Analele Universităţii de Vest din Timişoara
Vol. XLVIII, 2006
Seria Fizică

STRUCTURAL PROPERTIES OF Bi_2O_3 - PbO GLASSES DOPED WITH RARE-EARTH IONS

L. Pop[1], E. Culea[1], M. Culea[2], S. Rada[1], P. Pascuta[1], R. Fechete[1], M. Bosca[1], R. Chelcea[1]

[1] *Department of Physics, Technical University of Cluj-Napoca, Romania,*

[2] *Faculty of Physics, Babes-Bolyai University of Cluj-Napoca, Romania*

Abstract
Bi_2O_3 - PbO glass system with different content of rare-earth ions (Nd_2O_3, Eu_2O_3, Er_2O_3, CeO_2, Tb_4O_7) have been prepared and examined with the aim of determining their structural characteristics. Density measurements and IR spectroscopy were used to characterize the samples. From density data we calculated the Poisson's ratio using the Makishima and Mackenzie model, which permitted to observe the evolution of the packing degree of the atoms in the studied glasses with increasing the content of rare-earth oxide. IR spectra permitted to identify some of the structural units that built up the lead bismuthate vitreous network.
Keywords: glass system, density data, spectroscopic data.

1. Introduction

The multicomponent oxide glasses based on the unconventional network formers Bi_2O_3 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. At the same time, glass systems with rare-earth ions are of current interest because of their potentiality as materials for high power lasers and optical amplifiers for telecommunications. The broad range of applications of these glasses requires the evaluation of their spectroscopic properties. [1-3]

The effect of the rare-earth ions on the glass structure are studied on this paper. Therefore, we report structural characterization of [$3Bi_2O_3$·PbO] glass system for different concentration of rare-earth oxide (Nd_2O_3, Eu_2O_3, Er_2O_3, CeO_2, Tb_4O_7), based on density data and IR spectroscopy.

2. Method and samples

Samples of the xREO (1-x)[$3Bi_2O_3$·PbO] glass system, were prepared by mixing Bi_2O_3, PbO and Nd_2O_3, Eu_2O_3, Er_2O_3, CeO_2 or Tb_4O_7 of reagent grade purity. The mentioned oxides

were mixed in suitable proportions to obtain the desired compositions (table 1). The mixtures were milled in an agate ball mill for 30 minutes and then were melted at 1200^{o}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/cm^3.

Tabel 1 The xREO (1-x)[3Bi_2O_3·PbO] glass systems obtained

Glass systems	x [mol]								
xNd_2O_3·(1-x)[3Bi_2O_3·PbO]	1	–	5	–	10	–	15	20	25
xEu_2O_3·(1-x)[3Bi_2O_3·PbO]	1	–	5	–	10	–	15	20	25
xEr_2O_3·(1-x)[3Bi_2O_3·PbO]	1	–	5	–	10	–	15	20	25
xCeO_2·(1-x)[3Bi_2O_3·PbO]	1	3	5	7	10	–	–	–	–
xTb_4O_7·(1-x)[3Bi_2O_3·PbO]	1	3	5	7	10	12	–	–	–

The IR absorption spectra of the glasses were recorded using an Equinox 55 spectrometer in the 400-1300 cm^{-1} wave number range at room temperature. Sample pellets were prepared by mixing and grinding a small quantity of glass powder with spectroscopic grade dry KBr powder and then compressing the mixtures to form thin pellets for testing. All measurements were run at a 2 cm^{-1} resolution.

3. Results and Discussions

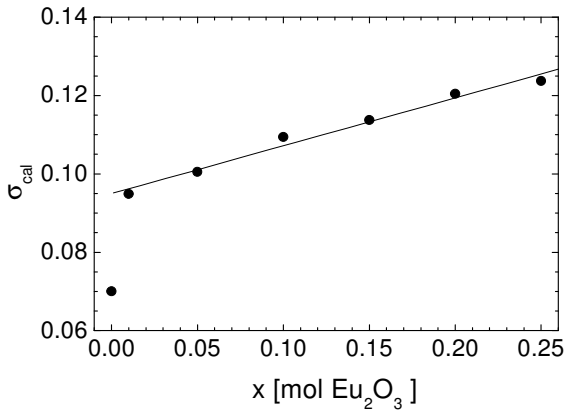

Fig. 1 Compositional dependence of the Poisson's ratio for the xEu_2O_3(1-x)[3Bi_2O_3·PbO] glass system.

