SYNTHESIS AND THERMAL PROPERTIES OF OXYCHALCOHALIDE GLASSES FROM THE $GeSe_2$-CdI_2-CdO SYSTEM

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Oxychalcohalide glasses from the $GeSe_2$-CdI_2-CdO system were synthesized using melt quenching technique. The obtained samples were characterized by visual, X-ray diffraction and electron microscopic analyses. Their temperatures of glass-transition, crystallization and melting were defined by differential thermal analysis. A correlation between these characteristics and the composition of the glasses is established and widely discussed.

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1. Introduction

When chalcogenide glasses are combined with oxide and halide glasses, new highly effective glassy materials for optical amplifiers and IR-lasers are expected to be obtained. In this sense the halide and the chalcogenide glasses are interesting at a first place because of their optical properties in the IR part of the spectrum [1,2]. Besides, together with the properties typical for the chalcogenide and the halide glasses new ones should be expected from the glassy chalcohalides, such as: high ionic conductivity, very low resistivity, porosity, absorbance and catalytic ability, etc., which would wider the application areas of these materials [3-9]. On the other hand, the oxyhalide glasses possess much better optical parameters from the halide glasses and they are much stable to chemical and thermal impacts [10].

The oxychalcohalide glasses are perspective materials for production of: membranes for ion-selective electrodes, sensitive elements in multifunctional sensoric elements, optical amplifiers and IR-lasers, gas sensors, nanosensitive quartz crystal microbalance sensors, galvanic elements, waveguides, catalysts, protective layers, condensators, optoelectronic elements, etc. [1,2,8,11,12].

The region of glassformation in the $GeSe_2$-CdI_2-CdO system is outlined by us and published in a previous work [13]. It lies partially on the $GeSe_2$-CdI_2 (0-78 mol % CdI_2) and $GeSe_2$-CdO (0-25 mol % CdO) sides of the Gibbs' concentration triangle. The maximum solubility of CdO in the glasses is about 35 mol %. No glasses were obtained in the CdI_2-CdO system.

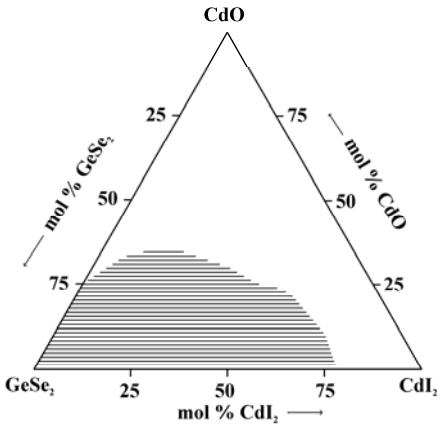
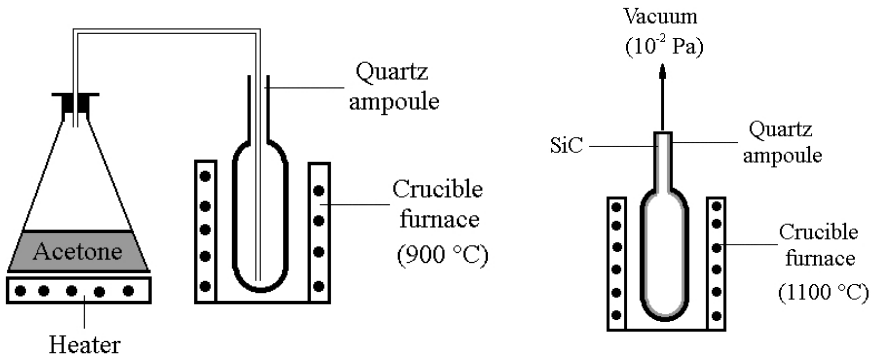


Fig. 1. Region of glassformation in the $GeSe_2$-CdI_2-CdO system

The aim of the present investigation is to synthesize oxychalcohalide glasses from the $GeSe_2$-CdI_2-CdO system and to define their main thermal characteristics.

2. Experimental

Preliminary synthesized $GeSe_2$ (5N Ge and 6N Se), as well as CdI_2 (≥ 99.0 %, Aldrich) and CdO (≥99.0 %, Fluka) were used for the synthesis of the glasses from the $GeSe_2$-CdI_2-CdO system. The glasses' synthesis was performed by standard method in evacuated quartz ampoules. Due to the high reactivity of CdO and CdI_2 with SiO_2, the inner sides of the quartz ampoules were graphitisized before the synthesis by pyrolisis of acetone vapors. For this purpose the scheme shown in Fig. 2,a was used.



a) *b)*

Fig. 2. Principle scheme for graphitization of quartz ampoules: a) graphitization; b) obtaining of inert SiC layer.

