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Glass-formation in the Ag_2Se–Zn(Cd,Hg)Se–$GeSe_2$ systems

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The glass-formation regions in the quasi-ternary systems Ag_2Se–Zn(Cd,Hg)Se–$GeSe_2$ were determined using XRD data. The maximum content of the modifier ZnSe is 10 mol.%, that of CdSe is 12 mol.%. The largest region of existence of glasses is observed in the mercury-containing system where it crosses the concentration triangle. The thermal properties of the glasses were characterized by the glass transition temperature, the crystallization temperature and the melting point of the crystallized alloy.

Chalcogenide glasses / Quasi-ternary systems / Characteristic temperatures

Introduction

Complex chalcogenide semiconductor glasses (CSGs) are widely used in various applications of optics and electronics (see *e.g.* [1]) due to good transparency in the infra-red spectral region. A proven approach to widen the range of applications and to progress into new fields consists in doping the material. For instance, when doped with rare-earth ions, CSGs with low phonon energies are expected to be efficient host materials for fiber-optic amplifiers and IR lasers [2].

Germanium selenide is an effective glass-forming compound that has recently drawn interest as the matrix for functional membranes in ion-selective potentiometry, particularly for heavy metal ions [3]. The use of glasses provides higher chemical stability in corrosive media and better selectivity in the presence of interfering ions than crystalline electrodes.

An investigation of glass formation in the quasi-binary system HgSe–$GeSe_2$ revealed a large region of existence of glasses – from 50 to 100 mol.% $GeSe_2$ [4]. These glassy alloys exhibit a photodarkening effect and are promising materials for devices of high-density optical recording of information. It was shown in [5] that addition of Cu_2Se (maximum content 6 mol.%) leads to a significant increase of the photoconductivity of the HgSe–$GeSe_2$ glasses, which makes possible their use as materials for photosensors. It is expected that the modification of these glasses with silver selenide – an analog of Cu_2Se – will increase the glass-formation region and thus widen the range of control over the properties of the glasses. Additionally, glasses modified with silver chalcogenides are expected to possess high ionic conductivity due to the Ag^+ ions, making them a promising base for the development of new materials. In some ternary Ag- and Ge-containing chalcogenide glasses the conductivity is almost entirely due to ionic transport, with an ionic transport number close to unity [6].

Considering the interesting properties of the glasses in the boundary systems, we decided to investigate the properties of multicomponent $GeSe_2$-based glasses modified with selenides of both silver and Group II-b elements. Presently, we report the results of the investigation of the glass-formation regions in the Ag_2Se–Zn(Cd,Hg)Se–$GeSe_2$ systems and thermal properties of the glasses.

Data on the glass formation and properties in the Ge–Cd–Se system were reported in [7]. It was discovered that the glass compositions in the $GeSe_2$–CdSe section occupy a minor concentration range near $GeSe_2$ that does not exceed a few mol.%. A similar picture was observed in the $GeSe_2$–ZnSe system [8]. A preliminary investigation of the Ag_2Se–$GeSe_2$ system [9] indicated that the glass-formation region is small and is localized near the binary eutectic at 57 mol.% $GeSe_2$.

An investigation of the phase equilibria in the Ag_2Se–ZnSe–$GeSe_2$ system [10] revealed no ternary or quaternary zinc-containing compounds. The study of the Ag_2Se–CdSe–$GeSe_2$ system, in addition to the known ternary compounds Ag_8GeSe_6 and Cd_4GeSe_6 [11], discovered the quaternary compounds

$Ag_2CdGe_2Se_6$ and $Ag_2CdGeSe_4$ [10]. The ternary compound Hg_2GeSe_4 was reported in [12]. The Ag_2Se–HgSe–$GeSe_2$ system was investigated in detail in [13]. A compound with the approximate composition $Ag_{1.4}Hg_{1.3}Ge_2Se_6$ was discovered, as well as four solid solution ranges along the section Ag_8GeSe_6–'Hg_4GeSe_6'. Their extent is expressed by the compositions $Ag_{7.12\text{-}6.32}Hg_{0.44\text{-}0.82}GeSe_6$, $Ag_{6.06\text{-}4.00}Hg_{0.96\text{-}2.00}GeSe_6$, $Ag_{3.4}Hg_{2.3}GeSe_6$, and $Ag_{2.24\text{-}2.00}Hg_{2.88\text{-}3.00}GeSe_6$. The quaternary compound $Ag_2HgGeSe_4$, reported in [14], was not observed.

