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Glass-forming region and physical properties of the glasses in the TeO_2 — MoO_3 — Bi_2O_3 system

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ABSTRACT

The glass-forming region of the TeO_2 — MoO_3 — Bi_2O_3 system was determined by melt quenching method at 850 °C. The nature of crystalline phases formed by heating a mixture of initial oxides up to the predetermined temperature was investigated by X-ray diffraction analysis. The physical properties of glasses were defined and the value of molar volume (V_m), oxygen molar volume (V_O), oxygen packing density (ODP), packing density (V_t) and Poisson's ratio were calculated at an equivalent substitution of TeO_2 + MoO_3 by Bi_2O_3. DSC curves for series of ternary glasses with different contents of bismuth trioxide were registered and glass transition temperature (T_g), crystallization temperature (T_x) and melting temperature (T_m) were found and the thermal stability range of glasses (ΔT) was calculated. The glass compositions stable to crystallization and suitable for fiber drawing were found.

1. Introduction

Tellurite glasses have unique physical and chemical properties, in particular, a low energy of phonons, high values of refractive indices, high dielectric constant, broad transparency window, relatively low temperatures of vitrification and melting, high thermal and chemical stability [1–9]. Therefore they are promising materials in photonics and optoelectronics for fabrication of solid-state lasers, optical fibers, optical fiber amplifiers, optical displays, various sensors, data storage devices and various optoelectronic converters [10–13]. The introduction of the oxides of heavy elements (PbO, Bi_2O_3, MoO_3, WO_3, Nb_2O_5 and others) into tellurite glass increases glass-forming ability and improves thermal, mechanical and optical characteristics [14–16].

The binary tellurite-molybdate system is one of the attractive systems with wide glass-forming range and high solubility of some heavy metal oxides in it. The study of its properties initiated in [17], the phase diagram description by [18], the region of vitrification was established in [19,20] and glass structural, optical and electrical properties were reported in [21–25]. Investigation of optical and electric properties at addition of elements oxides into TeO_2 — MoO_3 system was conducted in [23,26–30]. However, complete information about the effect of bismuth trioxide on the fundamental properties of TeO_2 — MoO_3 glasses has not published yet. There are only limited publications [31] devoted to investigation of Er^{+3} luminescence in the glasses of TeO_2 — MoO_3 — Bi_2O_3 system. The similar TeO_2 — WO_3 — Bi_2O_3 system has been investigated and glass forming range and crystalline phases formed during the crystallization of glasses were established [32,33]. Foregoing facts indicate that knowledge of ternary tellurite-molybdate system containing bismuth oxide is limited and they may be demanded in optical technology.

Therefore, the purpose of the work was to determine the glass-forming area in the TeO_2 — MoO_3 — Bi_2O_3 system and to study the important thermal and physical parameters of the prepared glasses as well as to investigate the phase formation processes during synthesis.

2. Experimental

2.1. Glass preparation

The glasses of system TeO_2 — MoO_3 — Bi_2O_3 were prepared from high-purity TeO_2, MoO_3 and Bi_2O_3, obtained by thermal decomposition of bismuth nitrate pentahydrate at 800 °C.

The oxides were weighed using the analytical balance Shimadzu AU-120 (with an accuracy of ±0.1 mg) and then thoroughly mixed in a porcelain mortar. The mixture with a mass of 5 g was placed in a porcelain crucible and melted in a furnace at 850 °C for 15 min in the air. The produced melt was poured into a polished steel mould and the formed glass was annealed in air at 310 °C during 1 h and then was cooled down to room temperature. The selected compositions of glass samples are given in Table 1.

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Table 1
Main parameters of the glasses in the $TeO_2-MoO_3-Bi_2O_3$ system.

