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Thesis title: " Pnictogen modified Ge-Ga-Se(Te)-based glasses for optoelectronic devices"

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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 Ga_2Se_3, $Bi_2Se_xTe_{3-x}$ and Te phases.

Apart from that, regarding applicatory context, the electrical resistivity has been measured in parallel with additional annealing. Gathered results for $Bi_5Ga_5Ge_{18}Se_{36}Te_{36}$ glass demonstrate a decrease of resistivity in the range of $10^5 \rightarrow 10^3 [\Omega \cdot m]$ 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 $Bi_5Ga_5Ge_{18}Se_{36}Te_{36}$ system occurs to be amorphous by volume with some initial traces of Ga_2Se_3 crystallites/seeds (100nm) and $Bi_2Se_{1.5}Te_{1.5}$ (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 → Sb, Se → Te to the $Ga_5Ge_{20}As_{10}Se_{65}$ matrix
- Substitution As → Sb to the Ga-modified As_2Se_3 matrix
- Substitution As → Ga to the $Te_{20}As_{22}Sb_8Se_{50}$ 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 As_2Se_3 glasses obtained through optimized dynamic distillation protocol, the lowest attenuation measured reached 0.2dB/m.