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STRUCTURAL AND MAGNETIC INVESTIGATIONS OF MANGANESE IONS IN $2B_2O_3 \cdot As_2O_3$ GLASS MATRIX

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Glasses of the $xMnO \cdot (100-x)[2B_2O_3 \cdot As_2O_3]$ system with $0 < x \leq 50$ mol % were investigated by means of electron paramagnetic resonance (EPR) and magnetic susceptibility measurements,. EPR of Mn^{2+} ions revealed their distribution on different structural units of $2B_2O_3 \cdot As_2O_3$ glass matrix doped with MnO. Distorted octahedral sites were detected. The progressive clustering of Mn^{2+} ions was evidenced for $x \geq 5$ mol %. Magnetic data revealed both 2+ and 3+ valence states for the manganese ions simultaneously present in the vitreous matrix for $x > 1$ mol %. The transition from isolated ions ($x < 1$ mol %) to those involved in dipole-dipole interactions ($x < 5$ mol %) and to antiferromagnetically coupled pairs ($x \geq 5$ mol %) was revealed.

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1. Introduction

There are many reports concerning the investigation of the valence states and the distribution of the transition metal ions (TMIs) in the network of oxide glasses, which depend on the glass matrix nature [1], preparation conditions [2] and nature of the TMIs [3].

The ESR absorption spectra due to paramagnetic ions in vitreous matrices are recommended as valuable in revealing the structural details of the diamagnetic host, the coordination and valence state of these ions. Manganese ions have been frequently used as paramagnetic probes for exploring the structure and properties of vitreous systems. Many oxide glasses such as borate [4-6], alkali-silicate [7] aluminium-silicate or phosphate [8], tellurite [9] and also chalcogenide [10] or halide [11] containing Mn^{2+} ions have been investigated by ESR.

The magnetic properties of oxide glasses containing manganese have been investigated in potassium – [3], lithium – [12], strontium – [13], lead – [14], cadmium – [15] – borate and also in tellurite [16] and bismuthate [17-19] systems. The type and strength of magnetic interactions concerning manganese were determined in various concentration range. Besides Mn^{2+} ions, the Mn^{3+} species are often detected [13, 17, 20].

This paper aims to present the results concerning the EPR and magnetic susceptibility measurements of MnO-B_2O_3-As_2O_3 glass system in order to obtain further information on the distribution and valence state of manganese ions in $2B_2O_3 \cdot As_2O_3$ glass matrix.

2. Experimental

We have prepared $xMnO \cdot (100-x)[2B_2O_3 \cdot As_2O_3]$ glasses with $0 < x \leq 50$ mol % using pure reagent grade $MnCO_3$, H_3BO_3 and As_2O_3. The mixtures, in suitable proportions corresponding to the

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desired concentration of MnO, were mechanically homogenized and melted in sintered corundum crucibles in an electric furnace, at 1200 °C. The molten material was kept at this temperature 0.5 h, then quenched at room temperature by pouring onto a stainless-steel plate. The structure of samples was analyzed by means of X-ray diffraction. The pattern obtained did not reveal any crystalline phase in the glasses up to 50 mol %.

EPR absorption spectra were obtained using a SEX-201/RADIOPAN spectrometer, at room temperature, in the X-frequency band (9.4 GHz).

Magnetic susceptibility measurements were performed in the 80-300 K temperature range, using a Faraday-type balance.

3. Results and discussion

The resonance absorptions are due to the Mn^2 ($3d^5$, $^6S_{5/2}$) ions entering the matrix as paramagnetic species. The detected spectra are presented in Fig. 1. Their shape depend on the MnO content of the samples. The estimated EPR parameters of the resonance line were the peak-to-peak width, ΔB, the line amplitude I and the intensity approximated by $J = I(\Delta B)^2$. Their corresponding concentration dependencies are presented in Fig. 2.

