GLASS FORMATION IN THE As-Te-Cd SYSTEM

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Chalcogenide glasses from the As-Te-Cd system were synthesized for the first time. The glass forming region was determined by the help of visual, X-ray diffraction and electron microscopic analyses. The basic physicochemical parameters such as density (d), microhardness (HV) and temperatures of phase transformations (glass transition T_g, crystallization T_{cr} and melting T_m) were measured. Compactness and some thermomechanical characteristics such as volume (V_h) and formation energy (E_h) of micro-voids in the glassy network as well as the elasticity module (E) were calculated. The glass-forming ability was evaluated according to Hruby's criteria (K_G). The correlation between composition and properties of the $As_xTe_yCd_z$ glasses was established and comprehensively discussed.

1. Introduction

The interest in chalcogenide glasses (ChG), especially those based on arsenic, as material suitable for infrared optical devices started years ago [1-7]. Due to the fact that these glasses exist not only in stoichiometric composition, but in a continuous variety of mixtures, it is often possible to prepare a glass of certain properties needed.

ChG are one of the most promising materials for fiber and thin film waveguides in the near-, mid- and far-IR regions of the spectrum [8-12]. The research workers have focused their efforts mainly on decreasing the transmission losses in the middle infrared range of the spectrum because the chalcogenide glasses have good transmission in this wavelength region and represent a suitable environment for the CO_2-lasers high-power emission [13]. Theoretical estimations [14,15] show that the minimum optical losses in ChG vary between 0.05 and 30 dB km^{-1} for the wavelength gap of 4-6 μm.

The refraction index n increases in the row $As_2S_3 \rightarrow As_2Se_3 \rightarrow As_2Te_3$ from 2.4 to 3.8 for wavelength of 2 μm [16]. Sanghera et al. [17] have investigated the optical properties of $As_{40}S_{60}$ and $Ge_{30}As_{10}Se_{30}Te_{30}$ and have obtained promising results of the refractive index and the optical losses for the Te-containing glass.

In the literature exists a data about investigations of amorphous thin films from the As-Te-Cd system [17,18,19], but the glass forming region of this system has never been outlined.

The aim of the present work is to outline the region of glass formation in the As-Te-Cd system and to investigate the main thermal, physicochemical and thermomechanical characteristics of the obtained glassy samples, with a view to enlarge the range of the As-Te-Me glasses with high molar mass and with suitable properties for application in the non-linear integral optoelectronics.

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2. Experimental

The glass forming region in the As-Te-Cd system was outlined by the help of 28 compositions – Table 1. The starting components for the synthesis were As and Cd with purity 4N and Te – 5N.

Table 1. Compositions used for outlining the glass forming region
in the As-Te-Cd system ($m=y/(x+y)$).

№	mol %			m	condition
	As	Te	Cd		
1	58.5	39	2.5	0.4	glassy
2	40	57.5	2.5	0.5897	crystalline
3	42.75	52.25	5	0.55	crystalline
4	52.25	42.75	5	0.45	glassy
5	45	45	10	0.5	crystalline
6	40.5	49.5	10	0.55	crystalline
7	47.5	47.5	5	0.5	glassy
8	57	38	5	0.4	glassy
9	61.75	33.25	5	0.35	crystalline
10	63.375	34.125	2.5	0.35	glassy+crystalline
11	53.625	43.875	2.5	0.45	glassy
12	48.75	48.75	2.5	0.5	glassy
13	60	40	0	0.4	glassy
14	43.875	53.625	2.5	0.55	glassy+crystalline
15	55.5	37	7.5	0.4	crystalline
16	50.875	41.625	7.5	0.45	glassy+crystalline
17	45.21	47.29	7.5	0.51	glassy+crystalline
18	55	45	0	0.45	glassy
19	62.5	37.5	0	0.375	glassy
20	45.125	49.875	5	0.525	glassy
21	59.375	35.625	5	0.375	glassy+crystalline
22	47.7	42.3	10	0.47	crystalline
23	48.1	44.4	7.5	0.48	glassy+crystalline
24	65	35	0	0.35	glassy
25	50	50	0	0.5	glassy
26	52.5	47.5	0	0.475	glassy
27	47.5	52.5	0	0.525	glassy
28	67.5	32.5	0	0.325	crystalline

The samples from the As-Te-Cd system were obtained via direct monotemperature synthesis in vacuumed (0.133 Pa) quartz ampoules under the following conditions: two-stage increase of the temperature to 500 and 900 °C with velocity of 5-8 and 4-5 °C/min and thermal treatment at these temperatures for 1 hour combined with continuous vibrational stirring of the smelter at the last temperature step. A decrease of the temperature to 750-800 °C follows, annealing for 0.5 h and after that the smelter was quenched in water+ice mixture.

