JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 4, April 2007, p. 840 - 843

EPR investigation of Fe_2O_3-B_2O_3-PbO-Ag_2O glass system

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Glasses of the $xFe_2O_3\cdot(100-x)[3B_2O_3\cdot 0.5PbO\cdot 0.5Ag_2O]$ system, with $0 < x \leq 20$ mol%, were investigated by means of EPR measurements. Started from the $xFe_2O_3\cdot(100-x)[3B_2O_3\cdot PbO]$ vitreous system, the effect of the partial substitution of PbO by Ag_2O as a glass matrix modifier was investigated. Diminishing the concentration range in which the homogeneous glasses are formed, from $0 \leq x \leq 50$ mol% (in the case of Fe_2O_3-B_2O_3-PbO system) at $0 \leq x \leq 20$ mol% (in the case of Fe_2O_3-B_2O_3-PbO-Ag_2O system) confirm the crystallized agent status for Ag_2O. The EPR spectra structure of Fe^{3+} ions mainly consists in absorption resonance centered at $g \approx 4.3$ and $g \approx 2.0$, 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 changes, the distribution and also different valence states of iron ions in the glass matrix. The magnetic interactions between iron ions were investigated.

(Received November 2, 2006; accepted February 28, 2007)

Keywords: Silver-lead-borate glasses; iron ions; local structure; EPR

1. Introduction

Glasses are materials that have an unlimited theoretical variety of compositions. This is the reason why their properties are very different, fact that leads to a large area of applications. An example is the borate glasses: today, they are an important material for insulation (glass wool) and textile (continuous filament) fiberglass. In the last few years, there have been reported many studies about the structure and properties of borate glasses from both fundamental and industrial points of view [1,2]. Borates are relative stable glasses, representing good matrices for transitional metals ions. The proportions of transitional metals ions that are accepted in glass structure without forming crystalline microprecipitates depend on transitional ion nature and concentration [2], matrix composition [3] and melting temperature [4]. 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. Glasses containing a large amount of silver are known to show various interesting properties like high ionic conduction and biomedical effect [5].

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. In this way, the Fe^{3+} ions are largely used as paramagnetic probes for revealing the local order in diamagnetic vitreous matrices [6-12]. EPR spectra of Fe^{3+} ions in oxide glasses are generally characterized by the appearance of resonance absorption at $g \approx 9.7$, 6.0, 4.28 and 2.0, their relative intensity being strongly dependent on composition [6-12]. The simultaneous presence of resonance absorption centered at $g \approx 9.7$ and 4.28 shows a predominant rhombic character of the distorted octahedral symmetry sites of the Fe^{3+} ions [6,13]. The $g \approx 6.0$ resonance line arises from axially distorted sites [7,14]. The $g \approx 4.28$ resonance absorption is characteristic for isolated Fe^{3+} ions predominantly situated in rhombically distorted octahedral or tetrahedral oxygen environments [6,7,10]. The $g \approx 2.0$ resonance is assigned to those ions, which interact by dipole-dipole or superexchange coupling [8,9].

This paper aims to present our results obtained by EPR measurements performed on

$3B_2O_3\cdot 0.5PbO\cdot 0.5Ag_2O$ glass matrix gradually doped with Fe_2O_3. Also, we discussed the similarities and differences that appear in behaviour of the studied glasses comparative to glasses of the $xFe_2O_3\cdot(100-x)[3B_2O_3\cdot PbO]$ system [9], due to the partial substitution of PbO by Ag_2O.

2. Experimental details

$xFe_2O_3\cdot(100-x)[3B_2O_3\cdot 0.5PbO\cdot 0.5Ag_2O]$ glasses have been prepared using pure reagent grade compounds, i.e. Fe_2O_3, H_3BO_3, PbO and Ag_2O. The mixtures, in suitable proportions corresponding to the desired concentration of Fe_2O_3, 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 onto a stainless steel plate.

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 with an Adani Portable EPR Spectrometer

PS8400, in the X-frequency band (9.4 GHz) and field modulation 100 kHz. Powdered samples were studied in tabular holders of the same caliber and quantity.

3. Results and discussion

The EPR absorption spectra were measured for the $xFe_2O_3\cdot(100-x)[3B_2O_3\cdot 0.5PbO\cdot 0.5Ag_2O]$ glasses with $0.5 \le x \le 20$ mol%. The spectra of Fe^{3+} ($3d^5$; ${}^6S_{5/2}$) paramagnetic ions consists in resonance lines centered at $g \approx 4.3$ and $g \approx 2.0$ having strong concentration dependence (fig. 1). Their prevalence in the spectrum depends on the Fe_2O_3 content. Up to x = 5 mol%, the $g \approx 4.3$ resonance line are predominant, while for x > 5 mol% the $g \approx 2.0$ resonance line become competitive.

