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Structural investigation of Fe_2O_3-B_2O_3-PbO-Ag_2O glass system by EPR spectroscopy

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Glasses of the $xFe_2O_3\cdot(100\text{-}x)[3B_2O_3\cdot(1\text{-}y)PbO\cdot yAg_2O]$ systems, with $0 < x \leq 20$ mol% and y = 0.1, 0.3, 0.5 were investigated by means of electronic paramagnetic resonance (EPR) measurements. The local order in diamagnetic vitreous matrices may be revealed by the Fe^{3+} paramagnetic ions used in EPR experiments. Following, in each system corresponding a value of y, the effect of increasing the Fe_2O_3 content in the samples was investigated. The shape of the EPR spectra of Fe^{3+} ($3d^5$; ${}^6S_{5/2}$) paramagnetic ions mainly consists in resonance absorptions centered at $g_{eff} \cong 4.3$ and $g_{eff} \cong 2.0$, their prevalence depending on the Fe_2O_3 content. The increasing of iron content in the samples generates the EPR absorption spectra modification, reflecting structural and magnetic interaction changes, the distribution and also different valence states of these ions in the glass matrices. The magnetic interactions between iron ions were also evidenced. The concentration range in which homogeneous glasses from studied systems are formed ($0 < x \leq 20$ mol%) isn't influenced on particular values of y. When increase the Ag_2O content in glasses matrices, the shape of EPR spectra is little modified. In addition, it observed a similitude concerning the way of variation from the characteristic parameters of resonance lines (J and ΔB) and also an increasing of values of these parameters at increasing of Ag_2O content.

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1. Introduction

In the last few years, there have been reported many studies about the structure and properties of borate glasses from both fundamental and application points of view [1,2]. Borates can form relative stable glasses, are relatively easy to obtain and are good matrices for transitional metals ions. In their structure appear a large variety of structural units over a wide range of modifiers concentration [1,3]. B_2O_3-PbO glasses have the desired characteristic against irradiation since the naturally occurring stable boron isotope is a good absorber of thermal neutrons and lead is known as a shielding material of γ-ray. The lead oxide (PbO) enhances the resistance against devitrification, improve the chemical durability and lower the melting temperature [4-7]. Glasses containing a large amount of silver show recently a great interest, due to the various interesting properties like high ionic conduction, chemical sensitivity and biomedical effect [8,9].

Structural properties of the vitreous systems were frequently studied by means of EPR, using Fe^{3+} ions as paramagnetic probes for revealing the local order in diamagnetic vitreous matrices [10-16]. EPR investigation may provide valuable information concerning the local structural details of vitreous matrices, due to the great sensitivity of the EPR absorption spectra to symmetry and strengths of the ligand field in the neighbourhood of paramagnetic ions. It is also possible to follow the structural changes in the matrix when iron ions concentration increase during a controlled doping process.

EPR spectra of Fe^{3+} ions in oxide glasses are generally characterized by the appearance of resonance absorption at $g_{eff} \cong 9.7$, 6.0, 4.28 and 2.0, their relative intensity being strongly dependent on composition [10-16]. The simultaneous presence of resonance absorption centered at $g_{eff} \cong 9.7$ and 4.28 shows a predominant rhombic character of the distorted octahedral symmetry sites of the Fe^{3+} ions [10,17]. The $g_{eff} \cong 6.0$ resonance line arises from axially distorted sites [11,18]. The $g_{eff} \cong 4.28$ resonance absorption is characteristic for isolated Fe^{3+} ions predominantly situated in rhombically distorted octahedral or tetrahedral oxygen environments [10,11,14]. The $_{eff} \cong 2.0$ resonance is assigned to those ions, which interact by dipole-dipole or superexchange coupling [12,13].

This work aims to present our results obtained by EPR measurements performed on $[3B_2O_3\cdot(1\text{-}y)PbO\cdot yAg_2O]$ glasses matrices (with y = 0.1, 0.3 and 0.5) gradually doped with Fe_2O_3.

2. Experimental details

Three series of samples from $xFe_2O_3\cdot(100\text{-}x)[3B_2O_3\cdot(1\text{-}y)PbO\cdot yAg_2O]$ system with y = 0.1, 0.3, 0.5 were prepared using pure reagent grade compounds, i.e. H_3BO_3, PbO, Ag_2O and Fe_2O_3 in suitable proportions. The mixtures were mechanically homogenized and melted in sintered corundum crucibles in an electric furnace at 1000ºC. For melting, the samples were put into the electric furnace directly at this temperature. The molten material was kept at this temperature for 15 minutes and then quenched at room temperature by pouring on the stainless-steel plates.

