

# EPR investigation of the $x\text{MnO}\cdot(100-x)[2\text{B}_2\text{O}_3\cdot\text{MO}]$ ( $\text{MO} \rightarrow \text{CdO}, \text{SrO}$ ) glass systems

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Electron paramagnetic resonance (EPR) of  $\text{Mn}^{2+}$  ions revealed their distribution on different structural units in  $2\text{B}_2\text{O}_3\text{-CdO}$  or  $2\text{B}_2\text{O}_3\text{-SrO}$  glass matrices doped with of  $\text{MnO}$ . Disordered octahedral symmetric sites were detected up to 5 mol %  $\text{MnO}$ . In case of  $\text{CdO}$  containing glasses the dipolar interactions were detected up to 20 mol%  $\text{MnO}$  but for  $\text{SrO}$  containing glasses up to 10 mol%. For higher  $\text{MnO}$  content in both glass systems appear the superexchange magnetic interactions. From these data results that the valence states and intensity of magnetic superexchange interactions are different in these two glass systems.

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## 1. Introduction

Structural properties of vitreous systems were frequently studied by means of EPR of  $\text{Mn}^{2+}$  ions used as paramagnetic probes. Information concerning the structural details of the vitreous matrix revealed by the paramagnetic ion distribution on different structural units building the network, their coordination and the valence states were obtained. Generally the spectra of  $\text{Mn}^{2+}$  ions consists of resonance lines centered at  $g_{\text{eff}} \approx 2.0, 4.3$  and  $3.3$  values. A special effort was made to elaborate the theoretical support for explaining the resonance lines  $g_{\text{eff}} \approx 4.3$  and  $g_{\text{eff}} \approx 3.3$  from the  $\text{Mn}^{2+}$  EPR spectra [1-4].

Various oxide glasses such as borate [5-8], silicate [9-10], phosphate [11] and tellurite [12], chalcogenide [13] and halide [4-14] glasses doped with manganese were investigated.

This paper aims to present our results concerning the structural details of the  $2\text{B}_2\text{O}_3\cdot\text{MO}$  ( $\text{MO} \rightarrow \text{CdO}, \text{SrO}$ ) vitreous matrices revealed by the distribution of manganese ions on various structural units, their valence states and the magnetic interactions involving them. Investigation were made by means of EPR measurements

## 2. Experimental details

Glasses of the  $x\text{MnO}\cdot(100-x)[2\text{B}_2\text{O}_3\cdot\text{MO}]$  ( $\text{MO} \Rightarrow \text{CdO}$  or  $\text{SrO}$ ) systems were prepared using reagent grade  $\text{MnCO}_3$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{CdO}$ ,  $\text{SrCO}_3$ , in suitable proportions. The mixture were mechanically homogenized and melted in sintered corundum crucibles in an electric furnace at  $1250^\circ\text{C}$ . The molten materials was kept at this temperature for 30 min and quenched at room temperature by pouring onto a stainless-steel plate. Typical glass samples were obtained. The structure of samples was analyzed by means of X-ray diffraction. The patterns

obtained did not reveal any crystalline phases up to  $x = 50$  mol%.

The EPR measurements were performed at room temperature by using JEOL-type equipment with 100 KHz field modulations in the X frequency band. Powdered samples were studied in fused quartz tubular holders of the some caliber (3 mm) and quantity.

## 3. Results and discussion

For all samples, the EPR absorption spectra due to  $\text{Mn}^{2+}$  ( $3d^5$ ,  $^6\text{S}_{5/2}$ ) were obtained. The structure of the absorption spectra strongly depends on the  $\text{MnO}$  content of the samples, as can be observed in Fig. 1. At low concentrations of  $\text{MnO}$  the spectrum consists in absorption lines centered at values of  $\approx 4.3, \approx 3.3$  and  $\approx 2.0$  for the effective  $g$  factor.

