5Se65	1.57 ± 0.05	17.42
Ga5Ge20As10Se45Te20	1.01 ± 0.05	18.14
Ga5Ge20As5Sb5Se45Te20	0.99 ± 0.05	18.17



Figure 3.12. Absorption coefficient vs wavelength of Ge-Se and Ge-Te-Se-based glasses and their corresponding cut-off wavelengths (a), complex character of n-IR absorption edge caused by (As, Sb) co-substitution into Ga-modified GTS matrix.

Figure 3.12a shows the absorption coefficient variation caused by studied substitutions $Ga_5Ge_{20}As_{10-x}Sb_xSe_{65-y}Te_y$ (x = 0, y = 0); (x = 5, y = 0); (x = 10, y = 0); (x = 0, y = 20); (x = 5, y = 20); (x = 10, y = 20). Major trend that can be observed is red-shift of cut-off wavelength (at 10 cm⁻¹) caused by an increased Sb content at the expense of As for Ga-modified Ge-Se-based glasses. On the other hand multi-chalcogen Ge-Te-Se-based matrices exhibit different nature of optical absorption edge formation (Figure 3.12b). It can be observed that coexistence of As and Sb atoms in the structure of Ga₅Ge₂₀As₅Sb₅Se₄₅Te₂₀ glass creates a coaction of two different mechanisms of absorption. The addition of Sb leads to enhancement of weak absorption (WAT) which typically occurs below 10 cm⁻¹, whereas As, reduces more intense absorption originating from optical gap – beyond wavelength cut-off (see Figure 3.12b) As many old research point out – this phenomenological parameter refers to region $10^2 - 10^3$ cm⁻¹ [7, 9].

Additionally, as-synthesized Ga₅Ge₂₀As₁₀Se₆₅ glasses modified with Te and Sb were tested towards their thermodynamic properties i.e. vitrification temperatures, crystallization temperatures, and parameter of glass stability.

The density of alloys has been checked using the Archimedes method performed in ethanol of known temperature. Results are listed in Table 3.6 including data published by other authors. Gathered density data reflects its consistency reflected in an insignificant scattering of density results specifically caused by As/Sb substitution. In particular substitution resulted in ~ 0.121 g/cm³ for Ge,Se-based glasses, and~ 0.1 g/cm³ for Ge,Te,Se-based glasses. This is also evidence of proper distillation of Sb in the 2-step purification process. However, in relation to results on density reported in [23] (focusing on Ga₅Ge₂₀Sb₁₀Se₄₅Te₂₀) Ge-Te-Se-based compositions reveal too high density, yet it is still marginal misfit of the data considering adequate for Archimedean method error reaching 0.005 – 0.02 g/cm³ depending on precision)

As it was previously stated Sb substituting As decreases the optical energy gap. Such a statement can be justified with the consistency of thermodynamic data on 2-step statically purified Ga₅Ge₂₀Sb₁₀Se₆₅ and Ga₅Ge₂₀Sb₁₀Se₄₅Te₂₀ glass reported by Abdellaoui et al. [23] and obtained during this work (see Table 3.6) To conclude, Sb substituting As – in synthesized alloys – causes an increase of T_g. Ga-As(Sb)-Ge-Se-Te-based systems are less stable than based on Ga-Ge-As(Sb)-Se, however, still enough stable for further forming processes having their Δ T's of around 20 – 40° above the technological threshold for fiber drawing process. Moreover, a progression of T_g values maintains the overall trend reported by other authors for corresponding systems (Table 3.6).

<i>Table 3.6.</i> Comparison of density and basic thermodynamic parameters of as-received glasses
on the basis of previous results (blue-coloured row indicates confirmed partial crystallization).
Data marked with $*$ corresponds to peak crystallization temperature (T_p) what influences the
presented glass stability region ΔT .

Composition	Density (g/cm ³)	Tg ^{on} , °C	T _x , °C	Δ Τ, °C	Reference
Ga5Ge20As5Sb5Se65	4.531	268	-	>130	
Ga5Ge20As10Se65	4.410	266	-	>130	This work
Ga5Ge20Sb10Se65	4.61	272	-	>150	
Ga5Ge20Sb10Se55Te10	4.79	249	-	>150	Abdellaoui et
Ga5Ge20Sb10Se45Te20	4.88	229	-	>150	al. [23] (2-step static purification process)
Ga5Ge20Sb10Se40Te25	5.02	221	355	134	
Ga5Ge20Sb10Se35Te30	5.06	215	335	120	
Ga5Ge20Sb10Se27.5Te37.5	5.21	207	280	73	
Ga5Ge20As5Sb5Se45Te20	4.843	222	-	>120	This work
Ga5Ge20As10Se45Te20	4.743	206	342	136	I his work
Ge25Sb10Se60Te5	4.53	278	403*	125	
Ge25Sb10Se55Te10	4.59	259	383*	124	Yin et al. [47] (melt-quench process)
Ge25Sb10Se50Te15	4.66	250	386*	136	
Ge25Sb10Se45Te20	4.78	241	375*	134	

Relatively high T_g value specifically for Ga₅Ge₂₀As₁₀Se₆₅ glass (266°C) – considering spread of the values within Ga₅Ge₂₀As_{10-x}Sb_xSe₆₅ substitution range – may refer to contamination of the glass with oxides (as it was not chemically purified in the mid-step of glass preparation). A lower purity of this glass has been proven in terms of its optical attenuation presented further. Meanwhile, a much more pronounced effect on the extent of T_g values (> 10°C) can be noticed looking at Ga₅Ge₂₀As_{10-x}Sb_xSe₄₅Te₂₀ substitution series.

Following the advice from gathered thermodynamic data, each one of the prepared glasses has been drawn into single-index fibers – 350 μ m in diameter. The results of the attenuation study presented in the next subchapter for as-drawn optical fibers are evidence of accomplishment (see Figures 3.13 – 3.16).

3.4.2. Optical attenuation study of Sb, Te-modified Ga₅Ge₂₀As₁₀Se₆₅ fibers

The review investigation on the potential of the modified $Ga_5Ge_{20}As_{10}Se_{65}$ matrix has been planned to reveal the importance of chemical purification during the synthesis procedure via static purification. The additional objective – presented in the previous subchapter – was to monitor changes of transmission window and thermodynamic properties of as-prepared glass preforms caused by partial substitution with Te and Sb (Figure 3.13).



Figure 3.13. Attenuation spectra collected in m-IR region for Ga₅Ge₂₀Sb₅As₅Se₆₅ optical fibers a),b),c) with averaged spectral response d) (glass 2-step purification process), and proposed representation of the attenuation data for estimations of optical loss e).

