Physical properties of chalcogenide glasses from the $GeSe_2$-Sb_2Te_3-CdTe system

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ABSTRACT

Chalcogenide glasses from the $GeSe_2$-Sb_2Te_3−CdTe are synthesized from the initial compounds by melt quenching technique. The density and the Vickers microhardness are determined. Using the density values the compactness C is calculated. The thermomechanical characteristics (micro-voids volume V_h and energy for formation of a micro-void E_h), as well as the elasticity modulus E of the glasses, are also calculated. A compositional dependence of the revealed properties is observed and discussed.

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INTRODUCTION

The chalcogenide semiconductor glasses are interesting because of the multiple possibilities for their applications in the optics, electronics, sensorics and other areas of the contemporary engineering[1-6]. The multicomponent chalcogenide systems have wider regions of glass formation compared to the element ones[7-11] and give to the researchers wider variety for choosing a composition, appropriate for a given application. Besides, due to their better glass forming ability, the multicomponent chalcogenide glasses allow the introduction of larger quantity of the component, which carries the required property of the material.

Before beginning the real application search of a given glassy material, some important properties as glass-transition temperature, density, compactness, microhardness, etc. have to be investigated. The knowing of the mechanical and the thermomechanical properties of the material by its side allows the investigators to evaluate, even hypothetically, the possibility for formation of the material.

The glassy materials from the $GeSe_2$-Sb_2Te_3−CdTe system are interesting due to their high ionic content and molecular mass, which, even provisionally, give grounds for assumption of the possibilities for their practical application (in the optics, sensorics, etc.).

The region of glass formation within the $GeSe_2$-Sb_2Te_3−CdTe system[12] is extended towards the $GeSe_2$ apex and lies partially on the $GeSe_2$-Sb_2Te_3 (from 0 to 32.5 mol % Sb_2Te_3) and $GeSe_2$-CdTe (from 0 to 27 mol % CdTe) sides (Figure 1). A small crystalline area is observed in the concentration interval 5-12 mol % CdTe with maximum solubility of Sb_2Te_3 in it of ~ 2 mol %. No glassy phases were obtained in the quasibinary Sb_2Te_3-CdTe system.

The aim of the present work is to determine the physicochemical (density d, compactness C and microhardness HV), mechanical (elasticity modulus E) and thermomechanical (micro-voids volume V_h and energy for formation of a micro-void E_h) properties of chalcogenide glasses from the $GeSe_2$-Sb_2Te_3-CdTe

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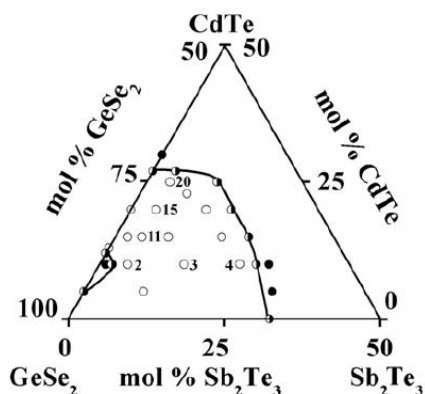system and to find an explanation of their compositional dependence, if such exists.

Figure 1 : Region of glass formation within the GeSe₂-Sb₂Te₃-CdTe system

EXPERIMENTAL

The initial components GeSe$_2$ and Sb$_2$Te$_3$, as well as the samples from the investigated system, were synthesized by direct monotemperature synthesis in evacuated to a residual pressure of 1.10^{-3} Pa quartz ampoules. The elements used for the synthesis of GeSe$_2$ and Sb$_2$Te$_3$ were with purity of 5N for Ge, Se and Te, and 4N for the Sb, respectively. The CdTe used for the synthesis of the samples was with purity "Coating material", produced by BALZERS.

The synthesis conditions were conformed to the physicochemical properties of the initial compounds and the used elements, as well as with the properties of the eventually formed intermediate compounds. By this reason the synthesis was performed by isothermal steps, as the last one, at temperature of $(1000-1150) \pm 10$ °C, was with duration of 3 h and continuous vibration stirring of the melt was applied. After decrease of the temperature to $(900-1050) \pm 10°C$ the melt was tempered for 10 min and quenched in water+ice mixture (cooling rate of $\approx$ 10-15°C s^{-1}).

The density of the glassy samples was measured by hydrostatic method in toluene as immersion fluid. The Vickers microhardness (HV) was measured using MIM-7 microscope with built in microhardnessmeter PMT-3 at loading of 20 g (30 measurements per sample). The accuracy of both measurements is $\pm$ 5 %.

