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ORIGINAL PAPER

EPR Study of MnO and MnO_2 Doped Barium Aluminoborate Glasses

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Abstract An off-equilibrium redox condition study of Mn^{2+} and Mn^{4+} ions added to the batch is reported for the case of the preparation of the barium aluminoborate glasses, by considering that the out of equilibrium reactions started already on the melt. It is shown that for lower dopant concentrations the relative concentrations of the oxidation states of the manganese are found out of equilibrium up to the added amount of 0.3 mol% of MnO_2, but on doping with MnO, the equilibrium state is achieved at the MnO added amount of 0.07 mol%. The change of the redox condition of the manganese ions toward the equilibrium was studied by tracking the Mn^{2+} amount as a function of the doping concentration in the two cases of MnO and MnO_2.

Keywords Aluminoborate glasses · EPR · Manganese · Redox

1 Introduction

The physical and chemical processes which occur in oxide glasses doped with transition metal elements such as manganese and/or co-doped with rare-earth elements are of great practical and theoretical importance. There are several possible applications for these glasses, such as lasers [1, 2], solar luminescent concentrators [3, 4], optical fibers, photosensors [5], radiation dosimeters [6, 7], coloring agents [8, 9], and nuclear wasteforms [10–12]. The behavior of Mn^{2+} ions content in manganese doped barium aluminoborate glass system, $x\text{TMO}(100-x)(0.20\text{Al}_2\text{O}_3 \cdot 0.50\text{B}_2\text{O}_3 \cdot 0.30\text{BaO})$ mol%, where TMO = MnO or MnO_2 is determined by amount of transition metal oxide. The changes is the oxidation state of manganese and also of the iron impurities, induced by irradiation, were studied using the EPR of Mn^{2+} and Fe^{3+} ions parameters.

The scope of this paper is to investigate the recovery behavior of the distribution of the equilibrium Mn^{3+}/Mn^{2+} rate in the $(30\text{BaO} \cdot 50\text{Al}_2\text{O}_3 \cdot 20\text{B}_2\text{O}_3)$ mol% base glass doped from starting amounts of manganese oxides containing either 100% of Mn^{2+} or 100% of Mn^{4+} ions.

2 Materials and Methods

The barium aluminoborate glasses containing different concentrations of manganese were prepared using a batch of weighed amounts of Al_2O_3, H_3BO_3, $Ba(OH)_2 \cdot 8H_2O$, MnO and MnO_2 in order to obtain the samples of the glass systems $x\text{TMO}(100-x)(0.20\text{Al}_2\text{O}_3 \cdot 0.50\text{B}_2\text{O}_3 \cdot 0.30\text{BaO})$ mol%, where TMO = MnO or MnO_2, as shown in Table 1.

The batch was melted in alumina crucibles at the temperature of 1150 °C in electric furnace for about three hours in air. The melt was then quenched in pre-heated moulds, discs of 25 mm of diameter and 4 mm thick being obtained. After solidification, the samples were annealed in another furnace at 500 °C during two hours. The electron paramagnetic resonance (EPR) measurements were performed using a homodyne Bruker EMX spectrometer with a rectangular TE_{102} cavity, at the frequency of about 9.75 GHz (X-band).

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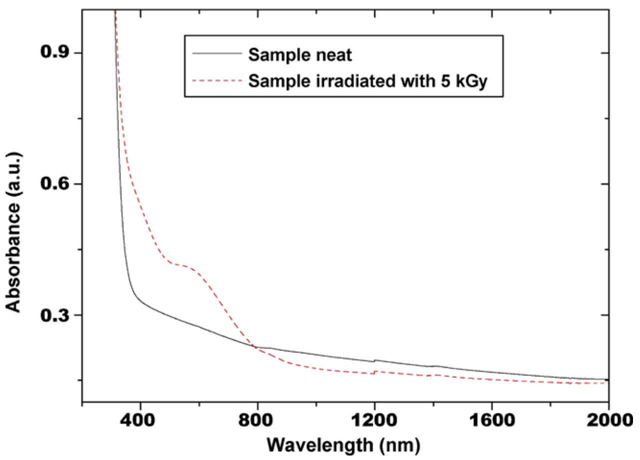

