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Review of the doctoral dissertation entitled "Pnictogen modified Ge-Ga-Se (Te) -based glasses for optoelectronic devices" by Mr Jakub Szlęzak MSci

Two aspects of the thesis under review make out of it a kind of monograph devoted to the fabrication, characterization and selected applications of the title glasses in comparison with typical PhD thesis. Firstly go the number and versatility of the experimental methods employed, with the results obtained thereof supported with the appropriate theoretical analyses well founded in the existing literature. Secondly, an important part of the overall text (164 pages without counting the Polish an French summaries) conveys an ample description of the experimental techniques worldly used in studies of similar systems.

The general subject of the thesis concerns so called chalcogenide glasses (ChG) i.e. those based on the chalcogen elements, e.g. sulfur S, selenium Se, and tellurium Te, alloyed with tathogens, usually Ge, and pnictogens such as P, As, Sb Bi, etc. Novel compounds of these materials are investigated for the perspective of applications in two main domains i.e. i) in thermoelectric and related semiconductor devices and ii) as optical fibres (waveguides) transparent in the infrared region of the electromagnetic radiation, used especially as fibre evanescent wave spectroscopy (FEWS) sensors.

In particular the systems under study are $Bi_xGa_5(Ge_{0.2}Se_{0.8})(Ge_{0.2}Te_{0.8})$, $Bi_xGa_5Ge_{20}Sb_{10-x}Se_{45}Te_{20}$, with the bismuth concentrations x = 1, 5 and 10. The first composition is given the name "GTS-s" for the equal concentration of selenium and tellurium, however it is intriguing why the composition $Bi_xGa_5Ge_{20}Sb_{10-x}Se_{45}Te_{20}$ is systematically called Te/Se=0.4 throughout the text, whereas the concentration ratio 20/45 = 0.444... ≠ 0.4. Further, the effect of phosphorus substitution of the Bi atoms on The GTS, Te/Se = 0.4 is studied with the Bi – P proportions 10 – 0, 7 – 3, 5 – 5, 1 – 9, and 0 – 10 denoted SBi10, SBi5, SBi3 and SBi1 and SBi0 respectively.

The studies of the Bi and Ga modified GTS, Te/Se = 1, glasses encompass the samples preparation in which the chemical compositions determined with the use of the energy dispersed X-ray spectroscopy (EDS) have been compared with the initially assumed ones (Table 2.1). The most significant differences have been noticed for the largest Bi content (Bi_{10}...). This may be related with a non-glass state of the as-prepared samples detected with the X-ray diffraction. The systems with Bi1 and Bi5 show two temperature regions of crystallization and the author states hypotheses on the particular crystalline phases that are precipitated giving rise to each peak in the DSC curves. A qualitatively different result has been obtained for the Bi_{10}... sample, where only the high-temperature thermodynamic manifestation of crystallization was observed as the sample had already been partly crystallized when quenched. The Ozawa plots allowed the author to estimate the activation energies with the use of Johnson-Mehl-Avrami (JMA) model. The attribution of the Raman bands does not seem very conclusive. The author explains that by possible shifts of vibrational eigenfrequencies due to the atoms substitutions in the mixed materials. The materials were also examined with the large-scale instruments, i.e. with Nanoscale Ordered Materials Diffractometer at the Spallation Source in Oak Ridge Laboratory and with X-ray synchrotron Advanced Photon Source at Argonne National Laboratory (USA). The results generally confirmed the X-ray diffractometer data obtained with the Bruker D8 diffractometer but allow the author to estimate the average size of the ordered regions to about 2.4 – 2.5 nm which is lower than the average size of the ordered regions detected with the electron microscopy images. Continuous Stiffness Measurement with an Ultra Nanoindentation Tester (UNHT) (not deciphered) show a rise in nanohardness and in the Young's modulus with increasing devitrification that grows with the Bi content. The Bi content also reduces the optical transmission in the range 2- 22 micrometers. The Bi10 system is practically opaque. DC electric conductivity exhibits features typical for semiconductors for Bi1 and Bi5 and increases significantly for Bi10.