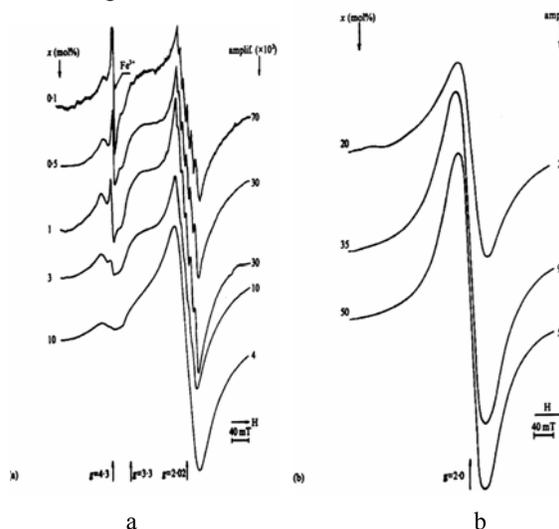


Fig. 1. EPR absorption spectra due to  $\text{Mn}^{2+}$  ions in  $x\text{MnO}(100-x)[2\text{B}_2\text{O}_3\cdot\text{CdO}]$  glasses for  $x \leq 10$  mol % (a) and  $20 \leq x \leq 50$  mol % (b).

The absorption line at  $g_{\text{eff}} \approx 2.0$  is prevalent in the spectrum and shows the hyperfine structure (hfs) characteristic of the  $^{55}\text{Mn}$  ( $I=5/2$ ) isotope that is well resolved for samples with  $x \leq 3$  mol% in both systems studied. The resolution depends on the  $\text{Mn}^{2+}$  ion concentration as can be seen in Fig. 3. The hfs sextet superimposes on a large absorption line, the envelope of all contributions at this absorption. At high  $\text{MnO}$  content, the spectrum reduces to a single absorption line, without hfs, centered at  $g_{\text{eff}} \approx 2.0$ .

The  $g_{\text{eff}} \approx 2.0$  absorption line was generally attributed to isolated paramagnetic  $\text{Mn}^{2+}$  ions in octahedral symmetric sites slightly tetragonal distorted, to dipolar or superexchange coupled pairs of ions [4]. Depending on  $\text{MnO}$  content, our samples show an evolution of the vitreous matrix structure from structural units involving  $\text{Mn}^{2+}$  ions in well defined vicinities having a certain symmetry, to structural formations containing clustered ions. This evolution was revealed by the changes in  $g_{\text{eff}} \approx 2.0$  absorption line when increase the  $\text{Mn}^{2+}$  ion content (Fig. 1 and Fig. 2).

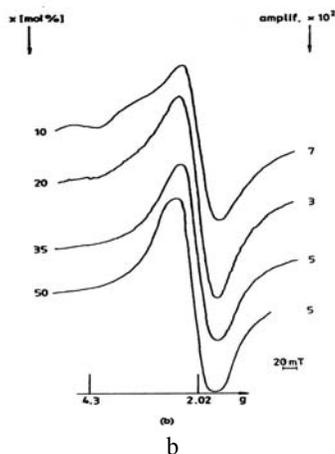
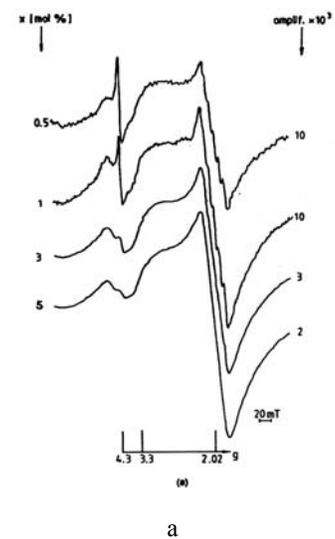


Fig. 2. EPR absorption spectra due to  $\text{Mn}^{2+}$  ions in  $x\text{Mn} \cdot (100-x)[2\text{B}_2\text{O}_3 \cdot \text{SrO}]$  glasses for  $x \leq 10$  % mol (a) and  $20 \leq x \leq 50$  % mol (b).