Fig. 1 Optical absorption of the barium aluminoborate glass, before and after γ-irradiation of dose 5 kGy

Table 1 Sample of the glass system $x\text{TMO}(100 - x)(0.20\text{Al}_2\text{O}_3 \cdot 0.50\text{B}_2\text{O}_3 \cdot 0.30\text{BaO})$ mol%, where TMO = MnO or MnO_2

	MnO (mol%)	MnO_2 (mol%)
Doping	0; 0.02; 0.04; 0.07; 0.70; 1.00	0; 0.04; 0.30; 0.50; 0.70

Gamma irradiation was performed with samples wrapped in a 10 mm thick polyethylene sheet and the surfaces covered with rectangular Lucite plates 3 mm thick. The samples were irradiated at room temperature with doses of 1 kGy and 5 kGy, respectively.

The optical absorption (OA) experiments were performed with the model 500 double-beam Cary spectrophotometer in the absorbance mode, in the wavelength range of 200 to 3000 nm.

3 Results

In Fig. 1 are shown the optical absorption (OA) of the non-doped sample before and after irradiation at room temperature. The band observed at $\lambda = 555$ nm (2.2 eV) is attributed to the boron-oxygen hole center (BOHC). As has been reported earlier [13], the boron electron center (BEC) was almost completely bleached at room temperature, so that photoelectrons trapped at other sites are remaining which still have remained stable, probably a boron electron center which has trapped two electrons (not seen by EPR) and the electron trapped by an Fe^{3+} impurity in which one has a previously trapped photoelectron.

The calibration curves of the Mn^{2+} EPR signal intensity versus (xTMO concentration) are shown in Fig. 2. The MnO_2 doping is represented in Fig. 2a and MnO-doping in Fig. 2b, respectively. The values measured below the dopant concentration of 0.1 mol%, highlighted in the insets, indicate that the Mn^{2+} content appears below the straight line for MnO_2 concentrations of 0.02; 0.04 and 0.09 mol%. In contrast, for MnO doping the points are very close and above the calibration line, approaching gradually for 0.02 and 0.04 mol% and reaching the straight line at 0.07 mol%.

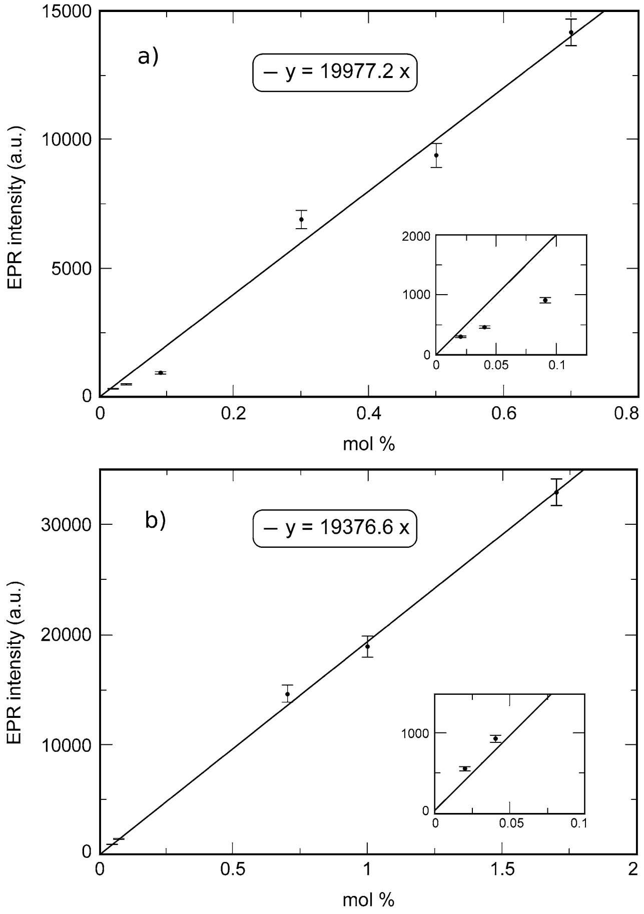

Fig. 2 Calibration of the EPR intensities with increasing concentrations of (**a**) TMO = MnO_2 and (**b**) TMO = MnO