Table 1. Molar Curie constants, effective magnetic moments, paramagnetic Curie temperatures and molar fractions of Mn^{2+} and Mn^{3+} ions for $xMnO\cdot(100-x)$ $[2B_2O_3\cdot As_2O_3]$ glasses.

x [mol % MnO]	C_M [emu/mol]x10^2	μ_{eff} [μ_B]	θ_p [K]	x_1 [mol% $Mn^{2+}O$]	x_2 [mol% $Mn^{3+}O$]
1	4.39	5.92	0	1	-
3	12.83	5.84	0	2.7	0.3
5	29.90	5.76	0	4.1	0.9
10	39.35	5.60	-8	6.6	3.4
20	75.22	5.48	-22	10.7	9.3
35	123.44	5.31	-44	12.9	22.1
50	164.89	5.14	-65	10.2	39.8

The temperature dependence of the reciprocal magnetic susceptibility of the investigated glasses is presented in Fig. 3. The composition dependencies of the molar Curie constant, C_M, and the paramagnetic Curie temperature, θ_p, are given in Table 1. The effective magnetic moments of manganese ions were estimated as $\mu_{eff} = 2.827\,(C_M/x)^{1/2}$. The obtained values of μ_{eff} for samples with $x \geq 1$ mol % (Table 1) lie between those corresponding to Mn^{2+} and Mn^{3+} in free ions state, i.e.: $\mu_{Mn^{2+}} = 5.92\ \mu_B$ and $\mu_{Mn^{3+}} = 4.90\ \mu_B$. Both valence states are supposed to be present in the glasses for $1 \leq x \leq 50$ mol %. The molar fraction of manganese ions in these two possible valence states were estimated in first approximation using relations:

$$x\mu_{eff}^2 = x_1\mu_{Mn^{2+}}^2 + x_2\mu_{Mn^{3+}}^2 \quad (1)$$

and

$$x = x_1 + x_2\ ,$$

where x_1 and x_2 are the molar fraction of Mn^{2+} and Mn^{3+} ions, respectively. The obtained values are given in Table 1.

The detected spectra exhibits a line centered at $g \cong 2.0$ having the main contribution to the EPR absorption (Fig. 1). At low manganese content ($x \leq 1$ mol %), the characteristic hyperfine structure (hfs) due to interaction with the nuclear spin I = 5/2, was resolved. The resolution decreases when the concentration increases, due to the ligand field fluctuations in the vicinity of the Mn^{2+} ion

and due to dipolar interactions. The absorption signals having a resolved hfs are due to isolated Mn^{2+} ions in sites of octahedral symmetry, poorly distorted. The strongly distorted versions of such vicinities give rise to the absorption lines at $g \cong 4.3$ representing the contribution to EPR of Mn^{2+} ions subjected to strong crystal field effects [9]. The most probable structural configurations at the origin of $g \cong 4.3$ signals are, in the case of Mn^{2+} ions, the octahedral ones, rhombically or tetragonally distorted [11]. For the investigated glasses the $g \cong 4.3$ lines were detected only at low Mn^{2+} ions concentration (Fig. 1a). Due to their extremely low intensity comparatively to those detected at $g \cong 2.0$, the lack of hfs, and their poor resolution, we may conclude that in glasses exists a small number of manganese ions involved in the above mentioned structural units and also great fluctuations in the crystal field parameters values, i.e. an appreciable structural variety of the corresponding units.

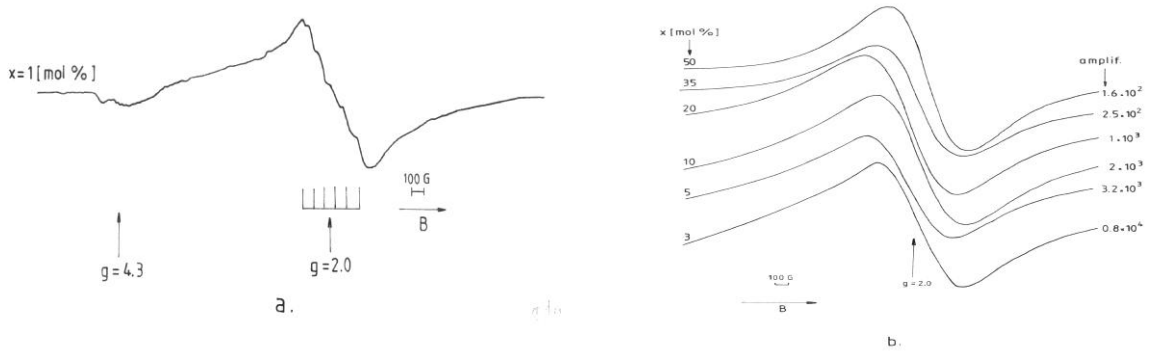


Fig. 1. EPR absorption spectra due to Mn^{2+} ions in $xMnO \cdot (100\text{-}x)[2B_2O_3 \cdot As_2O_3]$ glasses.