Acetone is heated in an Erlenmeyer flask and its vapors are led inside the ampoule. During this process the ampoule is heated up to 900 °C in a crucible furnace. By this way a sufficient by thickness graphite layer is deposited on the inner walls of the ampoule and the influx of acetone vapors must be stopped. The ampoule, without being removed from the furnace, has to be connected to a vacuum installation with quality of vacuum at least $\leq 10^{-2}$ Pa and the temperature of the furnace must be raised up to 1100 °C. The ampoule must be kept by this way for 30 minutes – Fig. 2,b. The obtained SiC on one side prevents the interaction between the quartz and the material

into the ampoule, and on the other – plays the role of "tampon" by absorbing the thermal strains during cooling, if such strains exist.

For the preparation of samples from the investigated system was preformed multi-step direct monotemperature synthesis from the initial components in evacuated to a residual pressure of 10^{-2} Pa graphitized quartz ampoules, conformed with the physicochemical features of the initial compounds ($T_m^{GeSe_2} = 740$ °C [14]; $T_m^{CdI_2} = 387$ °C [15], $T_{boiling}^{CdI_2} = 741$ °C [16]; $T_m^{CdO} = 900 - 1000$ °C [15]). The heating rate between the steps was 3-6 °C/min, as the duration of each of the first three steps (at 300, 450 and 600 °C) was 3 h and the next tree steps at temperatures of 700, 800 and 930 °C were with duration of 2 h, where a vibration stirring of the melt is performed. In the last phase of the synthesis the ampoules are taken out from the furnace and cooled in air to ~ 850 °C and rapidly quenched in ice cold water.

The obtained materials are characterized by visual, XRD and SEM analyses. The XRD investigations were performed on apparatus TUR-M61 using CuK_α-irradiation and Ni-filter, and the morphology of the samples was observed on scanning electron microscope Philips 515.

The thermal characteristics of the glasses (temperatures of glass-transition T_g, crystallization T_{cr} and melting T_m) are defined by differential thermal analysis. An apparatus from the F.Paulik-J.Paulik-L. Erdey system was used at heating rate of 15 ºC/min and reference substance γ-Al_2O_3. To avoid interaction of the investigated material and the air atmosphere the glasses (preliminary grinded) are closed in evacuated to a residual pressure of $\approx 1.10^{-3}$ Pa tubes, called Stepanov's pots.

3. Results and discussion

The results from the visual analysis show that the samples with composition presented in Table 1 possess shiny surface and well expressed shell-like surface. Their color changes from black to deep orange depending on the quantity of CdI_2 in them.

Table 1. Composition and thermal properties of glasses from the $GeSe_2$-CdI_2-CdO sysem.

№	Composition, mol %			m	T_g, ºC	T_{cr}, ºC	T_m, ºC
	$GeSe_2$	CdI_2	CdO				
1	90	0	10	0.0	253	354, 473	695
2	81	9	10	0.1	239	320, 444	646
3	54	36	10	0.4	210	258, 291	334, 593
4	27	63	10	0.7	158	201	358, 497
5	48	32	20	0.4	203	277	330, 354
6	45	30	25	0.4	197	296	330, 339

The XRD investigations show lack of reflexes and well-expressed X-ray amorphous plateau – Fig. 3.

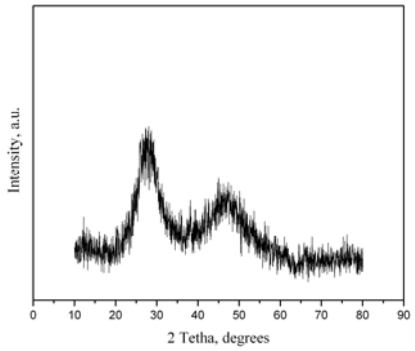


Fig. 3. XRD pattern of sample with composition $(GeSe_2)_{45}(CdI_2)_{30}(CdO)_{25}$.

The surface of the samples is smooth, without any crystalline inclusions and defects - Fig. 4.

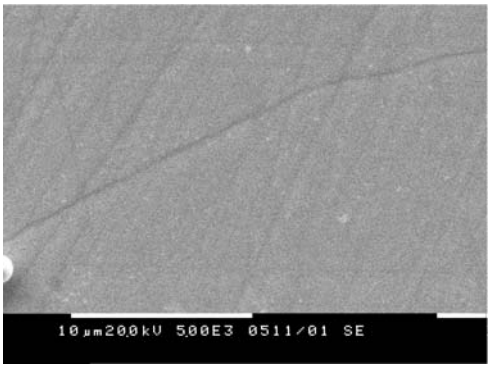


Fig. 4. SEM microphotograph of glass with composition $(GeSe_2)_{54}(CdI_2)_{36}(CdO)_{10}$.