The bulk samples were investigated by visual, X-ray (diffractometer TUR-M16 with CuK$_\alpha$-irradiation and Ni-filter) and electron microscopic (electron microscope TEM Philips-3003) analyses.

The characteristic temperatures of the glasses were defined by differential thermal analysis (DTA) using thermograph from the F.Paulic-J.Paulic-L.Erdey system (manufactured by MOM-Hungary) at heating rate of 10 °C min^{-1} and standard substance α-Al$_2$O$_3$.

The density (d) of the samples was measured by hydrostatic method using toluene as immersion fluid and the microhardness (HV) – by the Vicers' method (on metallographic microscope MIM-7 with a microhardnessmeter PMT-3 at loading of 10 g).

The elasticity modulus (E), the minimum volume of the micro-voids (V_h), the energy for their formation (E_h), the Hruby's criteria (K_G) and the compactness (C) were calculated by Eqs. (1)-(3) [20]:

$$E = 15HV, \ V_h = 5.04\frac{T_g}{HV}, \ E_h = 30.729T_g \tag{1}$$

$$K_G = \frac{T_{cr} - T_g}{T_m - T_{cr}} \tag{2}$$

$$C = d\left\{\sum_i \frac{M_i x_i}{d_i} - \sum_i \frac{M_i x_i}{d}\right\}\left[\sum_i M_i x_i\right]^{-1}, \tag{3}$$

where T_g, T_{cr} и T_m are the temperatures of glass transition, crystallization and complete melting; M_i и x_i – molar weight and fraction of the ith component.

3. Results and discussion

The synthesized bulk samples form the As-Te-Cd system are dark colored with a well-expressed shell-like surface.

The X-ray diffraction analysis (XRD) show a typical amorphous state diffractogram for the compositions lying within the glass forming region (group A): presence of X-ray amorphous plateau and lack of well-expressed diffraction reflexes (Fig. 1a). For the compositions situated on the boundaries of the glass forming region (group B) the diffractograms are richer of reflexes, even with poor intensity (Fig. 1b), while for the compositions outside the glass forming region (group C) the diffraction pattern is typical for the crystalline state (Fig. 1c).
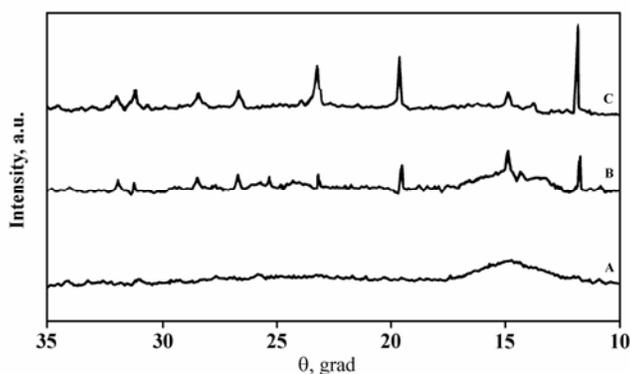

Fig. 1. Typical rentgenograms of samples from the As-Te-Cd system a) group A (composition $As_{48.75}Te_{48.75}Cd_{2.5}$); b) group B (composition $As_{50.875}Te_{41.625}Cd_{7.5}$); c) group C (composition $As_{45}Te_{45}Cd_{10}$)

The electron microscopic investigations showed that the surface of the samples from group A is homogeneous and smooth; for the samples from group B on the surface appear local islands of crystallization; for the samples from group C – the surface is rough without any areas belonging to a glassy phase.

