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The structural arrangement and the optical band gap in certain Quaternary PbO–ZnO–TeO_2–B_2O_3 glasses

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ABSTRACT

Eight PbO–ZnO–TeO_2–B_2O_3 glasses were prepared with a standard melting method from pure oxides. The substitution of TeO_2 by B_2O_3 leads to an increase in the glass-transition temperature from 292 to 457 °C and to an increase in the optical band gap from 3.66 eV to 4.03 eV. The values of the non-linear refractive index were estimated at around 6×10^{-12} esu. Raman scattering spectra suggest a transformation in TeO_2 and B_2O_3 based part of the glasses network.

1. Introduction

Glasses based on TeO_2 and B_2O_3, often called boro-tellurite glasses, combined with heavy metal oxide (HMO) are interesting for applications such as: (i) low-melting glasses [1], (ii) a matrix having a good solubility of rare earth elements, e.g. [2–5]., (iii) gamma ray shielding materials, e.g. [6,7]. and (iv) non-linear optical material in the visible spectral region, e.g. [8]. Certain optical properties and the structure of boro-tellurite glasses were studied in several papers. Pavani et al. [9] studied, for example, the glasses $(B_2O_3)_{0.5}(ZnO)_{0.5\text{-}x}(TeO_2)_x$ and for $0 \le x \le 0.5$ found the optical band gap E_g in the region 2.55 $(x = 0) \le E_g[\mathrm{eV}] \le 2.73(x = 0.5)$ and the refractive index (n) in the region 2.53 $(x = 0) \le n \le 2.47(x = 0.5)$. Based on the results of the infrared spectroscopy, the authors suggest that with an increase in ZnO content the conversion of $[TeO_4]$ and $[BO_4]$ proceeds to $[TeO_3]$ and $[BO_3]$ structural units, respectively, and the number of non-bridging oxygen increases. Zhao et al. [10] studied Bi_2O_3–B_2O_3–TeO_2 glasses. They determined the glass-forming region for glasses where the content of $B_2O_3 \le 0.4$. For glasses $(Bi_2O_3)_x(B_2O_3)_{0.3}(TeO_2)_{0.7\text{-}x}$ $(0.4 \le x \le 0.7)$ the refractive index lies in the region 2.011 $(x = 0.4) \le n \le 2.114$ $(x = 0.7)$ at the wavelength $\lambda = 632.8$ nm, the optical basicity and molar volume increases with an increase in x. It is suggested from Raman and XPS spectra that the network of the glasses is formed by $[BiO_6]$, $[TeO_4]$, $[TeO_3]$, $[BO_4]$ and $[BO_3]$ structural units and for an increase in Bi_2O_3 content the $[TeO_4]$ units are converted into $[TeO_3]$ while $[BO_3]$ units are converted into $[BO_4]$ units. The presence of Bi^{5+} was found for a high content of Bi. The quaternary $(Bi_2O_3)_x(ZnO)_{0.1}(B_2O_3)_{0.3\text{-}x}(TeO_2)_{0.6}$ glasses were studied by Kundu et al. [11]. The basic results obtained can be summarized as follows: (i) the glass-transition temperature decreases from 362 to 350 [°C] with an increase in Bi_2O_3 content, the density $[\mathrm{gcm}^{-3}]$ increases from 4.415 $(x = 0)$ to 6.036 $(x = 0.2)$ and the direct optical band gap decreases with an increase in x from 3.57 (3.56) [eV], $(x = 0)$ to 3.18 (3.25) [eV], $(x = 0.2)$. (ii) Bismuth forming $[BiO_6]$ structural units are a network modifier for $x < 0.2$ while for $x = 0.2$ bismuth behaves as a network former and forms $[BiO_3]$ trigonal units. ZnO acts as a network modifier forming $[ZnO_4]$ units, B_2O_3 exists in both $[BO_4]$ and $[BO_3]$ structural units and TeO_2 exists as $[TeO_4]$, $[TeO_3]$ units, even the presence of $[TeO_6]$ units is assumed. For $x = 0.05$ a maximum of $[TeO_4]$ units is suggested and with an increase in Bi_2O_3 content a transformation from $[TeO_4]$ to $[TeO_3]$ structural units proceeds. Elkhoshkhany et al. [12] recently studied some glasses Bi_2O_3–B_2O_3–TeO_2–TiO_2. They found the direct optical band gap in the region 2.9–3.05 eV and after some thermal treatment various nanocrystalline phases ($BiTe_3O_{7.5}$, $Bi_4Ti_3O_{12.4}TeO_2$, Bi_2O_3) were observed. They suggested from the infrared spectroscopy that the substitution of TeO_2 by TiO_2 leads to a transformation of TeO_4 to TeO_3 structural units and simultaneously to a transformation of BO_4 to BO_3 structural units.

