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EPR and magnetic susceptibility studies of B_2O_3·BaO glass matrix dopped with iron ions

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EPR and magnetic susceptibility measurements have been performed on $xFe_2O_3\cdot(1\text{-}x)\,[3B_2O_3\cdot BaO]$ glasses with $0 < x \leq 50$ mol%. The influence of a gradual increase in Fe_2O_3 content on the glass matrix (B_2O_3·BaO) structure and magnetic interactions involved iron ions have been discussed. By EPR data, the Fe^{3+} ions in sites of distorted octahedral symmetry were evidenced. EPR and magnetic susceptibility results indicate that in studied glasses the iron ions participate at the dipolar or/and superexchange magnetic interactions. From magnetic data it was evidenced that the iron ions are in Fe^{3+} and Fe^{2+} valence state and are antiferomagnetic coupled, these are depending on the iron content of the glasses.

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1. Introduction

The study of the vitreous oxidic materials with transitional metals ions has been rapidly developed due to their application in different domains, in the last years. The borate glasses e.g. exhibit interesting structural properties [1].

The investigation of the properties of borate glasses with iron ions was an attraction point for the researchers due to the possibility of those existing in the valence states Fe^{3+} and Fe^{2+} [2, 3]. EPR of Fe^{3+} ($3d^5$, $^6S_{5/2}$) ions in vitreous matrices may provide useful information about the short-range ordering in the paramagnetic ion vicinity due to the fact that the EPR absorption spectra show distinct resonance lines for the ions involved in structural units of well-defined symmetry and those connected in clusters. It can be observed the microstuctural changes in the network matrix when the concentration of the iron ions increases and their distribution on different structural entities and valence states.

There are several sites symmetries appropiate to split the ground state level of Fe^{3+} ion in three doublets. The EPR absorption spectra being characterized by the $g \approx 4.3$ resonance line arising from the isotropic transition inside one of the Kramers doublets [4-6]. Resonance line at $g \approx 2.0$ may also occur, duet to the ions distributed in clusters which interact by superexchange coupling [6-8]. Useful information about the valence states and interaction involving the iron ions in vitreous systems were obtained by means of magnetic measurements. An antiferromagnetic coupling between iron ions has been reported in phosphate [3, 9], borate[2, 10], teluritte [11, 12] oxide glasses. The presence of both Fe^{3+} and Fe^{2+} ionic species was also evidenced. The antiferromagnetic behavior depends on the concentration range of iron, the glass matrix structure, the preparation conditions and the Fe^{3+} / Fe^{2+} ratio [13, 14].

The aims of this paper are to show the results obtained by EPR and magnetic susceptibility measurements performed on the $3B_2O_3$·BaO glass matrix doped with Fe_2O_3 .

2. Experimental

Glasses of the system $xFe_2O_3\cdot(1\text{-}x)\,[3B_2O_3\cdot BaO]$ were prepared using reagent grade purity of Fe_2O_3, H_3BO_3, and $BaCO_3$ in suitable proportion. The mixtures mechanically homogenized were melting in sintered corundum crucibles at 1250 °C for 30 minutes. The mixtures were put into the electrical furnace directly at this temperature. No crystalline phases were revealed by X-ray diffraction,up to 50 mol % Fe_2O_3.

The EPR measurements were recorded at room temperature in X band frequency (9.4 GHz) and 100 KHz field modulations with an ADANI Portable EPR PS 8400 type spectrometer. The same quantities of powdered samples were studied in fused tubular holders of the same caliber.

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

3. Results and discussion

3.1. EPR data

The detected EPR spectra for all the samples are presented in Fig. 1. It can be observed that the spectra are typical for the Fe^{3+} ($3d^5$, $^6S_{5/2}$) ions in vitreous oxide systems. The EPR spectra for the glasses exhibit two resonance lines centered at g ≈ 4.3 and g ≈ 2.0 having a strong dependence on the Fe_2O_3 content of the samples.

