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Structural and optical characteristics of some bismuthate glass with rare earth ions

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Glasses of the (1-x)[$3Bi_2O_3 \cdot PbO$]xR_2O_3 system where R=Er and Nd were prepared using the melt-quench technique. These glasses were characterized by density and magnetic susceptibility measurements and optical and infrared spectroscopy. Density data were used to calculate the Poisson's ratio in terms of the Makishima-Mackenzie model. The temperature dependence of reciprocal magnetic susceptibility permitted to discuss the nature of complex interactions between rare earth ions localized in lead bismuthate glass matrix. The IR data permitted to identify some of the structural units that built up the lead bismuthate vitreous network. The optical spectroscopy data permitted to identify the electronic transition which occurs in these systems.

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1. Introduction

It is known that Bi and Pb are placed next to each other on the periodic table, and Bi^{3+} and Pb^{2+} ions have the same $6s^2$ electronic configurations. Therefore, a number of similarities have been confirmed in various properties for glasses with Bi_2O_3 and/or PbO, such as a high density, high refractive index, low bond strength, excellent IR transmission, high polarisability and high nonlinear optical susceptibility [1–3]. Glasses based on Bi_2O_3 and PbO were intensely investigated in the last decade because of their interesting technological applications such as thermal and mechanical sensors, wave-guides in non-linear optics, scintillation detectors in high-energy physics, optoeletronic circuits as ultrafast switches, infrared windows, optical isolators and also in advanced computer [4-6]

In the present study, Bi_2O_3 - PbO glasses containing erbium and neodymium ions were chosen to examine the glass structure. The structural information was collected from X-ray diffraction data, density and magnetic susceptibility measurements and optical and infrared spectroscopy investigation.

2. Experimental

Glasses of the $3Bi_2O_3 \cdot PbO$ composition doped with different quantities of rare-earth oxides were prepared by mixing Bi_2O_3, PbO and rare-earth oxides (Er_2O_3 and Nd_2O_3) of reagent grade purity. 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 1200ºC for 15 minutes. The glass samples were obtained by pouring the melts on a stainless steel block.

Structural characterization of all samples has been made by using X-ray diffraction, density measurements, optical and infrared spectroscopy.

X-ray diffraction was performed using an D8 Advance D8 Discover equipment in order to check the vitreous character of the samples.

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 0.02g/cm^3.

Magnetic susceptibility measurements were performed with a Faraday – Weiss balance in the temperature range 80 to 300 K.

Infrared spectra were recorded on a Equinox 55 Bruker spectrometer scanning a range from 400 to 1300 cm^{-1}. The samples were thoroughly mixed with dried KBr. The spectral resolution was about 4 cm^{-1}.

Optical spectra were recorded at room temperature in the 550 to 800 nm range for samples with different size. So, it was necessary to do some correction to the obtained spectra.

3. Results and discussion

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.

From density data we calculated the Poisson's ratio using the Makishima and Mackenzie model, which permitted to follow the evolution of the packing degree of the atoms in the studied glasses with increasing the composition [7]. 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.

In Fig. 1 is presented the dependence of the Poisson's ratio versus the concentration of the neodymium ion. The same behaviour was observed for the glasses dopped with erbium ions, too [8].

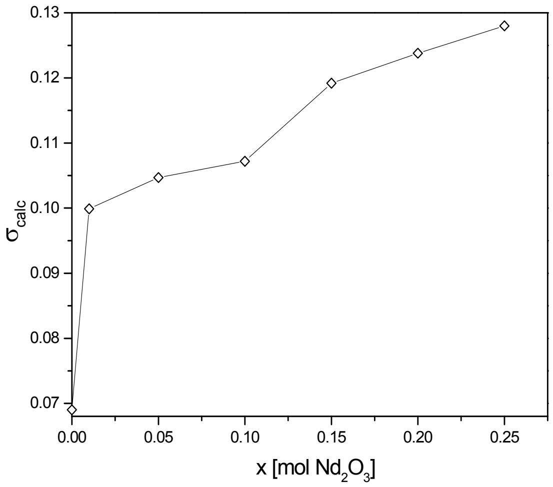

Fig. 1. Compositional dependence of the Poisson's ratio for the $xNd_2O_3(1-x)[3Bi_2O_3{\cdot}PbO]$ *glass system (the line is only a guide for the eye)*

The Poisson's ratio [7] was calculated from the expressions:

$$\sigma_{cal} = 0.5 - \frac{1}{7.2V_T} \tag{1}$$

$$V_T = \frac{\rho}{M}\sum_i V_i X_i \tag{2}$$

$$V_i = 6.023\times10^{23}\,\frac{4\pi}{3}\left(mR_A^3 + nR_O^3\right) \tag{3}$$

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.

