Chalcogenide Letters Vol. 5, No. 3, March 2008, p. 39 - 43

Glass formation in the As_2Se_3-Sb_2Te_3-CdTe system

V. Vassilev*, T. Hristova-Vasileva, L. Aljihmani
Department of Non-Ferrous Metals and Semiconductor Technologies, University of Chemical Technology and Metallurgy, 8 Kliment Ohridski blvd., 1756 Sofia, Bulgaria

Chalcogenide glasses from the As_2Se_3-Sb_2Te_3-CdTe system were synthesized. The glass-forming region was determined by the help of visual, X-ray diffraction and electron microscopic analyses. The temperatures of phase transformations (the glass transition T_g, crystallization T_{cr} and melting T_m) were measured. The glass-forming ability was evaluated according to Hruby's criteria K_G. A correlation between composition and properties of the As_2Se_3-Sb_2Te_3-CdTe glasses was established and discussed.

(Received February 21, 2008; accepted February 28, 2008)

Keywords: Chalcogenide glasses, Synthesis, X-ray diffraction, Thermal properties

1. Introduction

The chalcogenide glasses (ChG) differ from the ordinary silicate ones by their transparency in the IR-region of the spectrum, high refraction coefficient with a nonlinear dispersion, low softening temperature, which lies near to the temperature of crystallization. Besides, they are easy to obtain and are characterized by high chemical and radiation stability. Many physical effects are shown in them, such as thermo- and photo-electromotive tension, Hall effect, photoconductivity and photoluminescence, as well as the photodarkening effect as a result from the photostructural changes passing in them [1,2].

Thanks to their properties, the ChG find their application as materials for threshold switchers, memory elements, optical windows in different parts of the spectra, optical fibers, functional elements in integrated optic circuits and as photoresists. The ChG are used as medium for holographic records in the non-linear optoelectronics and acousto-optical devices [3, 4]. On the basis of ChG are also developed chemical sensors for potentiometric, amperometric, thermal and other measurements. Among the solid-state potentiometric sensors, particular interests excite the ion-selective electrodes (ISE) with membranes from ChG, as well as the multisensor systems [5-11].

The properties shown above, as well as the possibility for their practical application in different elements and devices, motivate more complete and extensive research of the already known materials, on one hand and the synthesis and investigation of the properties of new ones, on the other.

The aim of the present work is to outline the region of glass formation within the system As_2Se_3-Sb_2Te_3-CdTe and to investigate the thermal characteristics of the produced new ChG, which might serve in the future as a base for the production of Cd(II)–ISE or thin film waveguides.

2. Experimental

The glass forming region within the As_2Se_3-Sb_2Te_3-CdTe system is outlined by the help of 24 compositions – Table 1.

*Corresponding author: venciv@uctm.edu

Table 1 Compounds used for outlining the glass forming region within the As_2Se_3-Sb_2Te_3-CdTe system.

№	mol %			m	condition
	As_2Se_3	Sb_2Te_3	CdTe		
1	85.5	4.5	10	0.05	glassy
2	76.5	8.5	15	0.10	glassy+crystalline
3	72	18	10	0.20	glassy
4	71.25	23.75	5	0.25	glassy
5	90	10	0	0.10	glassy
6	80	20	0	0.20	glassy
7	68	17	15	0.20	glassy+crystalline
8	63	27	10	0.30	crystalline
9	57	38	5	0.40	crystalline
10	70	30	0	0.30	glassy
11	60	40	0	0.40	crystalline
12	55	45	0	0.45	crystalline
13	70.55	12.45	17	0.15	glassy+crystalline
14	67.5	22.5	10	0.25	glassy+crystalline
15	66.5	28.5	5	0.30	glassy+crystalline
16	65	35	0	0.35	glassy
17	81	9	10	0.10	glassy+crystalline
18	76.5	13.5	10	0.15	glassy
19	100	0	0	0	glassy
20	95	0	5	0	glassy
21	85.5	9.5	5	0.10	glassy
22	76	19	5	0.20	glassy
23	61.75	33.25	5	0.35	crystalline
24	62	38	0	0.38	glassy+crystalline