The analyses of "Te/Se = 0.4" are less complete with a general conclusion that the decrease in Te content does not provoke so strong devitrification for growing Bi content as in the case of Te/Se =1.0. Consequently the author is right when writing "The investigated Bi_xSb_{10-}

$_x Ga_5Ge_{20}Se_{45}Te_{20}$ alloys with chalcogenide ratio Te/Se = 0.4". [have] shown to be suitable for the incorporation of quite high concentration of Bi keeping the glassy state". The lack of structural, microscopic and vibrational-spectroscopic data explains the author's statement that the elucidation of the nature of recrystallization in this case requires further studies.

More experiments have been done on P substituted GTS Te/Se = 0.4 glasses. The planned and examined samples were not compared. An interesting effect of Anti-Arrhenius behaviour, i.e. a negative activation energy has been found. A general statement is that the addition of P enhances the stability of glass and prevents bulk crystallization during glass preparation as well as suppress the low-temperature (240 – 300 °C) crystallization under the heat treatments. Increase in P content shifts the absorption edge towards higher frequencies (energies) as shown in Fig. 2.34. The $Bi_7Ga_5Ge_{20}P_3Se_{45}Te_{20}$ composition (containing 7 at.% of Bi) maintaining homogeneous amorphous structure is selected as a promising candidate for further investigations.

Chapter 3 is devoted to the application of the studied glasses as IR sensing devices. The first 16 pages provide a review on the fabrication of the optical fibres with fibre drawing machine completed by the Glasses and Ceramics Team, Institute of Chemical Sciences of the University of Rennes as well as on optical and selected mechanical properties of similar systems. The original results concern measurements of transmission spectra, the related absorption edges and attenuation spectra in the systems $Ga_5Ge_{20}As_{10-x}Sb_xSe_{65-y}Te_y$ (x = 0, y = 0); (x = 5, y = 0); (x = 10, y = 0); (x = 0, y = 20); (x = 5,y = 20); (x = 10, y = 20). Additionally, measurements on the thermodynamical stability of the matrices have been done and presented in Table, 3.6. Different units of energy (wavelength, frequency) in Table 3.5. and Fig. 3.12 make a comparison of the results a bit difficult. The summary on p. 169 open the prospects of further studies rather than conveying firm conclusions. "Thus, next steps in this field should be made on optimization of doping and purification". The effect of addition of Sb on the Ga doped chalcogenide systems lead the author to measurements of TAS-235 in which "Confronting with previous studies for pure TAS system, better efficiency could be reached by better purification/distillation using chemical getters.". An annexure has been provided on viscosimetry and nanoindentation showing a bifurcation of the mechanical response.

The problem with the evaluation of this work is that it is difficult to separate the literature data from the results obtained by the author. The latter have usually no reference to the published articles with participation of the author. The articles, gathered at the last page of the thesis are however quite numerous (7). Being a good guide for novices of the subject the text suffers from some linguistic drawbacks such as omission or misuses of articles “a” and “the” which is understandable for a native speaker of a language lacking these parts of speech. A systematic use of “what” instead of “that” to translate Polish “co” or French “ce qui”/ “ce que” as well as occasional misunderstood expressions such as “as can be dented(?) from Figure”, “glass industry is dictated by”, “Se interruption into ...”, “basic state” instead of “ground state” make reading somewhat difficult.

Minor shortcomings noted above do not diminish the value of the results achieved by the author or his skills in using various experimental methods and theoretical analyses. Therefore, I am entitled to state that the thesis meets the requirements set for the doctoral dissertations by the Act of March 14, 2003 on academic degrees and academic title as well as on degrees and title in the field of art (Journal of Laws of 2016, item 882 and 1311) as amended (Journal of Laws of 2017, item 859) in connection with the Act of July 20, 2018 Law on Higher Education and Science (Journal of Laws of 2020, item 85 with amendments) and I hereby request that the author be admitted to further stages of the doctoral procedure.