Even though the Mn^{2+} ions given rise to $g \cong 2.0$ absorption lines in their vicinity exist an appreciable crystal field distributions which explaining the poor resolution of hfs and its disappearance when increasing concentration. The line reduces to the envelope of contributions at resonance. Besides the ions involved in well defined units, there are those of "uncertain" vicinity, which are no longer strictly coordinated with the surrounding oxygens, giving rise to a broad structureless line. From magnetic data results that in the studied glasses are present Mn^{3+} ions when the MnO content increases. Without giving rise to an EPR absorption, these ions interact with the Mn^{2+} ones and, consequently, influence their resonance line. In such circumstances manganese ions become involved in magnetic clusters of Mn^{2+} and Mn^{3+} species.

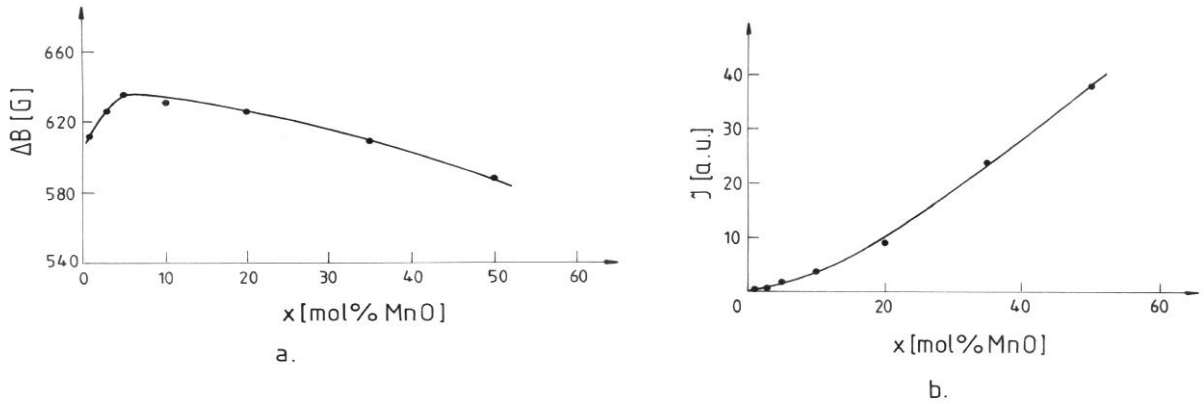


Fig. 2. Concentration dependence of the line-width (a) and the line-intensity (b) for signals at $g \approx 2.0$ in the EPR absorption spectra of Mn^{2+} ions in $xMnO \cdot (100\text{-}x)[2B_2O_3 \cdot As_2O_3]$ glasses.

The evolution of the EPR absorption line at $g \cong 2.0$ was revealed by the concentration dependence of its parameters (Fig. 2). The line-width (Fig. 2a) increases up to 5 % mol MnO due to

dipole-dipole interactions. For x > 5 mol % the line narrows suggest the presence of the superexchange-type magnetic interaction mechanisms between manganese ions. This assumption is confirmed by the magnetic data which revealed a change in the temperature dependence of the reciprocal magnetic susceptibility from a Curie-type behaviour characteristic to isolated magnetic ions or involved in dipolar interactions, to a Curie-Weiss-type one, specific to coupled ions by means of superexchange interactions (Fig. 3). This changement was evidenced at concentrations of about 5 mol % MnO. The negative values of θ_p indicate that these interactions are antiferomagnetic. The dependence of θ_p upon concentration (Table 1) shows an increasing of the absolute values for x > 5 mol % that reflects the increasing of the magnetic interactions with the increased number of involved manganese ions. This narrowing mechanism is balanced by the broadening ones, especially by the Mn^{2+}-Mn^{3+} dipolar interactions inside the clusters, and, consequently, the line-width decreasing for x > 5 mol % (Fig. 2a) is not very pronounced. According to Table 1 the Mn^{3+} ions content is appreciable in glasses with x ≥ 35 mol %. According to these data, it results that for x ≤ 1 mol % only Mn^{2+} ions are present in the studied glasses.