The source compounds Me_nCh_m (Me=As and Sb; Ch=Se and Te) and the glasses (4 g) from the $(As_2Se_3)_x(Sb_2Te_3)_y(CdTe)_z$ system are produced via direct single temperature synthesis in vacuumed and sealed under vacuum of 1.10^{-3} Pa quartz ampoules. The source materials used for the synthesis of Me_nCh_m are Se, Te and As with a purity of 5N (Fluka), Sb - 4N (Merck). CdTe produced by BALZERS with a purity "Coating material" is used. The characteristics of the syntheses (temperatures and the duration of the isothermal steps; the heating rate between them) have been conformed by the physical and chemical features of the source components and the intermediary and final phases. The maximum temperature of the synthesis of the glasses within the investigated system is 950±10 °C where, in the course of 2 hours a vibrational agitation of the smelter is included. The last has been tempered at a temperature of 850±10 °C and quenched in a mixture of water and ice with a cooling rate of 10-15 °C s^{-1}.

The characteristic temperatures of the glasses have been defined by differential thermal analysis (DTA) [12] performed on a device from the system F.Paulik-J.Paulik-L.Erdey of the company MOM-Hungary at a speed of heating 10°C/min. The standard sample (α-Al_2O_3) and the investigated substance to a quantity of ≈ 0,3 g are placed in Stepanov pots and sealed at residual pressure ~ 1.10^{-3} Pa.

The XRD is performed on a TUR-M61 device using CuK_α radiation (Ni-filter, θ=5-40°).

The surface of the samples is investigated in an electron microscope EM 4000 – Phillips.

3. Results and discussion

The synthesized bulk samples of the As_2Se_3-Sb_2Te_3-CdTe system are dark colored with a strong luster.

The results from the X-ray diffraction show that several compositions (group A) are typical glasses without peaks on the diffractograms – these compositions form the glass forming region (Fig. 1a). Some other compositions (group B, Fig. 1b) show diffraction peaks with small intensity (compositions on the region boundary). The diffractograms of the samples from group C show strong peaks (Fig. 1c), these samples are crystalline outside the glass forming region.

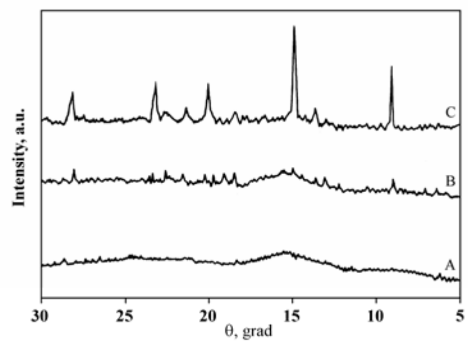

Fig. 1. Typical diffractograms of samples from the As_2Se_3-Sb_2Te_3-CdTe system:
a) composition $(As_2Se_3)_{85.5}(Sb_2Te_3)_{9.5}(CdTe)_5$ (in the glass forming region);
b) composition $(As_2Se_3)_{67.5}(Sb_2Te_3)_{22.5}(CdTe)_{10}$ (on the glass forming boundary);
c) composition $(As_2Se_3)_{57}(Sb_2Te_3)_{38}(CdTe)_5$ (outside the glass forming region).

The electron microscopic observations show a smooth and homogeneous surface of the samples from group A. Small crystalline regions are shown on the surface of the samples from group B. The surface of the group C samples is rough and there are no regions on it belonging to a glassy phase.

Based on the syntheses carried out and the results obtained from the visual X-ray diffraction analysis and the electron microscopic analysis we outlined the region of glass formation in the three-component system $(As_2Se_3)_x(Sb_2Te_3)_y(CdTe)_z$, where x+y+z=100 and m=y/(x+y) – Fig. 2.

