Journal of Non-Crystalline Solids 459 (2017) 63–67

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

On the structural arrangement and optical band gap $(PbO)_x(ZnO)_{10}(TeO_2)_{90-x}$ glasses

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ARTICLE INFO

Article history:
Received 1 November 2016
Received in revised form 20 December 2016
Accepted 3 January 2017
Available online xxxx

Keywords:
Tellurite glass
Raman spectra
Optical band gap
Non-linear refractive index

ABSTRACT

The glasses $(PbO)_x(ZnO)_{10}(TeO_2)_{90-x}$, where x = 10, 20, 30, 35 and 40 mol%, were prepared with a classic melting method from pure oxides. With an increase in x the density increases from 5.92 (x = 10) to 6.8 (x = 40) g/cm^3, the glass-transition temperature decreases from 299 to 254 °C and the optical band gap decreases from 3.73 to 3.48 eV. It is suggested from the Raman scattering spectra that the structural units inherent to $[Te_3O_8]^{4-}$ and $[TeO_3]^{2-}$ anions form the Te-O based network, that is with an increase in x the conversion proceeds from TeO_4 to TeO_3 structural units. The values of the non-linear refractive index were estimated from the optical band gap values in the region: $(6.5–8.4) \times 10^{-12}$ esu.

1. Introduction

Glasses based on tellurium dioxide (TeO_2) and modified by heavy metal oxides have properties promising for various optical applications namely non-linear optics, see e.g. [1,2], inclusive Raman amplifiers, see e.g. [3,4]. Certain glasses based on the PbO-TeO_2 system even seem to be interesting candidates in immobilization technology for certain spent electrochemical salts from the used nuclear fuel reprocessing [5]. Recently, the glasses from the system PbO-ZnO-TeO_2 were found to be interesting as a matrix which not only has appropriate optical properties such as a high refractive index and low phonon energy, but also quite high solubility of rare earth elements [6–8]. Consequently, attention has been given more recently to the study of the structural and thermal properties of PbO-ZnO-TeO_2 glasses. The network of the glasses studied ($(PbO)_y(ZnO)_{30-y}(TeO_2)_{70}$) was found to be rich in Te-O-Te bridges and with an increase in PbO content by a mixture of Te-O-Te and Te-O-Pb bridges [9]. We report in this communication the preparation, Raman spectra and optical band gap (E_g) and its temperature dependence ($E_g(T)$) in the series of $(PbO)_x(ZnO)_{10}(TeO_2)_{90-x}$ glasses. Attention is drawn to the structural arrangement inferred from Raman spectroscopy and to correct the determination of E_g and $E_g(T)$ because in TeO_2 based glasses the electronic contribution to the non-linear refractive index has been found to be at approximately 80% [10].

2. Experimental

Glasses of the chemical composition $(PbO)_x(ZnO)_{10}(TeO_2)_{90-x}$, where x = 10, 20, 30, 35 and 40 mol%, were prepared from PbO, ZnO and TeO_2 purity 99.95%, Sigma-Aldrich. Stoichiometric amounts of the oxides were thoroughly mixed, homogenized and melted in a platinum crucible for about 20 min in a preheated electrical furnace at a temperature (T) of about 850 °C. During the synthesis the melt was homogenized by a crucible frequent manual agitation. The melt was poured onto polished nickel plate annealed to $T \approx 200$ °C and slowly cooled down to room temperature. The prepared bulk glasses were clear, transparent with weak greenish-yellowish tint. No traces of the crystalline phase were detected within a sensitivity of X-ray diffraction and classical optical microscopy. The chemical composition of the prepared glasses was verified using a microprobe X-ray analysis (JEOL JSM 5500 LV, Japan). The hydrostatic density (ρ) of the glasses was determined using the Archimedean method. The dilatometric glass transition temperature (T_g) was determined from both the "low" and "high" temperature parts of the expansion curves using the slope intercept method similarly as in Ref. [11]. The optical transmission in the short wavelength absorption edge (SWAE) region was carried out with an optical thermostat placed in the sample compartment of the HP 8453 spectrophotometer in a temperature interval of 300–515 K. For a correct determination of the optical energy gap (E_g) values, samples with a thickness $d \approx 2–4$ μm were prepared with the glass blowing method [12]. The optical band gap values for the studied glasses were evaluated assuming non-direct transitions from relation $(\alpha h\nu)^{1/2} = B^{1/2}(h\nu - E_g)$, where $B^{1/2}$, the slope of the SWAE, is a parameter reflecting the sample disorder [13] and $h\nu$ is the photon energy. The values of the absorption coefficient (α) were calculated using the relation $\alpha = (1 / d)\ln\{(1 -$

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http://dx.doi.org/10.1016/j.jnoncrysol.2017.01.012
0022-3093/© 2017 Published by Elsevier B.V.

