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Structural investigation of crystallized Ge-Ga-Se chalcogenide glasses

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Abstract. Crystallization transformation in the $80GeSe_2$-$20Ga_2Se_3$ chalcogenide glasses caused by annealing at 380 °C during different duration (25, 50, 80 and 100 hours) are studied using X-ray diffraction and atomic force microscopy methods. It is established that $GeGa_4Se$ phase of low- and high-temperature modification, Ga_2Se_3 phase (α- and γ-modification) and $GeSe_2$ phases are crystallized during this process. It is shown that annealing duration over 50 h does not lead to further internal structural crystallization, while annealing for 80 h result in processes of surface crystallization.

1. Introduction

Development of modern IR photonics brings up the challenges of searching new functional media for effective transfer of wide-spectra electro-magnetic radiation and developing of novel miniaturization technologies of passive and active photonic elements (optical waveguides, resonators, splitters, multiplexers, detectors, signal amplifiers and converters, comparators etc). Among the most promising materials for such applications are special chalcogenide glasses (ChG) – non-oxide glassy-like materials with high content of chalcogens (S, Se, Te) [1-3]. To a great extent, the further success in this field relies on chemical-technological resolutions in development of ChG-based media with unique properties [4-6].

Basic approach in development of functional materials is based on the various methods of technological and post-technological structural modification using external factors such as thermal annealing, high-energy radiation treatment or laser beams [7-9]. It is known that the nearest atomic environment in glass matrix can be adequately studied using numerous experimental methods such as vibration and Raman scattering spectroscopy, X-ray diffraction (XRD), scanning electron microscopy etc. [10].

The aim of this work is the investigation of crystallization processes and features formation of crystalline phases in $80GeSe_2$-$20Ga_2Se_3$ chalcogenide glasses under different durations of thermal annealing above the glass transition temperature using XRD and atomic force microscopy (AFM) methods.

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2. Experimental details

The $80GeSe_2$-$20Ga_2Se_3$ samples were obtained from high purity (99.999%) Ge, Ga and Se 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 the highest temperature for 12 h. Then silica tube was cooled in water at room temperature and annealed at 30 ° C below the glass transition temperature T_g (370 °C) for 3 h and slowly cooled down to room temperature [11]. Samples with thickness of 1 mm were polished for further investigations [9, 12-14].

The crystallization of the $80GeSe_2$-$20Ga_2Se_3$ ChG was performed with a single step typical heat treatment at T_g+10 °C as described in [11,15]. 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 25 to 100 h [12].

The XRD measurements ($CuK_{\alpha 1}$ radiation) were carried out to determine crystalline phases in the studied glasses. The automatic STOE STADI P diffractometer ("STOE & Cie GmbH, Germany) with a linear position-precision detector was used for XRD measurements. All measurements were conducted in 2θ-step regime, the profiles of peaks being refined using WinPLOTR software [12,15].

The surface morphology of the glasses annealed at 25 and 80 h was studied by means of Solver P47-PRO AFM, the obtained images being processed with Image Analysis program (NT-MDT).

3. Results and Discussion

It is possible to assume that basic transformations can be related to inwardly-phase stratification in the $80GeSe_2$-$20Ga_2Se_3$ cut-section on individual components (stoichiometric $GeSe_2$ and Ga_2Se_3) which set the stage for further reaction forming of $GeGa_4Se_8$ triple phase [12]. This indicates that the stoichiometric $80GeSe_2$-$20Ga_2Se_3$ cut-section creates terms for crystallization of $GeGa_4Se_8$ phase due to segregation of preliminary selected $GeSe_2$ and Ga_2Se_3 phases with additional formation of $GeSe_2$-enriched residues. Since the stoichiometric $GeSe_2$ phase is outside glass formation [12] 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 [16]. $GeGa_4Se_8$ ($Ga_{0.5}Ge_{0.13}Se$) phase exists 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 ($GeGa_2Se_5$) structure has not been established exactly, however, lattice parameter *a* is known to be ~ 5,461 Å [16] indicating affinity in structures of these two modifications. It was also reported about existence of $GeGa_2Se_3$ but $GeGaSe_3$ phases [17]. Total structural relationship between these phases and binary Ga_2Se_3 $GeSe_2$ phases and various modifications are Ga [Se_4] and Ge [Se_4] tetrahedrons.

