

# Nanostructured phases in bismuthate glasses containing rare earth ions

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Glasses of the  $xR_2O_3(1-x)(Bi_2O_3 \cdot PbO)$  system where  $R=Gd, Eu, \text{ and } Nd$  and  $0 \leq x \leq 0.30$  were obtained and studied by magnetic susceptibility, X ray diffraction and SEM microscopy. Magnetic susceptibility data that the rare earth magnetic ions show a clusterization tendency even for low concentrations. Over certain limits, the increase of the rare earth oxide content of the samples generate the phase separation process. The crystalline phase evidenced was the  $3BiO \cdot PbO$   $\beta$  solid solution (built up of distorted  $[BiO_6]$  and  $[PbO_6]$  octahedral units in the body centered cubic crystallographic structure).

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## 1. Introduction

Vitreous systems containing rare-earth ions attracted a great attention due to their important applications in optical telecommunication, but also as sensors, up-converters or hole burning memory materials [1-8]. Thus, the use of bismuthate glasses containing rare earth ions represent in important domain because such material represent very important candidates for low loss optical fibres, Raman optical fibre amplifiers or IR transmitting windows [5]. It is interesting to be mentioned that the bismuth oxide is not a traditional network former, however, in combination with different oxides such as  $B_2O_3$  or  $PbO$ , glass formation is possible in a relatively large composition range [9]. The interest for such unconventional vitreous systems is increased by the fact that the bismuth ions are known to have more than one stable coordination and thus are able to generate several structural units in the glass matrix.

To extend the available information concerning glasses containing bismuthate glasses containing rare earth ions, in this work we performed the investigation of the  $xR_2O_3(1-x)(Bi_2O_3 \cdot PbO)$  glass systems where  $R=Gd, Eu, \text{ and } Nd$  and  $0 \leq x \leq 0.30$  using magnetic susceptibility and electron microscopy. Our attention was focused on the process of generation of nanostructured phases in the studied materials as function of composition and heat treatment.

## 2. Experimental

Samples of the the  $xR_2O_3(1-x)(Bi_2O_3 \cdot PbO)$  glass systems where  $R=Gd, Eu, \text{ and } Nd$  and  $0 \leq x \leq 0.30$  were

obtained using reagent grade  $Bi_2O_3$ ,  $PbO$  and  $R_2O_3$ . The mentioned oxides were mixed in suitable proportions. The mixtures were milled in an agate ball mill for 40 minutes and then were melted at  $1250 \text{ }^\circ\text{C}$  for 30 minutes. The glass samples were obtained by pouring the melts on stainless steel.

X-ray diffraction investigation of the samples did not reveal crystalline phases.

Magnetic susceptibility measurements were performed on a Faraday type balance in the temperature range 80 to 300 K. The sensitivity of the equipment was  $10^{-8} \text{ emu/g}$ . The measurements were performed on samples having a mass of 0.200-0.300 g.

Electron microscopic examination of the samples was made using a Jeol JSM 5600-LV scanning electron microscope.

## 3. Results and discussion

Fig. 1 presents the thermal variation of the inverse magnetic susceptibility for the  $xR_2O_3(1-x)(Bi_2O_3 \cdot PbO)$  with  $R=Gd$ .

The susceptibility data shown in this figure follow the Curie-Weiss behaviour, described by the equation:

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

where  $C$  is the Curie constant,  $\theta_p$  is the paramagnetic Curie temperature and  $T$  is the temperature. By fitting the experimental data according to Eq. 1, we determined the values of  $C$  and  $\theta_p$ .

This magnetic behavior was characteristic of all the glass systems studied in this paper and was assumed to be

due to the presence of the magnetic rare earth ions,  $R^{3+}$ , in the diamagnetic host glass matrix (all the experimental magnetic data were corrected taking into account the diamagnetic contribution of the host glass matrix).

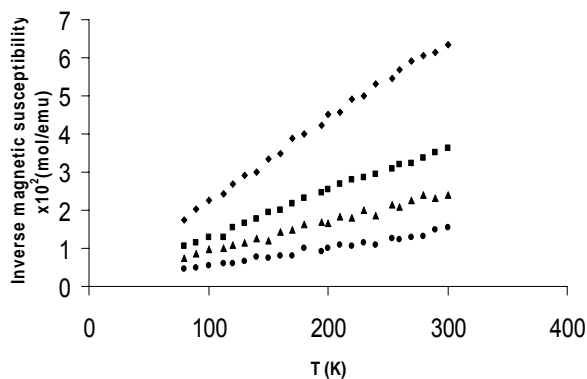


Fig. 1. Temperature dependence of the inverse magnetic susceptibility for the  $x\text{Gd}_2\text{O}_3(1-x)(\text{Bi}_2\text{O}_3\text{ PbO})$  glasses ( $x=0.10$  (◆),  $x=0.15$  (■),  $x=0.20$  (▲) and  $x=0.25$  (●).