Figures 3a and 3b show the behavior of EPR intensities of Mn^{2+} and Fe^{3+} of the $x\text{TMO}(100 - x)(0.20\text{Al}_2\text{O}_3 \cdot 0.50\text{B}_2\text{O}_3 \cdot 0.30\text{BaO})$ mol%, where TMO = MnO or MnO_2 and $x = 0.04$ mol%, respectively. The Fe^{3+} signal at $g = 4.3$ was found from the pervasive iron impurity often present in oxide glasses. Its concentration in aluminoborate glass has been measured earlier by EPR giving 1.1×10^{18} spins/cm^3 [14].

The samples doped with MnO presented a very pale pink coloration, even at the lower doses, whereas the samples doped with MnO_2 presented a considerably heavier pink coloration for comparable dopant concentrations.

4 Discussion

As the Mn^{3+} content can be easily evaluated by OA and Mn^{2+} by EPR, we can observe how the manganese ions oxidation state behaves, while they are recovering the equilibrium state.

From the EPR intensity of the Mn^{2+} concentration of the samples doped with MnO_2, shown in Fig. 2a, it is observed that for low manganese concentration the maximum Mn^{2+} deficiency occurs at about the fraction of 0.7 of the corresponding equilibrium value (represented by the straight line determined as $y = (20.0 \pm 1.3)x$, adjusted from the higher concentration values). The equilibrium $[Mn^{3+}]/[Mn^{2+}]$ fraction was evaluated using the calibrated straight line from de Mn^{2+} concentration of the MnO-doped samples, shown in Fig. 2b. From the off-equilibrium values highlighted in the inset of Fig. 2b, it was evaluated that $[Mn^{3+}]/[Mn^{2+}]$ equilibrium rate is ~0.6.

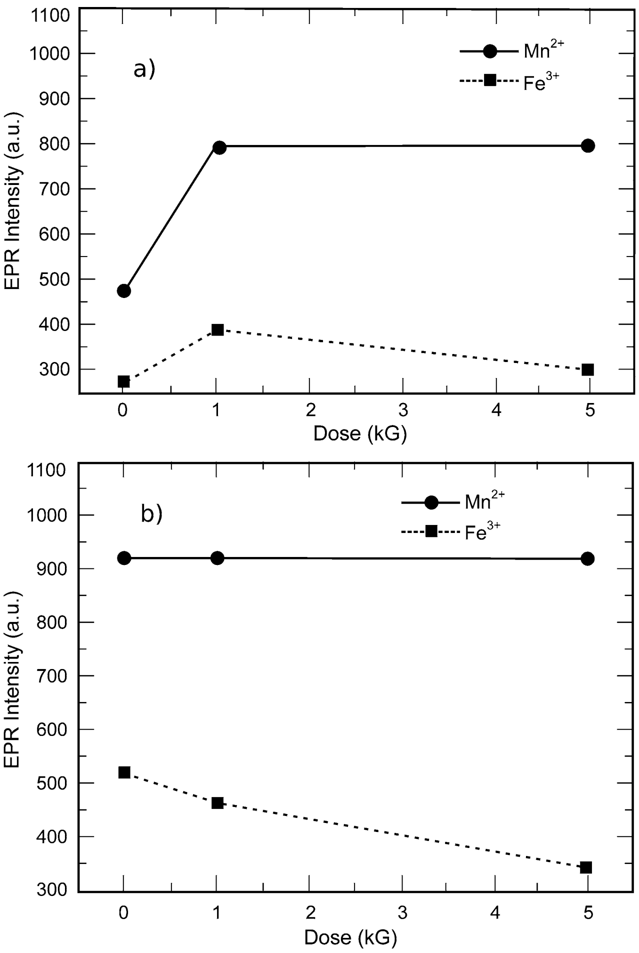

Fig. 3 EPR intensities of Mn^{2+} and Fe^{3+} of xTMO(100x) × ($0.20Al_2O_3 0.50B_2O_3 0.30BaO$) mol% with increasing dose of the gamma-ray exposure, where (**a**) TMO = MnO_2 and (**b**) TMO = MnO

Another interesting effect is the slightly different slope of the adjusted straight lines of the Mn^{2+} EPR *vs.* dopant concentration. For the case of MnO_2-doping $y = (20.0 \pm 1.3)x$ more oxygen is added to the glass composition, contributing to increase the glass basicity, or the pO index [15], as compared with $y = (19.4 \pm 0.9)x$ for the MnO-doping.

