

Crystallization ability of 80GeSe₂-20Ga₂Se₃ glasses caused by thermal treatment studied by XRD method

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Abstract—Crystallization ability of the 80GeSe₂-20Ga₂Se₃ chalcogenide glasses caused by annealing at 380 °C during different duration are studied using X-ray diffraction method. It is established that GeGa₄Se phase of low- and high-temperature modification, Ga₂Se₃ phase (α - and γ -modification) and GeSe₂ phases are crystallized during this process. It is shown that annealing duration over 50 h does not lead to further internal structural crystallization.

Keywords— chalcogenide glass; crystallization; annealing; phase composition; modification

I. INTRODUCTION

Modern development of IR photonics and sensor electronics put forward an actual task to search new functional media for effective transfer of wide-spectra electro-magnetic radiation and to develop novel miniaturization technologies of passive and active photonic elements (optical waveguides, resonators, splitters, multiplexers, detectors, signal amplifiers and converters, comparators, etc). One of the most perspective media for such applications are special chalcogenide glasses (ChG) – non-oxide glassy-like materials with high content of chalcogens (S, Se, Te) [1,2]. To a great extent, the further success in this field relies on chemical-technological resolutions in development of ChG-based media with unique properties. Thus, principal functionality of ChG revealed in their excellent IR transparency (including both commercially-important atmospheric telecommunication windows at 3-5 and 8-12 μm up to space telecommunication domain at 15-25 μm) can be effectively combined with transparency of halide compounds in a visible range by developing mixed chalcogenide-halogenide glasses and glass-ceramics [3-7].

Basic conceptions receipt of such media based on the varied methods technological and post-technological structural modification using external factors such as thermal annealing, high-energy radiation treatment laser beams. It is known that in the nearest atomic environment glass matrix can adequately studied using numerous experimental methods like vibration and Raman scattering spectroscopy, X-ray diffraction (XRD)

scanning electron microscopy, etc. [4,9].

The aim of this work is investigation of crystallization processes and features formation of crystalline phases in 80GeSe₂-20Ga₂Se₃ chalcogenide glasses under different durations of thermal annealing above the glass transition temperature using XRD method.

II. EXPERIMENTAL

The 80GeSe₂-20Ga₂Se₃ samples were prepared from high pure Ge, Ga and Se (99.999%) components in silica ampoule kept under 10⁻⁶ vacuum. Raw materials were heated from 20 to 850 °C at 2 °C/min and maintained at temperature for 12 h. Then silica tube was cooled in water at room temperature and annealed at 30 °C below the glass transition temperature (370 °C) for 3 h and slowly cooled at room temperature. Samples with thickness of 1 mm were polished for further investigations [4,10-18].

The crystallization of the 80GeSe₂-20Ga₂Se₃ ChG was performed with a single step of heat treatment at $T_g + 10$ °C [8,9,12,14]. This temperature has been chosen as an optimal temperature of ceramization as it permits to control the generation by simultaneous nucleation and growth of nanoparticles within the glassy matrix according to the heat treatment time. Thus, glass samples were placed in a ventilated furnace where the accuracy of temperature is ± 2 °C for various time varying from 10 to 100 h [9].

The XRD measurements (CuK α_1 radiation) were carried out to determine crystalline phases in the studied glasses. Powdered 80GeSe₂-20Ga₂Se₃ glasses were deposited on amorphous substrate and prepared to arrange experiments in optimal geometry. The automatic STOE STADI P diffractometer ("STOE & Cie GmbH, Germany) with a linear position-precision detector were used for XRD measurements. Experimental linear absorption coefficients were determined as logarithmic ratio of primary beam intensities after passing through background and studied samples. All measurements were conducted in 2 θ -step regime, the profiles of peaks being refined using WinPLOTR software [8].

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III. RESULTS AND DISCUSSION

Combined results obtained by XRD method for 80GeSe₂-20Ga₂Se₃ chalcogenide glasses before and after thermal annealing at 380 °C for 10, 25 and 50 h compared with the theoretical reflexes of the known GeGa₄Se₈, GeSe₂ phases are represented in Fig. 1 and Fig. 2.

