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How silver influences the structure and physical properties of chalcogenide glass $(GeS_2)_{50}(Sb_2S_3)_{50}$

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ABSTRACT

The presented study shows how the incorporation of silver changes the structure and physical properties of chalcogenide glass $(GeS_2)_{50}(Sb_2S_3)_{50}$. Nine samples with silver content (0–25 at. %) were studied to give a detailed picture. The structure and its changes were analyzed by Raman spectroscopy. The medium range order of the $(GeS_2)_{50}(Sb_2S_3)_{50}$ glass was identified. The structural motif of interconnected $SbS_{3/2}$ pyramids is the doorway for the silver incorporation in the $(GeS_2)_{50}(Sb_2S_3)_{50}$ glass. The material hardness is significantly increased by up to 26% due to silver addition. The ability of silver to fill cavities in a glass is responsible for the observed hardness increase. Electronic properties and silver ion mobility were examined by impedance spectroscopy and radioactive tracer diffusion. The purpose of the presented study is to give an instructive description of how silver change the structure of the studied chalcogenide glass and give a complex feeling of how the silver changes its physical properties.

1. Introduction

Silver doped chalcogenide glasses compared to undoped chalcogenide glasses exhibit red-shifted absorption, higher index of refraction and steep increase in electrical conductivity. Introduced silver into chalcogenide glass became cation Ag^+. The charge of the Ag^+ cation is compensated by C_1^- (one-fold coordinated chalcogen) [1, 2]. The silver doped chalcogenide glasses, with Ag concentration higher than ≈ 5 at. %, are a good ionic conductor [3]. Increase of the electrical conductivity could reach up to 11 orders of magnitude (from 0 to 30 at. % of Ag) [4].The good ionic conductivity and ability of silver to form a conductive filament make silver doped chalcogenide glasses a good candidate for a Conductive Bridge RAM memory. The Conductive Bridge RAM memory is today one of the most promising applications of silver doped chalcogenide glasses with an industrial significance [5]. The $(GeS_2)_y(Sb_2S_3)_{1-y}$ glasses belong among the important pseudo-binary chalcogenides. These glasses are attractive for silver doping because of two main reasons: 1) the $(GeS_2)_y(Sb_2S_3)_{1-y}$ glasses are well described, as they were object of numerous studies regarding glass-forming properties [6], structural properties [7–10], optical properties [11], and mechanical properties [12]; and 2) the silver doping of ternary GeSbS glasses has not yet been studied in detail. The aim of the present work is to describe how silver influences the structure and the physical properties of the chalcogenide bulk glass $(GeS_2)_{50}(Sb_2S_3)_{50}$. The structural changes, hardness evolution and electronic / ionic properties are of the special interest.

2. Experimental

2.1. Glass preparation

The samples $Ag_x((GeS_2)_{50}(Sb_2S_3)_{50})_{1-x}$ glasses where x = 0, 0.1, 1, 5, 7.5, 10, 12.5, 15, 17.5, 20, and 25 were prepared. Appropriate amount of elements (Ge, Sb, S, Ag) of 5 N purity was sealed into evacuated silica ampule. Each batch has about 10 g. Synthesis was done in a rocking furnace at temperature 970 °C for 36 h. Then the temperature was decreased to 700 °C and samples were quenched into the water and annealed for 3 h ca. 20 °C under Tg.Composition and glass homogeneity was tested by SEM microscope Lyra 3 (Tescan) equipped with EDX analyser AZtec X-Max 20 (Oxford Instruments), and Bruker AXS diffractometer D8. The DSC measurements were performed using Q2000 heat-flow calorimeter (TA Instruments). Microhardness was measured by Hanemann's microhardness-meter with Vickers' pyramid, supplied with a Zeiss-Neophot microscope. Density of samples was

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measured by Archimedes method.

2.2. Raman spectroscopy

Raman scattering spectra of the bulk samples were measured by Dimension P2 system (Lambda Solution, USA) Spectra were excited with a laser operating at 532 nm (output power 5 mW). Reduced Raman intensity of glasses Raman spectra were calculated considering the Gammon–Shuker equation [13].

2.3. Microhardness

The bulk samples were fixed in an epoxy resin. After hardening were the samples polished from the top side to an optical quality. Microhardness was measured by Vickers method. There was applied a load of 80 g for 10 s. The six measurements were done for each sample. The accuracy of the microhardness measurement was ± 5% (for the samples x = 20, 25 was accuracy ± 9%).

2.4. Electrical conductivity measurement

The dimension of each bulk sample was about 5 × 5 mm and thickness about 1 mm. The both sides were polished and Pt sputtered. Impedance spectroscopy measurement was performed by impedance spectrometer Autolab PGSTAT204 in frequency range 10 mHz – 100 kHz from 20 °C up to 150 °C. The sample of $Ag_{15}((GeS_2)_{50}(Sb_2S_3)_{50})_{85}$ composition was measured at Alpha-A Analyser from Novocontrol and at Keysight E4991B Impedance Analyser (in frequency range 0.1 Hz to 3 GHz, in temperature range − 100 °C to 140 °C). All impedance measurements were done in normal atmosphere.