The resonance line at g ≈ 4.3 is due to Fe^{3+} ions which are isolated and/or participate to the dipolar interactions. The Fe^{3+} ions are situated in sites of distorted octahedral symmetry (rhombic or tetragonal) subjected to strong crystal effects [4-6, 15, 16].

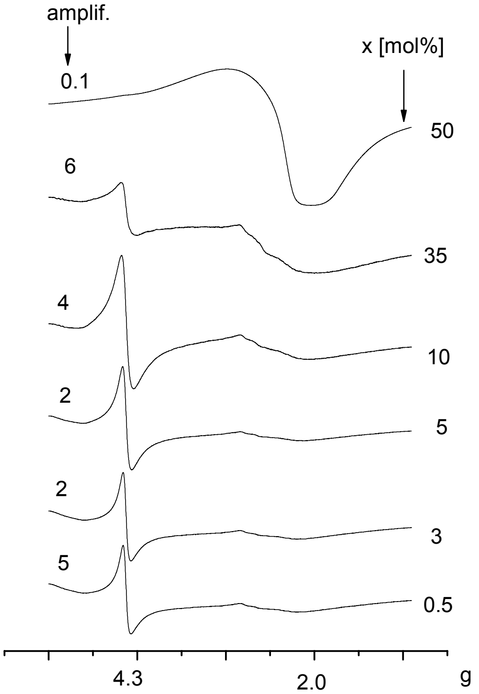

Fig. 1. EPR absorption spectra due to Fe^{3+} ions in $xFe_2O_3\cdot(1-x)\ [3B_2O_3\cdot BaO]$ glasses for $x \leq 50$ mol%.

The concentration dependence of the intensity, J, which was obtained as an integral of the area under the corresponding EPR signals and the line-width, ΔB, for the line at g ≈ 4.3 are presented in Fig. 2. The resonance line intensity at g ≈ 4.3 reaches a maximum value at about 5 mol % Fe_2O_3 and decreasing for higher content of iron ions (Fig. 2 (a)). The composition dependence of the absorption suggests the changes in Fe^{3+} neighborhood during the accumulation of iron ions in the matrix. The structural units of defined symmetry involving Fe^{3+} ions although randomly distorted, have at the origin the crystalline structure of glass matrix former, B_2O_3. These structural units assure the independence of the involved Fe^{3+} ions and their specific state of energy. The gradual increasing of the iron content in the matrix destroys the local ordering of the Fe^{3+} ion neighborhood, so the structural units as characteristic entities become less represented. As a result of these the line intensity at g ≈ 4.3 decreases. Compared to other vitreous oxide systems [17] studied before having a more compact structure than the borate ones the g ≈ 4.3 lines are well resolved being relative large in our spectra.

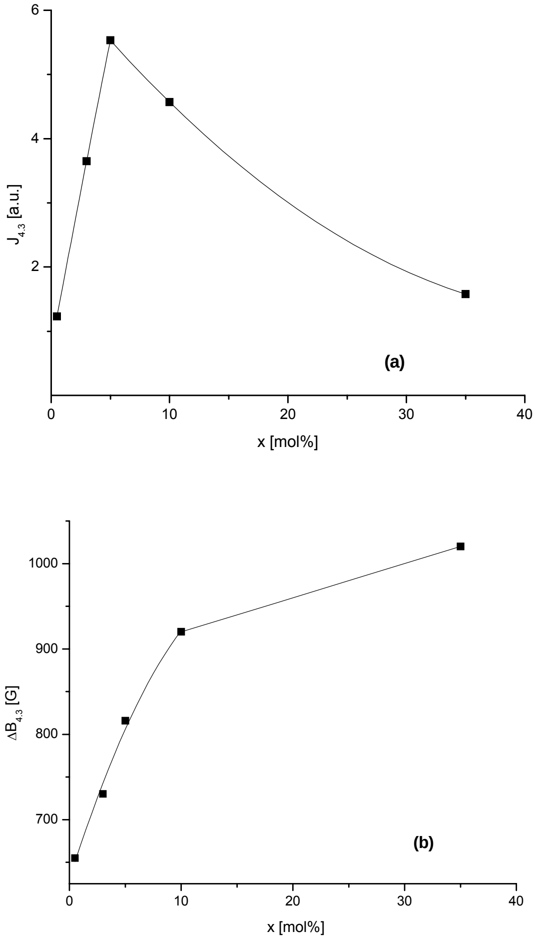

Fig. 2. Composition dependence of intensity (a) and the line-width (b) of the g ≈ 4.3 resonance absorption for the $xFe_2O_3\cdot(1-x)\ [3B_2O_3\cdot BaO]$ glasses.