The samples presented in table 1 were also investigated by X-ray diffraction method. From resulted pattern we can conclude that the samples are in vitreous state. Their vitreous nature could be also recognized by visual inspection, since they were homogeneous and transparent. The compositions that did not give pure glasses (either crystalline or vitroceramics) are opaque in appearance.

From density data we calculated the

Poisson's ratio using the Makishima and Mackenzie model [4], which 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.

In figure 1 is presented the dependence of the Poisson's ratio versus the concentration of the europium ions. A linear dependence of Poisson's ratio, σ as function of the concentration x can be observed for x greater than zero. In the same time the theoretical density value for x = 0 greater with 36 % than the measured density of the $3Bi_2O_3 \cdot PbO$ matrix. The same behaviour was observed, too, for the glasses doped with neodymium, erbium, cerium or terbium ions.

The compositional evolution of these parameters indicates that there are some structural changes of the glass matrix, namely that the rare-earth 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 [5, 6]. Thus, we decided to study the manner in which the rare-earth ions have influenced the structural change which occur in the xREO (1-x)[$3Bi_2O_3 \cdot PbO$] glasses studied by means of IR spectroscopy (RE = Nd_2O_3, Eu_2O_3, Er_2O_3, CeO_2 or Tb_4O_7). Figure 2 depicts the IR spectrum of the $3Bi_2O_3 \cdot PbO$ glass. The spectra of the glasses doped with rare-earth oxide are similar. 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 [7, 8]. The most important bands are structured and assigned in table 2. The most important absorption feature present in the studied IR spectra is located at 856 cm^{-1} and 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

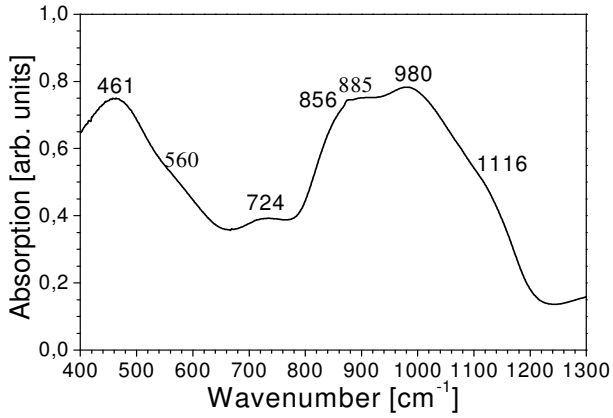

Fig. 2 IR spectrum of the $3Bi_2O_3 \cdot PbO$ glass matrix

obtained for $3Bi_2O_3 \cdot PbO$ 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.

Tabel 2. *IR bands and there assigned in case of the $3Bi_2O_3 \cdot PbO$ glass.*

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

4. Conclusions

The compositional evolution of the spectroscopic and density data suggests that the rare earth ions act as network modifiers in the studied glasses generating structural modifications. Poisson's ratio shows that with increasing the composition of the rare-earth oxide increase the packing degree of the atoms. IR spectroscopic data obtained for these glasses show the presence of BiO_6, BiO_3, PbO_n (n = 3 and/or 4) groups as basic structural units.

Acknowledgements

This work was supported by CEEX – MATNANTECH 47/2006 program.

References

[1] P.Srivastava, S.B.Rai and D.K.Rai, Spectrochimica Acta Part A 59 (14) (2003) 3303

[2] I.V. Kityk, J. Wasylak, D. Dorosz, J. Kucharski, S. Benet, H. Kaddouri, Opt.&Laser Technology 33 (2001) 511

[3] C. Duverger, M. Montagna, R. Rolli, S. Ronchin, L. Zampedri, M. Fossi, S. Pelli, G.C. Righini, A. Monteil, C. Armellini, M. Ferrari, J. Non-Cryst. Solids 280 (2001) 261

[4] A.Makishima, J.D.Mackenzie, J.Non-Cryst. Solids 17 (1975) 147

[5] A. El-Adawy, Y. Moustafa, J. Phys. D: Appl. Phys. 32 (1999) 2791

[6] L.G. Hwa, T.H. Lee, S.P. Szu, Mater. Res. Bull. 39 (2004) 33

[7] F.F. Bentley, L.D. Smithson, A.L. Rozek, Infrared Spectra and Characteristic Frequencies 700-300 cm^{-1}, Interscience Pub., New York (1968)

[8] Zs. Szaller, L. Kovacs, L. Poppl, J. Sol. State Chem. 152 (2000) 392