$R)^2 + [(1 - R)^4 + 4R^2T^2]^{1/2}) / 2T\}$, [14], where R is the reflectivity, $R \approx 0.11$ invariant to the wavelength within the narrow spectral region of SWAE was used, and T is the transmission. Raman spectra in the spectral region $100\ cm^{-1} < \nu < 1000\ cm^{-1}$ were recorded on a natural flat optical surface of bulk samples at room temperature employing an FTIR spectrometer Bruker model IFS 55 provided with FRA 106 Raman-module using a Nd:YAG laser beam (excitation light wavelength ($\lambda = 1064$ nm), a slit width of 4 cm^{-1}, laser power $\approx$ 300 mW) at the sample surface. Experimental spectra were reduced using the Bose-Einstein population factor, $I_{red} \sim \nu / (\nu_0 - \nu)^4[1 - \exp(-h\nu / k_BT)] \times I_{exp}$, where ν, ν_0, k_B and T represent the observed Raman shift, the wavenumber of the excitation light, the Boltzmann constant and the temperature, respectively.

3. Results

The chemical composition (x) of the studied glasses, their density, the molar volume, the dilatometric glass-transition temperature and the optical band gap values are summarized in Table 1. It is evident from Table 1 that the relative changes in the molar volume and optical band gap are quite small. The relative changes in the density and in the glass-transition temperature are significant since they exceed 10% of the maximal value of the corresponding quantity. The relative change in the density relates to the substitution of TeO_2 with PbO. The relative change, the decrease, in the T_g value can be primarily associated with the depolymerization of the network of the glasses studied as the changes in the overall cohesive forces due to the substitution of TeO_2 by PbO are in all probability not as critical since the bond energies (E) of Pb—O bond and Te—O bond are close ($E_{Pb\text{—}O} \approx 382$ kJ/mol and $E_{Te\text{—}O} = 376$ kJ/mol [15]). Fig. 1 shows, at various temperatures, the typical spectral dependencies of the absorption coefficient in $(\alpha h\nu)^{1/2}$ versus $h\nu$ coordinates assuming non-direct transitions between the valence and conduction band. Fig. 2 shows, for all glasses studied, the temperature dependencies of the optical band gap ($E_{g,non}(T)$) approximated by a simple relation: $E_{g,non}(T) = E_{g,non}(0) - \gamma T$ where γ is the coefficient of the temperature dependence of the optical band gap. The values of $E_{g,non}$ (300 K) are summarized in Table 1 and the values of γ are in the region: 6.7×10^{-4}–7.9×10^{-4} eV/K.

The reduced Raman spectra of glasses studied are shown in Fig. 3. The horizontal lines in Fig. 3 indicate the spectral region of Raman features (RF), the origin of which within the Lines approach [16,17] is as follows: (i) HM ($70 \le \nu\ [cm^{-1}] \le 170$) – the heavy metal atom motion, (ii) BO ($300 \le \nu\ [cm^{-1}] \le 600$) – the bridging oxygen motion which is the symmetric stretch motion in covalent C-O-C or C-O-C′ configuration where C and C′ are different cations, and (iii) NBO ($650 \le \nu\ [cm^{-1}] \le 900$) – the non-bridging oxygen asymmetric stretch motion in C—O—C′ configuration, where O—C′ bond is longer, or in C—O$^-$ configuration. It is widely accepted that the network of the TeO_2 based glasses consists of several structural units of which the actual structural configuration depends on the chemical composition specifically on the type of network modifiers and other additives which assist in network formation, see e.g. [18 and there cited references]. The basic structural units are trigonal bipyramids (tbp) and trigonal pyramids (tp) having

Table 1
Chemical composition of studied $(PbO)_x(ZnO)_{10}(TeO_2)_{90-x}$ glasses expressed as x(PbO), the values of density (ρ) and molar volume (V_m), the dilatometric glass transition temperature (T_g) and the values of the non-direct optical band gap ($E_{g,non}$ (300 K)).

x(PbO)/mol%	ρ/g cm^{-3}	V_m/cm^3 mol^{-1}	T_g/°C	$E_{g,non}$ (300 K)/eV
10	5.92	26.71	299	3.73
20	6.21	26.50	291	3.7
30	6.52	26.20	284	3.51
35	6.68	26.05	261	3.5
40	6.80	26.06	254	3.48

Relative changes $\delta X = (X_{max} - X_{min}) / X_{max}$ of the parameters considered: $\delta\rho \approx 13\%$, $\delta V_m \approx 2.5\%$, $\delta T_g \approx 15\%$, $\delta E_g \approx 6.7\%$.