The next step was to test the optical transmission properties of as-drawn optical fibers manufactured from these preforms. The experiment's importance relies on technological aspects of glass synthesis, or, more precisely, that all starting elements, used in syntheses were the same chemicals (prepared by the same initial purification procedure) for more grounded prove of their influence on output purity of as-synthesized glass.

To understand better the consequences of not using a chemical getter during a static purification process (typically for this work it is 100 wppm of 5N purity Al) $Ga_5Ge_{20}As_{10}Se_{65}$ system was intentionally chosen to elucidate the level of transmission losses in an as-drawn waveguide. Omitting – relatively to 2-step statically purified systems – the low mechanical strength of such optical fiber which may originate from surface crystallization of the fiber, their minimal attenuation loss is on average more than twice as higher than for the rest of optical fibers (minimal loss ~ 26 dB/m).

Simultaneously, each of the studied systems has been synthesized from already prepurified As (dynamic evaporation from the surface) and Se (dynamic melt evaporation of the oxide). Therefore, highly-attenuative $Ga_5Ge_{20}As_{10}Se_{65}$ optical fiber (~ 26 dB/m) ensures the necessity for an additional chemical purification step. Moreover, as can be denoted from Figure 3.14a, the poor optical quality of fiber enabled to measure merely short-distance attenuation, which reflects a slight difference between the concentration of hydrogen impurities for $Ga_5Ge_{20}As_{10}Se_{65}$ and $Ga_5Ge_{20}As_5Sb_5Se_{65}$ (i.e. compare Se-H absorption peak at ~ 3,5 µm).



Figure 3.14. Attenuation spectra collected in m-IR region for Ga₅Ge₂₀As₁₀Se₆₅ optical fiber a)(glass without chemical purification), normalized attenuation spectra in the vicinity of Se-H absorption-related peaks for two similar systems b)

Normalized data (Figure 3.14b) may be also the evidence that dynamically pre-purified As 5N (purified only on the surface) could be a reservoir of hydrogen. Thus, when As was substituted with 5at.% of 6N-purity Sb , Se-H absorption peaks are less pronounced.

Whereas the influence of Te on $Ga_5Ge_{20}As_{10}Se_{65}$ matrix should not be described as only positive. First of all, substitution up to 20at.% of Te significantly increases loss in n-IR region, below 4 µm (Figures 3.15 and 3.16). However, when comparing loss in m-IR region, above 9 µm, Te modified matrices (Figures 3.15 and 3.16) displays lower loss than similarly synthesized Se-based matrix (Figure 3.13), which is even consistent with previous investigations [23].



Figure 3.15. Attenuation spectra collected in *m*-IR region for $Ga_5Ge_{20}Sb_5As_5Se_{45}Te_{20}$ optical fiber *a*),*b*),*c*) with averaged spectral response *d*) (glass synthesized with 2-step purification).

This aspect was denoted as the existence of Si-O-related impurities. It can be assumed, that technique of removal of as-purified Se from silica setup should be performed paying sufficient attention for precise removal of a raw element (avoiding any silica powder residue).

To conclude, even 20 at% of Te substituting Se cause in both cases collapse of transmission in n-IR for both systems. Minimal loss is lower than for only Se-based systems which may be evidence of the effectiveness of dynamic distillation performed on raw Te.



Figure 3.16. Attenuation spectra collected in *m*-*IR* region for Ga₅Ge₂₀As₁₀Se₄₅Te₂₀ optical fiber a),b) with averaged spectral response c) (glass synthesized with 2-step purification).

As may be deduced from Figure 3.14 - glass without chemical purification and static distillation – exhibited poor quality, and m-IR region (above 9 µm) was totally inaccessible for signal detection. Besides, the substitution of Sb with isoelectronic but lighter As, increases signal loss around 5 µm, most probably due to the introduction of some hydrogen into the system (compare averaged loss spectra on Figures 3.15d and 3.16c), despite the initial purification process performed on As. This information has led to an idea for the preparation of raw As according to dynamic sublimation procedure, which was used for latter dynamic distillation processes.

By comparing two types of glasses: Ge-Se and Ge-Te-Se-based, the significant role of Te on transmission window in these systems should be considered. Ge-Se-based single-index fiber covers n-IR range of transmission, whereas, Ge-Te-Se-based single-index fiber transmits very well beyond 6 μ m. The explanation should be found in optical band-gap shift due to significant amount of heavier Te atoms creating lone pair electrons in the matrix (Figure 3.17).



Figure 3.17. Comparison of attenuation spectra for chemically not purified Ga₅Ge₂₀As₁₀Se₆₅ and 2-step statically purified Ga₅Ge₂₀As₁₀Se₄₅Te₂₀

3.4.3. Summary

In general, all Te, Sb (co-)modified Ge-As-Se-based systems prepared under 2-step static purification processes have been verified suitable for fiber drawing. The inevitable role of Al oxygen getter has been reflected in minimal loss observed on attenuation spectra. Minimal attenuation loss for the 2-step statically purified glasses varied in between ~ 5 - 10 dB/m, whereas glass synthesized without chemical getter revealed attenuation of more than 20 dB/m. The pronounced stability of these complex glass systems, together with confirmed effective RE doping of their chemical analogs, creates a positive notion for further RE-doping experiments. Thus, next steps in this field should be made on optimization of doping and purification procedures within Te-modified Ga₅Ge₂₀As₁₀Se₆₅ matrix.

 $Ga_5Ge_{20}As_{10}Se_{65}$ matrix could serve as convenient host for RE ions allowing to dissolve them in quantities of ~1000 wppm, while other widely studied systems like As-Se or Te-As-Se exhibit low solubility threshold for RE dopants. Thus, the following part of this work is devoted to the potential of Ga, Sb modification on As-Se and Te-As-Se glasses.

3.5. Effect of Sb addition on the homogeneity of Ga-doped chalcogenide systems

For a better understanding of the role of Sb addition in ChG, the glass-forming ability of Ga and Sb-modified As₂Se₃ and Te₂As₃Se₅ systems were studied. The addition of Ga promotes the solubility of RE metals in the glassy matrix. Doped with RE ions, such as Pr^{3+} or Dy^{3+} these glassy systems profit new functionality with remote light conversion due to many radiative transitions in the IR spectral range. On the other hand, an increased amount of Ga (typically up to ~5at.% or more) causes crystallization of Ga₂Se₃ phases [50].

