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NEW CHALCOGENIDE GLASSES IN THE $GeSe_2$ -As_2Se_3-CdTe SYSTEM

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Glass-forming region in the $GeSe_2$-As_2Se_3-CdTe system has been determined by visual, X-ray diffraction and electron microscope analyses. Glasses have been obtained in the $GeSe_2$-rich region. Glass-formation has been situated wholly on the $GeSe_2$- As_2Se_3 and partially on the $GeSe_2$-CdTe and As_2Se_3-CdTe (0 - 15 Mol. % CdTe) sides in the Gibbs diagram. The maximal dissolution of CdTe in the glasses has been found up to 20 Mol. % CdTe. The temperatures of glass transition (T_g), crystallization (T_{cr}) and melting (T_m) of the glasses have been examined in the temperature range 20÷950 °C. Two exothermic effects have been registered at 440 and 565 °C, which are connected with $GeSe_2$ and CdTe crystallization, respectively. The endothermic effect observed at 680±20 °C is related to the previous crystallized $GeSe_2$ phase. A small deviation from the melting temperature of $GeSe_2$ (T_m=740 °C) is probably due to a solid solution formation on the base of $GeSe_2$+As_2Se_3. According to the rule $\Delta t=T_c-T_m>100$ °C the glasses have been obtained stable. The density and microhardness of the glassy samples have been measured to be in the range 4.36÷4.58 g/cm^3 and 85-125 kgf/mm^2, respectively. It has been calculated some characteristics of synthesized glasses as follows: module of elasticity (E), minimal micro-voids volume (V_h) and micro-voids formation energy (E_h). The relations properties-average coordination number (Z) were clarified in terms of glassy network structure.

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1. Introduction

Recently, multicomponent chalcogenide glasses are widely applicable in the field of semiconductor technics. The great interest of these materials is due to their simply obtaining technology in bulk forms and thin films; chemical and radiation durability; their transparency and photosensitivity in IR and VIS spectral regions, as well as the possibility of wide varying of properties with the composition. That determine the possibilities for their application - for optical covers and optical fibers preparation, photoresists, optical recording media, threshold and memory-switching devices and so on. Multicomponent chalcogenide glassy materials have recently been used successfully in ion-selective potentiometry as functional membranes in ionselective electrodes for determination of heavy metal ions [1]. Chalcogenide glassy membranes are more stable and durable in corrosion media in respect to crystalline ones [2]. In this connection chalcogenide glasses are often used as membrane materials in ionselective electrodes for determination of Ag(I)-, Pb(II)-, Fe(III)- and Cu(II)-ions [2÷5].

The investigation of new glassy materials on the basis of Ge-chalcogenides and/or As with MeCh (Me=Zn, Cd, Ni, Sn, Tl, Cr and so on; Ch=S, Se, Te) provokes the scientific interest for new membranes materials production.

The aim of the present work is to synthesize multicomponent chlacogenide glasses in the system $GeSe_2$-As_2Se_3-CdTe and to investigate their physico-chemical properties. The idea of CdTe addition in glassy matrix is to increase the ionic conductivity [6]. It is expected the new synthesized glasses to be a suitable material for Cd^{2+}-ionselective electrodes.

2. Experimental

The glass-forming region was determined by the help of 24 synthesized compositions. The starting materials were Ge, As, Se with 5N purity and CdTe (Coating quality, BALZERS 99.999%). The starting compounds $GeSe_2$ and As_2Se_3, as well as the samples from the investigated system were prepared by direct monotemperature synthesis at 850-1000 ^oC depending on the CdTe content. The melts were kept for about 2 hours at the highest temperature of the synthesis and vibrational stirring was applied, and after that the melts were quenched in a ice-water mixture.

The glassy state of the obtained samples were checked by a visual, X-ray diffraction (diffractometer TUR – M 61 with CuK_α radiation and a Ni filter) and electron-microscope (Philips) analyses. The density of the samples (d) was measured by a hydrostatic method using toluene as immersion fluid and the microhardness (HV) was measured by Vickers' method. A thermograph (DTA) was used to record the thermal characteristics of the samples.

3. Results

The synthesized bulk samples from the $GeSe_2$ -As_2Se_3-CdTe system are dark colored with a strong lustre. 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. Some other compositions (group B) show diffraction peaks with small intensity (compositions on the region's boundary). The diffractograms of the samples from group C show strong peaks, these samples are crystalline and outside the glass-forming region.