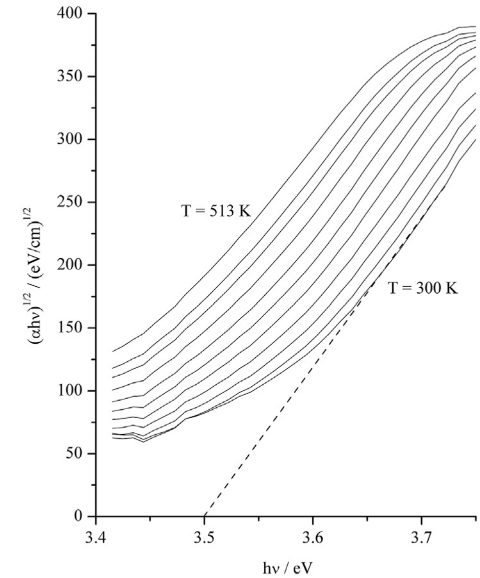

Fig. 1. Typical spectral dependence of $(\alpha h\nu)^{1/2}$ for $(PbO)_{30}(ZnO)_{10}(TeO_2)_{60}$ glass at various temperatures. In summary, 11 measurements were realized with a temperature step of around 20 K. Dashed line — the fit to relation: $(\alpha h\nu)^{1/2} = B^{1/2}(h\nu - E_g)$. The error in E_g determination is lower than ±0.03 eV.

a varying number of NBO and a net charge, for more details, see e.g. [19–21]. With respect to the references [17,18–20] it is clear that the most intensive Raman response in the spectral region 600–900 cm^{-1}, Fig. 4, can be attributed to a combination of tbp and tp units with non-bridging oxygens. We decomposed the reduced Raman spectra into four distinct Raman features (RF) marked A, B, C, D, see Fig. 4, and the RF are assigned as follows [18 and there cited references,22]:

(i) RF_A ($\approx$780 cm^{-1}) to stretching vibrations of Te = O double bonds in $O_{2/2}Te = O$ (N_3^0) and stretching vibration in Te—O$^-$ bonds of negatively charged terminal $O_{1/2}Te({=}O)\text{—}O^-$ (N_3^-) and/or to isolated $O = Te(\text{—}O^-)\text{—}O^-$ (N_3^{2-}) on tp based units and/or to stretching vibrations in $O_{3/2}Te\ \text{—}O^-$ (N_4^-) and $O_{2/2}Te(\text{—}O^-)\text{—}O^-$ (N_4^{2-}) tbp based units. N_k^m is here the so-called NMR notation [20] where k is the number of oxygen atom coordinated around Te atom and m is the net charge on non-bridging oxygen atoms in the unit.

(ii) RF_B ($\approx$720 cm^{-1}) to stretching vibration in Te—O$^-$ bonds and Te═O double bonds that is in N_3^-, N_3^0 and/or N_3^{2-} tp based units.

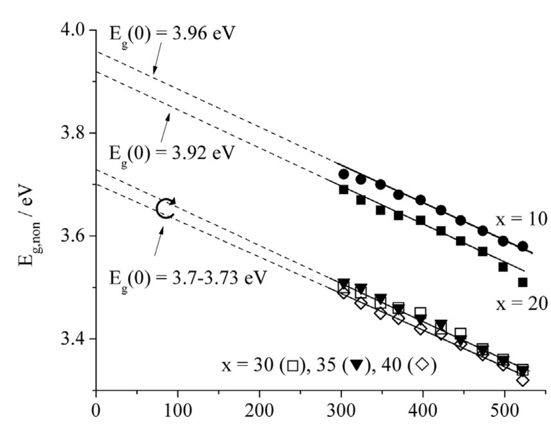

Fig. 2. Temperature dependences of the optical band gap for the studied $(PbO)_x(ZnO)_{10}(TeO_2)_{90-x}$ glasses. Full line fit to relation $E_{g,non}(T) = E_{g,non}(0) - \gamma T$.