Combined results obtained by XRD method for $80GeSe_2$-$20Ga_2Se_3$ chalcogenide glasses before and after thermal annealing at 380 °C for 25, 50, 80 and 100 h are shown in Figure 1. In the $80GeSe_2$-$20Ga_2Se_3$ ChG annealed for 25 h and 50 h the well-formed peaks of $GeGa_4Se_8$, Ga_2Se_3 and $GeSe_2$ phases appear. The maximal reflection corresponding to $GeSe_2$ phase is semi-amorphous halo while reflections from $GeGa_4Se_8$ and Ga_2Se_3 are relatively well formed, especially at maximum of $2\theta \sim 28.22°$ (Figure 1). The 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.

This process is accompanied by crystallization of $GeGa_4Se_8$ phase (in the structure of glass from chaotic arrangement of Ga [Se_4] and Ge [Se_4] tetrahedrons is 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 the diffraction peaks, reflecting mainly the formation of double and triple $GeGa_4Se_8$ and Ga_2Se_3 phases, just as for $80GeSe_2$-$20Ga_2Se_3$ glass, annealed for 50 h (Figure 1). Thus, further crystallization process registered by XRD and formation of long-range order during such annealing do not occur. The first maximum of semi-

amorphous halo at ~14.6 °2θ corresponds to the maximum intensity reflection (002) of $GeSe_2$ phase (monoclinic syngony, $P2_1/c$ space group).

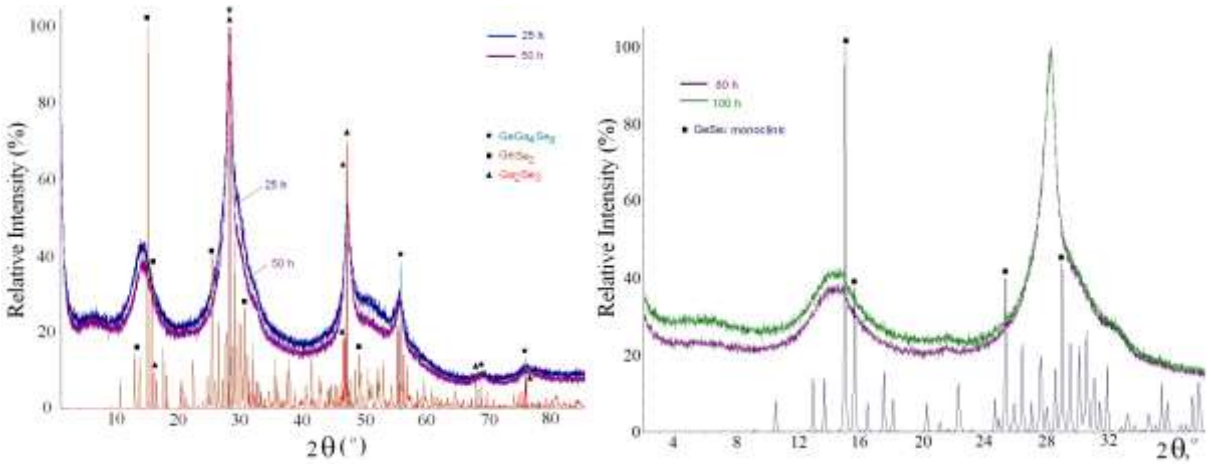


Figure 1. Experimental XRD patterns for initial 80GeSe2-20Ga2Se3 glasses and after annealing for 25, 50, 80 and 100 h: comparison of experimental results with theoretical lines.

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. Considering the state diagram for the Ga-Se system, temperature of existence of cubic Ga_2Se_3 (high-temperature $Ga_{0.67}Se$) begins above T = 730 °C. Below this temperature low-temperature monoclinic modification of Ga_2Se_3 exists. Distinguishing of monoclinic and cubic modification of Ga_2Se_3 phases is possible only on samples with the high degree of crystallization.

Assuming that in studied samples pure high-temperature Ga_2Se_3 phase is crystallized, most likely this is modification of α-Ga_2Se_3 (a ~ 5.44 Å). However, taking into account the fact that the peaks are extended, along with α-modification γ-modification of Ga_2Se is possible (Figure 2). Yet, one should pay attention to the raising of the background on diffraction pattern (indicated by ellipses in Figure 3).