2.5. Radioactive tracer diffusion measurement

Radioactive tracer diffusion (RTD) measurement was performed at three glass composition $Ag_x((GeS_2)_{50}(Sb_2S_3)_{50})_{1-x}$ where x = 0, 7.5, and 15. Seven samples were prepared from each composition. A drop of radioactive $^{110m}AgNO_3$ was deposited on top of sample. The drop was kept for a certain period and dried. The samples, containing radioactive silver on their surface, were encapsulated into the ampules and annealed at different temperatures from a couple of hours to a couple of days. The penetration profile of silver inside annealed samples was evaluated by a multistep process. As first, the total gama activity was measured by scintillation counter. After that, a few units of microns from top of the samples were grinded. The both steps were repeated ca. 8 times. The diffusion measurement was performed in the temperature range from 20 °C to 180 °C. This temperature range was chosen to coincide with the temperature range of the impedance measurement (from 20 °C to 150 °C). The temperature range for the sample x = 0 was higher (from 180 °C to 270 °C) because the diffusion process of silver at this sample is slower.

3. Results

3.1. General

The prepared sample without silver $(GeS_2)_{50}(Sb_2S_3)_{50}$ has a red colour but with an increasing content of silver the samples became gradually darker and metallic shiny. The density of the samples increases proportionally to the content of silver as shown in Fig. 1. The value of glass-transition temperature T_g declines steeply for small concentration x < 5, then decrease slowly as shown in Fig. 1. XRD and SEM microscopy prove that samples are glassy where silver concentration x ≤ 15. The samples are glassy with crystalline inclusions for x ≥ 17.5. The crystalline inclusions are separated by a glassy phase and represent a minor portion (< 5 vol%) of the whole sample (Fig. 2e).

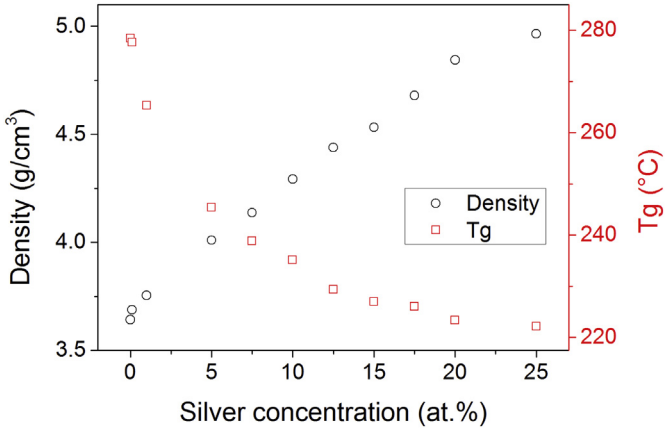

Fig. 1. Density and glass-transition temperature of the $Ag_x((GeS_2)_{50}(Sb_2S_3)_{50})_{1-x}$.

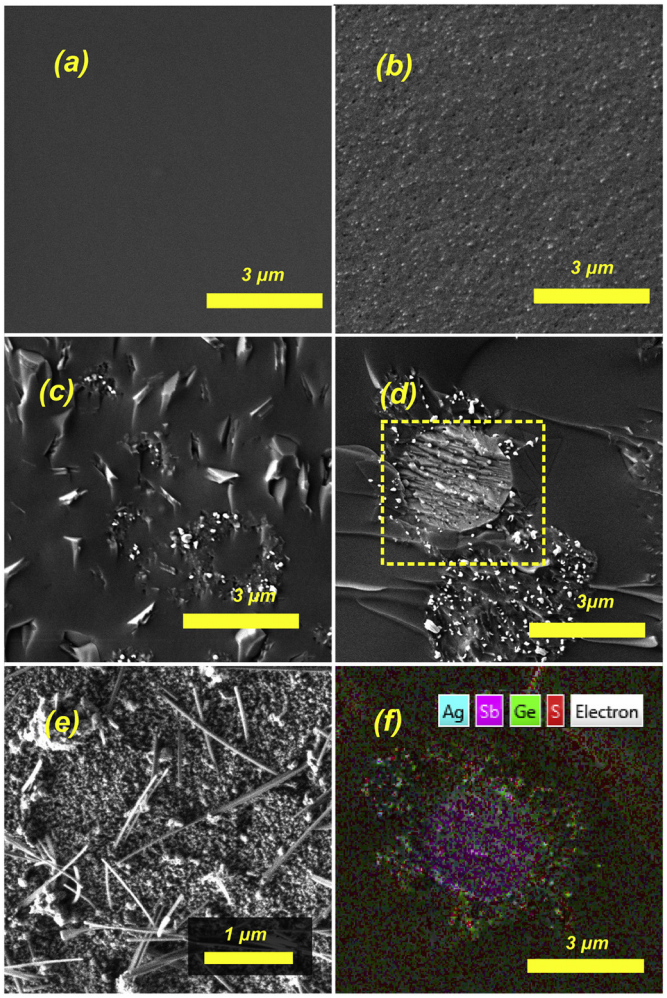

Fig. 2. a-f) SEM images of samples $Ag_x((GeS_2)_{50}(Sb_2S_3)_{50})_{1-x}$ a) x = 15 glass without a crystals, b) x = 17.5 with antimony crystals, c) x = 20 with antimony crystals d) x = 25 phase separated antimony sphere is visible e) x = 20 after wet etch in NaOH solution with needle like antimony crystals 1–2 μm in length, f) x = 25, EDX mapping identifies antimony sphere.

XRD results show that crystals are antimony for samples x = 17.5, 20, and 25 at. % and argyrodite [14] Ag_8GeS_6 for sample x = 25. The corresponding crystallization patterns are shown in the previous work [15]. The antimony crystals are rhombohedral (R3m – 166) – the lattice