The compactness C was calculated using the equation[13]:

$$C = d\left\{ \sum_i \frac{M_i x_i}{d_i} - \sum_i \frac{M_i x_i}{d} \right\}\left[\sum_i M_i x_i \right]^{-1} \qquad (1)$$

where M_i, x_i and d_i are the molar mass, the molar part and the theoretical density of the ith component, respectively.

For calculation of the thermomechanical properties (micro-voids volume V_h and energy for their formation E_h) the following equations were used[14]:

$$V_h = 5.04 \cdot 10^{-3} \frac{T_g}{HV} \text{[nm3]} \qquad (2)$$

$$E_h = 29.75 T_g \text{[J/mol]} \qquad (3)$$

The T_g values, needed for calculation of the thermomechanical properties, are taken from our previous work[15].

The elasticity modulus was calculated using Eq. (4)[14]:

$$E = 0.147 \cdot HV \text{ [GPa]}, \qquad (4)$$

RESULTS

The results obtained from the density d and microhardness HV measurements of chalcogenide glasses from the GeSe$_2$-Sb$_2$Te$_3$-CdTe system are presented in TABLE 1. For convenience during the analysis of the results the m parameter is introduced, which expresses the ratio between the GeSe$_2$ (x) and Sb$_2$Te$_3$ (y) – $m = Sb_2Te_3/(GeSe_2+Sb_2Te_3) = y/(x+y)$. Due to the same reason the third component from the system (CdTe) is marked with z in the dependencies.

TABLE 1 : Composition and physical properties of glassy samples with composition (GeSe₂)$_x$(Sb₂Te₃)$_y$(CdTe)$_z$

№	Composition			m	d, g/cm³	HV, kgf/mm²
	GeSe₂	Sb₂Te₃	CdTe			
2	85.5	4.5	10	0.05	4.400	114
3	76.5	13.5	10	0.15	4.705	95
4	67.5	22.5	10	0.25	4.903	81
11	80.75	4.25	15	0.05	4.469	94
15	76	4	20	0.05	4.525	88
20	71.25	3.75	25	0.05	4.583	77

The results from the calculation of the compactness (C), the elasticity modulus (E) and the thermomechanical characteristics (V_h and E_h) of the investigated glasses are presented in TABLE 2.

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TABLE 2 : Compactness, elasticity modulus, glass-transition temperature and thermomechanical properties of chalcogenide glasses with composition $(GeSe_2)_x(Sb_2Te_3)_y(CdTe)_z$ (m=y/(x+y))

| №	z	m	C	E, GPa	T_g, K[15]	$V_h.10^{-3}$, nm³	E_h, kJ/mol
2	10	0.05	-0.0504	16.76	495	0.0219	14.73
3	10	0.15	-0.0488	13.97	505	0.0268	15.02
4	10	0.25	-0.0608	11.91	510	0.0317	15.17
11	15	0.05	-0.0463	13.82	500	0.0268	14.88
15	20	0.05	-0.0454	12.94	505	0.0289	15.02
20	25	0.05	-0.0443	11.32	510	0.0334	15.17

DISCUSSION

The density values of the investigated samples (TABLE 1) fall between the density values of the initial components (d_{GeSe_2} = 4.34 g.cm⁻³[16], $d_{Sb_2Te_3}$ = 6.57 g.cm⁻³ and d_{CdTe} = 5.86 g.cm⁻³[17]). At both $d(z)_{m=const}$ and $d(m)_{z=const}$ dependencies an increase of the density is observed with the increase of z and m.

The microhardnesses of the initial components influence directly on the HV of the glasses with the change of their composition – TABLE 1. Their microhardness decreases in the row $GeSe_2 \rightarrow CdTe \rightarrow Sb_2Te_3$ with 100-200[16] → 60[18] → 18 kgf/mm²[19], respectively. Due to this reason the $HV(m)_{z=10}$ and $HV(z)_{m=0.05}$ dependencies show well expressed tendency towards decrease with both increase of the Sb_2Te_3 content at z=10 mol % CdTe and the CdTe content at m=0.05.

In the $C(m)_{z=10}$ dependence the compactness shows a tendency towards decrease with the increase of the m ratio – TABLE 2. This is most probably related to the breakage of the Se-bridges, which connect the separate structural units in the $GeSe_2$, and following building of the $Sb_2Te_{3/2}$ structural units (s.u.) into them by the scheme:

$$- Se - Se - \xrightarrow{Sb_2Te_3} \underset{-Se-Te}{\overset{-Se-Te}{\langle \Delta V \rangle}} Sb - Te-$$
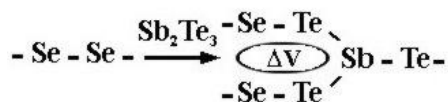
This leads to increase of V_h with additional volume V, proportional to the $Sb_2Te_{3/2}$ structural units, as a result of which the compactness decreases.

