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Glass formation in the Se–Ge–Zn and $GeSe_3$–ZnSe–Ag_2Se systems

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The glass-forming region in the Se–Ge–Zn (I) and $GeSe_3$–ZnSe–Ag_2Se (II) systems are determined, as well as some physical and chemical properties (temperatures of softening, crystallization and melting, density and microhardness). The glass-forming region in system I on the Se–Ge side (concentration limits 0–43% Ge). The maximum solubility of Zn is around 6% (at Se : Ge = 9 : 1). The glass-forming region in system II lies on the side Ag_2Se–$GeSe_3$ (from 54 to 100% GeSe) and ZnSe–$GeSe_3$ (from 78 to 100% $GeSe_3$) of the Gibbs' concentration triangle for $GeSe_3$–ZnSe–Ag_2Se.

1. Introduction

The chalcogenide glasses can be used as materials for threshold switches and memory devices [1], for thin film waveguides in integrated-optical circuits [2], in photothermoplastic photography [3] and for ion-selective potentiometry [4]. They possess radiation resistance which makes them applicable in devices for space research.

The systems Se–Ge–Zn (I) and $GeSe_3$–ZnSe–Ag_2Se (II) are not studied. The purpose of the present investigation is to determine the limits of glass-forming in these systems and to investigate some physical and chemical properties of the glasses obtained. The investigation of the first system became necessary to find the glass-forming area in the $GeSe_3$–ZnSe system, which is an edge of the second system.

2. Experimental details

Twenty-one samples of system I and 31 samples of system II were synthesized. The starting materials are of 99.999% (5N) purity. The synthesis regime is governed by the physical and chemical properties of the starting components. Quartz ampoules with stoichiometric quantities of the starting components, evacuated in advance to a residual pressure of 0.1 Pa and sealed, were heated step-wise to the maximum temperature of the synthesis that does not exceed $1000 \pm 10\,^{\circ}C$. After vibrational agitation of the melt, the latter is quenched in a mixture of water and ice. The synthesized samples undergo visual analysis, X-ray phase analysis (diffractometer TUR M62 with CuK_{α} radiation and Ni filtering), and electron microscopic analysis (electron microscope Philips). The glassy phases had their density (hydrostatic method), microhardness (Vickers) and thermal characteristics (differential thermal analysis) determined.

3. Results and discussion

The compositions rich in Se (system I) and $GeSe_3$ (system II) have a dark colour with well expressed conchoidal fracture.

The X-ray analysis showed that some composition (nos 7, 13, 14, 16–21 from system I and Nos 1–4, 6–8, 12–14, 18, 21, 22, 25, 27, 28 from system II) have diffractograms typical of those of the amorphous state, i.e. presence of a X-ray-amorphous plateau and absence of clearly expressed diffraction reflections (these compositions fall in the glass-forming region of the first and second system, respectively). Other compositions (nos 6, 8–11 from system I and nos 5, 11, 15, 19, 23, 26, 30 from system II) have roentgenograms that are much richer in diffraction reflection, although with weaker intensity (these compositions are along the borders of the glass-forming regions of the first and second system, respectively). The remaining compositions have diffraction patterns typical of the crystalline state (these compositions lie outside the glass-forming regions).

The electron microscope investigations showed that the surface of one part of the samples is homogeneous and smooth. On the surface of other samples there are

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regions, although small in size, with crystalline formations (crystalline phase). On the surface of a third group of samples there are no regions belonging to the glassy phase, or if there are any such regions, they have a small area (the surface is typical of a crystalline phase). The first samples are located in the glass-formation region, the second, along their borders, and the third, outside them.

In the $GeSe_3$–ZnSe–Ag_2Se system there is a concentration region marked with a dashed line, in which the samples tend to liquation. The increase in the synthesis temperature of about 50–100 °C diminishes strongly the probability of liquation processes taking place.

On the basis of visual, X-ray phase and electron microscopic analyses, the glass-forming regions of the two systems were determined. In the Se–Ge–Zn system, the glass-forming region lies on the Se–Ge side in the concentration limits 0 to 43% Ge (Fig. 1). The maximum solubility of Zn in the glassy phase is about 5% at a Ge:Se ratio of 9:1.

