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GLASS-FORMATION IN THE As_2Se_3-$GeSe_2$-ZnTe SYSTEM

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ABSTRACT

New chalcogenide samples from the As_2Se_3-$GeSe_2$-ZnTe system are synthesized by melt quenching technique in evacuated to a residual pressure of 1.10^{-3} Pa quartz ampoules. The specimens from the investigated system are prepared by direct mono-temperature synthesis with conditions conformed to the physico-chemical features of the initial compounds. The state of the bulk samples (glassy, crystalline, glassy + crystalline) is proven by visual, X-ray diffraction, and microscopic analyses. The glass-forming region within the system is outlined using the results of the performed syntheses and analyses. It lies on the As_2Se_3-$GeSe_2$ side and partially on the As_2Se_3-ZnTe (from 0 to 5 mol % ZnTe) and $GeSe_2$-ZnTe (from 0 to 15 mol % ZnTe) sides. The maximum solubility of ZnTe in the glasses is 20 mol %. A presence of a crystallizing phase As_2ZnGe is registered in the XRD-investigated samples.

Keywords: *chalcogenide glasses, glass-formation, synthesis, X-ray diffraction.*

INTRODUCTION

Multi-component chalcogenide systems in which the initial components are compounds have been intensively studied as suitable materials for integrated optoelectronic devices [1], sensors [2], switches [3], and memories [4]. The systems complication aims to obtain new glasses with preset properties and widen the glass-forming region. $GeSe_2$ and As_2Se_3, such excellent glass-formers, enable to expand of the glass region, increasing the concentration of the component which imparts the desired property [5 - 7]. Adding Zn (in the form of ZnTe) in the system improves the optoelectronic properties [8, 9]. $ZnGeAs_2$ compound's properties could be used in optoelectronic, thermal, and electrical devices [10], solar cells [10 - 12], non-linear optics [13], and low-loss optical fibers [14].

The subject of the present study is the multi-component As_2Se_3-$GeSe_2$-ZnTe system, data for which are not found in the literature. The goal is sintering new chalcogenide materials and outlining the glass-forming region within the system.

EXPERIMENTAL

The initial compounds and samples from the As_2Se_3-$GeSe_2$-ZnTe system are synthesized in evacuated quartz ampoules. High-purity elements (Se, Te, As, and Ge - 5N) and commercial ZnTe 4N (Balzers) are used. The heating rate and the duration of the heat treatments are chosen experimentally. Stepwise heating regimes are employed for the synthesis of $GeSe_2$ and As_2Se_3: for $GeSe_2$, heating at 300°C, 620°C, and 975°C for 2 h, reducing the temperature to 800°C; for As_2Se_3, heating at 300°C and 400°C for 1 h and at 900°C for 2 h. Samples from the investigated system are synthesized with temperature holds for 1 h at 420°C, 750°C, 1000°C, and 1150°C. A continuous vibrational stirring of the melt is performed at the maximum synthesis temperature. The quenching of the melt is done on air for the initial compounds and in ice water (cooling rate of 10 - 15°C s^{-1}) for the samples. The synthesis is carried out in a vertical crucible furnace with a thermoregulating device, which guarantees to maintain the temperature with an accuracy of ± 10°C.

To classify the samples' state as glassy, crystalline, or glassy-crystalline, XRD (Philips PW 1050 diffractometer with CuKα, radiation, and a Ni filter) and microscopic analyses (RH-2000 digital microscope, HIROX; MXB-2500REZ zoom lens) are used. A fraction with particle size < 0.063mm is subjected to XRD investigations.

RESULTS AND DISCUSSION\

From the investigated system, 22 bulk samples are synthesized. The composition and state of the samples are presented in Table 1.

The samples are observed visually and using a binocular magnifier. According to the characteristic fracture of a freshly exposed surface, the state of the samples is determined as glassy, crystalline, or glassy-crystalline. The glassy specimens are dark colored, with a strong luster and a well-defined shell fracture. Crystalline samples have a matte and rough surface, while mixed glass-crystalline samples, which lie on the glass-forming boundary, are characterized by the presence of both phases.