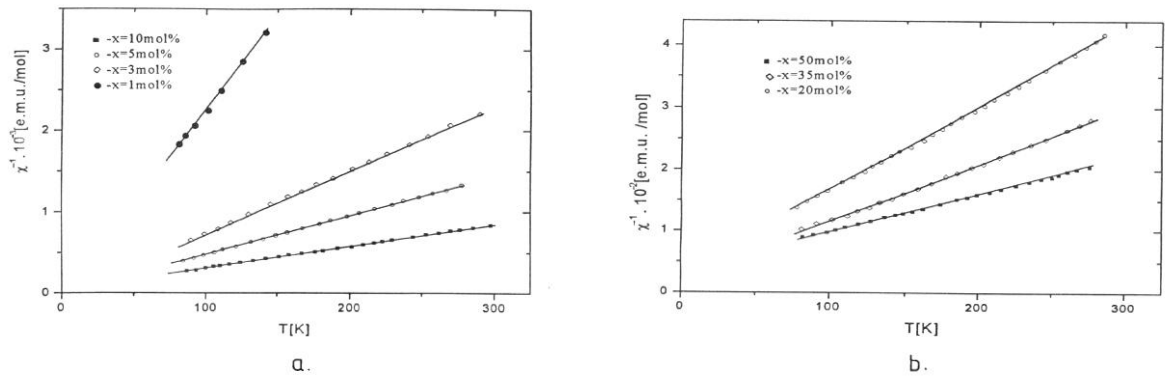


Fig. 3. Temperature dependence of the reciprocal magnetic susceptibility of some glasses of the system $xMnO\cdot(100-x)[2B_2O_3\cdot As_2O_3]$ for 1 ≤ x ≤ 10 mol % (a) and 20 ≤ x ≤ 50 mol % (b) concentration range.

The intensity of the absorption line increases progressively with the MnO content in the glasses, especially for x > 5 mol %, when passing from samples containing preponderantly isolated Mn^{2+} ions to those where magnetic clusters are prevalent (Fig. 2b). This evolution suggests that the intensity of the absorption line depends on the Mn^{2+} ions concentration, Mn^{2+}-Mn^{3+} interactions and degree of disorder in the studied glasses.

4. Conclusions

EPR absorption spectra due to Mn^{2+} were recorded for all studied glasses. Up to 1 mol % Mn^{2+} ions enters in the matrix involved in low-symmetric structural units subjected to strong crystal field effects, resulting in g ≅ 4.3 resonance lines. The high symmetric configurations of structural units involving Mn^{2+} ions give rise to the g ≅ 2.0 lines showing a resolved hfs. The matrix is not structurally stable when manganese accumulates in the glasses so that the concentration range of isolated Mn^{2+} ions in well defined structural units is relatively narrow and hfs rapidly smears out. Broaden unresolved lines at g ≅ 2.0 due to cluster formation show manganese as agglomerated in disordered vicinities for x > 5 mol %. For such compositions the magnetic susceptibility data evidenced manganese ions as experiencing negative magnetic interactions and predominantly antiferromagnetic coupling. The superexchange mechanisms narrow the EPR resonance lines at g ≅ 2.0 but this narrowing is balanced by Mn^{2+}-Mn^{3+} interactions. The Mn^{3+} valence state was detected for glasses with x > 1 mol % by means of magnetic susceptibility measurements. Both valence states coexist for 1 < x ≤ 50 mol %, the molar fraction of Mn^{3+} ions exceeding that of Mn^{2+} ions for x ≥ 35 mol %.

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