The structure of samples was analyzed by means of X-ray diffraction using a Bruker D8 ADVANCE X-ray Diffractometer. The pattern obtained did not reveal any crystalline phase in the samples up to 20 mol%.

EPR measurements were performed at room temperature using an ADANI Portable EPR PS 8400-type spectrometer, in the X frequency band (9.4 GHz) and a field modulation of 100 kHz. To avoid the alteration of the glass structure due to the ambient conditions, samples of equal quantities were enclosed immediately after preparation in the tubular holders of the same caliber.

3. Results and discussion

It is observed that the concentration range in which homogeneous glasses from studied system are formed ($0 < x \leq 20$ mol%) isn't influenced on particular values of y. Thus, in our system, the crystallized agent status of Ag_2O content wasn't evidenced.

Recorded EPR spectra show resonance lines due to Fe^{3+} ($3d^5; {}^6S_{5/2}$) paramagnetic ions for all investigated concentrations. As can be observed in Fig. 1 (a, b and c), the shape of the EPR spectra depends on the Fe_2O_3 content of the samples and is little influenced by the Ag_2O concentration in matrices. The spectra consist mainly of resonance lines centered at $g_{eff} \cong 4.3$ and $g_{eff} \cong 2.0$ values, their relative intensity depends on the iron content of the samples. For all the three systems, up to x = 5 mol%, the $g_{eff} \cong 4.3$ resonance line is prevalent in the spectrum, while for x > 5 mol% the $g_{eff} \cong 2.0$ resonance line become competitive. The resonance line at $g_{eff} \cong 4.3$ is due to the isolated Fe^{3+} ions situated in sites of rhombically distorted octahedral symmetry subjected to strong crystal field effects [11,14,19]. The $g_{eff} \cong 2.0$ line may be attributed either to Fe^{3+} species participating at the dipole-dipole interactions in sites of less tetrahedral distorted octahedral field or to superexchange coupled pairs [19,20].

The evolution of the resonance lines with increasing of iron ions content was followed in the dependence of the EPR characteristic parameters, i.e. the line intensity J (obtained as an integral of the area under the corresponding EPR signal) and peak-to-peak line-width, ΔB. The corresponding variations of these parameters are plotted in Figs. 2 and 3 for the resonance lines centered at $g_{eff} \cong 4.3$ and respectively $g_{eff} \cong 2.0$. For each case, the analyzed parameter (J and ΔB) presents the similar evolutions for all systems investigated, their effective values at the same x being higher for great values of y. This result may be attributed to the increasing of the Fe^{3+} ions concentration in the glasses structure following an increasing of the Ag_2O content in matrix, fact that releave the decisive status of vitreous matrix for distribution of Fe^{3+} ions in different structural sites that determine specific EPR absorption and nature/strength interactions between them.