In this part of the work, the material engineering strategy was to substitute As atoms with four-fold coordinated Ga and three-fold coordinated Sb. Ga dopant possessing its peculiar electron configuration s²p¹ is four-fold coordinated due to the creation of a dative bond with a p-lone pair on Se atoms. From theoretical accounts, Ga and Sb with glass-forming element Se exhibit relatively higher heteropolar bond energy than in the case of As (exceeding 2.32 eV, 1.87eV, and 1.8eV respectively). Therefore, theoretically, it can be stated that elements like Ga and Sb, apart from their well-defined influence on optical properties, could be a good glass-forming constituent. During planning experimental approach for a novel (based on As₂Se₃ and TAS-235) chemical compositions, information concerning the amount of Ga at.% which is not destructive for amorphousness gave the direction for investigations.

The binary stoichiometric As₂Se₃ are typical formers of transparent glasses in the region up to 18µm [51]. The network-forming ability of Ga-doped As₂Se₃-based materials had been earlier thoroughly studied within Ga_x(As_{0.4}Se_{0.6})_{100-x} system (x = 0, 1, 2, 3, 4, 5) [50]. The role of Sb on Ga-modified As-Se has been also widely-investigated through described substitutions: Ga₂(As_{0.40-x}Sb_xSe_{0.60})₉₈ (x = 0.04, 0.12, 0.20), and Ga_y(As_{0.40-x}Sb_xSe_{0.60})_{100-y} (x = 0, 0.04, 0.12, 0.20, y = 5, 8) carrying out classical melt-quench technique with initially pre-purified raw elements [20]. In the next step, the role of Sb and Ga compositional variation was investigated according to the following formula: Ga_x(As_{0.4-y}Sb_ySe_{0.6})_{100-x} (x=2, y=0; x=2, y=0.12; x=5, y=0.12), though, an approach to glass preparation has been changed by implementing additionally chemical purification (oxygen getter) combined with static distillation. The optical transmittance spectra of these ChG (synthesized within 2-step static purification procedure) in the IR (3.2 – 25µm) are presented in Figures 3.18 and 3.19.

As it was expected multiphonon absorption edge of such systems significantly shifts into longer wavelengths due to the addition of a much heavier antimony constituent. However,

comparing only Sb-containing systems (element significantly heavier than matrix elements As and Se) the competitive mechanism of multiphonon cut-off shift can be observed regarding the simultaneous change in Ga content (element a little lighter than matrix constituents). The same logical explanation can be employed for the process of optical bandgap shift. In addition, specifically for Sb-containing systems, the transmittance relatively increases, with an increased atomic percentage of Ga, even above 5%.



Figure 3.18. m-IR transmission spectra collected for bulk 2mm thick discs of glasses from $Ga_x(As_{0.4-y}Sb_ySe_{0.6})_{100-x}$ (x=2, y=0; x=2, y=0.12) substitution range. Inset charts present the position of the multi-phonon absorption edge.

The atomic density changes caused by Ga and Sb addition in the studied As-Se samples correlate well with previous results for Ga-doped As₂Se₃. Indeed, the atomic packing increases with Ga due to the filling of structural voids in the matrix (Table 3.7). The effect of densification induced by Sb can be explained simply by the relatively high atomic mass of this constituent.

Composition	Density (g/cm ³)	Tg ^{on} , °C	T _x , °C	ΔT, °C	Reference
As40Se60	4.619	184	-	-	
Ga1(As0.4Se0.6)99	4.629	182	-	-	
Ga2(As0.4Se0.6)98	4.635	182	307	125	
Ga3(As0.4Se0.6)97	4.631	180	283	103	
Ga4(As _{0.4} Se _{0.6})96	4.642	182	277	95	Shpotuuk at al
Ga5(As0.4Se0.6)95	4.662	180	276	96	[50, 20]
Ga2(As0.36Sb0.04Se0.6)98	4.727	187	-	-	process from
Ga2(As0.28Sb0.12Se0.6)98	4.900	191	-	-	purified raw
Ga2(As0.20Sb0.20Se0.6)98	5.073	196	306	110	elements)
Ga5(As0.36Sb0.04Se0.6)95	4.715	193	287	94	
Ga5(As0.28Sb0.12Se0.6)95	4.873	195	325	130	
Ga5(As0.20Sb0.20Se0.6)95	5.049	208	328	120	
Gas(As0.28Sb0.12Se0.6)92	4.856	207	295	88	
Ga2(As0.4Se0.6)98	4.634	184	309	120	
Ga2(As0.28Sb0.12Se0.6)98	4.884	189	323	131	
Ga5(As0.28Sb0.12Se0.6)95	4.865	200	296	96	this work
Ga2(As0.36Sb0.04Se0.6)98 dyn. distill.	4.701	186	-	-	
Ga5(As0.36Sb0.04Se0.6)95 dyn. distill.	-	191	290	99	

Table 3.7. Comparison of density and thermodynamic parameters of studied glasses on a basis of previous results (dark rows indicate amorphousness, bright – partial crystallization).



Figure 3.19. m-IR transmission spectra collected for bulk 2mm thick discs of glass from $Ga_x(As_{0.4-y}Sb_ySe_{0.6})_{100-x}$ (x=5, y=0,12) substitution. Inset charts present the position of the multi-phonon cut-off.

3.5.1. Study of optical attenuation for Ga, Sb-modified As₂Se₃ optical fibers

 $Ga_2(As_{0.28}Sb_{0.12}Se_{0.6})_{98}$ and $Ga_5(As_{0.28}Sb_{0.12}Se_{0.6})_{95}$ 2-step statically purified glasses were drawn into a single-core optical fiber ($\phi = 350\mu m$), however, they were too brittle to measure attenuation, perhaps due to lack of stress relaxation when subjected to the priorplanned temperature of the annealing process. It turned out from further DSC characterization, that T_g of As₂Se₃ modified with Sb and Ga raised notably comparing with Sb-free glass, therefore hypothetically it might be reasonable to try to modify the temperature regime.

The only characterized fiber (made through 2-step static purification) was not modified with Sb (Figure 3.20) and indeed DSC scan revealed relaxation of the enthalpy attributed to metastable amorphous state what is in agreement with relative mechanical durability of asdrawn waveguides.



Figure 3.20. Attenuation loss spectra of 2-step statically purified $Ga_2(As_{0.4}Se_{0.6})_{98}$ glass with indicated absorption bands of bond impurities.

3.5.2. Working out dynamic distillation process for Ga- and Sb- enriched nearly stoichiometric As-Selenides

Glass purification performed under high vacuum-dynamic conditions ($\sim 10^{-6}$ mBar) maintained in silica glassware reactors is inseparably connected with the thermodynamic behavior of each processed glass constituent.