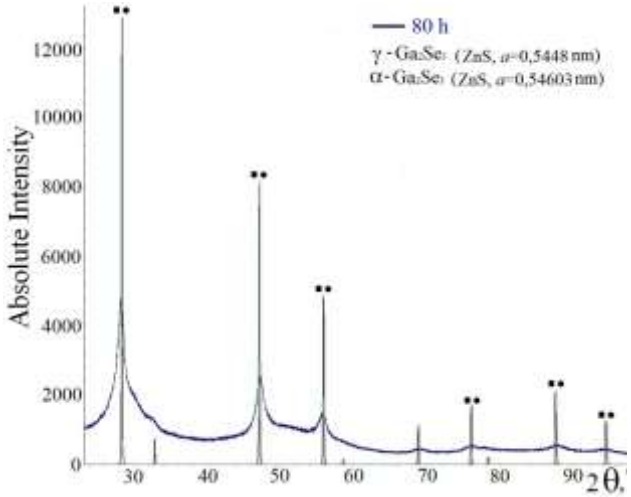


Figure 2. Comparison of experimental XRD patterns for ChG annealed for 80 h with theoretical reflexes of α-Ga_2Se_3 and γ-Ga_2Se_3 phases

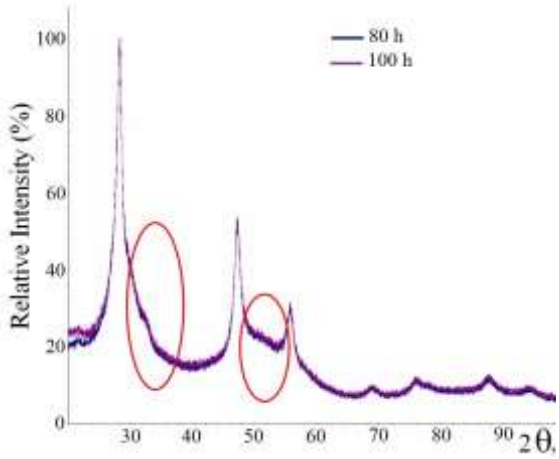


Figure 3. Raising of the background on experimental XRD patterns for samples annealed for 80 and 100 h.

These raising may correspond to peaks from experimental diffraction pattern for high- and low-temperature modification of Ga_4GeSe_8 (Figure 4) but we can also assume that crystallized high-temperature α-Ga_2Se_3 phase may exist. Amorphous phase of glass is likely to be responsible for the features on the pattern in Figure 4 outlined by ellipses.

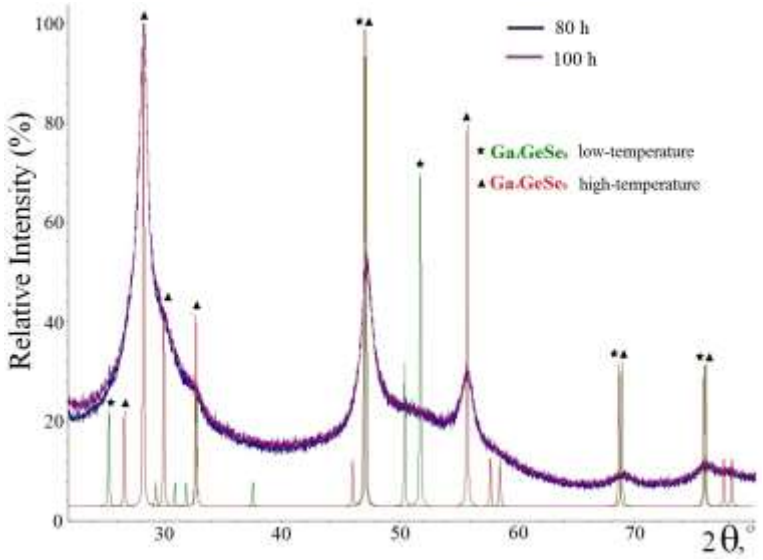
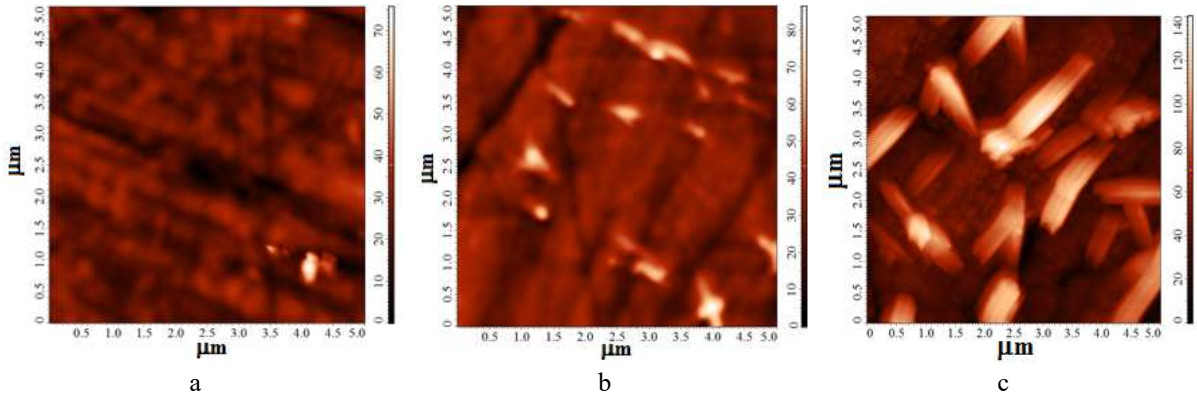


