

The influence of erbium ions on Bi₂O₃ – PbO glass structure

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Some properties of the xEr₂O₃(1-x)[3Bi₂O₃·PbO] glasses with 0 < x ≤ 0.25 prepared using the melt-quenching technique are reported in this paper. The influence of erbium ions on the host vitreous system was evidenced by analyzing the compositional dependence of the spectroscopic and density data. Raman data permitted to identify some of the structural units that built up the lead bismuthate vitreous network and to follow their evolution with respect to the erbium ion content of the samples.

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1. Introduction

Bismuthate glasses are interesting amorphous systems considered to have important technologic applications in optical communication due to their high refractive index, good infrared transmittance and high optical non-linearity. At the same time, the multicomponent oxide glasses based on the unconventional network formers Bi₂O₃ and PbO are of great interest because they form vitreous materials without traditional network formers and they are very attractive hosts for rare-earth ions [1-3]. In this paper, we report some density and Raman spectroscopic data obtained for the xEr₂O₃(1-x)[3Bi₂O₃·PbO] glass system, with 0 < x ≤ 0.25.

2. Experimental

Glasses with the xEr₂O₃(1-x)[3Bi₂O₃·PbO] composition were prepared where x increased from 0 to 0.25 mol Er₂O₃. High purity PbO, Bi₂O₃ and Er₂O₃ powders were used as starting materials. The mentioned oxides were mixed in suitable proportions to obtain the desired compositions. The mixtures were milled in an agate ball mill for 30 minutes and then were melted at 1200 °C for 15 minutes. The glass samples were obtained by pouring the melts on a stainless steel block.

Density measurements were performed using the picnometric method with water as the reference immersion liquid. The estimated error for the determined density values was less than 0.02 g/cm³.

The Raman spectra of these glasses were recorded in the 0 to 900 cm⁻¹ range using an Equinox 55 spectrometer equipped with a Nd:YAG laser as excitation light source (wavelength 1064nm) and a germanium detector, cooled with liquid nitrogen. The spectral resolution was about 4 cm⁻¹.

3. Results

The X-ray diffractograms of the samples show only broad diffuse scattering at low angles characteristic of long-range structural disorder, confirming the amorphous nature of the samples in the studied composition range.

In order to elucidate the structure of the xEr₂O₃(1-x)[3Bi₂O₃·PbO] glass system, we studied this system by Raman spectroscopy and density measurements.

From density data we calculated the Poisson's ratio (Fig. 1) using the Makishima and Mackenzie model [4], that permitted to follow the evolution of the packing degree of the atoms in the studied glasses with increasing the composition. The Poisson's ratio, σ, is small if the atoms are loosely packed in the oxide glass whereas tightly packed glass has a higher Poisson's ratio.

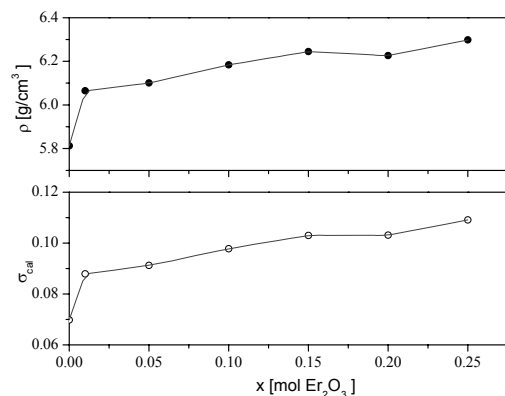


Fig. 1. Dependence of density and Poisson's ratio by the concentration of erbium ions in case of xEr₂O₃(1-x)[3Bi₂O₃·PbO] glass system (the lines are only guides for the eye).