The line-width at g ≈ 4.3 is increasing almost linear (Fig. 2 (b)) until x ≤ 10 mol% which suggests that the Fe^{3+} ions are involved in dipolar interaction responsible for the EPR line broadening [16]. For the higher content of Fe_2O_3 the increasing is very small, almost stops. In according with the decreasing of the line intensity for x > 5 mol% (Fig. 2 (a)) the stopping of ΔB increasing is due to the progressive decrease of the concentration of Fe^{3+} ions in structural vicinities giving rise to the g ≈ 4.3 absorption line.

The line intensity at g ≈ 2.0 increases up to x ≤ 10 mol% and decreases for higher content of iron ions (Fig. 3 (a)).

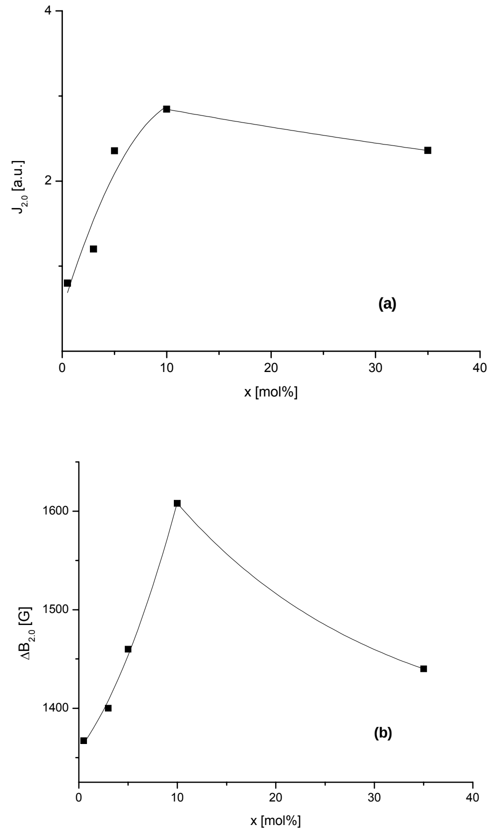

Fig. 3. Composition dependence of intensity (a) and the line-width (b) of the g ≈ 2.0 resonance absorption for the $xFe_2O_3{\cdot}(1-x)$ $[3B_2O_3{\cdot}BaO]$ glasses.

The composition dependence of line intensity suggests other valence states of iron ions, different from Fe^{3+} valence state, which do not contribute directly to the EPR absorption. This valence state of the iron ions, which can be Fe^{2+}, enters progressively in the matrix during the preparation process over 10 mol% content of Fe_2O_3. The interaction of the Fe^{3+} and the Fe^{2+} ions and the disorder of the glass structure determined by the increasing of the Fe_2O_3 content broaden this absorption line. The line-width dependence for the g ≈ 2.0 absorption line (Fig. 3 (b)) proves its cluster origin for x > 10 mol% showing narrowing effects due to exchange mechanisms. In other previously studied glasses [10, 18] the resonance line corresponding to the clustered Fe^{3+} ions appeared at lower concentrations, while other glasses do not show this line at all [17].

3.2. Magnetic susceptibility data

The temperature dependence of the reciprocal magnetic susceptibility for studied samples are presented in Fig. 4.