The electron microscopic observation shows a smooth and homogeneous surface of the samples form group A. Small crystalline regions are shown on the surface of the samples from group B while the samples placed outside of the glass-forming region (group C) are completely crystallized. Thermal characteristics of the samples - temperatures of glass transition (T_g), crystallization (T_{cr}) and melting (T_m) were determined by DTA-analysis and the results are summarized in Table 1. The obtained values for density and microhardness are given in Table 1.

Table 1. Thermal and physical properties of the $(GeSe_2)_x(As_2Se_3)_y(CdTe)_z$ glassy samples, where x+y+z=100.

Composition			m	T_g, °C	T_{cr}, °C	T_m, °C	d, g/cm^3	HV, kgf/mm^2
x	y	z						
90	0	10	0.0	155	445	680	4.40	125
81	9	10	0.1	140	445,565	685	4.44	120
63	27	10	0.3	125	445,565	685	4.49	115
45	45	10	0.5	120	440,565	675	4.50	104
27	63	10	0.7	120	440,565	670	4.56	96
9	81	10	0.9	120	440	665	4.60	89
0	90	10	1.0	130	440	660	4.62	85

4. Discussions

4.1. Glass-forming region

The glass-forming region was determined on the basis of the results from the visual, X-ray diffraction and electron microscopic analyses of the samples from ternary $(GeSe_2)_x$ $(As_2Se_3)_y(CdTe)_z$ system, where x+y+z = 100 and m = y/(x+y) - Fig. 1. The region is situated in the $GeSe_2$ –rich region and lies wholly on the $GeSe_2$- As_2Se_3 side partially on the $GeSe_2$-CdTe and As_2Se_3-CdTe sides from 0 to 17 Mol.% CdTe. The glasses dissolves up to 20 Mol.% CdTe - Fig. 1.

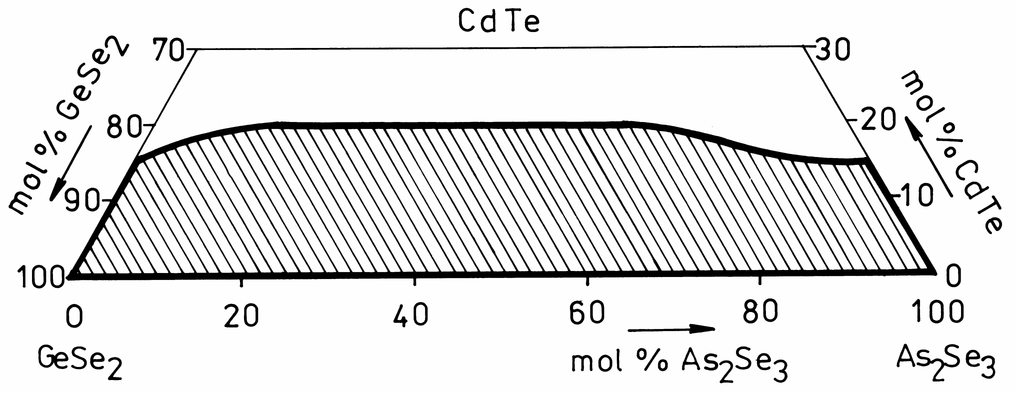

Fig. 1. The glass-forming region in the $GeSe_2$-As_2Se_3-CdTe system.

4.2. Thermal characteristics

Three different effects are observed in the thermograms of the glasses: the first endothermic effect is connected to the glass transition temperature (T_g), next exothermic effect is related to the crystallization temperature (T_{cr}) (part of samples show two consecutive exothermic peaks), and last endothermic effect correspondent with melting of the crystallized phases (solid solutions). Glass transition temperatures, T_g, of the glasses decreases with increasing of m (z = const). The obtained T_g values are in the range 120÷150 °C. The influence of the composition variation on the crystallization temperature is negligible, it is evidence that identical phases are crystallized at the all compositions. The quantity of the glassformers $GeSe_2$ and As_2Se_3 have no influence on T_{cr}. It is observed one or two crystallized phases under glassy samples heating. The first crystalline phase was observed at (440±5)°C and the second at (565±5)°C, respectively. We supposed that the low temperature crystallized phase belongs to $GeSe_2$ and high temperature crystallized phase corresponds to CdTe, taking into account that the melting point of starting compositions are as follows: $T_m^{GeSe_2}$ =740 °C, $T_m^{As_2Se_3}$ =360 °C and T_m^{CdTe} =1095 °C.