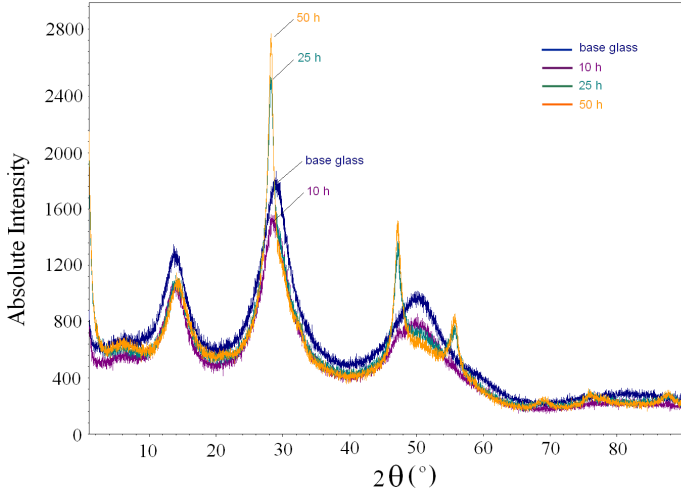


Fig. 1. Experimental XRD patterns for 80GeSe₂-20Ga₂Se₃ glasses before (base glass) and after annealing for 10, 25 and 50 h

It is shown that annealing at 380 °C for 10 h almost does not change the structure of glasses. However, in the diffraction angles of $2\theta < 1.5^\circ$ there is the increase of intensity that testifies to formation of fractals aggregates and structures. It is possible to assume that basic transformations can be related to inwardly-phase stratification in the 80GeSe₂-20Ga₂Se₃ cut-section on individual components (stoichiometric GeSe₂ and Ga₂Se₃) which set the stage for further reaction forming of GeGa₄Se₈ triple phase [8]. This indicates that the stoichiometric 80GeSe₂-20Ga₂Se₃ cut-section creates terms for crystallization of GeGa₄Se₈ phase due to segregation of preliminary selected GeSe₂ and Ga₂Se₃ phases with additional formation of GeSe₂-enriched residues. Since the stoichiometric GeSe₂ phase is outside glass formation [8,9,14] then in future it will be formed in a separate crystalline phase.

The Ge-Ga-Se system (polythermal and isothermal cut-sections, crystal structure of intermediate phase) was studied in [19,20]. The existence of GeGa₄Se₈ (Ga_{0.5}Ge_{0.13}Se) phase is in two modifications with polymorphic transformation temperature of ~898 K (625 °C). High-temperature modification is crystallized in ZnS structural type (cubic crystal system, *F*-43*m* space group, *a* ~5.45 Å), whereas for low-temperature modification (GeGa₂Se₅) structure precision has not been established, however, parameter *a* is ~5.461 Å [19] indicating affinity in structures of these two modifications. It was also reported about existence of GeGa₂Se₃ but GeGaSe₃ phases [21]. Total structural relationship between these phases and binary Ga₂Se₃ GeSe₂ phases and various modifications are Ga [Se₄] and Ge [Se₄] tetrahedrons.

In non-annealed ChG and annealed for 10 h semi-amorphous halo testify dipped ordering of these tetrahedrons in the glass structure without clear their belonging to some of the

mentioned phases. However, with increasing annealing time from 25 to 50 h the well-formed peaks of GeGa₄Se₈, Ga₂Se₃ and GeSe₂ phases appear. The maximal reflection corresponding to GeSe₂ phase is semi-amorphous halo while reflections from GeGa₄Se₈ and Ga₂Se₃ are relatively well formed, especially at maximum of $2\theta \sim 28.22^\circ$ (Fig. 2).