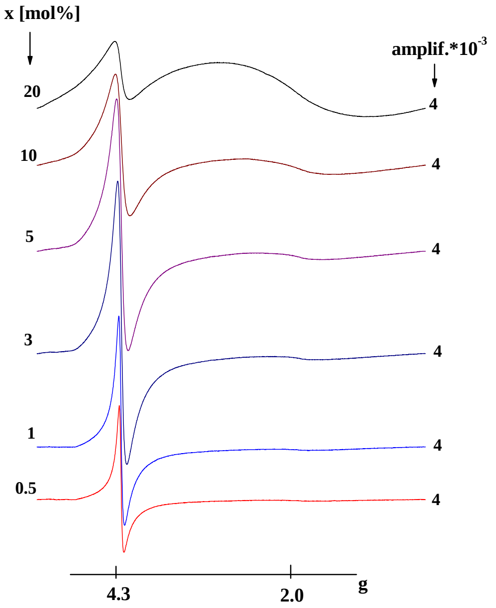

Fig. 1. EPR absorption spectra of Fe^{3+} ions in $xFe_2O_3\cdot(100-x)[3B_2O_3\cdot 0.5PbO\cdot 0.5Ag_2O]$ glasses.

The resonance line at $g \approx 4.3$ is due to the isolated Fe^{3+} ions situated in sites of rhombically distorted octahedral symmetry subjected to strong crystal field effects [7,10,15]. The $g \approx 2.0$ line may be attributed either to Fe^{3+} species interacting by dipole-dipole interaction in sites of less tetrahedral distorted octahedral field or to superexchange coupled pairs [15,16].

The evolution of the resonance lines with increasing of iron ions content was followed in the dependence of the EPR parameters, i.e. the line intensity, J 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 $g \approx 4.3$ and respectively $g \approx 2.0$.

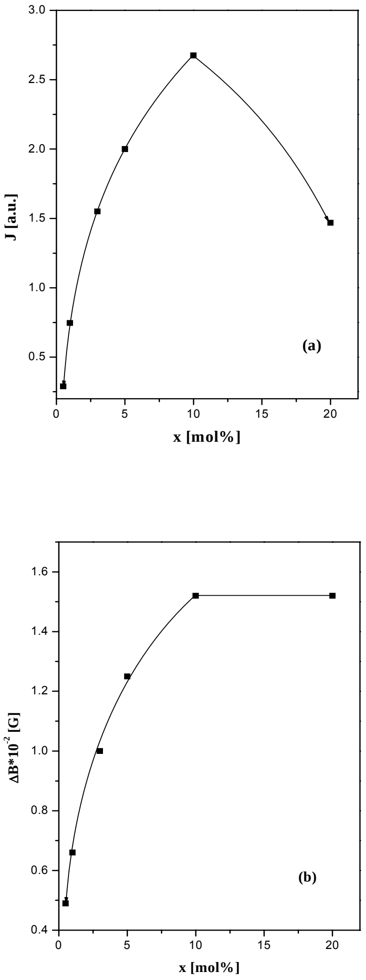

Fig. 2. Composition dependences of the line-intensity (a) and line-width (b) of resonance absorptions at $g \approx 4.3$ for $xFe_2O_3\cdot(100-x)[3B_2O_3\cdot 0.5PbO\cdot 0.5Ag_2O]$ glasses.

The $g \approx 4.3$ resonance line intensity has a complex evolution, showing a quasi-linear increasing in the concentration range $0.5 \le x \le 10$ mol% followed by a decreasing for x > 10 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 destruction of the configuration from the iron ions neighbourhoods, which ensures their magnetic isolation. The line-width evolution of the $g \approx 4.3$ lines (Fig. 2(b)) shows an increasing up to 10 mol% due to increasing of Fe^{3+} ions concentration [15]. 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 vicinities giving rise to the $g \approx 4.3$ absorptions.

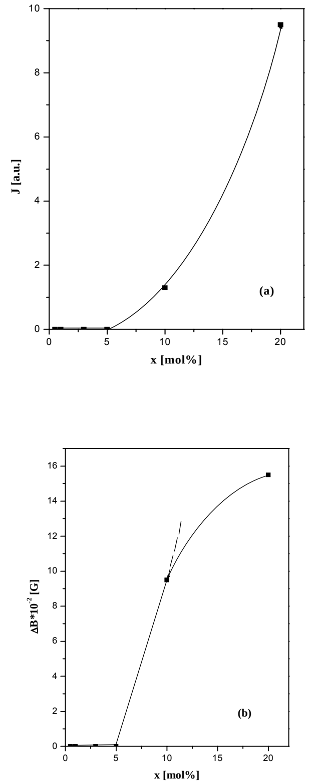

Fig. 3. Composition dependences of the line-intensity (a) and line-width (b) of resonance absorptions at g ≈ 2.0 for $xFe_2O_3\cdot(100\text{-}x)[3B_2O_3\cdot0.5PbO\cdot0.5Ag_2O]$ glasses

The composition dependence of the g ≈ 2.0 absorptions intensity is presented in fig. 3(a). In the concentration range $0.5 \leq x \leq 5$ mol%, the g ≈ 2.0 resonance line is very large and with short intensity. Over x = 5 mol%, the increasing of the Fe_2O_3 content in the samples determine an increasing of the 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 ≈ 2.0 line intensity reflect seeming an increase of the Fe^{3+} ions concentration involved in new structural vicinities of glasses. The line-width of the g ≈ 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 ≈ 2.0 resonance is due to dipole-dipole interactions between Fe^{3+} ions, but does not exclude the increase of disorder in the glass structures or/and the presence of magnetic interaction between iron ions in different valence states. For higher concentrations of Fe_2O_3, the line-width linearly increases and evidences the Fe^{3+} ions participation at superexchange magnetic interactions, which leads to the narrowing of this resonance line.