For the investigation of the compositional dependence of the thermal characteristics of the glasses (temperatures of glass-transition T_g, crystallization T_{cr} and melting T_m) – Table 1, the index m is used for convenience, which refers to the ratio between the concentrations of the components $GeSe_2$ and CdI_2. It is given by the expression m=y/(x+y), where with x and y are presented the mol % of the different components of the glasses, written as $(GeSe_2)_x(CdI_2)_y(CdO)_z$.

The temperature of glass-transition T_g of the glasses from the $GeSe_2$-CdI_2-CdO system depend on their composition. When the content of the CdI_2 (z=const) and CdO (m=const) is increased, the T_g decreases – faster for the first dependence and swoler for the second (Table 1). This path of the dependencies is logical since it is related to increase of the ionic content in the chemical bond of the glasses. At the increase of the CdI_2 a breakage of the linear chains in the investigated oxychalcohalide glasses structure passes and they are closed with iodine atoms, while when the CdO is increased it is built into the linear chains without closing them and taking into account the specifics of the cadmium in the CdO (coordination number 4) explains to a great degree the much weaker influence of the CdO concentration on T_g.

During the heating of the glasses the typical for the crystallization process exoeffects appear on the thermograms. The area of these effects depends on the concentrations both of CdI_2 and CdO. A specific feature of these glasses is that two exoeffects are observed, which temperature decreases with the increase of the CdI_2-content (z=const) – Table 1. This pate is expected if the characteristics of the CdI_2 are taken into account. The interesting in this case is that the T_{cr} decreasing rate for both exoeffects is different, as the two temperatures equalize at m=0.7 (z=10 mol % CdO). In the binary $GeSe_2$-CdI_2 system, in the region around 30 mol % $GeSe_2$, an intermediate phase with composition $GeSe_2.2CdI_2$ exists [17] and most probably this compound influences on the T_{cr} of the samples, lying on the $GeSe_2.2CdI_2$-CdO section (especially these rich of $GeSe_2.2CdI_2$). Moreover, the fact that this compound goes trough a phase transition at 220-225 °C which will exert influence on the low-temperature effects should not be ignored.

The CdO concentration change leads to a weak alternation of the T_{cr} and in a first approach one can talk about a weakly expressed diluted maximum at z=20 % CdO (Table 1). The interpretation of this path is difficult because of the fact that in the concentration region 30-100 mol % $GeSe_2$ complicated physicochemical interactions are passing which are caused by the nonvariant eutectic equilibrium at 280 °C and the nonvariant sintectic equilibrium at 375 °C in the $GeSe_2$-CdI_2 system [17]. This means that the exoeffects in the temperature range 270-300 °C are most probably related to a crystallization of solid solution between the $GeSe_2.2CdI_2$ and CdO.

The presence of doubled effects corresponding to the crystallization process presumes in most of the cases presence of two endoeffects of melting too. If these effects are less than two this means that either the crystallized phase or the formed solid solutions in which it participates melt at higher temperatures outside the investigated temperature region. At content of CdO of 10 mol %, the samples with $m<0.4$ show just one endoeffect and at $m\geq0.4$ - two (Table 1). The high-temperature melting effect depends strongly on the CdI_2 concentration, which is expected taking into account the lower melting temperature of this compound. The low-temperature effect (at

m≥0.4) weakly depends on m and must be related to the influence of the nonvariant sintectic equilibrium at 375 °C in the binary $GeSe_2$-CdI_2 system [17], and taking into account the presence of 10 mol % CdO.

The T_m alternation on the $(GeSe_2)_{60}(CdI_2)_{40}$-CdO section is characterized by two melting effects (high- and low-temperature) – Table 1. The path of the $T_m(z)$ dependence for both of the effects looks similar to the path of the $T_m(m)$ dependence. The low-temperature effect can be again related to the nonvariant equilibria in the binary $GeSe_2$-CdI_2 system. The temperature dependence of the second effect, the equalization of T_m at z=25 mol % CdO and the presence of one crystallization effect for this composition can be related only to the nonvariant syntectic equilibrium and the presence of limited area of two non-mixable liquids. The addition of CdO leads to decrease of this area, i.e. to decrease of the temperature difference between the T_m and the temperature of the nonvariant synthectic equilibrium.

4. Conclusions

Chalcohalide glasses from the $GeSe_2$-CdI_2-CdO are synthesized. The samples are characterized by visual, X-ray diffraction and electron microscopic analyses.

The temperatures of glass-transition, crystallization and melting are defined and lie around 158-253 ºC, 201-473 ºC and 330-695 ºC, respectively. A correlation between these characteristics and the composition is established, widely discussed and approaches for its explanation are proposed.

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