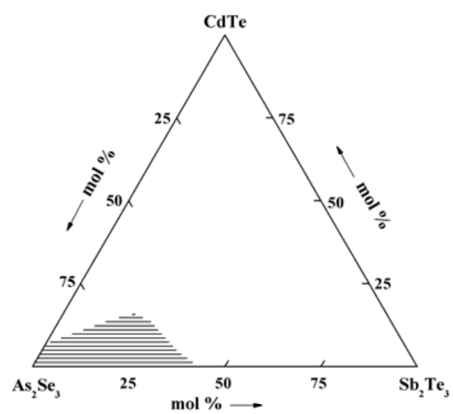

Fig. 2. Glass forming region in the As_2Se_3-Sb_2Te_3-CdTe system

It lies partially on the As_2Se_3-Sb_2Te_3 and As_2Se_3-CdTe sides (from 0 to 38 mol % Sb_2Te_3 and from 0 to 15 mol % CdTe, respectively), which are side of the Gibbs's concentration triangle. The maximum solubility of CdTe in the glasses is ≈ 15 mol %. On the side Sb_2Te_3-CdTe glasses were not obtained.

The investigated thermal characteristics T_g, T_{cr} and T_m of the samples, defined by DTA, are shown in Table 2. Some typical derivatograms are presented at Fig. 3. Three different effects could be seen on the thermograms. The first is connected to the glass transition temperature (change of the angle coefficient of the T(τ) dependence); the second is exothermal with well expressed maximum and is related to the crystallization process; the last effect is endothermal and is obtained as result of the melting of already crystallized phase or solid solution.

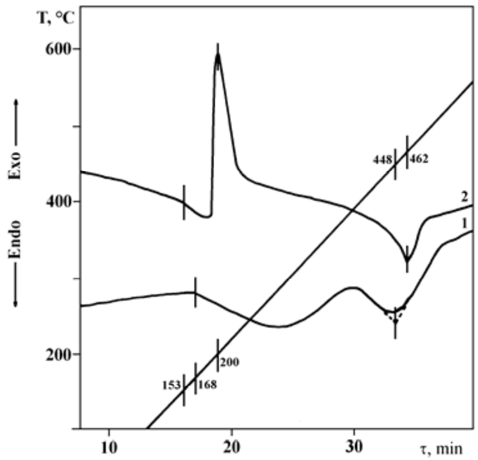

Fig. 3. Typical thermograms of samples from the As_2Se_3-Sb_2Te_3-CdTe system: 1) sample with composition $(As_2Se_3)_{70}(Sb_2Te_3)_{30}(CdTe)_0$; 2) sample with composition $(As_2Se_3)_{66.5}(Sb_2Te_3)_{28.5}(CdTe)_5$.

The glass transition temperature (T_g) depending on the composition alters within the framework between 148 to 182 °C (Table 2). Upon the increase of the contents of As_2Se_3 (z = const) T_g of the glasses from the investigated system grows considerably as As_2Se_3 is one of the best glass forming agents. CdTe has an extremely restricted influence on the values of T_g. This is most probably connected with the "domination" of the trigonal pyramids $AsSe_{3/2}$ and $SbTe_{3/2}$, as their quantity when increasing m and z remains practically the same, while CdTe covers the structure with a net and connects the separate pyramids on a flat plane without altering their quantity.

The temperature of crystallization (T_{cr}) is within 200 to 256 °C. When the concentration of CdTe increases, T_{cr} increases too. In the compounds, rich in As_2Se_3, stable ChG have been produced, due to whom no effect of crystallization has been established in them (table 2).

The temperature of complete melting (T_m) depends slightly on the composition and alters within the 375-462 °C - Table 2. The near values of T_m for the different compositions, as well as the weak influence of the concentration of CdTe over T_m are most probably due to the very good glass forming properties of As_2Se_3, on one hand and to the influence of Sb_2Te_3, which seems to be a very good modifying agent, on the other.