Based on the XRD results, three types of diffractograms (Fig. 1) are distinguished: a group of diffractograms typical of amorphous substances - the absence of clearly defined peaks and the presence of a characteristic amorphous halo (samples 4, 6, and 7, lying in the glass-forming region); a group of diffractograms shows diffraction peaks with slight

Table 1. Composition and state of the samples synthesized to outline the glass-forming region within the As_2Se_3-$GeSe_2$-ZnTe system.

Sample	As_2Se_3, mol %	$GeSe_2$, mol %	ZnTe, mol %	State
1	95	0	5	Glassy + crystalline
2	93	0	7	Crystalline
3	81	9	10	Glassy + crystalline
4	63	27	10	Glassy
5	45	45	10	Glassy
6	27	63	10	Glassy
7	9	81	10	Glassy
8	0	90	10	Glassy
9	26.25	61.25	12.5	Glassy + crystalline
10	68	17	15	Glassy + crystalline
11	59.5	25.5	15	Glassy + crystalline
12	42.5	42.5	15	Glassy + crystalline
13	25.5	59.5	15	Crystalline
14	8.5	76.5	15	Glassy
15	0	85	15	Glassy + crystalline
16	64	16	20	Crystalline
17	40	40	20	Crystalline
18	24	56	20	Crystalline
19	16	64	20	Glassy + crystalline
20	0	80	20	Crystalline
21	52.5	22.5	25	Crystalline
22	37.5	37.5	25	Crystalline

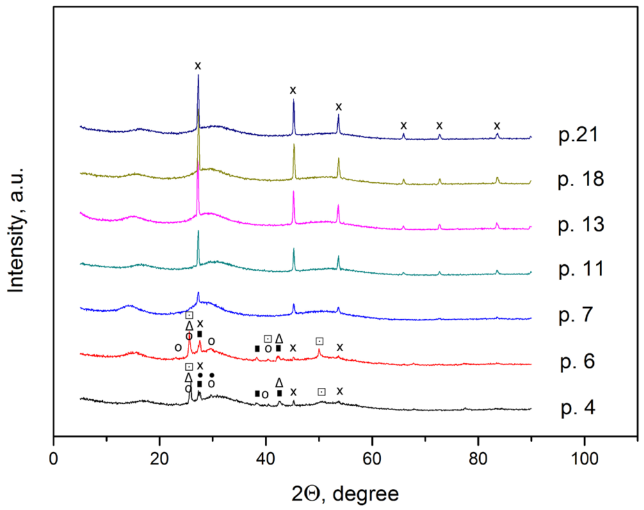

Fig. 1. XRD patterns of samples from theAs_2Se_3-$GeSe_2$-ZnTe system; x - As_2ZnGe; Δ - ZnTe; ■ - Te; o - Se; ⊡ - GeSe; • - AsSe.

intensity characteristic for the compositions on the glass-forming region's boundary (sample 11); the third group is formed by diffractograms with strong peaks of the crystalline samples situated outside the glass-forming area (samples 13, and 18, and 21).

The indexing of the XRD patterns (Fig. 1) shows that:

- No initial compounds' peaks are observed.

- For all samples, a crystallizing phase As_2ZnGe is registered. For the crystalline and glassy-crystalline samples, only As_2ZnGe [15] reflexes are observed, while for the glassy ones, peaks of ZnTe [16], Te [17], Se [18], GeSe [19], and AsSe [20] are also observed.

- During the high-temperature synthesis, the $GeSe_2$ decomposes to GeSe and Se, good glass formers; Se forms and links the linear chains formed by structural units GeSe2/2.

- For the As-rich glass (p. 4), the amorphous AsSe-reflexes are distinguished.

The microscopic observation shows a smooth and homogeneous surface of glassy samples (Fig. 2(a)). Small crystalline regions (micro-crystals) are shown on the surface of the glassy-crystalline samples (Fig. 2(b)). In comparison, the samples placed outside of the glass-forming region are completely crystallized (Fig. 2(c)).