The Poisson's ratio [4] was calculated from the expressions:

$$\sigma_{cal} = 0.5 - \frac{1}{7.2V_T} \quad (1)$$

$$V_T = \frac{\rho}{M} \sum_i V_i X_i \quad (2)$$

$$V_i = 6.023 \times 10^{23} \frac{4\pi}{3} (mR_A^3 + nR_O^3) \quad (3)$$

where R_A and R_O are the respective Pauling's ionic radius of metal A and oxygen O, ρ is the glass density, M the glass molecular weight, X_i the mole fraction of oxide component i , V_i is the packing factor of oxide A_mO_n , V_t the packing density of glass and σ_{cal} is the theoretically calculated Poisson's ratio.

Fig. 2 shows the Raman spectra of $3\text{Bi}_2\text{O}_3\cdot\text{PbO}$ and $x\text{Er}_2\text{O}_3(1-x)[3\text{Bi}_2\text{O}_3\cdot\text{PbO}]$ glass systems. For all compositions, we observe a strong band about 142 cm^{-1} which dominates the spectra. Other bands characteristic of these spectra can be seen on the Fig. 2 and it is clearly visible that the increase of the erbium oxide content produces some structural changes in the glass matrix.

4. Discussion

In the case of the $[3\text{Bi}_2\text{O}_3\cdot\text{PbO}]$ glass matrix the packing density is equal to 0.323 cm^3 . By introducing the rare earth oxide Er_2O_3 with a packing factor equal to 25.81 cm^3 , the packing density of the glass increases until 0.355 cm^3 for the glass with $x=0.25$ mol Er_2O_3 . This causes the increase in Poisson's ratio from 0.0879 to 0.1091 as shown in Fig. 1. The compositional evolution of these parameters indicates that there might be some structural changes of the glass matrix, namely that the erbium ions play an important role in these glasses influencing the Bi- and Pb- coordination number. The lower Poisson's ratio of the host glass matrix is due to the fact that most of the bonds are covalent, in comparison with Er_2O_3 , which is predominantly ionic [5-8].

Therefore, we decided to follow in what manner erbium ions have influenced the structural change which occur in the $x\text{Er}_2\text{O}_3(1-x)[3\text{Bi}_2\text{O}_3\cdot\text{PbO}]$ glasses studied by means of Raman spectroscopy.

The assignment of the Raman bands for the $x\text{Er}_2\text{O}_3(1-x)[3\text{Bi}_2\text{O}_3\cdot\text{PbO}]$ glass systems is discussed by comparing the experimental data obtained for these vitreous systems with the Raman spectra of the Bi_2O_3 and PbO crystalline compounds [9, 10].

By comparing the Raman spectra of the $[3\text{Bi}_2\text{O}_3\cdot\text{PbO}]$ glass matrix to the spectra obtained for the

samples doped with erbium oxide, remarkable structural changes can be seen as a consequence of the addition of erbium ions. These structural changes are related to the rearrangement of the surroundings of the bismuth and lead ions, namely to the $\text{BiO}_6 \rightarrow \text{BiO}_3$ and $\text{PbO}_3 \rightarrow \text{PbO}_4$ conversion processes.