The region of glass formation in the As-Te-Cd system was outlined on the basis of the syntheses led and the results from the visual, XRD and electron microscopic analyses – Fig. 2.
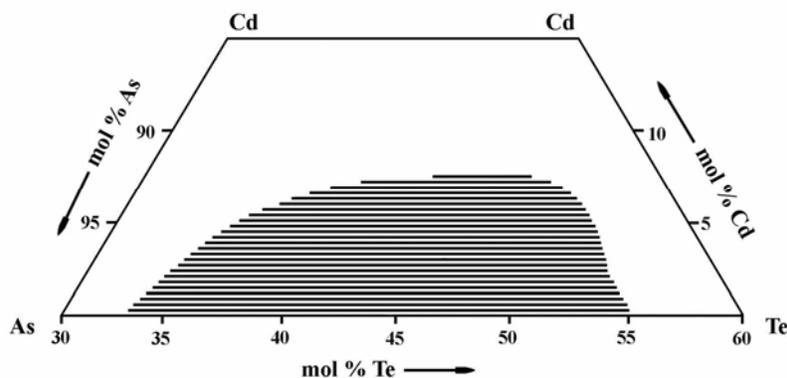

Fig. 2. Glass forming region in the As-Te-Cd system

It lies on the As-Te side (33-55 mol % Te). In the binary systems As-Cd and Te-Cd were not obtained glassy phases. The maximum solubility of Cd in the glasses from the binary system As-Te is ≈7.5 %.

The thermal characteristics of the ChG from the investigated system: temperature of glass transition (T_g), crystallization (T_{cr}) and complete melting (T_m), defined from the derivatograms, are summarized in Table 2.

Table 2. Thermal properties of some glassy phases from the $As_xTe_yCd_z$ system, m= y/(x+y).

Composition			m	T_g, °C	T_{cr}, °C	T_m, °C	ΔT, °C	K_G
x	y	z						
65	35	0	0.35	195	290	391	95	0.9406
60	40	0	0.4	196	271	390	75	0.6303
55	45	0	0.45	198	255	390	27	0.1636
52.5	47.5	0	0.475	198	228	385	30	0.1911
50	50	0	0.5	199	239	388	40	0.2685
57	38	5	0.4	185	-	390	-	-
52.25	42.75	5	0.45	190	249	388	59	0.4245
47.5	47.5	5	0.5	193	222	382	29	0.1813
45.125	49.875	5	0.525	195	220	380	25	0.1563

On the thermograms of the glassy samples are observed three effects: the first is connected with the glass transition temperature T_g; the next is exothermal with well-expressed maximum and is related with the crystallization process of two phases; the last is endothermal and shows the melting of already crystallized phase (solid solution). Typical thermograms for some of the investigated glassy samples are shown on Fig. 3
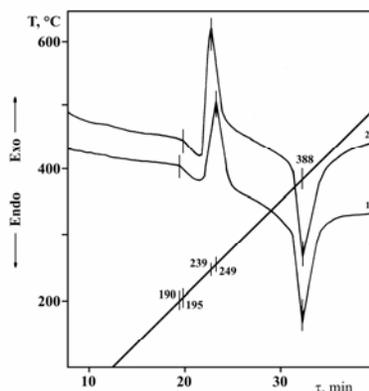
Fig. 3. Typical thermograms of glassy samples from the As-Te-Cd system
1) sample $As_{52.25}Te_{42.75}Cd_5$.; 2) sample $As_{50}Te_{50}Cd_0$.

The temperature of glass transition (T_g) changes in dependence of the composition in the range from 185 to 199 °C – Table 2. A correlation between T_g and the composition of the glasses exists. At increase of m (z=const) the dependence $T_g(m)$ slightly increases. When z increases, T_g weakly decreases.

The crystallization temperature (T_{cr}) varies between 220 and 290 °C and decreases when increasing m (at z = const). The increase of the Cd-content does not exert influence on T_{cr}, which is probably due to two reasons: 1) the cadmium content in the glass is slight and does not lead to sudden changes in the structure of the glass and 2) at z=0 and z=5 % crystalizes one and the same phase. Most probably, the crystalizing phase is As_2Te_3 or a solid solution on its base (rich of As at z=0 or with cadmium dissolved in As_2Te_3 at z=5).

The temperature of complete melting (T_m) practically does not depend from the content of Te (at z = const) and Cd (at m=const) - Table 2. This temperature (about 385±5 °C) should be connected with T_m of the As_2Te_3 ($T_m^{As_2Te_3} = 381$ °C) [21].

The Hruby's criteria K_G (Table 2) characterises, though roughly, the glass forming ability of the glasses. The decrease of K_G, at z=const and m=const, shows that the glass forming ability of the compositions in this order decreases, which is logical because the contents of Te and Cd increase in the same order.

At the analysis of the thermomechanical properties of the glasses (V_h, E_h, E)- Table 3, a good agreement between the change of these characteristics and the composition is observed.