Fig. 2 shows the compositional dependence of the paramagnetic Curie temperatures for some of the  $x\text{R}_2\text{O}_3(1-x)(\text{Bi}_2\text{O}_3\text{ PbO})$  glasses. The paramagnetic Curie temperatures were almost zero for low  $\text{R}_2\text{O}_3$  concentration and became relatively small and negative for higher rare earth oxide concentrations suggesting that the magnetic interactions between the rare earth ions weak and of antiferromagnetic nature. This behavior is characteristic of oxide glasses containing rare earth ions [8].

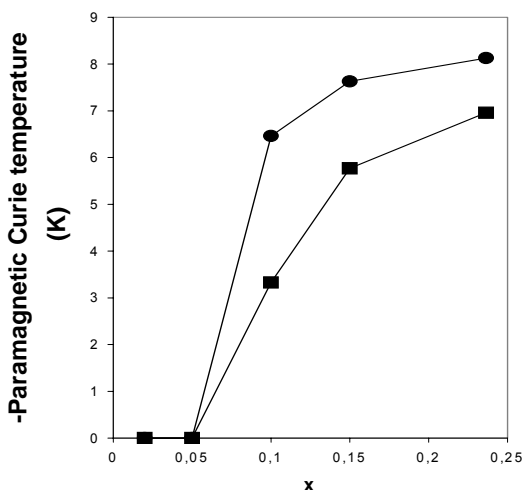


Fig. 2. Compositional dependence of the paramagnetic Curie temperatures for the  $x\text{R}_2\text{O}_3(1-x)(\text{Bi}_2\text{O}_3\text{ PbO})$  glasses with  $R=\text{Nd}$  (■) and  $\text{Eu}$  (●).

The X ray analysis of the studied samples evidentiates that at high rare earth oxide content,  $x$ , a phase separation

process including the occurrence of crystalline phases. Fig. 3 show the X ray powder diffraction spectra of the  $x\text{Gd}_2\text{O}_3(1-x)(\text{Bi}_2\text{O}_3\text{ PbO})$  glasses. The crystalline phase that appears in the  $x\text{Gd}_2\text{O}_3(1-x)(\text{Bi}_2\text{O}_3\text{ PbO})$  glasses was found to be the  $3\text{BiO-PbO}$   $\beta$  solid solution which is built up of distorted  $[\text{BiO}_6]$  and  $[\text{PbO}_6]$  octahedral units in the body centered cubic crystallographic structure [10].

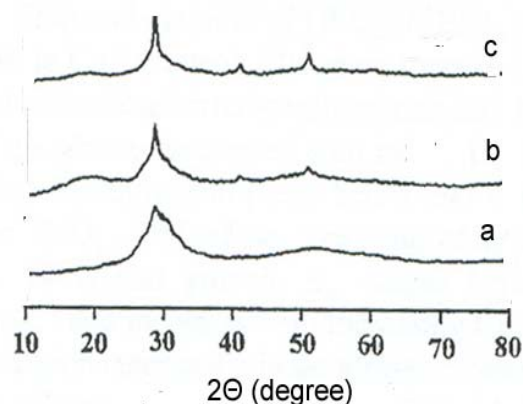


Fig. 3. X ray diffraction spectra of the  $x\text{Gd}_2\text{O}_3(1-x)(\text{Bi}_2\text{O}_3\text{ PbO})$  glasses with  $x=0.20$  (a),  $x=0.25$  (b) and  $x=0.30$  (c).

SEM microscopy investigation of the studied glasses confirms the appearance of the phase separation process with increasing their rare earth oxide content (see Fig. 4). The dimensions of the droplet phase are of hundreds of nanometers and increase up to thousands of nanometers for high rare-earth oxide content.

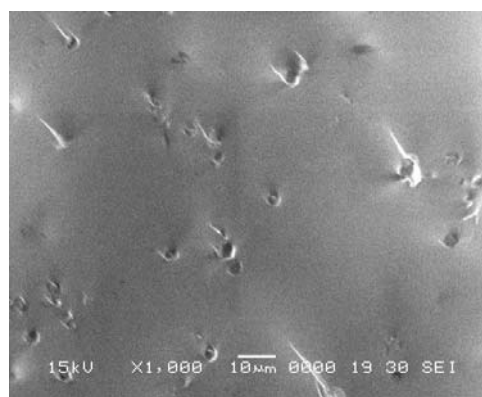


Fig. 4. SEM microscopy image of the  $x\text{Eu}_2\text{O}_3(1-x)(\text{Bi}_2\text{O}_3\text{ PbO})$  glass with  $x=0.20$ .

#### 4. Conclusions

Magnetic susceptibility, X-ray diffraction and SEM investigation was performed on  $x\text{R}_2\text{O}_3(1-x)(\text{Bi}_2\text{O}_3\text{ PbO})$  glasses with  $R=\text{Gd}$ ,  $\text{Eu}$ , and  $\text{Nd}$  and  $0 \leq x \leq 0.30$ . Vitreous samples were obtained for all the composition ranges. A droplet-type phase separation was evidenced for the

samples with high rare earth oxide content. For very high rare earth oxide contents the  $3\text{BiO}\cdot\text{PbO}$   $\beta$  crystalline phase was detected. All the samples show weak ferromagnetic behavior.

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