Dynamic distillation of binary or ternary amorphous systems consisting of chalcogenide (S, Se, Te) with structure modifiers like As or Ge is well-elaborated. The next direction for the development of this technique is the improvement of a distillation of multi-component ChG. Especially modifiers with less tendency to distillate as Sb and Ga, create a new path for further research to optimize process parameters. Concerning this at least two different important parameters of solid-state matter have to be considered:

- Vapor pressure of each elemental component (see Figure 3.21)
- The bond energy of possible bonds located in amorphous or crystalline phases which are created in the processed material



Figure 3.21. Vapor pressure vs T curves of chalcogen atoms and common ChG modifiers (boiling point relates to ambient atmospheric conditions) [52].

Having this information one may estimate or suspect at which stage (temperature, time) of distillation each component will be vaporized/condensed or sublimed/resublimed. Also, the type of transition between the state of matter is important regarding the control of an appropriate zone for the distillate to appear. As a good example, elemental As thermally treated under high vacuum conditions tend to sublime, therefore when the process runs too rapidly with heating ramp, the charge may resublime in an undesirable zone of silica setup, leading to compositional discrepancies.

3.5.3. Optimal conditions of dynamic distillation for Ga₂(As_{0.36}Sb_{0.04}Se_{0.6})₉₈

The experiment has been planned to estimate possibilities to perform purification of As-Se-based glass matrices modified with highly-refractory Sb and Ga under high-vacuum conditions (10⁻⁶ mBar) adding chemical getters of oxygen Al and hydrogen TeCl₄.

It turns out, that initial problems to distillate statically As-Se glass containing up to 4at.% of Sb as a modifier, also affects dynamic processes. Therefore, it is important to figure out which element – Ga, Sb, or potentially their compound with selenium – causes those difficulties (see Figure 3.22).



Figure 3.22. The residue of not distilled material after dynamic distillation process (marked in the circle) a); SEM image of microstructure at the surface of not distilled matter b) (magnification proves a hexagonal type of structure for this polycrystal).

3.5.3.1. Initial chemical purification of the melt

Before final synthesis and dynamic distillation of the glass, all of the pre-purified elemental constituents were weighted in a glovebox and vacuum-sealed in a straight silica reactor, being mixed with Al 100 wppm (oxygen removal) and TeCl₄ 1000 wppm (hydrogen removal) as it is presented in Figure 3.23.

One of the benefits resulting from a dynamic distillation method lies in the fact that elemental gallium and antimony (typically used as high purity raw element -6N) can be also subjected to chemical purification procedure. This aspect is not achievable in terms of a two-step static process, in which, Sb pre-melted/chemically-purified with the rest matrix constituents (As, Se) can be clumsily statically distilled. Whereas, there is no possibility to distillate Ga through a 2-step static process, as it tends to form highly-refractory Ga₂Se₃.

On the other hand, the preliminary step for a chemical purification can be done for the final composition of the glass – including Sb and Ga – because an optimized dynamic distillation process allows to fully distillate material at 1000° C.



Figure 3.23. Initial melt purification with chemical getters (a), and exemplary melt-quench regime for this step (b)

3.5.3.2. Optimization of dynamic distillation protocol for Ga₂(As_{0.36}Sb_{0.04}Se_{0.6})₉₈

Three dynamic distillation processes, with moderately different approach has been realized (see Figure 3.24).

The 1-st process has been provided covering with heating wire whole dynamic setup tube, maintaining in this zone ~ 120° C – from half of the distillate batch up to vacuum-sealed valve section shown in Figure 3.24d – what caused partial loss of highly volatile elements (suspected loss of As due to the low solubility of this over-distilled material to strong aqua regia solution). Nonetheless, the positive aspect of such an approach should be highlighted, because of absolute distillation (at 1000° C) – including highly-refractory Ga₂Se₃ has been observed. Moreover, such absolute distillation, is the less possible event, regarding 2-nd and 3-rd approach (despite similarly heated tube furnace up to 1000° C)

The 2-nd and 3-rd process has been done covering with resistance heating wire from half of the distillate batch to several millimeters above distillate batch of the silica setup (see Figure 3.24e), simultaneously increasing temperature at this zone to $\sim 150^{\circ}C \pm 20^{\circ}C$. Such wire heating regime has been maintained up to the end of a distillation of the highly volatile matrix elements/ compounds like As, Se, or As-Se-mixed molecules. Besides, after the temperature for a tube furnace came to \sim 440°C (ensuring full distillation of highly volatile part of a batch), the heating wire zone has been disassembled. The reason for that relates to not correctly conducted 1-st. distillation process, in which, due to maintenance of extended wire heating zone at temperatures > 440°C have led to the intense distillation up to the valve zone, hence, losing part of the distillate.





Figure 3.24. Dynamic distillation procedure for Ga₂(As_{0.36}Sb_{0.04}Se_{0.6})₉₈: initial dynamic drying of setup a); temperature regime used for distillation b); photograph showing distillation process c); scheme presenting distillation with an extension of heating wire zone (1-st distillation) d); scheme presenting distillation with a shortened zone of heating wire (2-nd and 3-rd distillation) e).

Precisely, 2-nd and 3-rd approach were similar in terms of dynamic distillation process, however the only optimization has been done to quenching temperature occurring in asprepared ChG rod. Indeed, the reduction of quenching temperature from 700°C to 675°C, resulted in a much shorter hollow core zone of the ChG rod.

The raw elements As, Se, were initially purified (as described in 1st Chapter). Wherein, 3rd synthesis was done with a lower temperature of quenching increasing the technological usefulness of preform.

Definitely, an attenuation study performed on a set of single-index $Ga_2(As_{0.36}Sb_{0.04}Se_{0.6})_{98}$ optical fibers revealed its incontestable purity comparing with statically distilled glasses of nearly the same chemical composition. In general, their minimum attenuation loss localized between 6 – 7µm does not exceed 1 dB/m and the best obtained optical fiber showed minimal loss at the level of 0.2 dB/m. An interesting feature concerning the first glass distilled in much more radical conditions for impurities removal seems to reveal the promotion of pollutant H location rather with constituent Se than with As (see inset of Figure 3.25).



Figure 3.25. Comparative attenuation spectra for a dynamically distilled set of glasses gathered on 125µm optical fibers (inset shows differences in glass impurities content.