It should be noted that semi-amorphous halo presented in diffraction pattern of non-annealed ChG and annealed for 10 h does not disappear. Overall, the picture is completely consistent with the results given in [5]. For samples annealed for 25 h and 50 h raising intensity at low diffraction angles of 2θ is shown suggesting that the fractal formation in the glass during annealing will not disappear, but become larger (Fig. 2).

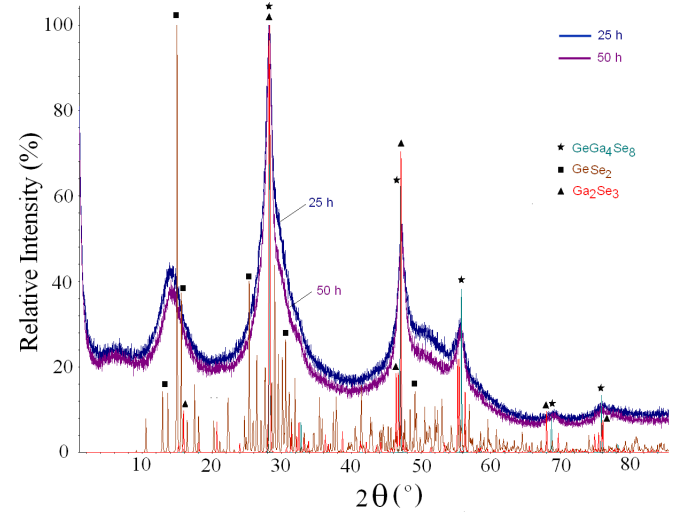


Fig. 2. Experimental and theoretical XRD patterns for 80GeSe₂-20Ga₂Se₃ glasses after annealing for 25 and 50 h

However, at detailed analysis of maximum halo, it is possible to notice that even at insignificant time of heat treatment (10 h), the changes in glass structure are performed (Fig. 3).

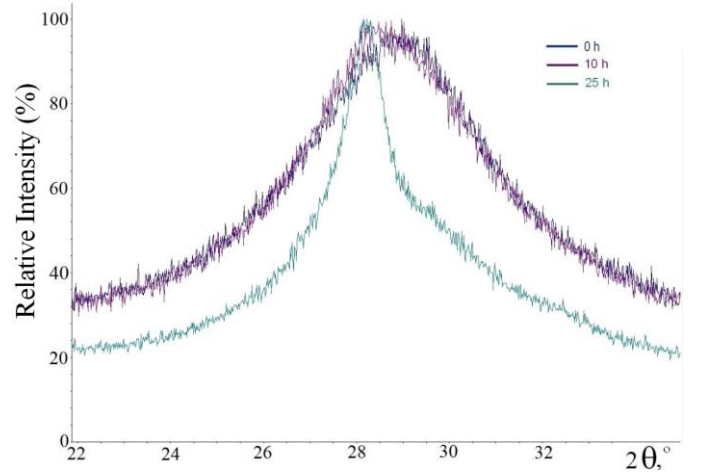


Fig. 3. Comparison of maximum of diffraction peaks for ChG before and after annealing for 10 and 50 h

This process is accompanied by crystallization of GeGa_4Se_8 phase (in the structure of glass from chaotic arrangement of Ga $[\text{Se}_4]$ and Ge $[\text{Se}_4]$ tetrahedrons characterized by only short-range order, the transition to the formation of long-range order characteristic of crystalline structure of GeGa_4Se_8 with ZnS structural type ZnS occurs).

Further increasing in annealing duration to 80 and 100 h does not affect on the diffraction peaks, reflecting mainly the formation of double and triple GeGa_4Se_8 and Ga_2Se_3 phases, just as for 80 GeSe_2 -20 Ga_2Se_3 glass, annealed for 50 h (Fig. 2 and Fig. 4). Thus, further crystallization process registered by XRD and formation of long-range order in times of such annealing does not occurs. First maximum of semi-amorphous halo at $\sim 14.6^\circ 2\theta$ (Fig. 4) corresponds to the maximum intensity reflection (002) of GeSe_2 phase (monoclinic syngony, $P2_1/c$ space group).