Table 3. Physicochemical and thermomechanical properties of samples from the As-Te-Cd system.

Composition			m	T_g	d	HV	E	V_h, 10^{-3}	E_h	C
x	y	z		°C	g/cm^3	kgf/mm^2	kgf/mm^2	Å^3	kJ/mol	
65	35	0	0.35	195	5.30	57	855	17.24	5992	-0.117
60	40	0	0.4	196	5.55	56	840	17.64	6023	-0.078
55	45	0	0.45	198	5.69	55	825	18.14	6084	-0.060
52.5	47.5	0	0.475	198	5.70	51	765	19.57	6084	-0.060
50	50	0	0.5	199	5.75	47	705	21.34	6115	-0.054
57	38	5	0.4	185	5.87	28	420	33.30	5685	-0.044
52.25	42.75	5	0.45	190	5.85	24	360	39.90	5839	-0.050
47.5	47.5	5	0.5	193	5.90	24	360	40.53	5931	-0.045
45.125	49.875	5	0.525	195	6.00	21	315	46.80	5992	-0.031

The dependence E(m) goes over the dependence HV(m) by definition. Analogically, the course of the dependence $E_h(m)$ repeats $T_g(m)$.

A characteristic feature of the ChG is the presence of a great nuber of micro-voids. It is logical, when the glass forming ability increases, the probability for increase of the volume of these micro-voids to raise too, which finds its expression by the property minimal volume of the micro-voids (V_h). A decrease of V_h should be expected when increasing the cadmium content at m=const, but in the investigated system it raises. This could be explained by the following way - it is possible that when increasing the Cd content in the glasses, the last to break the–Te–Te– bonds or to unite two structural fragments from the–As–Te– type in one chain fragment–As–Te–Cd–Te–As–, due to which the minimal volume of micro-voids to increase too. Because of lack of tellurium atoms in the binary system As–Te (As:Te<1.5) it is not likely structural fragments from the kind –As–Te–Cd–Te–Te– to come out. The formation of bonds –As–Cd– and –Cd–Cd– in the same matrix is also unexpected, especially at low concentration of cadmium.

The microhardness of the investigated samples varies in the range 21-57 kgf/mm^2 and depends of the composition of the glassy phases - Table 3. When m (z = const) is increased, the HV slightly decreases. In addition of Cd to the As-Te system, the microhardness of the obtained glasses decreases much more than expected, which probably is connected with the sudden increase of V_h.

The density (d) of the samples changes between 5.3 and 6.0 g/cm^3 - Table 3. When m (z = const) and z (m = const) increase, d lightly increases, since d_{Te} (6.27 g cm^{-3}) > d_{As} (5.78 g cm^{-3}) and d_{Cd} (8.42 g cm^{-3}) > d_{Te} > d_{As} [22].

The compactness C (Table 3) of the glasses has negative value and depending on the composition changes within very narrow limits (the experimental values of C fall in the range from -0.03 to -0.11). The low values of C indicate a high compactness of the glasses similar to that of the crystalline samples with the same composition. Despite the slight change of C, the following regularity is outlined: when increasing the contents of Te (at z=const) and of Cd (at m=const), the strucutre of the glasses becomes more compact, which seems absolutely logical, since the atomic radiuses of both Te and Cd are larger than this of As. Besides, the increase of C with the rise of the tellurium, respectively of the cadmium content, should affect the glass forming ability, which is confirmed by the values of K_G (Table 2).

It is logical that the properties compactness and minimal volume of the micro-voids are connected by inversely proportional dependence, but in Table 3 it is directly proportional. This could be explained by the following way. The presence of defective triangular pyramids AsTe$_{3/2}$ with one or two free bond, as well as the formed fragments with participation of cadmium atoms, creates favorable conditions for internal netting of the structure, which is related with a decrease of the micro-voids number (n). In view of fact that d=m/(V_g+nV_h), where nV_h and V_g are the total volume of micro-voids and the volume taken by the glass, respectively. When adding cadmium in the system, n and V_g+nV_h will decrease and d will increase, which according to Eq (3) will have direct influence on the compactness.

4. Conclusions

New chalcogenide glasses were synthesized and the glass forming region in the As-Te-Cd was outlined.

A number of physicochemical (density, microhardness, temperatures of glass transition, crystallization and melting) and thermomechanical properties of the glassy phases were investigated. A correlation between these properties and the composition of the glasses from the studied system was established and a principle for its explanation has been proposed.

Acknowledgements

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