The melting effects are probably connected to the melting of the crystallized solid solutions of $GeSe_2$. Melting temperatures are independent on the composition of the samples.

4.3. Density and microhardness

The density values of the samples are in the range 4.40 - 4.62 g/cm^3. The results are given in Table 1. The values increase with As_2Se_3 content when z = const. These results are expected because the density of As_2Se_3 is bigger compared to these of $GeSe_2$ (d_{GeSe_2} = 4.34 g/cm^3 [7], $d_{As_2Se_3}$ = 4.8 g/cm^3 [8], d_{CdTe} = 5.86 g/cm^3[9]). The density values increase with CdTe content at a constant value of m since the density of CdTe is bigger in respect to the density values of $GeSe_2$ and As_2Se_3.

The values obtained from microhardness (HV) measurements are in the ranges 85÷125 kgf/mm^2 and depend on the glassy compositions – Table 1. An increase of the microhardness is observed in cases when As_2Se_3 content increases (m decreases and z is constant), as well as when CdTe content decreases (z –decreases and m is constant). This relation is determined by the higher microhardness of $GeSe_2$ and As_2Se_3, respectively compared to the microhardness of cadmium telluride ($HV_{GeSe_2} = HV_{As_2Se_3}$ =150 kgf/mm^2 [7,10] and HV_{CdTe} = 60 kgf/mm^2 [7]).

4.4. Thermo-mechanical characteristics

According to the free-volume theory Sanditov [11] proposed a follow equation for microhardness of glasses:

$$HV=\frac{E_h}{V_h}, \tag{1}$$

where E_h is the energy of micro-void creation in a volume V_h. According to Bartenev [12] and Nemilov [13] the microhardness is related to the module of elasticity (E) and a Poison's coefficient, μ, by the relation:

$$HV=\frac{1-2\mu}{6(1+\mu)}E \tag{2}$$

On the other hand [11]:

$$\Delta\alpha.T_g=3(1-2\mu).\frac{HV}{E}\quad, \tag{3}$$

where $\Delta\alpha=\alpha_f-\alpha_g$ is the variation of the coefficient of thermal expansion at T_g and

$$\Delta\alpha.T_g\cong 0{,}1 \tag{4}$$

The equation (4) is given by Simh-Boyer and it is valid for the glasses possessing equal values of Poison's coefficients. Combining the equations (2) and (3) we can write the relation:

$$\Delta\alpha.T_g=\frac{(1-2\mu)^2}{2(1+\mu)} \tag{5}$$

According to Bartenev and co-authors [15]:

$$\Delta\alpha.T_g=f_g\ln\left(\frac{1}{f_g}\right). \tag{6}$$

Thus at $T=T_g$ the partition of fluctuational free volume, f_g, depends also on the Poison's coefficient fg=f(μ).

$$HV=\left(\frac{gk}{V_h}\right)T_g, \tag{7}$$

where k is the Boltzmann's constant and $g=\ln\left(\frac{1}{f_g}\right)$. It is logical to expect existing the correlation between HV and T_g values for the glasses from one and the same type which possess $V_h\cong$const and $g(f_g)\cong$const.

Integration of the equations (1) and (7) gives the relation of T_g, as well as HV, towards f_g and E_h:

$$T_g=\left(\frac{1}{gk}\right)E_h, \tag{8}$$

From the equations' systems (4) and (5), and (4) and (6) we can determine $\mu=0.25$ and $f_g\cong0.028$ ($g\cong3.58$). In order to determine V_h, E_h **E** the relations (7), (8) and (2) we can be written as:

$$V_h=3.58\ k\ \frac{T_g}{HV};\quad E_h=3.58\ k\ T_g;\quad E = 15\ HV, \tag{9}$$

Table 2 presents the calculated values of V_h, E_h , E as a function of the glassy composition (m) and average coordination number ($Z=x_iz_i$, x_i, z_i - are the molar part and coordination number of i^{-th} component of the glass).