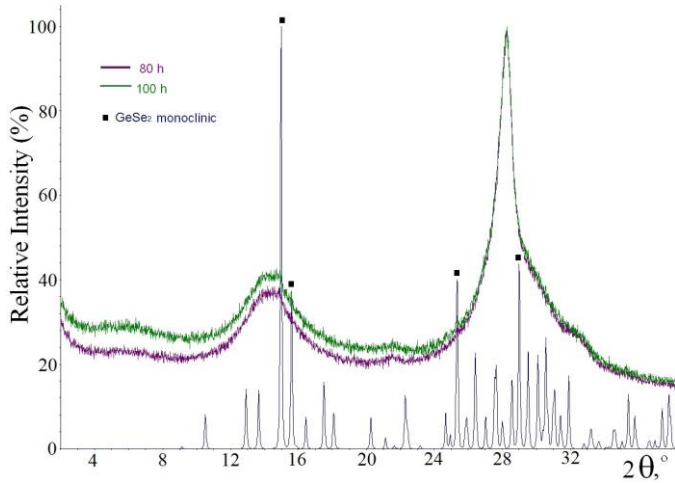


Fig. 4. Comparison of small-angle diffraction experimental plot for glasses annealed for 80 and 100 h with theoretical reflections of GeSe_2 phase

For ChG samples annealed at high duration of 80 and 100 h the additional analysis of Ga_4GeSe_8 and Ga_2Se_3 crystallization phase was performed. Taking into account the state diagram for the Ga-Se system, temperature of existence of cubic Ga_2Se_3 (high-temperature $\text{Ga}_{0.67}\text{Se}$) begins above $T = 730^\circ\text{C}$. Below this temperature is low-temperature monoclinic modification of Ga_2Se_3 . Distinguish monoclinic and cubic modification of Ga_2Se_3 phases is possible only on samples with the high degree of crystalline.

Assuming that in studied samples pure high-temperature Ga_2Se_3 phase is crystallized, then most likely this is modification of $\alpha\text{-Ga}_2\text{Se}_3$ ($a \sim 5.44 \text{ \AA}$). However, taking into account that the peaks are extended, along with α -modification γ -modification of Ga_2Se_3 is possible (Fig. 5).

However, it should pay attention to raising of background on diffraction pattern (indicated by ellipses in Fig. 6).

These raising correspond to peaks from experimental diffraction pattern for high- and low- temperature modification of Ga_4GeSe_8 (Fig. 7).

Otherwise, we can assume that crystallized high-temperature $\alpha\text{-Ga}_2\text{Se}_3$ phase (stabilization with minor Ge impurities lowers the temperature of its existence from 730°C to 385°C , which dependence for glass annealing) and amorphous phase of glass, which is responsible for halo circled ellipses, are present in ChG.

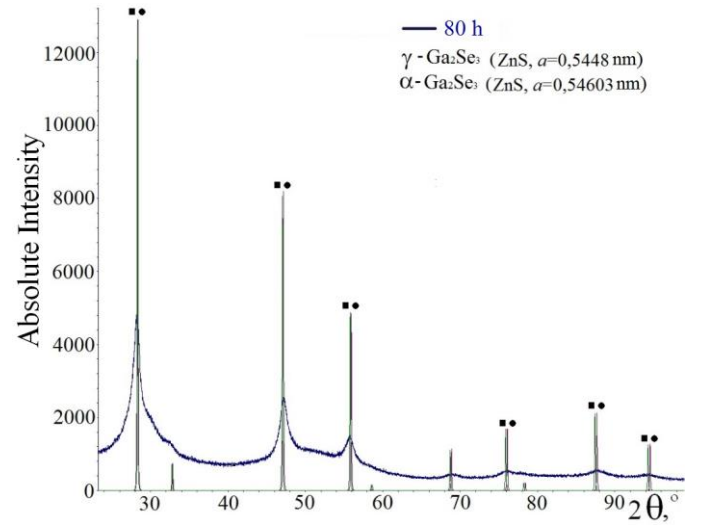


Fig. 5. Comparison of experimental XRD patterns for ChG annealed for 80 h with theoretical reflexes of $\alpha\text{-Ga}_2\text{Se}_3$ and $\gamma\text{-Ga}_2\text{Se}_3$ phases