Based on the syntheses carried out and the results obtained from the visual, XRD, and microscopic analyses, the region of glass-formation in the As_2Se_3-$GeSe_2$-ZnTe system is outlined (Fig. 3).

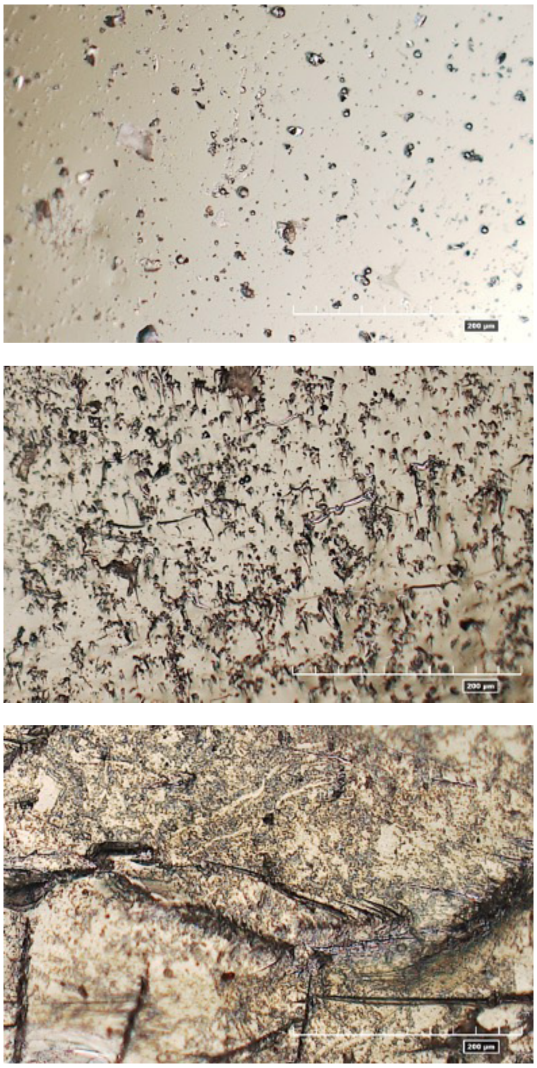

Fig. 2. Microscopy images of the samples' surface: a) glassy sample (p. 4); b) glassy-crystalline sample (p. 11); c) crystalline sample (p. 21).

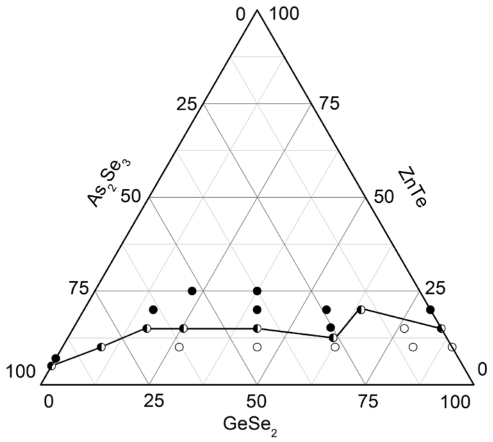

Fig. 3. Glass-formation region in the As_2Se_3-$GeSe_2$-ZnTe system.

It lies on the As_2Se_3-$GeSe_2$ side and partially on the As_2Se_3-ZnTe (from 0 to 5 mol % ZnTe) and $GeSe_2$-ZnTe (from 0 to 15 mol % ZnTe) sides. The maximum solubility of ZnTe in the glasses is 20 mol %.

CONCLUSIONS

New chalcogenide glasses from the As_2Se_3-$GeSe_2$-ZnTe system are synthesized. The glass-forming region is outlined using visual, XRD, and microscopic analyses. The glassy phases cover the area on the As_2Se_3-$GeSe_2$ side and lies partially on the As_2Se_3-ZnTe and $GeSe_2$-ZnTe sides. Crystallizing phases As_2ZnGe, ZnTe, GeSe, AsSe, Se, and Te are registered of XRD-investigated samples from the system.

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