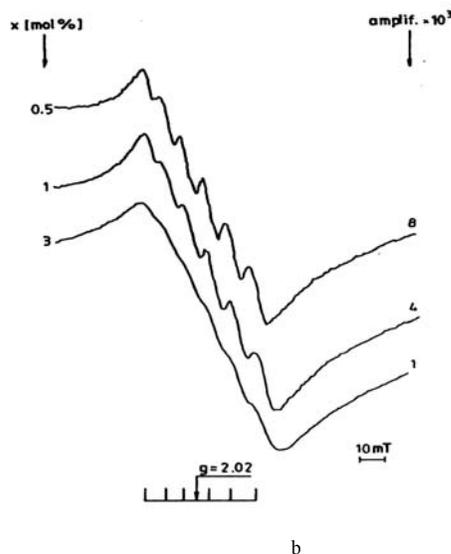
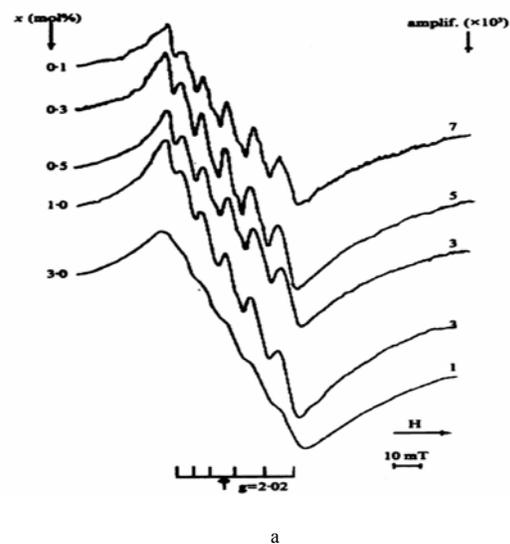


Fig. 3. The evolution of the hfs at the  $g_{\text{eff}} \approx 2.02$  EPR absorption when increasing the  $\text{Mn}^{2+}$  ions concentration for glasses containing CdO (a) and SrO (b).

For both glass systems, within the low concentration range ( $x \leq 3$  mol %), has a resolved hfs (Fig. 3). The hyperfine sextet is due to isolated  $\text{Mn}^{2+}$  ions in high symmetric sites (octahedral) that are separated well enough from each other to avoid strong dipolar interactions. The  $g$  factor and hyperfine coupling constant values and the well resolved hfs support this statement and also evidence the predominantly ionic character of the bonding between  $\text{Mn}^{2+}$  and the  $\text{O}^{2-}$  ions generating the octahedral symmetric ligand field. These are weak axial distortions superimposed on this field varying from one vicinity to another [15]. Their random orientation determines the broadening of the absorption line. The random distribution of  $\text{Mn}^{2+}$  ions in the vitreous matrix,

together with this broadening, results in a large background line that is the envelope of all contributions at  $g_{\text{eff}} \approx 2.0$  having superimposed the hfs sextet. When the  $\text{Mn}^{2+}$  ions concentration increases, the hfs smears out and the intensity of the symmetric absorption line at  $g_{\text{eff}} \approx 2.0$  increases for glasses containing CdO. In the case of glasses containing SrO, the intensity of this absorption line increase up to 20 mol % MnO after decrease evidenced that in this samples are present manganese ions in other valence states, which no contribute to the EPR absorption in our experiment.