3.5.4. Preparation of Sb-modified As-Se with a high content of Ga – Ga₅(As_{0.36}Sb_{0.04}Se_{0.6})₉₅

The number of attempts to dynamic distillation process advised trying distillate the glass $As_{36}Sb_4Se_{60}$ doped with 5at.% of Ga. Conditions of initial chemical purification, as well as dynamic distillation details, were similar to the 2-nd and 3-rd dynamic distillation approach described previously (see subchapter 3.5.3.1 and 3.5.3.2), also including a reduction in quenching temperature for the final step of the synthesis. The whole process resulted in a technological problem with the fiber drawing process caused by a hole inside ChG rod, despite a decrease in quenching temperature to $675^{\circ}C$ (i.e. within ~ 12 cm of rod length only 11.5 cm had hollow core). Considering phenomenon of highly wetting silica glass chalcogenide melt, the influence of Ga on melt viscosity should be precisely investigated for quenching optimization. Nevertheless, it turns out to be the promising measurement of its bulk transmittance on roughly 1mm of a bulk disc without any observable absorption bands. The random part of the rod was chosen also for DSC study and ΔT of the material is slightly lower than 100° (Figure 3.26).



Figure 3.26. DSC spectra gathered using 10°/min heating rate for Ga₅(As_{0.36}Sb_{0.04}Se_{0.6})95.

Subtly wider transmittance window towards lower energies, comparing with two-step statically purified glass of richer in Sb (12at.%) composition (see Figure 3.19) than discussed material (Figure 3.27), may refer to better effectiveness of dynamic distillation considering highly refractory Sb (and consequently its relatively higher content in as-prepared glass).


Figure 3.27. m-IR transmission spectra collected for bulk 1mm thick discs of glasses for $Ga_{5(A}s_{0.36}Sb_{0.04}Se_{0.6})_{95}$ glass.

3.5.5. Summary

Ga, Sb-modified As-Se system has been most intensely studied towards its RE-doping potential. Indeed, As-Se matrix may be treated as the material being able to accept even up to 5at.% of Ga, maintaining its amorphousness, despite demonstrating uncertain Dietzel parameter $\Delta T = 99^{\circ}$ (regarding potential shaping methods). Such an affirmative result has been obtained through the most sophisticated glass purification approach under dynamic vacuum conditions, taking special care to manipulation/process purity and appropriate thermal regime. Moreover, satisfying IR attenuation results of minimal loss around 0.2 dB/m between 6 – 7 µm collected for dynamically distilled Ga₂(As_{0.36}Sb_{0.04}Se_{0.6})₉₈ glass, give a basis for further research. Since results on Ga-enrichment of Sb-modified As-Se were agreeable and stable (regarding three insignificantly different attempts to dynamic distillation realized for the same composition), the next step would be to work on an appropriate RE-doping procedure for Ga₂(As_{0.36}Sb_{0.04}Se_{0.6})₉₈ glass. The subsequent study in this field should be concentrated on finding appropriate ratio between Ga, As and Sb in order to obtain stable glass with higher amount of Ga.

Following the same strategy of Ga, Sb modifications to ChG matrix, the next objective was to optimize compositional boundary parameters for TAS-235 glass.

3.6. TAS-235 glass systems for active applications in fiber optics

3.6.1. Description of Te-As-Se system and current results on Ga, Sb modification

The development of glasses transmitting as widely as possible in the IR range can give capabilities for further advancement in IR fiber optics performance. For better propagation of light often passing through meters of fibers it is crucial to lower the loss in the low phonon range. Increasing the average atomic mass of the chalcogen components by adding an appropriate molar combination of Se and Te regarding their glass stability range may lead to the previously mentioned improvement. However, the use of Te as a significant content of the glass can be hazardous due to an increase in the tendency to create microcrystals and electron delocalization of bonds. Therefore, the solution for the development of such a group of glass possessing a wide IR transmission window is to maintain the Se character of chalcogen matrix bonding, which means sufficient separation of Te atoms to suppress the formation of π bonding.

As it results from the ternary diagram for Te-As-Se system (Figure 3.28) the most stable vitreous compound, completely non-crystalline is $Te_{20}As_{30}Se_{50}$. So-called TAS-235 glass has the atomic percentage proportion of Se more than twice as much as Te which increases the solubility of Te in the melt preventing the creation of Te-Te bonding. The following TAS-based systems have been studied $Ga_2As_{20}Sb_8Se_{50}Te_{20}$ and $Ga_5As_{17}Sb_8Se_{50}Te_{20}$ (see Table 3.8).



Figure 3.28. Te-As-Se phase diagram investigated by [53].

Such behavior leads to the construction of cross-linked by Arsenic, -Se-As-Se-Te-Se-As-Te-Se-As-Se- chains, forming a ramified 2D structure. The TAS glass regarding its high stability against crystallization is a convenient matrix for fiber drawing. Moreover, its thermomechanic properties allow carrying out fiber tapering [54]. According to the ternary diagram (Figure 3.28) TAS-235 glass is placed near the center of the glass-forming region. Due to excellent transparency up to 20 μ m, these ChG are interesting media for IR fiber applications.

Composition	Density (g/cm ³)	Tg ^{on} ,°C	T _x ,°C	Δ Τ, °C	Reference
Ga2As20Sb8Se50Te20	5.070	132	-	-	this work
Ga5As17Sb8Se50Te20	4.968	131	230	99	
As30Se50Te20	4.888	134	-	-	Shpotyuk et al. [50,55] (melt-quench process)
Ga1As29Se50Te20	4.912	131	-	-	
Ga2As28Se50Te20	4.920	128	228	100	
Ga2As31.2Se46.8Te20	4.940	132	239	107	
Ga5As25Se50Te20	4.940	126	223	97	
Ga10As20Se50Te20	4.899	118	231	113	

Table 3.8. Comparison of density and basic thermodynamic parameters of as-received 2-step statically purified glasses on a basis of previous result (dark rows indicate confirmed amorphousness, bright – partial or absolute crystallization).

For an active application, glass is doped with RE ions and co-doped with Ga (to increase RE solubility) [55]. A sufficient amount of Ga atoms (up to 1at.%) in the host TAS-235 system has a positive effect on RE ions dispersion, without triggering the devitrification. On the other hand, too high Ga at.% values cause the formation of Ga₂Se₃ cubic phase crystallites. Moreover, XRD patterns (Figure 3.29) ensures that Ga addition affects MRO in the atomic structure which are non-significantly reflected by the shape and location parameters of FSDP.

