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Study of the structural units in some chalcogenides of the As–Sb–S–Se–I system by X-ray and DSC analysis

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The paper describes a study carried out with the aim of establishing the elements of structural network of the five-component non-crystalline samples. X-ray powder diffraction at room temperature and temperatures up to 620 K and differential scanning calorimetry (DSC) studies of the glasses from the pseudo-binary system $(As_2Se_3)_{100-x}(SbSI)_x$ have been realized. On the basis of the obtained results, it was possible to identify the appearance of different structural units in the crystallization processes above glass transition temperature T_g in the materials with various atomic percent of SbSI. The DSC experiments, carried out up to 700 K, showed that the temperature regions of crystallization translates to lower temperatures with increasing SbSI content. Structural unit of antimony-sulfoiodide exists in materials with $x \geq 50$ at. %. Thermal analysis showed the presence of two distinctive temperature domains of crystallization of the glasses with 70 and 80 at. % SbSI. Also, partial overlapping of glass transition and crystallization processes were found in the sample with $x=80$ at. % SbSI.

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1. Introduction

In the last several decades, chalcogenide glasses, with their amorphous internal structure, have attracted considerable interest of researchers in the field of materials science, primarily due to their interesting optical, and electrical properties. Their high transparency in the visible and IR ranges, high values of refraction index, semiconducting properties, and the possbility of stimulated alteration of some physical characteristics under the light or thermal treatment, are only some of their significant characteristics [1-4]. If one bears also in mind their relatively simple synthesis by melt vitrification and the possibility of altering some of their properties either by changing continuously their composition within the amorphicity region or by varying preparation regime parameters (maximal temperature of the synthesis and cooling rate) [5,6], then it is understandable why these materials have aroused strong interest.

Arsenic chalcogenides of the type As_2X_3 (X – S, Se, Te) are generally known and well studied glass-forming materials. The introduction of new elements into their composition, increase to a great extent the number of materials with amorphous internal structure and having a wide range of physical properties. In the case of the $(As_2Se_3)_{100-x}(SbSI)_x$ system, the introduction of antimony, sulfur, and iodine into the composition of the typical glass-former is carried out with the aim of preparing new materials in which the subsequently induced partial crystallization of SbSI in the crystalline lattice will enhance their dielectric properties.

For this reason it is important to study the crystallization process in the glasses of this system, primarily with the aim of preparing glass-ceramic materials with higher dielectric constant. In this respect, of special importance is information offered by the experimental techniques of high-temperature X-ray powder diffraction and differential scanning calorimetry (DSC). This X-ray diffraction procedure allows study of the appearance and composition of structural units in the amorphous matrix with increase in temperature, their changes and/or disappearance. On the other hand, DSC studies allow exact characterization of the crystallization processes on the temperature scale and the potential separation of these processes.

2. Experimental

Glasses from the system $(As_2Se_3)_{100-x}(SbSI)_x$ (x=20, 30, 50, 70 and 80 at. %) were synthesized from the high-purity (99.999 %) elemental components in evacuated quartz ampoules, applying the cascade regime of temperature raising [7]. The ampoules with starting substances were placed in a furnace that oscillated in the course of the synthesis, to achieve more efficient interaction of the melted components. Amorphous character of the structures was confirmed by X-ray diffraction analysis at room temperature and by reflected-light polarization microscopy.

High-temperature X-ray powder diffraction analysis of glassy samples was performed on a Philips 1373 - PW 1965/50 diffractometer, equipped with an HTK-10 (Anton Paar) camera. Small amounts of investigated materials were placed in the special Pt or Ta holders and heated in the evacuated chamber to the temperature at which is expected the appearance of crystalline fractions (phases) in the glass structure. Experiments were carried out up to 620 K.

The DSC experiments involving powder glassy samples (5−10 mg) were performed on a Perkin-Elmer Pyris 6 instrument in the range from room temperature to 700 K in the dynamic nitrogen atmosphere. The heating rate of samples in aluminum crucibles was 10 K/min. Characteristic phase-transformation temperatures were determined, first of all the glass transition temperature T_g, the crystallization onset temperature T_{ons}, the temperature of maximal enthalpy effect of crystallization T_p, and the melting temperature T_m. Because of partial overlapping of the processes of crystallization and softening, on the one hand, and crystallization and melting, on the other hand, characteristic onset temperatures of melting or vitrification could not be clearly determined.