In the $GeSe_3$–ZnSe–Ag_2Se system (Fig. 2) the glass-forming region is at the vertex of Gibbs' concentration triangle, corresponding to $GeSe_3$, and is located on the $GeSe_3$–Ag_2Se (from 54 to 100% $GeSe_3$) and $GeSe_3$–ZnSe (from 78 to 100%$GeSe_3$) sides. The glass-forming region is limited by composition (nos 5, 11, 15, 19, 20, 23, 26 and 30). The maximum solubility of ZnSe in the glassy phases is about 22% at a ratio $GeSe_3$: Ag_2Se = 9 : 1. (Calculated with respect to elemental Zn, this solubility is about 6.5% Zn.)

The relatively low solubility of Zn in both systems, which also governs the relatively narrow glass-forming region, is related to the nature of the chemical bonds formed. These have a high degree of delocalization of the electrons. On the other hand, it is known that metallization of the chemical bond reduces the glass-forming capacity. A similar conclusion was drawn about the Se–As–Zn system, where the maximum solubility of Zn is 10% [5].

The results from the differential thermal analysis (DTA) of the glasses from both systems are summarized in Table I. The softening temperature (T_g), crystallization temperature (T_{cr}) and melting temperature (T_m) depend on the composition and rise with increasing Ge content (system I). The softening temperature of the glassy phases from system II is in the range 200–275 °C and rises with increasing ZnSe content, compared to Ag_2Se. The crystallization temperature depends slightly on the composition and varies within narrow limits (336–366 °C). On increasing the content of ZnSe, compared to Ag_2Se, and keeping the ratio between the other two components constant, T_m increases. This result is logical since the melting temperatures of ZnSe and Ag_2Se are considerably higher than that of $GeSe_3$.

The density of the glasses from system I varies in the range 3.99–4.12 g cm^{-3} (Table I). These values are typical of chalcogenide glasses. The density of the glassy phases from system II increases and with increasing content of ZnSe Ag_2Se respectively, keeping a constant ratio between the other two components. This is determined by the fact that ZnSe and Ag_2Se have higher densities than that of $GeSe_3$ (Table I).

The dependence of the microhardness, H_V, on the composition is similar (Table I). On increasing the Ge content at a constant Zn content the microhardness increases and is in the range 30.6–111.2 kg mm^{-2}

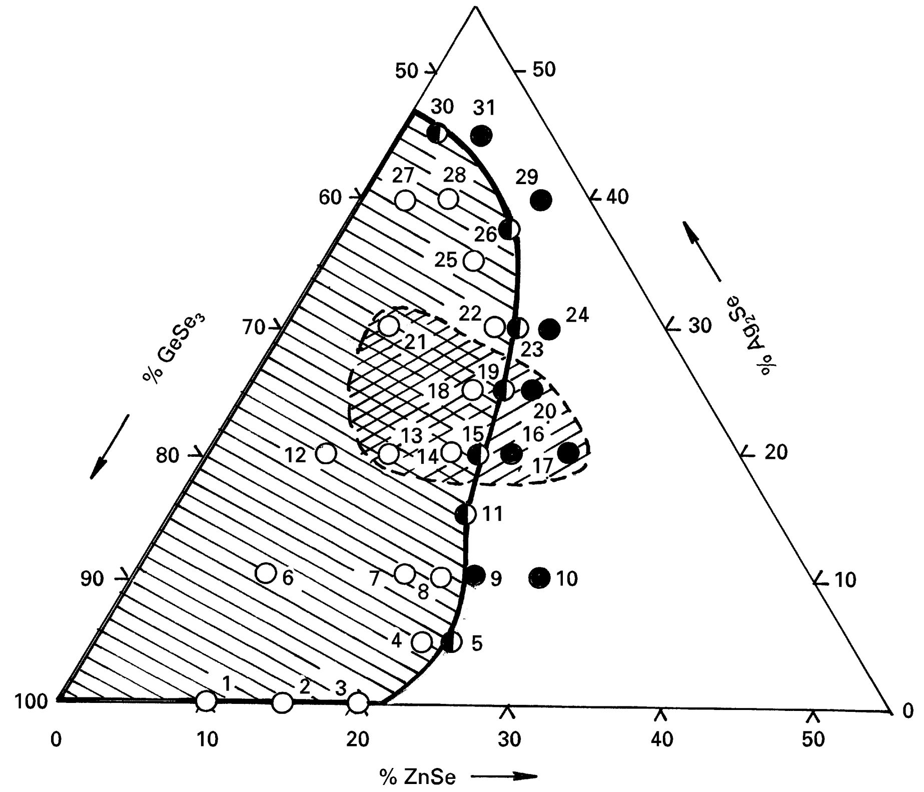

Figure 1 Region of glass-formation in the Se–Ge–Zn system.