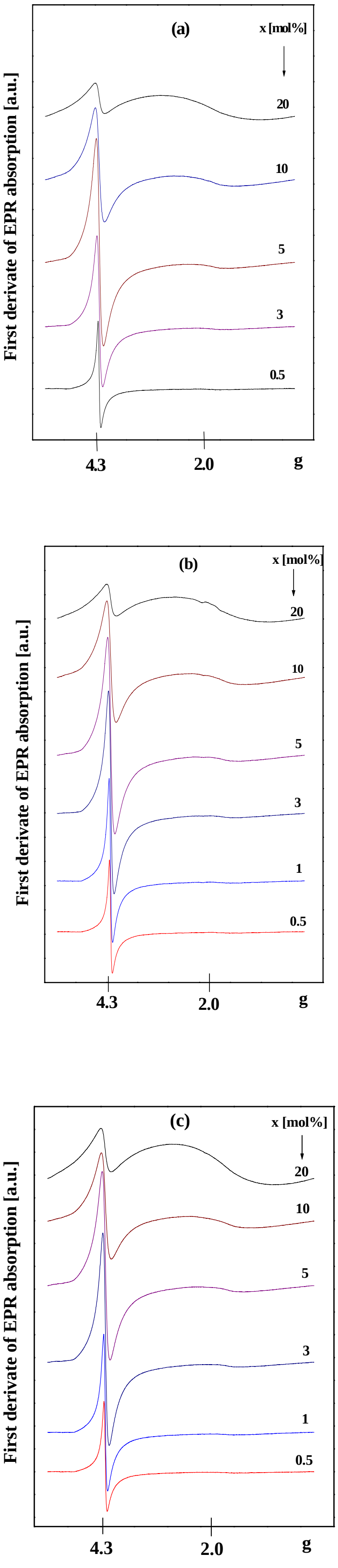

Fig. 1. EPR spectra of Fe^{3+} *ions for* $xFe_2O_3 \cdot (100-x)[3B_2O_3 \cdot (1-y)PbO \cdot yAg_2O]$ *glasses with* $y = 0.1$ *(a), 0.3 (b), 0.5 (c) and* $0.5 \leq x \leq 20$ *mol%.*

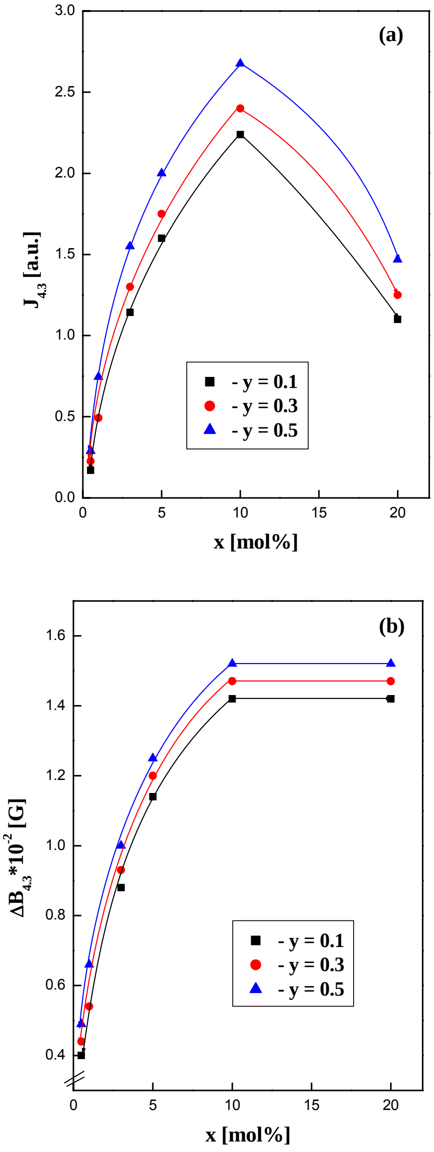

Fig. 2. Composition dependences of the line-intensity (a) and line-width (b) of resonance absorptions at g ≅ 4.3 for $xFe_2O_3\cdot(100-x)[3B_2O_3\cdot(1-y)PbO\cdot yAg_2O]$ glasses, with y = 0.1, 0.3, 0.5 and $0.5 \leq x \leq 20$ mol%.

The $g_{eff} \cong 4.3$ resonance line intensity has a complex dependence, showing an increasing in the concentration range $0.5 \leq x \leq 10$ mol% followed by a decreasing for x = 20 mol% (Fig. 2(a)). The structural units of defined symmetry involving Fe^{3+} ions so that those to be isolated have at the origin the structure of glass matrix former, B_2O_3. The decreasing of this resonance line intensity at the same time with the increasing of the Fe_2O_3 content is due to the modification of the configuration from the Fe^{3+} ions neighbourhoods, which no more assure their magnetic isolation. The line-width dependence of the $g_{eff} \cong 4.3$ lines (Fig. 2(b)) shows an increasing up to 10 mol% due to the increasing of Fe^{3+} ions concentration [19]. This increasing is stopped for higher concentration of Fe_2O_3, due to the progressive decrease of the concentration of Fe^{3+} ions disposed in structural configurations giving rise to the $g_{eff} \cong 4.3$ absorptions.

The composition dependence of the $g_{eff} \cong 2.0$ absorptions line intensity is presented in figure 3(a). In the concentration range $0.5 \leq x \leq 5$ mol%, the $g_{eff} \cong 2.0$ resonance line is very large, having a very small intensity. Over x = 5 mol%, the increasing of the Fe_2O_3 content in the samples determine an increasing of these line-intensity. Generally the signal intensity is proportional to the number of EPR active species involved in the resonance absorption, so the increase of the $g_{eff} \cong 2.0$ line intensity reflect seeming an increase of the Fe^{3+} ions concentration involved in new structural vicinities of glasses. Following, from analyse of the intensity variation with Ag_2O content (Fig. 3(a)) result that in studied glasses, at high concentration of Fe_2O_3, increasing of the Ag_2O content favorized rising of the Fe^{3+} ions number which participate at the $g_{eff} \cong 2.0$ resonance.