Experimental

Glassy alloys of the studied systems were synthesized from high-purity elements (at least 99.99 wt.% of the principal component) and previously synthesized HgSe for the mercury-containing system. The alloys were heated to 1270 K at a rate of 40-50 K/h, held at this temperature for 10 h for homogenization of the melt, and quenched into a saturated aqueous sodium chloride solution. The cooling rate during quenching was estimated to ≥200 K/s [15]. The obtained glasses were black ingots with a characteristic shine. The samples were studied by powder XRD (a DRON 4-13 diffractometer, 10–60° 2θ range, 3 s exposure) for the determination of the glass-formation region. The characteristic temperatures of the glassy alloys were determined by DTA (a Paulik-Paulik-Erdey derivatograph, heating rate 10 K/min). The accuracy of the measurements of the thermal effects was ±5 K.

Results and discussion

The results of the determination of the glass-formation regions in the quasi-ternary systems Ag_2Se–Zn(Cd,Hg)Se–$GeSe_2$ are presented in Fig. 1. The glass-formation region in the boundary system Ag_2Se–$GeSe_2$ is limited to the range 53–56 mol.% $GeSe_2$. The maximum amount of zinc or cadmium selenide that can be introduced into the glass is 10 mol.% ZnSe or 12 mol.% CdSe. The maximum $GeSe_2$ content is 63 mol.% at 4-6 mol.% ZnSe, whereas for the Cd-containing glasses it equals 62 mol.% at 8 mol.% CdSe. It is suggested that at this ZnSe or CdSe concentration the glass-formation regions are localized near the binary or ternary eutectics in the respective stable phase diagrams.

Increase of the covalent component of chemical bonding and decrease of the liquidus temperature from ZnSe to CdSe, and especially to HgSe, are the main contributing factors to the existence of a much larger glass-formation region in the Ag_2Se–HgSe–$GeSe_2$ system (Fig. 1), where it crosses the concentration triangle. The minimum content of the glass-forming component is 43 mol.% $GeSe_2$. For $GeSe_2$ concentrations over 80 mol.% the glass-formation region narrows along the HgSe–$GeSe_2$ side, and the content of the modifier Ag_2Se does not exceed 3 mol.%.

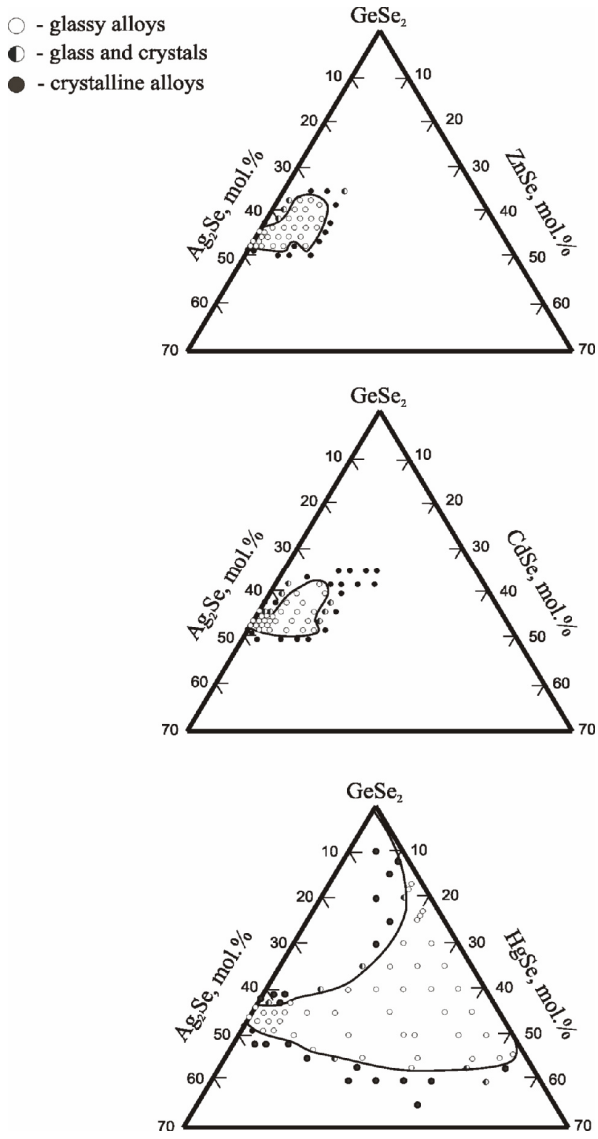

Fig. 1 Glass-formation regions in the Ag_2Se–Zn(Cd,Hg)Se–$GeSe_2$ systems.

Characteristic temperatures of the glassy alloys, namely the glass transition temperature (T_g), the crystallization temperature (T_c), and the melting point (T_m) of the crystallized alloy, were measured. Using these data, the reduced glass-formation temperature T_{gr} was calculated as $T_{gr}=T_g/T_m$. The results are presented in Tables 1-3. If more than one exothermic effect of crystallization was recorded (*e.g.* alloys 1-4, 2-9, 3-14), the alloys in question were composed of several glassy phases.