The compositional evolution of these parameters indicates that there might be some structural changes of the glass matrix, namely that the rare-earth (erbium and/or neodymium) 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 rare-earth oxide, which is predominantly ionic [9-12].

The susceptibility data were analysed considering a superposition that the magnetic ions follows a Curie-Weiss law behaviour:

$$\chi^{-1} = (T - \theta_p)/C \tag{4}$$

where C is the molar Curie constant and θ_p is the paramagnetic Curie temperature.

The composition dependence of two important magnetic parameters, derived from the plot of χ^{-1} as function of temperature was shown in Fig. 2. These parameters are the paramagnetic Curie temperature, θ_p, and the effective magnetic moment per rare-earth ion, μ_{eff}, calculated from:

$$\mu = 2.827\sqrt{\frac{C}{n\cdot x}} \tag{5}$$

where n is the number of the magnetic ions from one molecule and x is the molar concentration.

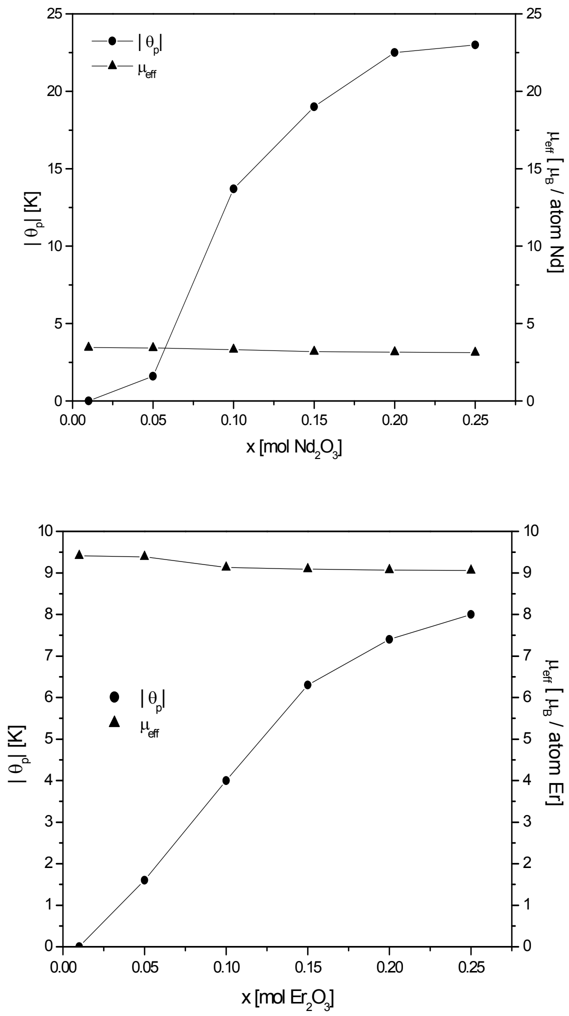

Fig. 2 Composition dependence of the paramagnetic Curie temperature, θ_p, *and of the effective magnetic moment per rare-earth ion,* μ_{eff}.

The $3Bi_2O_3{\cdot}PbO$ host glass matrix was found diamagnetic and the experimental magnetic susceptibility data obtained for these glasses were corrected taking into account this diamagnetic contribution. Therefore, the magnetic behaviour of these glasses was assumed to be due to the presence of the Nd^{3+} and Er^{3+} ions. The effective magnetic moment of these free rare-earth ions are presented in table 1.

The paramagnetic Curie temperature, θ_p, is a rough indicator of magnetic interaction between rare-earth ions. The negative values of θ_p suggest the presence of antifferomagnetic interaction between rare-earth ions. The assumption of the antifferomagnetic nature of the interaction between rare-earth ions is also supported by the fact that effective magnetic moment per rare-earth ion is less than or between of the free rare-earth ions.