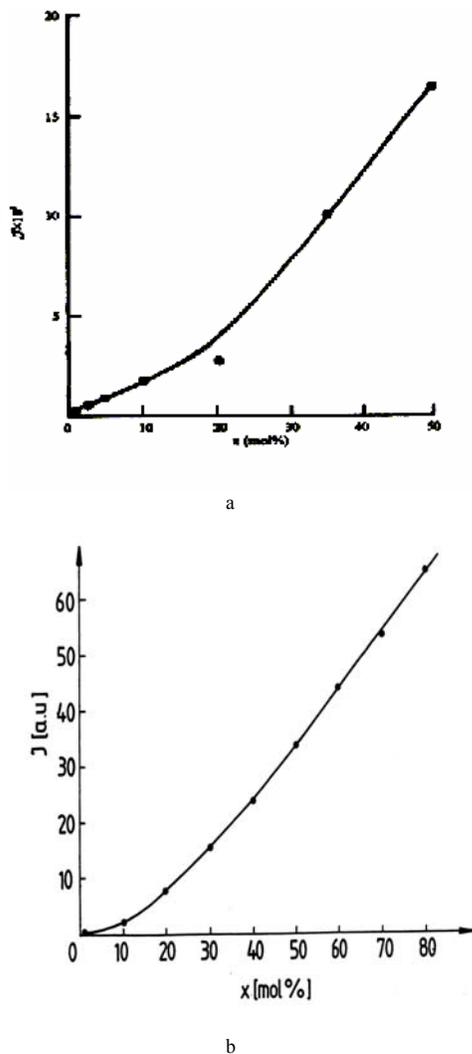


Fig. 4. The composition dependence of the line intensity centered at  $g_{\text{eff}} \approx 2.0$  for glasses containing CdO (a) and SrO (b).

From this variation of line intensity (Fig. 4. a and b) we can remark that the concentration of  $\text{Mn}^{2+}$  ions differs in these two glass systems studied. Therefore, existence in glass matrix of the CdO or SrO influenced in different way the valence states of manganese ions. The  $g_{\text{eff}} \approx 2.0$  absorption line width follows the variation presented in

Fig. 4. In case of glasses containing CdO the dipolar broadening are evidenced up to 20 mol % MnO and for glasses containing SrO this interactions are manifest only up to 10 mol % MnO. For higher concentration this broadening is balanced by narrowing mechanisms due to superexchange type interactions between the manganese ions close enough to each other. The reached doping level of the matrix imposes the progressive clustering of manganese. In case of the glasses containing SrO, for  $x > 25$  mol% the narrowing is balanced by broadening effects due to another mechanisms so as the interaction between mixed valence states of manganese or the progressive disordering of the vitreous system. At high MnO content, besides the  $\text{Mn}^{2+}$  ions species, the only one given rise to EPR absorption in our experiment, superior valence states may occur in the samples.  $\text{Mn}^{3+}$  ions have been frequently reported as progressively involved when increasing the MnO content [16, 17]. It is observed (Fig. 5) that as well as broadening and also narrowing mechanisms is different for this two glass systems. Therefore, the  $\text{Cd}^{2+}$  and  $\text{Sr}^{2+}$  ions determine the different structure of the glass matrix ( $2\text{B}_2\text{O}_3 \cdot \text{MO}$ ) in which they play the modifiers role of the glass network.

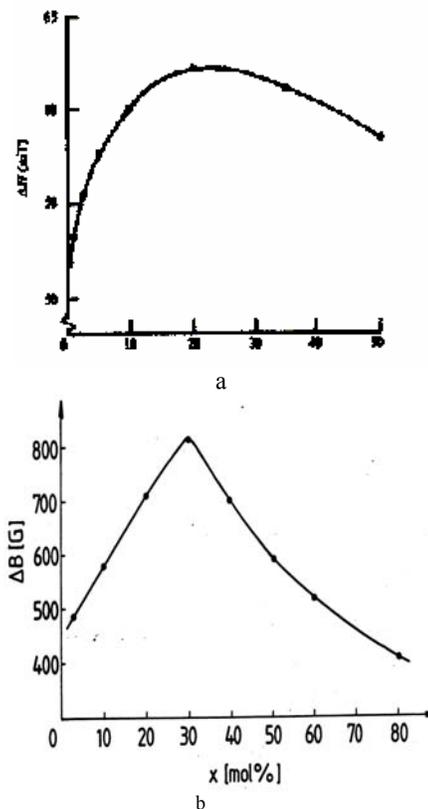


Fig. 5. The composition dependence of the peak-to-peak line width of the  $g_{\text{eff}} \approx 2.0$  absorption for glasses containing CdO (a) and SrO (b).