The glass transition temperature of the ZnSe- and the CdSe-containing glasses lies in a fairly narrow range (526±8 K), probably because the regions of glass existence are themselves rather small. The temperature range agrees well with the data for the HgSe-containing alloys with similar modifier concentration (up to 20-25 mol.% of the Group II selenide).

Table 1 Composition of glassy alloys of the quasi-ternary system Ag_2Se–ZnSe–$GeSe_2$ and their characteristic temperatures.

No.	Composition, mol.%			T_g, K	T_c, K	T_m, K	T_{gr}
	Ag_2Se	ZnSe	$GeSe_2$				
1-1	47	–	53	528	603, 627	859	0.61
1-2	45	2	53	520	612	856	0.61
1-3	43	2	55	526	624, 640	859	0.61
1-4	41	2	57	528	585, 622	859	0.61
1-5	43	4	53	523	610	851	0.61
1-6	41	4	55	527	621	851	0.62
1-7	39	4	57	530	619	850	0.62
1-8	37	4	59	526	617	858	0.61
1-9	35	4	61	522	616	850	0.61
1-10	33	4	63	533	615	867	0.61
1-11	41	6	53	526	615	853	0.62
1-12	39	6	55	526	607	849	0.62
1-13	37	6	57	526	617	850	0.62
1-13	35	6	59	519	620, 667	850	0.61
1-15	33	6	61	527	612, 670	842	0.63
1-16	31	6	63	526	610	858	0.61
1-17	37	8	55	523	605	852	0.61
1-18	35	8	57	526	603	846	0.62
1-19	28.5	9.5	62	526	603	878	0.60

Table 2 Composition of glassy alloys of the quasi-ternary system Ag_2Se–CdSe–$GeSe_2$ and their characteristic temperatures.

No.	Composition, mol.%			T_g, K	T_c, K	T_m, K	T_{gr}
	Ag_2Se	CdSe	$GeSe_2$				
2-1	45	2	53	526	623	852	0.62
2-2	42	3	55	525	622	855	0.61
2-3	42	4	54	534	624	869	0.61
2-4	40	4	56	526	620	860	0.61
2-5	35	5	60	527	623	863	0.61
2-6	41	7	52	527	622	863	0.61
2-7	39	7	54	526	624	860	0.61
2-8	37	7	56	525	624	858	0.61
2-9	30	8	62	526	617, 669	867	0.61
2-10	38	10	52	531	622, 628	861	0.62
2-11	36	10	54	527	623	861	0.61

However, the HgSe glasses exhibit a much wider divergence of values of both T_g and T_c. The dependences of T_g and T_c on the HgSe concentration are plotted for an Ag_2Se concentration of 5 mol.% (Fig. 2) and for a fixed $GeSe_2$ concentration of 50 mol.% (Fig. 3) (to illustrate more fully the findings, we extended the range of the graphs by including data for samples with 2 mol.% Ag_2Se–46 mol.% $GeSe_2$–52 mol.% HgSe and 2 mol.% Ag_2Se–83 mol.% $GeSe_2$–15 mol.% HgSe.).

The glass transition temperature near the HgSe–$GeSe_2$ boundary system (Fig. 2) decreases gradually with increasing HgSe content and features a minimum near 45-50 mol.% HgSe. The T_c values decrease as well, but to a lesser extent.

Within the concentration triangle, the values of T_g can be subdivided into three sharply defined regions (Fig. 3): 528±6 K for a HSe content up to 20-25 mol.%, 498±6 K for the HgSe range 25-40 mol.% and a distinct T_g minimum at 465-470 K near 45-50 mol.% HgSe. These regions most likely correspond to different fields of primary and secondary crystallization in the stable phase diagram of this quasi-ternary system (which is not yet fully investigated). The transition between different fields of crystallization leads to a different order of the formation of structural units that, in glasses, results in regions of different glass-formation temperature. The variations of T_c within the triangle are not pronounced.

Table 3 Composition of glassy alloys of the quasi-ternary system Ag_2Se–HgSe–$GeSe_2$ and their characteristic temperatures.