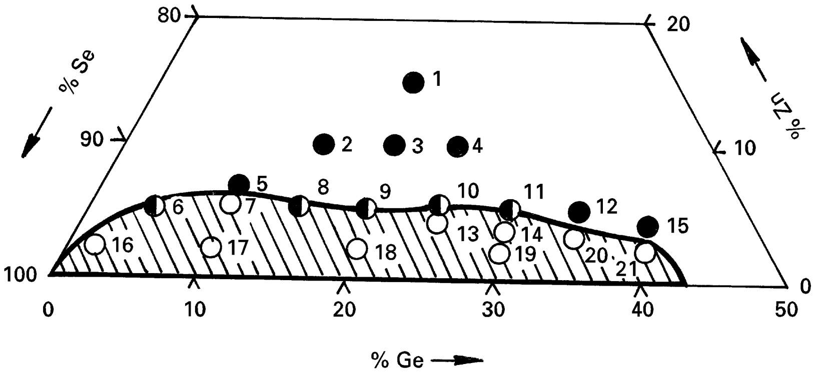

Figure 2 Region of glass-formation in the $GeSe_3$–ZnSe–Ag_2Se system.

TABLE I Thermal and physical properties of some samples from the $Se_xGe_yZn_z$ and $(GeSe_3)_x$ $(ZnSe)_y$ $(Ag_2Se)_z$ systems

	Sample no.	Composition			T_g (°C)	T_{cr} (°C)	T_m (°C)	d (g cm^{-3})	H_V (kg mm^{-2})
		x	*y*	*z*					
System I	16	96	2	2	49	160	269	3.99	30.6
	17	88	10	2	86	243	287	4.02	47.5
	18	78	20	2	92	360	435	4.04	68.8
	19	69	29	2	104	441	531	4.07	90.0
	21	59	39	2	115	445	571	4.12	111.2
System II	1	90	10	–	200	336	370	4.36	85.2
	6	81	9	10	202	341	373	4.55	86.1
	12	72	8	20	246	354	398	4.68	89.8
	21	63	7	30	253	359	436	5.02	91.6
	28	54	6	40	270	366	479	5.24	95.1
	3	80	20	–	215	340	380	4.45	98.0
	7	72	18	10	224	343	412	4.69	99.2
	14	64	16	20	260	360	435	5.14	102.2
	22	56	14	30	275	366	460	5.28	102.5

(system I). On one hand, this is related to the increasing number of Ge–Se bonds that are stronger than Se–Se bonds, and on the other hand, to the fact that the microhardness of Ge is higher than that of Se. On increasing the content of ZnSe, respectively Ag_2Se, at a constant ratio of the other two components (system II), the microhardness increases and is in the range 85.2–102.5 kg mm^{-2} (Table I).

4. Conclusions

Glasses from the Se–Ge–Zn (I) and $GeSe_3$–ZnSe–Ag_2Se (II) systems were synthesized and the glass-forming regions in the two systems determined. The maximum solubility of Zn (ZnSe) is around 5% (25%) at a ratio Se:Ge ($GeSe_3$:Ag_2Se) = 9:1. The density, microhardness, softening temperature, crystallization temperature and melting temperature of glassy phases from the investigated systems were determined.

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References

1. J. A. SAVAGE and S. NIELSEN, *Infrared Phys.* **5** (1965) 195.
2. L. M. ANDRIESH and U. A. BYKOVSKY, Proceedings of the Conference "Amorphous Semiconductors' 80", Kishinev, 1980 pp. 250–254.
3. L. M. PANASYIK, Proceeding of the Conference "Amorphous Semiconductors' 80", Kishinev, 1980, p. 238.
4. Yu. G. VLASOV and E. A. BYCHKOV, *Sens Actuators* **12** (1987) 275.
5. G. Z. VINOGRADOVA, "Glass Formation and Phase Equilibria in Chalcogenide Systems" (Nauka, Moscow, 1984).

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