An increase of the compactness is observed in the $C(m)_{z=const}$ dependence (TABLE 2). With the increase of z the number of the linear units, which are brought by the CdTe, increases. The experiment shows that the compactness increases, instead of

decrease, which leads to the assumption that the linear fragments of the CdTe are not built between the Se-, Te- or (Se-Te)-bridges, but fall into the micro-voids in the form of micro-crystals (their quantity is proportional to the quantity of the introduced CdTe). This assumption is confirmed to a large degree by the presence of more than one amorphous plateau in the XRD patterns of these samples, for example p. 15 (Figure 2) at about 2θ=13, 28 and 49°.

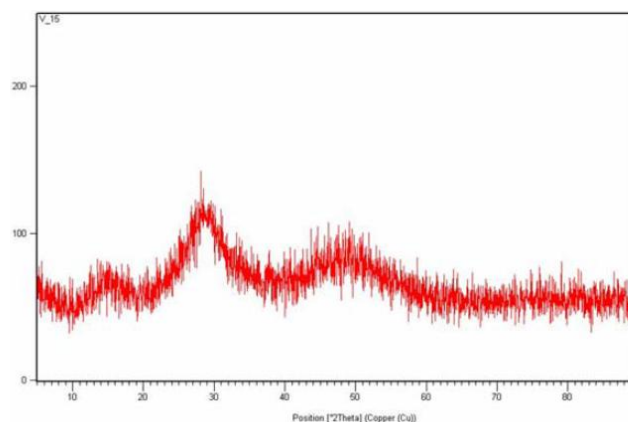**Figure 2 : XRD pattern of sample with composition $(GeSe_2)_{76}(Sb_2Te_3)_4(CdTe)_{20}$**

The concentration dependencies $E(m)_{z=10}$ and $E(z)_{m=0.05}$ (TABLE 2), in conformity with Eq. (4), are shifted in relation the analogical $HV(m)_{z=10}$ and $HV(z)_{m=0.05}$ dependencies. They show that the elasticity modulus decreases with the increase of both the Sb_2Te_3 content at z=10 mol % CdTe and the CdTe content at m=const.

With the increase both Sb_2Te_3 (z=10) and CdTe (m=0.05) content, the minimal micro-voids volume shows well expressed tendency towards increase, which regardless of the scant amount of points, can be qualified as linear.

The path of these two concentration dependencies is related to:

- the behavior of the new-built s. u. $SbTe_{3/2}$ (trigonal pyramids) and $CdTe_{1/2}$ (linear chains);
- the influence of the composition in the T_g and HV characteristics (Eq. (2)). The concentration dependencies of T_g[15] and HV (TABLE 1) show clearly expressed tendency towards increase of T_g and decrease of HV, which in accordance with this equation synonymously leads to increase of the V_h.

It is logical with the increase of T_g in accordance with Eq. (3) the energy for formation of the micro-voids

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E_h to increase too (TABLE 2). Besides, with the increase of Sb$_2$Te$_3$ or CdTe, as well as when they are both increased, considerable structural changes occur (breakage of the –Se–Se– and/or –Se–Te– bridges, building of different structural units SbTe$_{3/2}$ and CdTe$_{1/2}$, etc.), which require additional energy.

CONCLUSIONS

Chalcogenide glasses from the GeSe$_2$-Sb$_2$Te$_3$-CdTe were synthesized and their densities and microhardnesses were measured and vary between 4.4-4.9 g/cm^3 and 77-114 kgf/mm^2, respectively. The density d increases, while the Vickers microhardness HV decreases with the increase of m and z.

The compactness, the elasticity modulus and the thermomechanical characteristics of the samples were calculated and the influence of the composition on them was investigated. The compactness C and the elasticity modulus E decrease with the increase of both Sb$_2$Te$_3$ (z=0.1) and CdTe (m=0.05) content. The minimal micro-voids volume V$_h$ and the energy, needed for their formation E$_h$ increase with both Sb$_2$Te$_3$ (z=0.1) and CdTe (m=0.05) increase.

The path of the concentration dependencies of the investigated characteristics of the chalcogenide glasses was explained on the basis of the limiting influence of the structural units SbTe$_{3/2}$ (trigonal pyramids) and CdTe$_{1/2}$ (linear chains) and their building into the glass-former structure by breakage of – Se – Se – and/or – Se – Te – bridges.

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