In this paper we report the preparation, Raman spectra and optical band gap (E_g) of series of $(PbO)_{30}(ZnO)_{10}(TeO_2)_{60\text{-}x}(B_2O_3)_x$ and $(PbO)_{20}(ZnO)_{20}(TeO_2)_{60\text{-}x}(B_2O_3)_x$ glasses which can be taken as an PbO analogue of $(Bi_2O_3)_x(ZnO)_{10}(B_2O_3)_{30\text{-}x}(TeO_2)_{60}$ studied in Ref. [11].

2. Experimental

The stoichiometric mixtures of PbO, ZnO, TeO_2 and B_2O_3 (purity 3 N5) for 15 g batches were homogenized in platinum crucibles, melted for approximately 20 min in a preheated electrical furnace at

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temperatures of $T \approx 720–830\,°C$. After the synthesis and homogenization, the melt was poured into a polished nickel plate at $T \approx 200\,°C$ and slowly cooled to an ambient temperature. The obtained glasses were clear, transparent and colorless or with a very weak yellowish tint. No crystalline inclusions were detected within a sensitivity of X-ray diffraction and optical microscopy in the glasses prepared. The chemical composition of the glasses prepared was verified using a microprobe X-ray analysis (JEOL JSM 5500 LV). The density (ρ) of the glasses was measured with bulk samples (a sample mass around 5 g) in the distilled water employing the Archimedean method. The values of the dilatometric glass-transition temperature (T_g) were determined by a thermomechanical analysis (TMA), for more details see e.g. Ref. [13].

The Raman spectra were recorded using the Fourier transform infrared (FTIR) spectrometer (Bruker model IFS 55 equipped with the FRA 106 Raman module) similarly as described in Ref. [13]. The Bose-Einstein correction has been applied to the spontaneous Raman scattering data.

The optical transmission (*T*) was measured on the samples prepared by glass blowing with the thickness (d) varying in the region of $2 \le d \le 4\,\mu m$. The chemical composition of the bulk and blown samples prepared was verified using a microprobe X-ray analysis (JEOL JSM 5500 LV). UV–Vis transmission spectra were measured as described in Ref. [13]. The optical band gap values (E_g) were determined from the equation: $(Kh\nu)^{1/2} = B^{1/2}(h\nu - E_{g,non})$, where $E_{g,non}$ is the non-direct optical band gap, the $B^{1/2}$ reflects the sample disorder [14], $h\nu$ is the photon energy, K is the absorption coefficient calculated from the relation $K = (1/d)\ln\{[(1-R)^2 + ((1-R)^4 + 4R^2T^2)^{1/2}] / 2\,T\}$ and R is the reflectance [15]. The values of $R \approx 0.11$ invariant to the wavelength within a short wavelength absorption edge were used to determine the *K* values.

3. Results

3.1. Summary of the characteristics of the studied glasses

The chemical composition, the density, the molar volume, the deviation in molar volume, see Table footnote, the dilatometric glass-transition temperature, the optical band gap and the estimated non-linear refractive index values are summarized in Table 1. For a calculation of the additive molar volume ($V_{m,add}$), see the footnote to Table 1. We used the density value of B_2O_3, $\rho = 2.56\,g/cm^3$. It is problematic to use the widely accepted value of the density for glassy B_2O_3, $\rho = 1.85\,g/cm^3$ [16] in the present case because it is valid for a glass which is composed mainly (up to 75%, [17]) of boroxol rings. For the chemical composition of our glasses the presence of boroxol rings as constituent components of the glassy network can be excluded. For crystalline B_2O_3 two modifications are known. (i) Low pressure phase of B_2O_3, $\rho = 2.56\,g/cm^3$, with hexagonal unit cell. The structure of this B_2O_3 consists of infinitely linked BO_3 triangular units. (ii) High pressure phase of B_2O_3, $\rho = 3.11\,g/cm^3$ with the orthorhombic unit cell. The structure of this B_2O_3 consists of interconnected BO_4 units with six and eight membered rings [18]. Consequently, for a calculation of $V_{m,add}$ we used $\rho(B_2O_3) = 2.56\,g/cm^3$. The following facts are evident from Table 1. The substitution of TeO_2 by B_2O_3 leads to a decrease in the density, to a decrease in the molar volume but also to a negative deviation in molar volume ($V_{m,exp} < V_{m,add}$) and to an increase in both the glass-transition temperature and the optical band gap. These facts indicate that an increase in B_2O_3 content increases the overall cohesive forces and the glasses compactness.