With regard to the preliminary study on Ga-doped TAS-235 systems, it was intriguing to try subtly change the chemical composition by substituting Sb on the cost of As. The suspected result was to increase the capability of the glass to dilute Ga without the crystallization referring to chemical bond approach assumptions which inform that Sb creates stronger bonds with dominant Se atoms (~1.86 eV) than As (~1.8 eV). The theoretical bond energy of homogeneous bonds (Sb-Sb ~1.31 eV) is weaker than (As-As ~1.38 eV) [56] what is in favor of a better glass-forming ability of Sb with dominant Se than it is in the As case.



Figure 3.29. XRD patterns of Ga_xAs_{30-x}Se₅₀Te₂₀ (x=0,1,2,5,10) glasses [55].

Apart from that, Sb-modified glass with Ga up to 5at.% was tested with XRD to estimate whether crystallization is subtle by volume or microscopic. Measurements performed on asprepared glasses have not revealed any crystalline peaks, however, the glass heat-processed through fiber drawing procedure showed the beginning of devitrification (see Figure 3.30).



Figure 3.30. XRD patterns of Sb-modified TAS glass with different amount of Ga.

3.6.2. Effect of Ga, Sb addition on optical properties of TAS-235 matrices

A positive, side effect of Sb addition into TAS glass can be observed regarding an insignificant shift of the multi-phonon cut-off towards lower photon energies. The substitution of As with Sb (8at.%), didn't allow to introduce 5at.% of Ga, which was proven with bulk transmittance spectra, indicating scattering mechanisms induced by the matrix (Figure 3.31).



Figure 3.31. m-IR transmission spectra collected for bulk 2mm thick discs of modified with Ga and Sb TAS glasses. Inset charts present the position of the multi-phonon cut-off.

Collected attenuation spectra for Ga, Sb-modified TAS glass (Figure 3.32) confirms that the 2-step static purification process was not as efficient as dynamic distillation performed on genuine TAS-235 glass – when comparing overall losses localized in a detection range of MCT unit. Nonetheless, the intriguing feature has occurred as an intense peak from Se-H-attributed absorption (relatively to As-H bond absorption peak), what stays in contradiction with previous results on common TAS glass, where As-H associated peak dominates on insignificant Se-H impurity contribution (see Figure 3.32). The explanation may be found in deficiency of As caused by notable substitution with Sb (relatively to common TAS glass), which creates higher probability for Se-H bond creation. Moreover, an evident slope on attenuation spectra may be attributed to optical band gap contribution and/or weak absorption loss mechanism. Moreover, repeatability of the slope below 6 μ m, in the direction of the visible range, can be considered as a universal feature of Te-containing matrices (see Figure 3.32, Figure 3.15 – 3.16).



Figure 3.32. Attenuation of $Ga_2Sb_8Te_{20}As_{20}Se_{50}$ two-step statically purified glass. In the right upper corner loss spectra of not modified TAS-glass is presented (Image Courtesy \mathbb{O} [6]).

3.6.3. Summary

The Ga, Sb- modified TAS glasses reveals less promising results for an increase in Ga content, competing with Ga, Sb-modified As-Se glass. However, there is indication for increase in Ga solubility (from 1 to 2 at.% without crystallization) under the substitution of 8 at% As by Sb comparing with results for the system without Sb. Thus, TAS-based glasses should not be neglected as host matrix for RE-dopants.

It can be stated that synthesized by 2-step static purification TAS glass, under the substitution of 8at.% As by Sb, and 2at.% As by Ga, has been successfully drawn into IR-transparent fiber, exhibiting ~ 6 dB/m at 7 and 9 μ m minimal attenuation loss. Confronting with previous study of this system – as pure TAS glass – good efficiency of oxide bond removal by precisely added amount of chemical getter should be highlighted. On the other hand, Ga₅As₁₇Sb₈Se₅₀Te₂₀ alloy revealed signs of bulk crystallization, causing intense light scattering.

Further advances, concerning TAS glasses as host matrices for RE-doping, should be concentrated on the optimization of the ratio between Ga, As, and Sb in order to obtain more stable glass, as well as improvement of the purification and distillation processes in order to decrease the attenuation level and extend the transmission window.

3.7. Annexure (supplementary research data)

3.7.1. Parallel-plate viscometry: determination of Littleton's point

For a better understanding of significant changes in the drawing temperature between different types of glasses, comprehensive research on viscosity change via temperature was performed with the use of a parallel-plate viscometer equipped with a Linear Variable Differential Transformer sensor (TA instruments). Data on Littleton softening point temperature were deduced from collected characteristics and presented together with optimal temperatures elaborated during fiber drawing processes (see Table 3.9).

An important statement from this study is that compositional shifts of temperatures adequate both for Littleton points and drawing temperatures are not proportional. The cause of that is the difference in thermodynamic conditions between viscosity measurement (static heating conditions) and drawing temperature (dynamic conditions originating from heat dissipation due to process gas flow). However, comparing Ga₂(As_{0.4}Se_{0.6})₉₈, and Ga₂(As_{0.28}Sb_{0.12}Se_{0.6})₉₈ can be stated that the addition of Sb into the glass, significantly decreases heat conductivity of drawn fiber preform, leading to a bigger difference of T_L and T_{draw} . More precisely, drawing temperature is the temperature of an inert gas ambient zone monitored with a furnace thermocouple, therefore, including heat gradient occurring in ChG preform it is estimated that real temperature in the center of rod is around 10% lower. Nevertheless, this estimation should be proved by measuring directly heat conductivity.

Composition	Preparation	TL, °C	T _{draw} , °C	Fiber diameter, µm
Ga2(As0.4Se0.6)98	2-step statically purified, preform φ=7mm	246	320	- 350
Ga2(As0.28Sb0.12Se0.6)98		253	350	
Ga5Ge20As10Se45Te20		326	430	
Ga5Ge20Sb5As5Se65		375	520	

Table 3.9. Comparison of Littleton's softening point temperature (T_L) and the temperature of the drawing process (T_{draw}) measured in the closest vicinity of the heating zone in the furnace (to inspect viscometric characteristics see Figure 1.23 in Chapter 1).

3.7.2. Nanoindentation surface mapping of Ga_x(As_{0.40}Se_{0.60})_{100-x} systems

Glass preparation conditions for nanoindentation study

Samples were prepared via a melt quenching technique using high purity commercial elemental precursors As(5N), Se(5N), Ga(7N). Special purification was performed for matrix elements (As, Se) to avoid any contamination such as H₂O, O₂, SiO₂, C. The ampoule of 1cm of inner diameter was sealed under vacuum, heated up to 900°C, homogenized for 10h, and quenched in water at 700°C. In sequence, after quenching samples were annealed for 5h at a temperature 10°C lower than T_g .