It is interesting to observe what happens when a low manganese concentration sample, such as doped with 0.04 mol% of MnO_2 and MnO, is submitted to ionizing radiation. Thus, for the MnO_2-doped sample (see Fig. 3a) the Mn^{2+} concentrations increases pushing the manganese ion oxidation state toward the equilibrium value.

As the equilibrium was attained, for higher γ-irradiation dose the $[Mn^{2+}]$ value remains constant, because the manganese ions are located outside the glass-forming tetrahedral structural units, i.e., in the glass modifier ions site. A model for a probable site of Mn^{3+}, where the trivalent ion is compensating the change of three neighboring BO_4 tetrahedral units, is illustrated in Fig. 4.

For the sample doped with MnO the $[Mn^{3+}]/[Mn^{2+}]$ has already attained its equilibrium value, so that no reaction is noticed for the manganese ion (see Fig. 3b). The Fe^{3+} ion impurity behavior indicates that a fraction of Fe^{2+} ions were affected by the out of equilibrium condition of manganese ions, in the case of the MnO_2-doping, up to the dose of 1 kGy. As the manganese ions do not take part in redox reactions with higher dose, the $[Fe^{3+}]$ decay due to the electrons trapped from the neighboring oxygen ionization is observed in the site where a hole was left by forming a boron-oxygen hole center (BOHC).

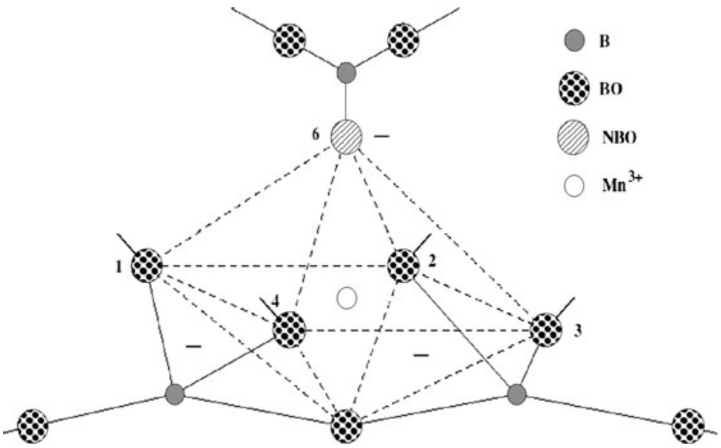

Fig. 4 Model of a probable local Mn^{3+} site in manganese doped barium aluminoborate glasses

5 Conclusion

The [Mn^{3+}]/[Mn^{2+}] equilibrium rate is constant for each of the MnO_2 and MnO doped barium aluminoborate glass systems, provided [MnO_2] $\geq$ 0.3 mol% and [MnO] $\geq$ 0.07 mol%.

For the lower [TMO] values the [Mn^{2+}] is (a) lower for MnO_2-doped and (b) higher for MnO doped values determined by the equilibrium condition. It was assumed that the presence of the Mn^{4+} ions in the oxide glasses can be neglected.

The equilibrium [Mn^{3+}]/[Mn^{2+}] rates of 0.7 for the MnO_2 doped and 0.6 for the MnO doped $30BaO \cdot 50Al_2O_3 \cdot 50B_2O_3$ mol% glass were evaluated.

The γ-irradiation of the glasses doped with 0.04 mol% [TMO] with a dose of 1 kGy has recovered the [Mn^{3+}]/[Mn^{2+}] equilibrium condition.

The [Fe^{3+}] impurity was affected by the presence of manganese ions under glass γ-irradiation up to the dose of 1 kGy, only for the MnO_2-doped glasses.

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