Table 1 Magnetic moment of neodymium and erbium ions

Rare-earth ion	μ_{eff} [μ_B]	Ref.
Nd^{3+}	3.62	[13, 14]
Er^{3+}	9.6	[14, 15]

Based on the data provided by the magnetic susceptibility measurements, magnetic behaviour of these glass systems are considered to be of mictomagnetic type where both isolated and superexchange coupled neodymium or erbium ions are present in the glass matrix.

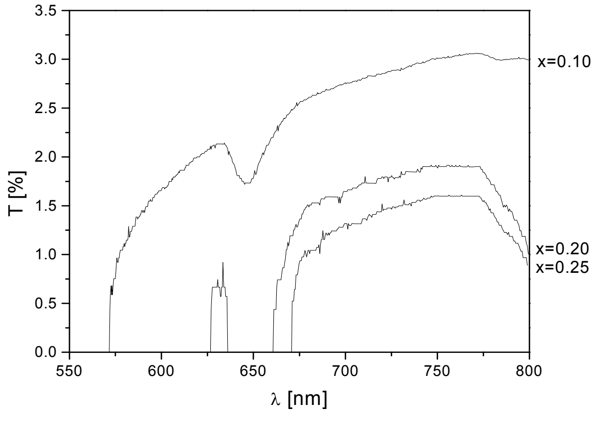

Fig.3 Visible spectra of some samples of the $xEr_2O_3(1\text{-}x)[3Bi_2O_3{\cdot}PbO]$ glass system.

The characteristic features of the electronic structure of trivalent lanthanides, namely the 4f shells, are partly occupied. The 4f electrons are shielded by the outer 5s and 5p orbitals. As a result, the energetic positions of excited electronic states relative to the ground state are nearly equal in energy for a given lanthanide and do not depend on the host lattice.[17].

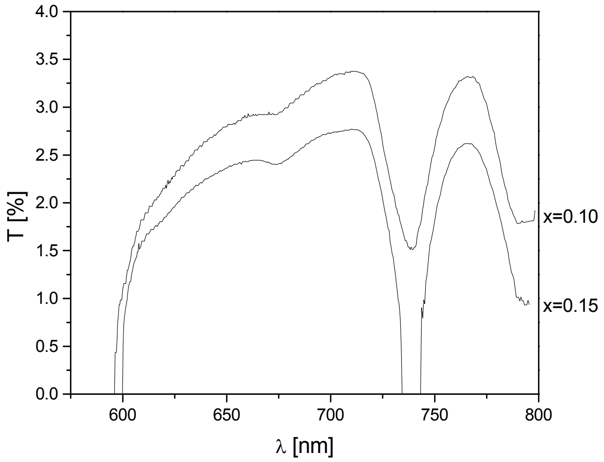

Fig.4. Visible spectra of some samples of the $xNd_2O_3(1\text{-}x)[3Bi_2O_3{\cdot}PbO]$ glass system.

From the optical spectra presented in figure 3 and 4 it can be determined the electronic transitions that occur in these systems. The transitions were assigned according to figure 4 who depicts the energy of the electronic states for Er^{3+} and Nd^{3+} [16]. The energetic positions of the transitions are given in table 2 and they are very close to the values obtained for the other studied systems [17-20].

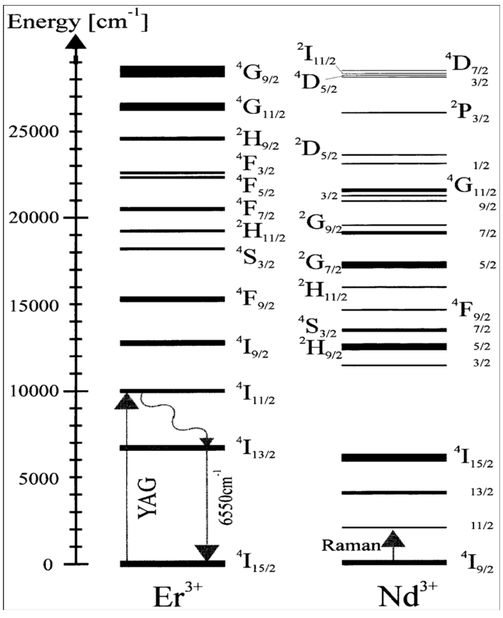

Fig. 5 Energetic position and term symbols of the electronic states for the Er^{3+} and Nd^{3+} ions [17].