3. Results and discussion

In Figs. 1-3 are shown the results of recording X-ray diffractograms for the samples of the glasses from the system $(As_2Se_3)_{100-x}(SbSI)_x$ at different temperatures. Position of diffraction peaks of crystalline phases (structural units) was marked with suitable symbols, while indices Pt and Ta relates to the specimen holders. All samples were originally amorphous and temperature increase yielded gradual appearance of crystalline fractions in the glass matrix. In the samples with x=20 and 30 at. % SbSI, arsenic selenides (As_2Se_3 and AsSe) and antimony selenide (Sb_2Se_3) were identified. Small contents of antimony, sulfur and iodine were obviously insufficient to form the structural unit SbSI or the contents of these elements were below their detection limits.

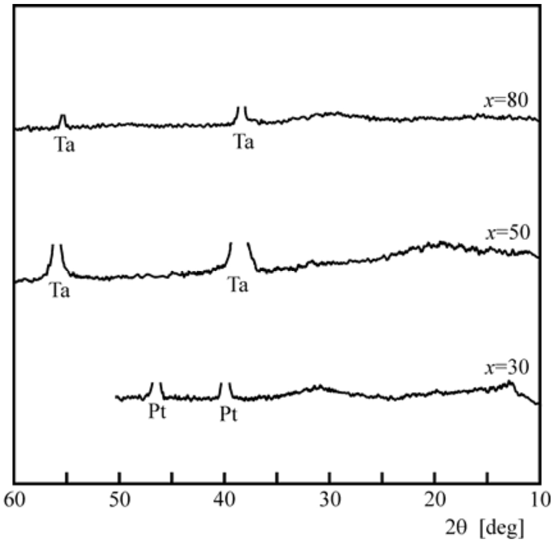

Fig. 1. X-ray diffractograms for the glasses $(As_2Se_3)_{100-x}(SbSI)_x$ at room temperature.

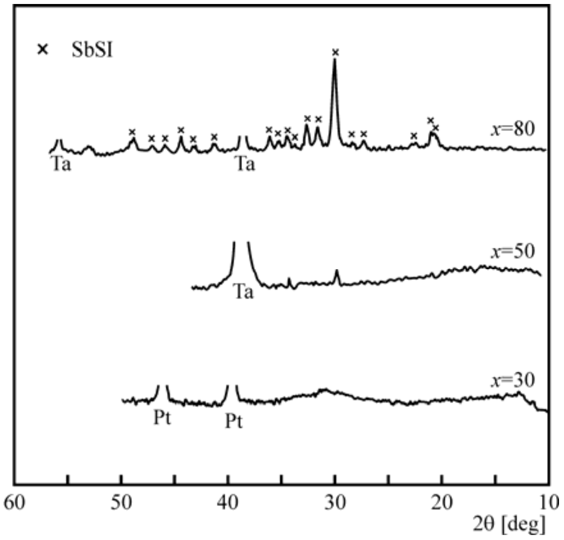

Fig. 2. X-ray diffractograms for the glasses $(As_2Se_3)_{100-x}(SbSI)_x$ at 470 K..

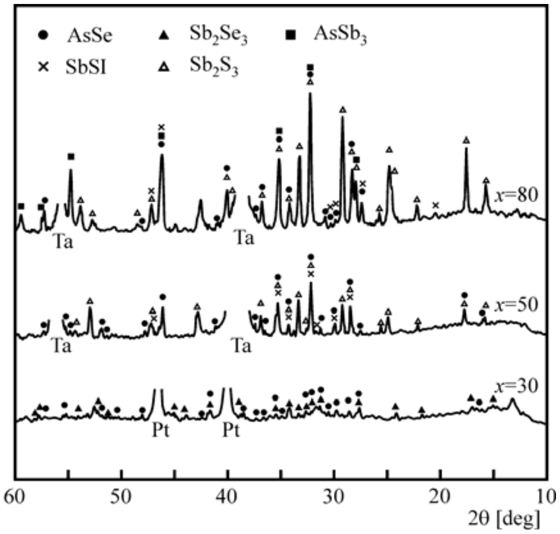

Fig. 3. X-ray diffractograms for the glasses $(As_2Se_3)_{100-x}(SbSI)_x$ at 570 K.