Nanohardness mapping tests were performed by means of CSM nanoindentation instrument (CSM Instruments SA., Peseux). Data analysis was done according to Oliver-Pharr's method (see Chapter 1).

Investigations were performed with a load rate of 20mN/min (max load 10mN and dwell time 15s). The studied sample's surface was investigated through scanning mode (creation of uniform grating of 10 separate nanoindentation sequences Figure 3.33a).



Figure 3.33. Scaling of nanohardness tests performed on $Ga_x(As_{0.40}Se_{0.60})_{100-x}$ glass a) and load-displacement curve shift due to Ga dopant b).

Such an approach eliminates the influence of size effects for the maintenance of sufficient locality for each test [57]. Represented measurements of nanohardness and modulus of elasticity E were statistically averaged for each sequence and whole indented area in total. With the enhancement of Ga doping both measured parameters display probable tendency as the common behavior of other glassy alloys (addition of dopant which enlarges density causes similar effect).

3.7.3. Bifurcation of the mechanical response

The structural state of glassy Ga-doped As-Se reveals the major appearance of As₂Se_{4/2} blocks which consist of As-As homonuclear covalent bonds. Another constituent of the structure is Ga-centered polyhedral units (GaSe_{4/2} tetrahedrons). The described mechanism of forming originates from growing input of atomic-deficient volumes which creates bond-free solid angles around contiguous atoms of Se ended with As₂Se_{4/2} parts. With Ga addition, void collection tendency saturates rapidly what in turn promotes the gathering of Ga-based fragments of the structure. Bifurcation of mechanical response can be even explained on the basis of the alloy doped with 4at.% of Ga. Partial disintegration of Ga₄(As_{0.4}Se_{0.6})₉₆ alloy reveals an increase of statistical scattering of the nanohaedness data (Figure 3.34) what suggests more radical changes in the microstructure.



Figure 3.34. Compositional mapping of statistical data for GAS systems: a) modulus of elasticity and b) nanohardness.

An alloy containing 5at.% of Ga clearly demonstrates two subareas of different mechanical properties. The evident reason for free-volume void evolution is an activation of the crystallization process of a well-defined Ga₂Se₃ phase [58].

3.8. Conclusions

The studied glassy systems pursuing the goal of rich in RE ion ChG media, keeping the simultaneously high optical transmission in the n-IR and m-IR, revealed several informative features for further improvement in this matter. Foremost, all Ga₅Ge₂₀As₁₀Se₆₅ alloys, subjected to modifications, substituting 20at.% of Se with Te and 5at.% of As with Sb, have led to fully amorphous matrices, allowing shaping them into IR-transparent optical fibers. 2-step statically purified glasses have shown their minimal attenuation level in the range of 5 – 10 dB/m inm-IR region. This, in turn proves the efficiency of chemically-assisted distillation (with Al chemical getter) by the fact that lack of getter generates minimal attenuation level ~26 dB/m eliminating such material as being functional in view of FEWS, or even more certainly as remote sources of IR light.

Apart from experiments concerning $Ga_5Ge_{20}As_{10}Se_{65}$, the As_2Se_3 matrix as the most common type of ChG has been tested for crucial modifications with Sb and Ga. It turned out that enriching As-Se matrix with 12at.% of Sb, allowed to fully vitrify an alloy doped with 5at.% of Ga. The IR attenuation measurements for dynamically distilled $Ga_2(As_{0.36}Sb_{0.04}Se_{0.6})_{98}$ glass resulted in minimal loss around 0.2 dB/m between 6-7 µm. Thus, these glasses are shown to be suitable for further improvements by RE doping.

Another important conclusion examining TAS-235 matrices prepared under 2-step static distillation protocol, in which As was substituted by 5at.% Ga, and stabilized with 8at.% of Sb. This type of alloy revealed partial crystallization, causing intense light scattering, which may suggest a saturation point for this modification. On the other hand, the optical fiber was successfully drawn from $Ga_2As_{20}Sb_8Se_{50}Te_{20}$ glass, exhibiting ~ 6 dB/m minimal attenuation loss at 7-9 µm. Confronting with previous study for pure TAS system, better efficiency could be reached by better purification/distillation using chemical getters.

Further advances, concerning these glasses as host matrices for RE-doping, should be concentrated on the optimization of glass composition (the ratio between Ga, As, and Sb), as well as improvement of the purification and distillation processes.

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General conclusion

Pnictogen modified Ge-Se-Te-based materials

The concept of TE glass-ceramics (also termed as phonon-glass electron-crystal approach) for energy harvesting, redirected the attention of researchers from entirely crystalline materials to composites. Among many optimal temperature ranges of operation, the family of pnictogen (Bi, Sb, and P) modified Ge-Se-Te-based glass-ceramics could be eventually used in low-temperature domain. Thus, in this work, an insightful study was performed for the first time for novel complex ChG alloys of Bi_xGa₅(Ge_{0.2}Se_{0.8})_{50-(x+5)/2}(Ge_{0.2}Te_{0.8})_{50-(x+5)/2}, Bi_xGa₅Ge₂₀Sb_{10-x}Se₄₅Te₂₀, as well as Bi_xGa₅Ge₂₀P_{10-x}Se₄₅Te₂₀ systems.

$Bi_xGa_5(Ge_{0.2}Se_{0.8})_{50-(x+5)/2}(Ge_{0.2}Te_{0.8})_{50-(x+5)/2}$ alloys with x=1, 5 and 10.

Considering outcomes from the interrelated structural-thermodynamic study of $(Bi_xGa_5(Ge_{0.2}Se_{0.8})_{50-(x+5)/2}(Ge_{0.2}Te_{0.8})_{50-(x+5)/2})$ alloys, the possible crystallization remnants were analyzed for either as-prepared or post-annealed materials. It was shown that up to 5 at.% of Bi the matrix occurs to be amorphous by volume with some initial traces of Ga_2Se_3 crystallites/seeds (~100 nm) and Bi_2Se_{1.5}Te_{1.5} (~5 nm) partially-ordered nanoscale inclusions, which were identified with TEM. Only sample with 10% of Bi showed pronounced crystallization already after quenching. The Raman spectroscopy testifies that crystallized samples are dominated by the vibrations of Te-based structural units within 80-160 cm⁻¹ range.