Table 2. Energy levels [cm^{-1}], wavenumber [nm] and assignment of electronic transitions of the xEr_2O_3 (1-x)[3Bi_2O_3·PbO] and xNd_2O_3 (1-x)[3Bi_2O_3·PbO] glasses.

xEr_2O_3 (1-x)[3Bi_2O_3·PbO]			xNd_2O_3 (1-x)[3Bi_2O_3·PbO]		
Energy [cm^{-1}]	λ [nm]	Assignment $^4I_{15/2} \to$	Energy [cm^{-1}]	λ [nm]	Assignment $^4I_{9/2} \to$
			16181	618	$^2H_{11/2}$
15456	647	$^4F_{9/2}$	14837	674	$^4F_{9/2}$
12739	785	$^4I_{9/2}$	13532	739	$^4F_{7/2}+^4S_{3/2}$
			12642	791	$^2H_{9/2}+^4F_{5/2}$

The IR spectra of the glasses doped with erbium and neodymium oxide are similar. The most important bands are structured and assigned in table 3.

All of the IR bands have been assigned to the stretching frequencies of the Bi-O and Pb-O bonds. The assignment of the IR absorption bands is discussed by comparing the experimental data obtained for this vitreous system with the absorption spectra of the Bi_2O_3 and PbO crystalline compounds [21, 22].

Tabel 3. IR bands and there assigned in case of the 3Bi_2O_3·PbO glass matrix.

Wavenumber [cm^{-1}]	Assignment
~ 461	Bi-O bending vibrations in BiO_6 units Pb-O bonds vibrations in PbO_4 units
~ 560	Bi-O stretching vibrations in BiO_6 units
~ 724	Pb-O bonds vibrations from PbO_n pyramidal units (n = 3 and/or 4)
~ 856	Bi-O stretching vibrations in BiO_3 units
~ 885	Bi-O stretching vibrations in BiO_6 units
~ 980, ~ 1116	Pb-O vibration from Pb-O-Bi connections

The IR spectral features characteristic of lead bismuthate glasses show the presence of two types of environments associated to structural units involving Bi^{3+} and Pb^{2+} ions. Thus, the bands and shoulders located around 461, 560, 856 and 885 cm^{-1} are associated with the presence of BiO_6 and BiO_3 units, while those located around 461, 724, 980 and 1116 cm^{-1} suggest the presence of PbO_3 and/or PbO_4 units in the glass matrix [23-26].

The most important absorption feature present in the studied IR spectra located around 856 cm^{-1} indicates the presence of the BiO_3 units in the glass network. This feature increases with the increasing the amount of the rare earth oxide. Therefore, the presence of rare-earth ions influences the surrounding of the Bi^{3+} ions, favoring the formation of BiO_3 units.

Based on the IR spectra obtained for 3Bi_2O_3·PbO glass system, we assumed that the structure of these glasses is built up of both BiO_3 and BiO_6 structural units. The analysis of these IR spectra suggests that PbO_n structural units (where n= 3 and/or 4) are present, too, in the glass network of the studied glasses.

4. Conclusions

The 3Bi_2O_3·PbO glasses doped with erbium and neodymium ions were prepared and studied.

Poisson's ratio shows that with increasing the composition of the rare-earth oxide increase the packing degree of the atoms in the studied glasses.

Magnetic susceptibility data evidence that for low rare-earth oxide contents, x < 0.05, the rare-earth ions appear as isolated species randomly distributed in the 3Bi_2O_3·PbO glass matrix. For higher x values the rare-earth ions are submitted to antiferromagnetic interactions.

IR spectroscopic data obtained for these glasses show the presence of BiO_6, BiO_3, PbO_4 and/or PbO_3 groups as basic structural units.

In the visible range several peaks specific for the electronic transition of the erbium and neodymium ions were observed and assigned to the corresponding electronic transitions.

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