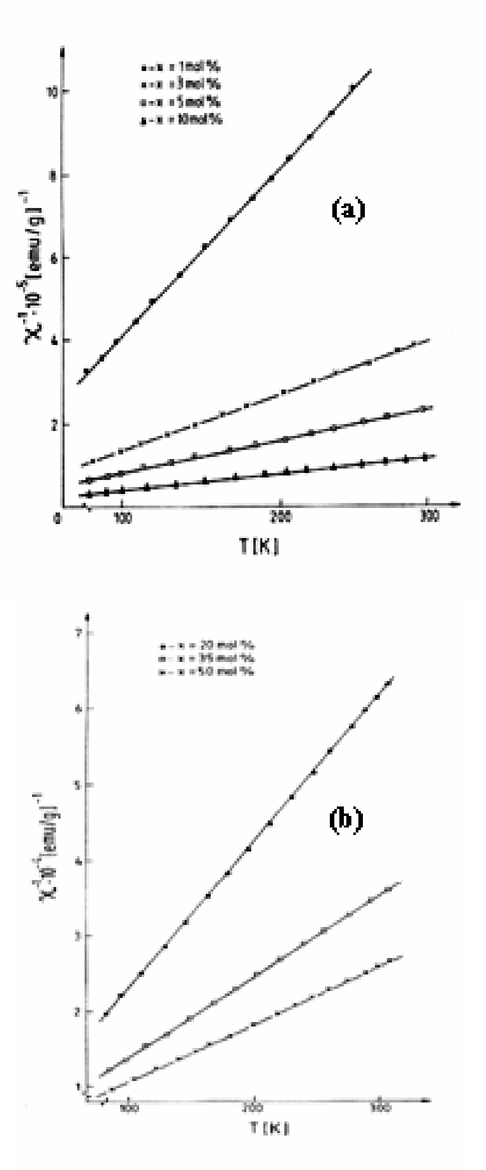

Fig. 4. Temperature dependence of the reciprocal magnetic susceptibility for $xFe_2O_3{\cdot}(1-x)$ $[3B_2O_3{\cdot}BaO]$ glasses(a) with $1 \leq x \leq 10$ mol% and (b) with $20 \leq x \leq 50$ mol%.

These data show a Curie-type behaviour for samples with x ≤ 10 mol % (Fig. 4(a)). For higher Fe_2O_3 content the temperature dependence of of the reciprocal magnetic susceptibility (χ^{-1}) is described by Curie-Weiss law with negative paramagnetic Curie temperature (θ_p) (Fig. 4(b)). This dependence suggests that for x ≤ 10 mol % are predominant the isolated iron ions and those which participate to the dipole-dipole interactions. For higher concentrations of Fe_2O_3 these data indicate that the iron ions in the glasses experience negative superexchange interactions and are predominantly antiferromagnetically coupled. Therefore, in the $3B_2O_3{\cdot}BaO$ glass matrix, the iron ions behave magnetically similarly as in lead- [2], cadmium- [19], strontium- [10] borate, phosphate [9, 14], lead- [20], antimony- [11, 12] tellurite and lead-bismuthate [21] oxide glasses. For samples with x > 10 mol% negative values of the paramagnetic Curie temperature were obtained, increasing in absolute magnitude with the iron ion concentration. This reflects an increase of the intensity of exchange interactions between iron ions and has narrowing effect upon the EPR absorption line.

The absolute magnitude of the values of θ_p increased x > 10 mol % (Fig. 5). In general the exchange integral increases as the concentration of the magnetic ions is increased in the glass [22]. As a result the absolute magnitude of the paramagnetic Curie temperature increases.

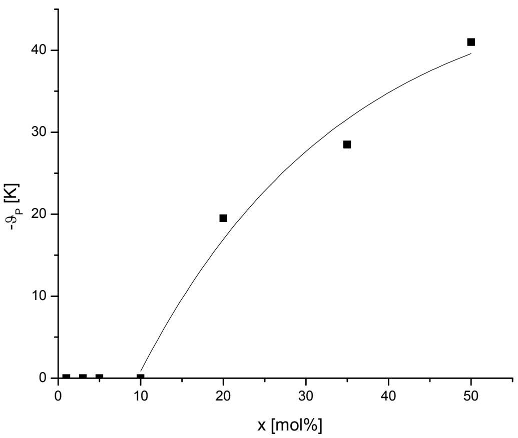

Fig. 5. Composition dependence of the paramagnetic Curie temperature.