On the DSC curves for the composition with x=30 at. % (Fig. 4) there is one enthalpy exothermic peak related to the simultaneous crystallization of all crystalline phases involved. However, for the sample with x=20 at. %, enthalpy maxima related to crystallization could not be registered at the given scanning rate, so that the corresponding curve was omitted from the figure. On the temperature scale, the crystallization processes are closer to the endothermic maximum ascribed to melting, which suggests a higher thermal stability of this composition. Namely, the further crystallization processes from the softening range are (that is the closer to the temperature range of melting), the thermally stabler is the materials. In Table 1 are shown the characteristic temperatures of phase transition in the glasses of the investigated system obtained at a scanning rate of 10 K/min. The higher T_g values for the samples with 20 and 30 at. % SbSI mean also a wider temperature interval of the existence of the solid glassy phase, which is one of the indicators of thermal stability of the material.

Table 1. Glass transition temperature T_g, crystallization onset temperature T_{ons}, temperature of maximal crystallization rate T_p, and melting temperature T_m, determined from the DSC analysis (β=10 K/min).

x [at. %]	T_g [K]	T_{ons} [K]	T_p [K]	T_m [K]
20	432.7	—	—	—
30	426.0	512.5	540.8	588.5
50	416.9	475.1	500.2	608.8
70	402.6	443.1	469.5	615.2
70 *		416.5	428.5	
80 *	—	396.2	405.2	631.2

* Temperatures for the first of two registered crystallization enthalpy peaks.

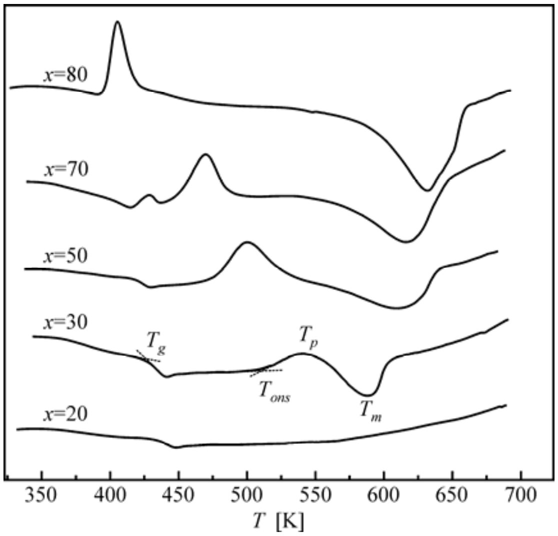

Fig. 4. DSC curves recorded at (β=10 K/min) for the samples of the glass $(As_2Se_3)_{100-x}(SbSI)_x$

In the material with x=50 at. % SbSI new structural units appeared, first of all of antimony sulfoiodide SbSI and antimony sulfide Sb_2S_3, along with the existence of AsSe. The increased contents of Sb, S and I facilitate their crystallization, which is also evident from the shifts of these processes to lower temperature range.

In the sample with x=80 at. %, the softening and crystallization processes are even partly ovelapped, and it appeared that the prolonged exposure (for at least 30 min) of the sample to a temperature of 370 K resulted in the appearance of SbSI crystalline phase. The presence of two crystallization enthalpy maxima on the DSC curves of heat flow, of which the first is related to the SbSI phase and second to the other crystalline phases, was observed only for the compositions with x=70 and 80 at. %. This unambiguously shows that these two materials are very prone to crystallization.

4. Conclusion

Differential scanning calorimetry and high-temperature X-ray diffraction analysis of the glasses of the $(As_2Se_3)_{100-x}(SbSI)_x$ type showed that increase in contents of Sb, S and I change gradually the composition of crystalline phases observed in their crystallization processes. Arsenic and antimony selenides, already in the composition with x=50 at. %, are gradually replaced by antimony sulfide and antimony sulfoiodide. The DSC analysis indicated significant shift of crystallization effects on the temperature axis to the direction of softening area and lowered thermal stability.

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