DSC analyses with implemented Gaussian and Frazer-Suzuki fitting approaches indicated at least five separate crystallization processes caused by heating up to 350° C. It was possible to provoke crystallization of certain phases starting from Bi₂Se_xTe_{3-x}, Ga₂Se₂Te, Te – at a low-temperature domain (~210-300°C), ending with a variety of high-temperature (~320-370°C) phases such as GeSeTe, GaGeTe, and GeBi₂Te₄. Thus, to induce crystallization of specific Bi₂Se_xTe_{3-x}, the heat treatment should be applied close to a low-temperature region of crystallization. Accordingly, crystallization of Bi-Se-Te (already known as the low-temperature TE phase) could be enhanced at the expense of the pure Te phase by annealing at 250°C.

Although their electrical transport properties are still insufficient, notably they possess much higher heat resistivity contributing to a high Seebeck coefficient in the range above room temperature up to 160°C. Considering promising result for a notable increase in electronic charge mobility caused by an increase of Bi-Se-Te phase concentration induced by moderate devitrification process – annealing at ~ 5° below the T_g of an amorphous constituent, it was possible to decrease electrical resistivity by two orders of magnitude from (10⁵ to 10³ Ω ·m).

In addition, IR light attenuation effect was observed in this system. Small changes in Bi content allowed to fabricate ~mm thick glass fully transparent or opaque in ~3-16 µm region.

$Bi_xGa_5Ge_{20}Sb_{10-x}Se_{45}Te_{20}$ alloys with x = 0, 1, 3, 5 and 10.

The investigated $Bi_xSb_{10-x}Ga_5Ge_{20}Se_{45}Te_{20}$ alloys with chalcogenide ratio Te/Se = 0.4 shown to be suitable for the incorporation of quite a high concentration of Bi keeping the glassy state. With Bi addition, the increase in density and decrease in glass transition and glass stability criterion is observed as well as a decrease in the optical bandgap. The complete opacity of ~2mm thick sample with 10 at.% of Bi is observed in a wide visible and IR range.

The glass transition temperature T_g of all investigated samples is higher than 200°C. Analysis of the crystallization kinetics reveals only a few crystallization processes which can be described with JMA model, while the majority of them do not pass JMA applicability test. The activation energies of crystallization show a tendency to increase with Bi content, which is associated with an overall shift of the crystallization processes to lower temperatures. Glassceramics formation by crystallization becomes more rapid in Bi-rich glasses. On the basis of previous studies, the predominant crystallization of Bi-based compounds (like Bi₂Se_xTe_{3-x}) is expected in the low-temperature region, while crystallization processes of stable Ge- and Sbbased chalcogenide phases should occur in the high-temperature range beyond ~320°C.

$Bi_xGa_5Ge_{20}P_{10-x}Se_{45}Te_{20}$ alloys with x = 0, 1, 3, 5, 7 and 10.

It was shown, that extension of glass-forming ability of Ga, Bi-modified Ge-Se-Te alloys is possible by P addition. P – being known as the element of many possible coordination states, thus suspected to support the desired disorder in a glassy state. Indeed, by the cosubstitution of 3at% P and 7at.% Bi it was possible to vitrify material by a melt-quench process. Therefore, it might be also tempting to check its behavior under low-temperature conditions of post-annealing, and investigate its TE properties. Generally, P-based glasses showed to be the most stable against crystallization during Bi addition. DSC analysis of the crystallization kinetics showed to be similar to the results obtained for BixSb10-xGa5Ge20Se45Te20 system. P addition suppresses low-temperature crystallization between 240 – 300 °C, or even in parallel shifts and merges these two peaks to the high-temperature range at the onset of crystallization at ~ 330°C into one peak, which is most probably attributed with Bi-Se-Te phase. Nonisothermal and isothermal crystallization kinetics analyzed with Frazer-Suzuki fit function reveals negative apparent activation energy for crystallization of two phases in the Bi₁P₉Ga₅Ge₂₀Se₄₅Te₂₀. This anti-Arrhenius behavior is explained by a dominant role of free energy of nucleus formation in the crystallization rate if crystallization occurs in proximity to melting points of these phases.

General conclusion

The activation energies of crystallization for the glasses with both P and Bi in their network are smaller than for the edge compositions with only Bi or P. This is consistent with the idea that an increase in E_a can be caused by a shift of the crystallization processes to lower temperatures. Owing to the obtained results, the developed P-containing glass matrix can be also considered as a good candidate for IR photonics.

Glasses for active fiber device applications

The efficient IR sensing devices already support many fields like biotechnology, drug industry, medicine, environmental pollution detection, etc. Research in this field follows an idea to create precise, miniaturized detection units that enable *in-situ* and *in-vivo* analysis of many important molecules affecting our health, environment, etc. For this purpose, the "active" IR transparent fibers are of high interest. Thus, this work is devoted to study potential matrices for further fiber drawing and RE-doping focusing on Ge-Se-based and As-Se-based systems.

In general, all Te, Sb (co-)modified Ge-As-Se-based systems prepared under 2-step static distillation processes as well as+ basal $Ga_5Ge_{20}As_{10}Se_{65}$ matrix (1-step static process) has been verified as vitreous alloys, suitable for fiber drawing process. The inevitable role of Al oxygen getter has been reflected in minimal loss observed on attenuation spectra. Roughly estimated minimal attenuation loss for the 2-step statically purified glasses varied within ~ 5 – 10 dB/m, whereas glass distilled without chemical getter revealed attenuation of 26 dB/m.

Apart from $Ga_5Ge_{20}As_{10}Se_{65}$, the As_2Se_3 matrix as the most common ChG has been tested for Ga, Sb modifications. It turned out that enriching As-Se matrix with 12at.% of Sb, allowed to fully vitrify an alloy doped with 5at.% of Ga. The IR attenuation measurements for dynamically distilled $Ga_2(As_{0.36}Sb_{0.04}Se_{0.6})_{98}$ glass resulted in minimal loss ~0.2 dB/m between 6-7 µm. Thus, these glasses are shown to be suitable for further improvements by RE doping.

Another important conclusion examining TAS-235 matrices prepared under 2-step static distillation protocol, in which As was substituted by 5at.% Ga, and stabilized with 8at.% of Sb. This type of alloy revealed partial crystallization, causing intense light scattering, which may suggest a saturation point for this modification. On the other hand, the optical fiber was successfully drawn from Ga₂As₂₀Sb₈Se₅₀Te₂₀ glass, exhibiting ~ 6 dB/m minimal attenuation loss at 7-9 μ m. Confronting with the previous study for pure TAS system, better efficiency could be reached by better purification/distillation using chemical getters.

Further advances, concerning these glasses as host matrices for RE-doping, should be concentrated on the optimization of glass composition (the ratio between Ga, As, and Sb), as well as improvement of the purification and distillation processes.

Dissemination of the obtained results

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