No.	Composition, mol.%			T_g, K	T_c, K	T_m, K	T_{gr}
	Ag_2Se	HgSe	$GeSe_2$				
3-1	2	15	83	552	639	962	0.57
3-2	2	52	46	500	608	852	0.59
3-3	3	20	77	543	636, 726	939	0.58
3-4	4	20	76	544	634, 715	943	0.58
3-5	5	20	75	527	640	938	0.56
3-6	5	25	70	526	648, 730	922	0.57
3-7	5	30	65	503	641, 728	920	0.55
3-8	5	35	60	493	626	888	0.56
3-9	5	40	55	492	613	876	0.56
3-10	5	45	50	466	604	855	0.55
3-11	5	50	45	469	603	841	0.56
3-12	10	30	60	492	629	895	0.55
3-13	10	45	45	470	606, 672	848	0.55
3-14	12	45	43	469	600, 648	850	0.55
3-15	15	25	60	527	630	886	0.59
3-16	18	32	50	495	596	863	0.57
3-17	20	15	65	526	618	893	0.59
3-18	20	25	55	527	607, 690	871	0.61
3-19	20	35	45	498	607, 633	849	0.59
3-20	25	15	60	526	619	875	0.60
3-21	30	10	60	527	625, 632	869	0.61
3-22	30	25	45	494	602, 645	863	0.57
3-23	35	10	55	527	612	866	0.61
3-24	35	20	45	492	602	847	0.58
3-25	38	15	47	504	604	866	0.58
3-26	40	10	50	528	589, 608, 613	861	0.61
3-27	43	6	51	528	626	861	0.61
3-28	45	4	51	533	620	861	0.62
3-29	10	40	50	492	610	828	0.59
3-30	20	30	50	494	603	862	0.57
3-31	30	20	50	527	605	861	0.61

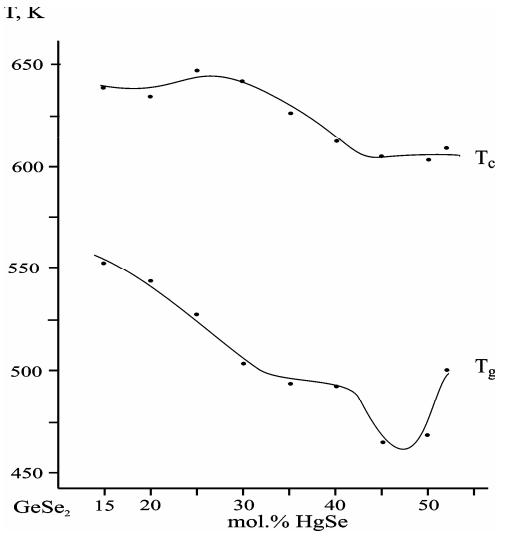

Fig. 2 T_g and T_c *vs.* the HgSe content (Ag_2Se concentration 5 mol.%, except for the left-most and the right-most samples, which contain 2 mol.% Ag_2Se).

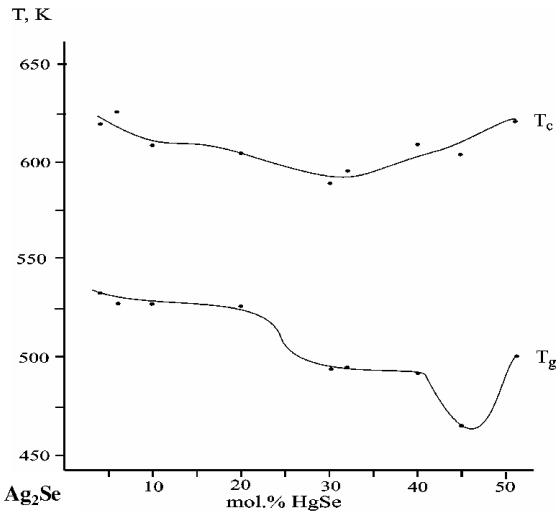

Fig. 3 T_g and T_c *vs.* the HgSe content ($GeSe_2$ concentration 50 mol.%, except for the right-most sample, which contains 46 mol.% $GeSe_2$).

The presented data show that the glass transition temperature is in the range typical of chalcogenide glasses. As the crystallization temperature remains fairly steady, the softening range (T_c–T_g) tends to increase with increasing content of the modifier, which is especially clear in the mercury-containing system. This range extends from ~85 to 100 K in the cadmium- and zinc-containing systems, whereas in the mercury-containing system it reaches 130 K for alloys near the T_g minimum. Using the Kauzmann criterion [16], one can see that the glasses of these systems have higher crystallization ability and so may be obtained in the glassy form only by applying a high quenching temperature. Indeed, several quenching attempts were often required to obtain the compositions with high germanium diselenide content in the glassy state.

Conclusions

Glass formation in the quasi-ternary systems Ag_2Se–Zn(Cd,Hg)Se–$GeSe_2$ was investigated. The largest glass-formation region is observed in the mercury-containing system. The thermal properties of the glassy alloys were characterized by the glass transition and the crystallization temperature and the melting point of the crystallized alloy. The glasses of these systems have high inclination for crystallization.

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