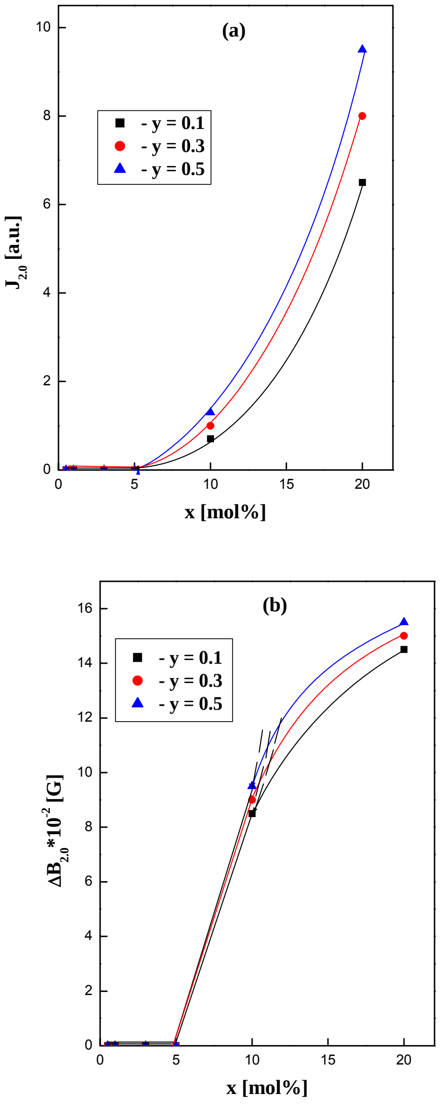

Fig. 3. Composition dependences of the line-intensity (a) and line-width (b) of resonance absorptions at g ≅ 2.0 for $xFe_2O_3\cdot(100-x)[3B_2O_3\cdot(1-y)PbO\cdot yAg_2O]$ glasses, with y = 0.1, 0.3, 0.5 and $0.5 \leq x \leq 20$ mol%.

The line-width of the $g_{eff} \cong 2.0$ lines depends also on the Fe_2O_3 concentration (Fig. 3(b)). The line-width increasing for $5 \leq x \leq 10$ mol% of $g_{eff} \cong 2.0$ resonance is due to the dipole-dipole interactions. For higher concentrations of Fe_2O_3, the line-width increase, but their slope decrease. This fact show that a part of the Fe^{3+} ions participate at the superexchange interactions, which determine narrowing of this resonance line. Also, increasing of the Ag_2O concentration in the studied glasses, at high concentrations of Fe_2O_3, determine increasing of the line-width for these line, and through following decreases of the intensity for superexchange interactions. From J and ΔB dependences presented in figure 3 result that the increasing of the Ag_2O content determine increases of disorder in the studied glasses.

4. Conclusions

Homogeneous glasses of the three systems $xFe_2O_3 \cdot (100-x)[3B_2O_3 \cdot (1-y)PbO \cdot yAg_2O]$, with y = 0.1, 0.3 and 0.5 were obtained over the $0 \leq x \leq 20$ mol% iron oxide concentration range.

EPR absorption spectra due to Fe^{3+} ions were recorded within $0.5 \leq x \leq 20$ mol%. The shape of the spectra and the values of the EPR parameters of resonance lines depend on the Fe_2O_3 concentration. At the same time, the Ag_2O content influenced little the shape of EPR spectra, what is reflected by values of characteristic parameters of the resonance lines. This influence consists in increasing of the J and ΔB values at the same time with increasing of the y.

The isolated Fe^{3+} in sites of distorted octahedral symmetry subjected to strong crystalline field effects ($g_{eff} \cong 4.3$) were detected over a relatively broad concentration range, attesting the structural stability of the vitreous matrix in receiving these ions.

The EPR measurements revealed both dipolar and superexchange type interactions involving Fe^{3+} ions ($g_{eff} \cong 2.0$). For all the samples with x > 10 mol%, a fraction of the Fe^{3+} ions participate at superexchange interactions and the intensity of these interactions decreases with increasing of the Ag_2O content.

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