There are also distorted sites of  $\text{Mn}^{2+}$  ions in octahedral vicinities subjected to strong crystal field effects. These give rise to absorption lines at  $g_{\text{eff}} \approx 4.3$  and  $g_{\text{eff}} \approx 3.3$  (Fig. 1 and 2). These resonance lines are less intense and their hfs is unresolved. There is a relative

small concentration of  $\text{Mn}^{2+}$  ions involved in such structural units. Superimposed on  $g_{\text{eff}} \approx 4.3$  broad absorption line the narrow, well resolved line corresponding to accidental impurities of  $\text{Fe}^{3+}$  ( $3d^5$ ,  ${}^6\text{S}_{5/2}$ ) ions was also detected (Fig. 1 and 2). The lack of hfs at the  $g_{\text{eff}} \approx 4.3$  and  $g_{\text{eff}} \approx 3.3$  absorption lines is due to fluctuations of the ligand field parameters in the paramagnetic ion neighborhood and the random distribution of the octahedral vicinity distributions [4]. Some of the low-symmetric centers no longer contribute to the isotropic absorption and the resulting EPR line is broadened due to anisotropy and the ligand parameters distribution [18]. The absorption lines at  $g_{\text{eff}} \approx 4.3$  and  $g_{\text{eff}} \approx 3.3$  reach their maximum intensity at about 5 mol% MnO in these two glass system. The increase in the MnO content reduces the possibility for  $\text{Mn}^{2+}$  to structure their vicinity so that structural units involving  $\text{Mn}^{2+}$  ions in low symmetric crystal field sites become less well represented and the paramagnetic ions are gradually involved in clusters. This clustering process generalizes for concentrations exceeding 20 mol% MnO in case of glasses containing CdO and 10 mol% MnO in case of SrO.

From the variety of symmetries efficient in splitting the  ${}^6\text{S}_{5/2}$  state the tetragonal and tetragonally distorted cubic vicinities are of particular interest and give theoretical isotropic  $g_{\text{eff}}$  values of 4.285 and 3.3 very close to the experimentally detected [18]. These values correspond to transition within the lowest field approximation.

#### 4. Conclusions

EPR absorption due to  $\text{Mn}^{2+}$  ions were detected in  $x\text{MnO}\cdot(100-x)[2\text{B}_2\text{O}_3\cdot\text{MO}]$  ( $\text{MO} \rightarrow \text{CdO}$  or  $\text{SrO}$ ) glasses within a large concentration range, i. e.  $0.5 \leq x \leq 50$  mol%. In the low concentration range, the  $\text{Mn}^{2+}$  ions were identified in sites of octahedral symmetry slightly tetragonally distorted. They give rise to intense absorption lines centered at  $g_{\text{eff}} \approx 2.0$  showing well resolved hfs up to  $\approx 3$  mol% MnO.  $\text{Mn}^{2+}$  ions in tetragonal sites give resonance lines at  $g_{\text{eff}} \approx 4.3$  and  $g_{\text{eff}} \approx 3.3$ . Their intensity is small enough to indicate a relatively low concentration of  $\text{Mn}^{2+}$  ions involved in such structural units.

The intensity and line – width of  $g_{\text{eff}} \approx 2.0$  resonance absorption depends in different way for glasses containing CdO or SrO. In case of glasses with CdO the intensity of this absorption line increase progressively with MnO content, but in SrO containing glasses that increase up to 20 mol% after decrease. The line-width dependence of the MnO content indicate that in the glasses containing CdO the dipolar interactions between  $\text{Mn}^{2+}$  ions occur up to 20 mol % MnO, but in that containing SrO only up to 10 mol % MnO. At the higher content of MnO in both glass systems occur superexchange interactions. These results indicate that the valence states and interactions of the manganese ions is different in these two glass matrices ( $2\text{B}_2\text{O}_3 \cdot \text{MO}$ ) ( $\text{MO} \rightarrow \text{CdO}$  or  $\text{SrO}$ ).

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