Table 2. Thermal properties and Hruby's criteria of glassy phases from the system $(As_2Se_3)_x(Sb_2Te_3)_y(CdTe)_z$, m=y/(x+y)

№	Composition, mol %			m	T_g, °C	T_{cr}, °C	T_m, °C	K_G
	x	y	z					
19	100	0	0	0.00	182	-	375	-
6	80	20	0	0.20	172	237	400	0.40
10	70	30	0	0.30	168	-	448	-
21	85.5	9.5	5	0.10	167	217	420	0.25
22	76	19	5	0.20	158	208	430	0.23
15	66.5	28.5	5	0.30	153	200	462	0.18
1	85.5	4.5	10	0.05	155	-	457	-
17	81	9	10	0.10	155	-	443	-
18	76.5	13.5	10	0.15	153	256	429	0.60
3	72	18	10	0.20	148	222	453	0.32

A criterion for the evaluation of the impact of the compound on the glass formation ability is the Hruby's criteria K_G [13]: $K_G = (T_{cr} – T_G)/(T_m – T_{cr})$ - Table 2. As it was mentioned above, a large part of the obtained ChG do not show any crystallization effect or if there is one, it is insignificant. Due to this fact, no correlation between K_G and the glass composition could be made.

4. Conclusions

New chalcogenide glasses were synthesized and the glass forming region of the As_2Se_3-Sb_2Te_3-CdTe system was outlined.

The thermal properties of the glassy phases were studied. A correlation was established between these properties and the composition of glasses from the studied system and a principle for its explanation was suggested.

It is determined that Sb_2Te_3 is a good modifying agent in the investigated system.

Acknowledgements

The authors acknowledge thankfully the financial support for this work from the Ministry of Education and Science (Fund "Scientific investigations" - contract TN-1503/05) and the Science Research Sector of the University of Chemical Technology and Metallurgy.

Referentes

[1] E. Marquez, J..B. Ramirez-Malo, J. Fernandez-Pena, P. Villares, R. Jimenez-Garay, P. J. S. Ewen, A.E. Owen, J. Non-Cryst. Solids, **164-166**, 1223 (1993).
[2] E. Marquez, J. B. Ramirez-Malo, J. Fernandez-Pena, P. Villares, R. Jimenez-Garay, P. J. S. Ewen, A. E. Owen, Opt. Mater., **2**, 3, 143 (1993).
[3] H. Nasu, K. Kubodera, M. Kobayashi, M. Nakamura, K. Kaniya, J. Amer. Ceram. Soc., **73**, 1794 (1990).
[4] E. Hajto, P.J. Ewen, A.E. Owen, J. Non-Cryst. Solids, **164-166**, 901 (1993).
[5] Yu.G. Vlasov, E.A. Bychkov, Ion-Sel. Electrode Rev., **9**, 5 (1987).
[6] Yu..G. Vlasov, E..A. Bychkov, B..L. Seleznev, Sensors and Actuators B, **2**, 1, 23 (1990).
[7] C.E. König, E.W. Grabner, Electroanalysis, **7**, 11, 1090 (1995).
[8] E. Pungor, Anal. Sci., **14**, 4, 249 (1998).
[9] D. Lezal, J.Pedlikova, J.Zavadil, Chalcogenide Letters, **1**, 1, 11 (2004).
[10] V. S. Vassilev, S.H. Hadjinikolova, S.V. Boycheva, Sensors and Actuators B, **106,** 401 (2005).
[11] V. S. Vassilev, S. V. Boycheva, Talanta, **67,** 1, 20 (2005)
[12] M. Hichri, C. Favotto, H. Zamali, Y. Feutelais, B. Legendre, A. Sebaoun, M. Jemal, J. Therm. Anal. Cal., **69,** 2, 509 (2002).
[13] A. Hruby, Czech. J. Phys., **B22,** 1187 (1972).