Figure 4. Comparison of experimental XRD patterns for ChG annealed for 80 and 100 h with theoretical reflexes of Ga_4GeSe8 phase low- and high-temperature modifications.

The width of the peak at 2θ ~ 28,22° indicates the presence of nanoparticles dispersed in the form of nanocrystalline inclusions with the size of 9-10 nm (determined by the Debye-Scherrer equation [12,18]) in the crystal matrix. It should be underlined that the height of this peak in glasses annealed at 80 and 100 h does not change essentially as compared to ChG treated at 50 h. Such behavior speaks in favor of saturated crystallization at longer durations of annealing.

The maxima associated with $GeSe_2$ phase appear on the XRD patterns of thermally annealed $80GeSe_2$-$20Ga_2Se_3$ glass as well [14] but (in contrast to [19]) they cannot be well distinguished as separate crystalline peaks even for prolonged annealing. It means that $GeSe_2$ crystals appear only in a small amount.

To better understand these processes on the surface, the glasses were examined by AFM (Figure 5).



a b c

Figure. 5. AFM images of unannealed $80GeSe_2$-$20Ga_2Se_3$ glasses (a) and annealed at 380 °C for 25 h (b) and 80 h (c).

As was shown in [15,20], that surface of base unannealed $80GeSe_2$-$20Ga_2Se_3$ glass is mostly morphologically uniform (Figure 5, a). At various cycles of potential scan, surface irregularities and individual features appear. It can be caused by hitting with microparticles from air since microscope stand is not placed in a vacuum chamber. The elemental analysis of the surface testifies stoichiometric composition of $Ge_{23,5}Ga_{11,8}Se_{64,7}$ glass [21-23]. However, the thermal annealing of glasses for 25 h

causes obvious changes in the surface morphology (Figure 5, b). After analysing the images, we can conclude that thermal annealing at 380 °C for small durations leads to internal transformation of free volume in the $80GeSe_2$-$20Ga_2Se_3$ glass due to the formation of additional crystalline phase on the surface [15,20,24]. However, after longer treatment (over 50 h), surface crystallization occurs more efficiently. As shown in Figure 5, crystallization of $GeSe_2$ phase in samples annealed for 80 h at 380 °C is a surface phenomenon. With respect to AFM and SEM data [15], the $GeSe_2$ crystals in form of wires with 1-3 μm lengths are non-uniformly distributed on sample surface (Figure 5,c).

4. Conclusions

It is established that crystallization processes in the $80GeSe_2$-$20Ga_2Se_3$ ChG caused by annealing at 380 °C for 25, 50, 80 and 100 h indicate 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 $80GeSe_2$-$20Ga_2Se_3$ glasses leads to obtaining of thermally stable glasses and glass-ceramic media. Longer annealing durations result in surface crystallization of $GeSe_2$ phase.

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