To determine accurately the values of the Curie constants, a correction due to the diamagnetism of the glass matrix and Fe_2O_3 was taken into account. The composition dependence of the molar Curie constant (C_M) are presented in Table 1.

For x ≥ 20 mol % the experimental values obtained for molar Curie constants and consequently for effective magnetic moments are lower than those which correspond to Fe_2O_3 content, considering that all iron ions are in Fe^{3+} valence states. The two valence states of iron ions could be explained by the presence of B^{3+} and Ba^{2+} ions which form the basic vitreous network. The presence of Fe^{3+} and Fe^{2+} ions has been evidenced in other oxide glasses [2, 9-12, 19,20]. In this way we consider that in these glasses are presented both, Fe^{3+} and Fe^{2+} ions. Having in view this supposition and using the atomic magnetic moment values of isolated Fe^{3+} and Fe^{2+} ions: $\mu_{Fe^{3+}} = 5.92\,\mu_B$ and $\mu_{Fe^{2+}} = 4.90\,\mu_B$ [23], we can estimate in first approximation the molar fraction of these ions in the investigated glasses using the relations:

$$x \cdot \mu_{eff}^2 = x_1 \cdot \mu_{Fe^{3+}}^2 + x_2 \cdot \mu_{Fe^{2+}}^2$$

$$x = x_1 + x_2 \ ,$$

where $\mu_{eff} = 2.827[C_M/2x]^{1/2}$ are experimental effective magnetic moments, x_1 and x_2 the molar fraction of iron ions in Fe^{3+} and Fe^{2+} valence states. The results are presented in Table 1. According to the obtained data the glasses with x < 20 mol % contain only Fe^{3+} species while for glasses with higher Fe_2O_3 content the Fe^{3+} and Fe^{2+} ionic species coexist.

Table 1. Molar Curie constants C_M, experimental magnetic moment values μ_{eff} and molar fraction of iron ions $Fe^{3+}(x_1)$ and $Fe^{2+}(x_2)$ ions for $xFe_2O_3\cdot(1-x)$ $[3B_2O_3\cdot BaO]$ glasses.

x [mol %]	$C_M\cdot 10^2$ [emu/mol]	μ_{eff} [μ_B]	x_1 [mol % $Fe_2^{3+}O_3$]	x_2 [mol % $Fe_2^{2+}O_3$]
1	8.763	5.92	0	0
3	26.185	5.90	3	0
5	43.757	5.90	5	0
10	87.677	5.90	6	0
20	160.556	5.50	16	4
35	270.194	5.22	22	13
50	366.798	5.18	24	26

It was observed the progressive increasing for both Fe^{3+} and Fe^{2+} ions concentration with the increasing of the Fe_2O_3 content, the proportion of Fe^{2+} ions being prevalent for x > 35 mol %.

The magnetic properties of the studied glasses may be explained by dipolar and/or superexchange interactions within Fe^{3+} - Fe^{3+}, Fe^{3+} - Fe^{2+}, Fe^{2+} - Fe^{2+} ionic pairs.

4. Conclusions

Glasses of the system $xFe_2O_3\cdot(100\text{-}x)$ $[3B_2O_3\cdot BaO]$ were obtained in the range 0 < x ≤ 50 mol %.

EPR absorption spectra due to Fe^{3+} ions were detected within 0.5 ≤ x ≤ 50 mol%. The shape of the spectra and the values of the EPR parameters of resonance lines depend on the Fe_2O_3 content. The Fe^{3+} ions in sites of distorted octahedral symmetry subjected to strong crystalline field effects were detected, underline the structural stability of the vitreous matrix in receiving these ions.

The EPR and magnetic measurements revealed both dipolar and superexchange interactions involving iron ions. For the x > 10 mol% antiferromagnetically coupled iron ions were detected.

The Fe^{2+} ionic species was detected in samples with x ≥ 20 mol%, together with Fe^{3+} ions.

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