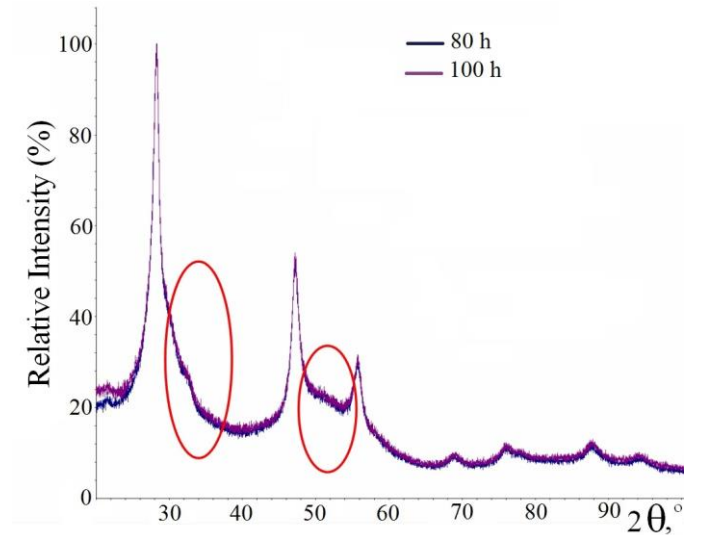


Fig. 6. Raising of background on experimental XRD patterns for samples annealed for 80 and 100 h

The width of the peak at $2\theta \sim 28,22^\circ$ indicates the presence in the crystal matrix of nanoparticles dispersed in the form of nanocrystalline including by a size of 9-10 nm (determined by the Debye-Scherrer equation [8,24]).

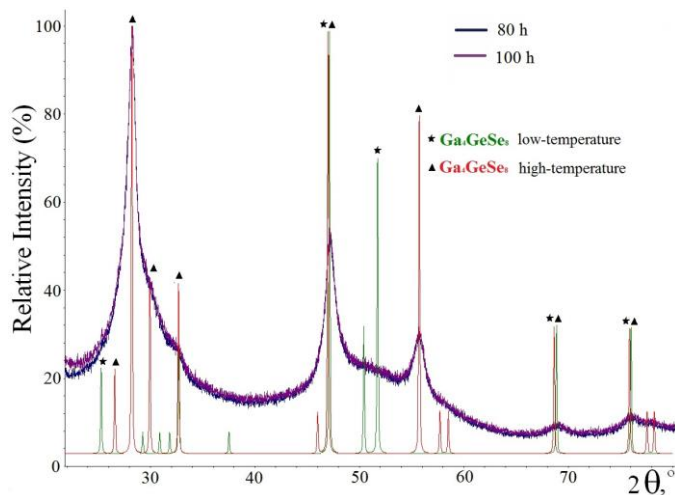


Fig. 7. Comparison of experimental XRD patterns for ChG annealed for 80 and 100 h with theoretical reflexes of Ga_4GeSe_8 phase low- and high-temperature modifications

CONCLUSIONS

It is established that crystallization processes in the $80\text{GeSe}_2\text{-}20\text{Ga}_2\text{Se}_3$ ChG caused by annealing at 380°C for 10, 25, 50, 80 and 100 h indicating the formation of GeGa_4Se (high- and low-temperature modification), Ga_2Se_3 (α - and γ -modification) and GeSe_2 crystals with size of 9-10 nm. Increasing duration of thermal treatment for $80\text{GeSe}_2\text{-}20\text{Ga}_2\text{Se}_3$ glasses leads to obtaining of thermal-stable glasses and glass-ceramic media.

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