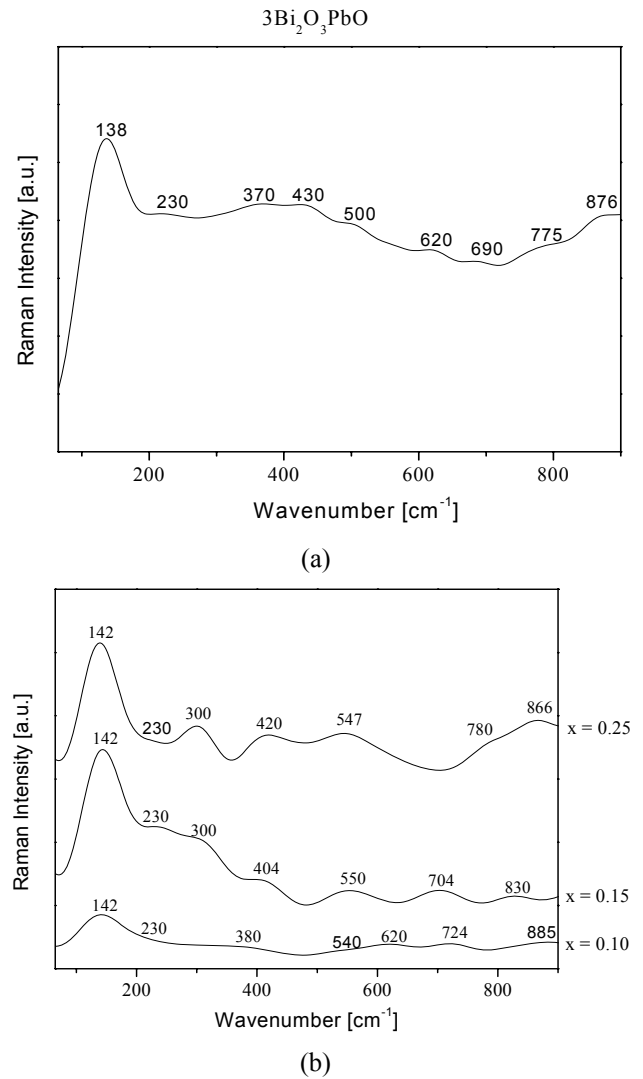


Fig. 2. Raman spectra of $x\text{Er}_2\text{O}_3(1-x)[3\text{Bi}_2\text{O}_3\cdot\text{PbO}]$ glass system for (a) $x = 0$ and (b) $x = 0.10$; $x = 0.15$; $x = 0.25$.

The low-frequency vibration mode around 142 cm^{-1} can be marked out for all the glasses and is assigned to the vibration of Bi^{3+} and Pb^{2+} ions from different structural units [9,11]. The Raman bands in the range from 230 cm^{-1} to 420 cm^{-1} are assigned to the Bi-O-Bi stretching vibrations in BiO_6 and BiO_3 octahedral units and to the Pb-O symmetric bending vibrations in the PbO_n ($n=3$ and/or 4) units [10,12].

The Raman band at $540\text{--}550\text{ cm}^{-1}$ is assigned to the Pb-O vibration from the PbO_4 units [13]. The presence of the PbO_4 units can be observed only in the case of the $x > 0$ samples, suggesting the influence of the erbium ions in determining the nature of the structural units in the host glass matrix. The broad band situated at 620 cm^{-1} for the

$x=0.10$ mol Er₂O₃ sample corresponds to the Bi-O bending vibration in BiO₆ octahedral units [14] and disappears for high erbium contents ($x \geq 0.10$ mol Er₂O₃). This suggests the reduction of the number of BiO₆ in favour of BiO₃ units.

The broad bands at 724 cm⁻¹, 704cm⁻¹ and 780 cm⁻¹ evidence the presence of Pb-O vibrations from PbO₃ units, while the Raman bands from 885 cm⁻¹, 830 cm⁻¹, 866 cm⁻¹ belong most probably to the Bi-O⁻ and Pb-O⁻ vibrations from different structural units [13]. Thus, shifts of the Raman bands are due to changes of the local symmetry involving the Bi-O and Pb-O bonds.

5. Conclusion

The evolution of the density and Raman spectroscopic experimental data obtained for the $x\text{Er}_2\text{O}_3(1-x)[3\text{Bi}_2\text{O}_3\cdot\text{PbO}]$ glass system suggesting that the erbium ions play a network modifier role in case of these glasses.

Raman spectroscopic data obtained for the $x\text{Er}_2\text{O}_3(1-x)[3\text{Bi}_2\text{O}_3\cdot\text{PbO}]$ glasses show the presence of BiO₆, BiO₃, PbO₄ and PbO₃ basic structural units and Er-O bonds. The increase of the Er₂O₃ content of the samples leads to the BiO₆ → BiO₃ and PbO₃ → PbO₄ conversion processes. The structural changes occurring in the studied glasses as function of the rare earth oxide content were evidenced by the density data, too.

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