3.2. Optical band gap

The typical spectral dependencies of the absorption coefficient in $(Kh\nu)^{1/2}$ versus $h\nu$ coordinates (assuming non-direct transitions between the valence and conduction band) are shown in Fig. 1. The temperature dependencies of the optical band gap ($E_{g,non}(T)$) for all glasses can be approximated by the 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, see Fig. 2. The values of $E_{g,non}(300\,K)$, summarized in Table 1, and the values of γ ($6.7 \times 10^{-4} \le \gamma \le 7.9 \times 10^{-4}$ [eV/K]) are comparable to E_g and γ of various other heavy metal oxide glasses (HMO), see e.g. [19]. With substitution of TeO_2 by B_2O_3, the optical band gap increases (Table 1). This is not a surprising result because the bond strength of B—O bond (≈498 kJ/mol for boron coordination number 3 and ≈372 kJ/mol for boron coordination number 4) is higher than the bond strength of Te—O bond (≈285 kJ/mol), [20], and an increase in the bond strength usually implies an increase in overall cohesive forces and an increase of E_g. With an increase in overall cohesive forces, the glass-transition temperature also increases, see Table 1. We note that for the glasses studied we found a simple empirical correlation between E_g and T_g: $E_g \approx 2.78 + 2.54 \times 10^{-3} T_g$ [°C]. Assuming that the electronic contribution to the non-linear refractive index (n_2) has the main influence on its magnitude, we using the relation $n_2 = 1.26 \times 10^{-9}/E_g^{\,4}$ [21] estimated n_2 values for studied glasses in the region $(4.8–8.6) \times 10^{-12}$ esu, see Table 1. These values are comparable to the n_2 values of various HMO glasses, see e.g. [22,23].

3.3. Raman spectra

Typical Raman spectra (RS) for glasses with high (x = 50) and low (x = 10) content of B_2O_3 are shown in Fig.3. The full horizontal lines indicate the region of Raman activity due to (i) heavy metal atom motion, (HM, $\approx 70 \le \nu[cm^{-1}] \le 170$), (ii) bridging oxygen motion that is a symmetrical stretch motion in covalent Te—O—Te and/or Te—O—C configuration where C is a cation, (BO, $\approx 300 \le \nu[cm^{-1}] \le 600$), (iii) non bridging oxygen asymmetrical stretch motion in Te—O—C configuration (here C—O bond is longer than Te—O bond), and in $Te—O^-$ configuration, (NBO, $\approx 630 \le \nu[cm^{-1}] \le 850$), see e.g. [24,25]. The dashed horizontal lines indicate the region of BO motion in B—O—B and/or B—O—C configuration where C is an cation (BO, $\approx 650 \le \nu[cm^{-1}] \le 900$) and NBO motion namely in $B—O^-$ configuration, (NBO, $\approx 900 \le \nu[cm^{-1}] \le 1500$), see e.g. [26,27]. It is evident from Fig. 3 that the Raman activity of B—O based part of the network in the NBO region is weak in comparison with the Raman activity of Te—O based part of the network. This is in agreement with Refs [24,25,28]. The Raman intensity (B_0) for BO and NBO optic modes can be expressed in the form [28]: $B_0 \propto d^5 \Lambda^2 Z_A^{\,10/3} Z_C^{\,2/3} \cos^2(\Theta/2)/m_O \omega_0$, where d is the bond length, Λ is the fractional variation of the polarizability (χ) of the bond with a fractional change in bond length d for the same bond, Z_A, Z_C is the formal valency of anion and cation, respectively, Θ is the bond angle of Te—O—Te and/or Te—O—C and B—O—B and/or B—O—C configuration, m_O is the oxygen mass and ω_0 is the mode frequency. It is valid in our case: $d_{Te—O}(\approx 1.9\,Å–2.08\,Å) > d_{B—O}(\approx 1.32\,Å–1.48\,Å)$, see for instance [27,29,30], and $Z_{Te} > Z_B$. Due to $d_{Te—O} > d_{B—O}$ and also $\chi_{Te—O} > \chi_{B—O}$ [31] we assume that $\Lambda_{Te\text{-}O} > \Lambda_{B—O}$. Since for the BO and NBO optic modes is valid: $\omega_{0(B—O)} > \omega_{0(Te—O)}$ it is reasonable to expect that B_0 for the part of the network based on B—O bonds will be lower than B_0 for the part of the network based on Te—O bonds. This is namely valid for the case of NBO modes because in this case for $C—O^-$ bond the $\cos^2(\Theta/2)$ term can be neglected [28].

4. Discussion

In the evaluation of our Raman spectra we were not successful in an unambiguous decomposition of reduced RS within the entire spectral region $70–1500\,cm^{-1}$. In the spectral regions $70–550\,cm^{-1}$ and $900–1500\,cm^{-1}$ due to an uncertainty in the number of individual bands and their parameters (position, half-width and intensity) we obtained good fits for a varying number of Raman bands and for various values of their parameters. For this reason we decomposed the RS only