Table 2. Thermo-mechanical characteristics of glasses from $(GeSe_2)_x(As_2Se_3)_y(CdTe)_z$ system.

Composition			m	Z	T_g, °C	HV, kgf/mm^2	V_h, $Å^3$	E_h, kJ/mol	E, 10^3 kgf/mm^2
x	y	z							
90	0	10	0.0	2.60	155	125	17.26	13.15	1.88
81	9	10	0.1	2.58	140	120	17.35	9.65	1.80
63	27	10	0.3	2.53	125	115	17.44	8.60	1.73
45	45	10	0.5	2.48	120	104	19.05	8.45	1.56
27	63	10	0.7	2.43	120	96	20.63	8.45	1.44
9	81	10	0.9	2.38	120	89	22.26	8.45	1.34
0	90	10	1.0	2.36	130	85	23.89	8.75	1.28

The graphical presentation of $V_h(Z)$, $E_h(Z)$ and E(Z) shows a kink at Z = 2.53 which corresponds to a composition $(GeSe_2)_{63}(As_2Se_3)_{27}(CdTe)_{10}$ (more gradual changes in V_h and E are observed when Z>2.53 while E_h increases significantly) – Fig. 2.

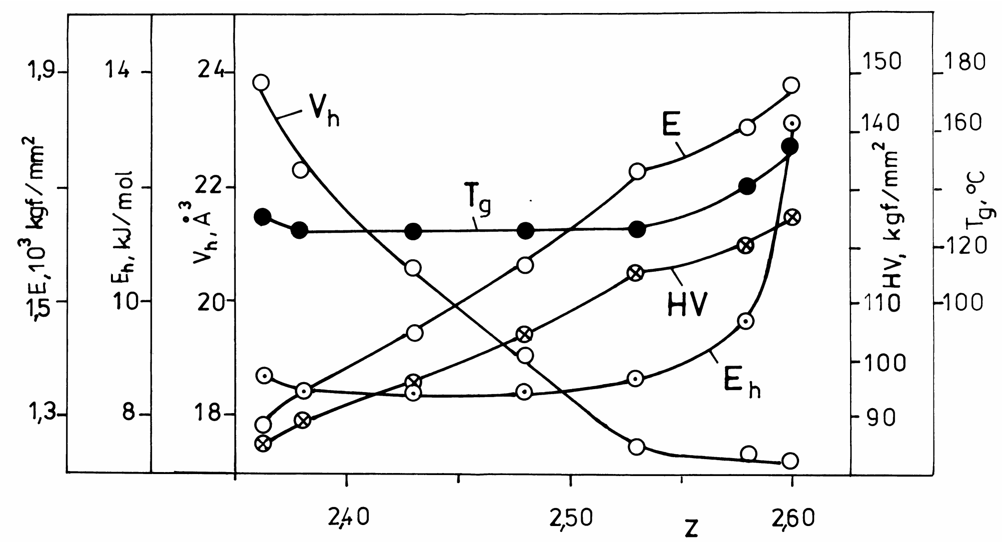

Fig. 2. Dependencies of V_h, E_h and E on Z of glasses.

The trend of the V_h curve could be explained by the cross-linking process of the glassy structure and saturation in the glassy network with bonds of tethraedrical $GeSe_{4/2}$ units. The further increase in $GeSe_2$ content is not related to a variation in the minimal sizes of micro-voids. The structure corresponds to an optimal energy of interatomic forces and system equilibrium. The deviation from these conditions is connected with a structure resistance and increase of energy values necessary for free volumes densification. In this reason the negligible decreasing in V_h at Z>2.53 corresponds to a quite increasing in values of necessary energy for micro-voids formation - Fig. 2. The values of elastic module presented in Fig. 2 show dependence similar to those of microhardness which is predictable result from eq. 9.

4. Conclusions

New chalcogenide glasses from the systems $GeSe_2$-As_2Se_3-Sb_2Se_3-CdTe are synthesized. The basic physico–chemical characteristics of the glasses are investigated – density, microhardness and temperatures of transformation, crystallization and melting. A compositional dependence of these properties is shown. A correlation between glassy structure and thermo-mechanical properties is proposed based on the structure deviations at Z = 2.53. The relation is connected with saturation of the glassy network.

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