Sample ID	Glass compositions (mol. %)			T_g (°C)	T_c/T_m, (°C)	ΔT	ρ, 25 °C (g cm^{-3})	ρ_{cal} (g cm^{-3})	V_M (cm^3·mol^{-1})	V_O (cm^3·mol^{-1})	OPD (mol L^{-1})	μ_{cal}	μ'_{cal}	$\overline{n}_c$	n_b ($\times 10^{21}$ cm^{-3})
	TeO_2	MoO_3	$BiO_{1.5}$												
Te:Mo = 2:1															
TMB1	63.3	31.7	5.00	318	–	–	5.29	5.52	29.93	13.06	76.59	0.252	0.218	2.73	95.26
TMB2	56.7	28.3	15.0	326	–	–	5.69	5.88	29.20	13.23	75.60	0.252	0.215	2.87	100.34
TMB3	50.0	25.0	25.0	333	390	57	6.07	6.23	28.67	13.49	74.12	0.251	0.213	3.00	105.02
Te:Mo = 1:1															
TMB4	47.5	47.5	5.00	313	–	–	5.05	5.37	30.86	12.59	79.40	0.259	0.212	3.05	98.55
TMB5	42.5	42.5	15.0	317	–	–	5.49	5.74	29.86	12.71	78.69	0.260	0.210	3.15	103.85
TMB6	32.5	32.5	35.0	337	378	41	6.27	6.48	28.74	13.37	74.81	0.255	0.207	3.35	112.10
Te:Mo = 1:2															
TMB7	28.3	56.7	15.0	311	364/418	53	5.22	5.60	30.98	12.43	80.43	0.263	0.206	3.43	105.62
TMB8	25.0	50.0	25.0	324			5.65	6.00	30.11	12.68	78.88	0.264	0.205	3.50	110.00
Te:Mo = 4:1															
TMB9	76.0	19.0	5.00	327	442	115	5.49	5.65	29.20	13.49	74.15	0.245	0.223	2.48	92.40
TMB10	68.0	17.0	15.00	331	392	59	5.86	6.00	28.66	13.68	73.10	0.245	0.220	2.64	97.50

2.2. Thermal analysis

Thermal properties of the glasses were investigated by differential scanning calorimetry analysis (DSC) in simultaneous system Netzsch STA 409 PC Luxx under flowing argon gas with a heating rate of 10 °C/min. Glass transition temperature (T_g) and crystallization temperature (T_c) are defined as the onset of DSC curves. The glass stability (ΔT) against crystallization is calculated as the difference between the temperatures of crystallization and glass transition $\Delta T = T_c - T_g$.

2.3. X-ray phase analysis

The nature of the amorphous and crystalline samples was checked by X-ray phase analysis (XRD) on Shimadzu XRD-6000 using the radiation of Cu K_α in the range of 2θ from 10 to 60° with voltage on the tube of 40 kV and current of 30 mA.

2.4. Physical properties of glasses

The density of glasses (ρ) was determined at room temperature by Archimedes principle using distilled water as immersion liquid (error for the determined was 0.02 g/cm^3) and a digital balance of sensitivity 10^{-4} g. The density was obtained from the relation

$$\rho = \rho_b \frac{W_{air}}{W_{air} - W_{water}}$$

where ρ_b is the density of distilled water, W_{air} и W_{water} – weight of the glass sample in air and in distilled water, respectively.

Theoretical density (ρ_{cal}) was calculated as the additive contribution of each oxide to glass by formula [34]

$$\rho_{cal} = \sum \rho_i x_i$$

where ρ_i – density of each component i, x_i – the molar fraction of each component i.

The molar volume of glasses (V_m) was calculated as a function of the mole fraction of each component using the relation

$$V_m = \sum \frac{x_i M_i}{\rho}$$

where x_i and M_i – the molar fraction and molecular weight of i-th component, ρ is the density of glass.

Oxygen molar volume (V_O) was calculated by the following formula:

$$V_O = V_m \left(\frac{1}{\sum x_i n_i} \right)$$

where n_i is the number of oxygen atoms in each constituent oxide.

Oxygen packing density (OPD) was calculated by formula

$$\mathrm{OPD} = 1000C(\rho/M)$$

where C is the number of oxygen atoms per each composition, ρ is the density and M is the molecular weight of the glass sample.

2.5. Structural investigations

Average cross-link density ($\overline{n}_c$) of the glasses was calculated using the relation [34]:

$$\overline{n}_c = \frac{\sum x_i (n_c)_i (N_c)_i}{\sum x_i (N_c)_i}$$

where x_i is the molar fraction of each component i; N_c is the number of cations per glass formula unit, $n_c = n_f - 2$, n_f is coordination number of the cations (4 for TeO_2 and 6 for MoO_3 and Bi_2O_3).

Number of bonds per unit volume of the glasses (n_b), was calculated by the following formula

$$n_b = \frac{N_A}{V_m} \sum (n_f x)_i$$

where N_A is the Avogadro's number, V_M molar volume of the glass.

Poisson's ratio of the glasses by Makishima and Mackenzie theory (μ_{cal}) was calculated theoretically according to the following expressions [35]

$$\mu_{cal} = 0.5 - \frac{1}{V_t}$$

and by the theory of Bridge (μ'_{cal}) according to the equation [36]

$$\mu'_{cal} = 0.28\ (\overline{n}_c)^{-1/4}.$$

The packing density (V_t) was calculated by formula

$$V_t = (1/V_m) \sum V_i x_i$$