For a comparative discussion between our studied glass, $xFe_2O_3\cdot(100\text{-}x)[3B_2O_3\cdot0.5PbO\cdot0.5Ag_2O]$ (S_1) and the similar system without Ag_2O in matrix, $xFe_2O_3\cdot(100\text{-}x)[3B_2O_3\cdot PbO]$ (S_2), it is necessary to present the main results obtained for system S_2 [9].

The EPR absorption spectra obtained for Fe^{3+} ions in the $3B_2O_3\cdot PbO$ glass matrix are presented selectively in Fig. 4. It can be remarked that in this case appear resonance lines centered at g ≈ 6.0, 4.3 and 2.0, their evolution being strongly dependent on composition.

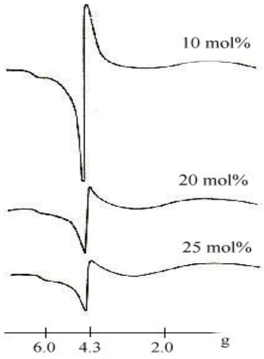

Fig. 4. EPR absorption spectra of Fe^3 ions in $xFe_2O_3\cdot(100\text{-}x)[3B_2O_3\cdot PbO]$ glasses.

In the analysis of results was ignored the g ≈ 6.0 resonance line because it has low intensity, due to the implication in these absorption of a small number of the isolated Fe^{3+} ions. The resonance absorptions from systems S_1 and S_2 are of the same nature.

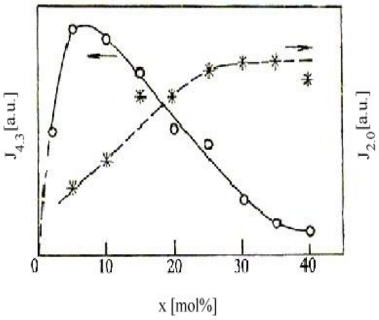

Fig. 5. Composition dependences of the line-intensity of resonance absorption at g ≈ 4.3 (o) and g ≈ 2.0 (*) for $xFe_2O_3\cdot(100\text{-}x)[3B_2O_3\cdot PbO]$ glasses.

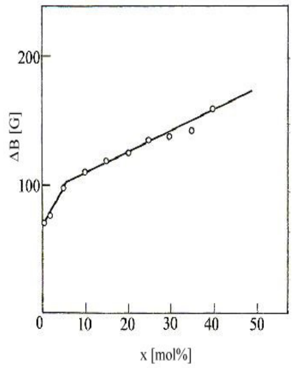

Fig. 6. Composition dependences of the line-width of resonance absorption at g ≈ 4.3 for $xFe_2O_3\cdot(100\text{-}x)[3B_2O_3\cdot PbO]$ glasses.

In Fig. 5 are presented the dependence on composition of line-intensity for g ≈ 4.3 and g ≈ 2.0 resonance. In the case of g ≈ 4.3 absorption resonance, corresponding to isolated ions, the line-intensity increases up to ≅5 mol%, then gradually decreases with increasing of the Fe_2O_3 content. The line-intensity of g ≈ 2.0 absorption resonance increases quasi-linearly with the increase of the Fe_2O_3 content, up to ≅25 mol%, followed by the modification of the curve slope. Over 25 mol%, the line-intensity increase is very small. In Fig. 6 was presented on the dependence composition - line-width for g ≈ 4.2 absorption. This dependence is linear and presents a change of slope at 5 mol%. It is necessary to mention that the line-width of g ≈ 2.0 absorption is very large (~10^3 G), that is why the estimation of Fe^{3+} ions number implicated in this absorption are realized with high error [9].

A first observation that can be made is related to the decreasing of the concentration range in which the homogeneous glasses are formed, from $0 \leq x \leq 50$ mol% in case of system S_2, at $0 \leq x \leq 20$ mol% in case of system S_1, due to the partial substitution of PbO by Ag_2O in the glassy matrix. This result, obtained by means of X-ray diffraction, confirms the crystallized agent status for Ag_2O. It is possible that the vitreous network of glasses from the system S_2 to be more disordered comparatively with the network from system S_1.

Through comparative analyses of EPR absorption spectra of Fe^{3+} ions in case of mentioned systems one remarks the presence of the lines centered at g ≈ 4.3 and g ≈ 2.0. Their characteristic parameters (J, ΔB) varied in different way depending on Fe_2O_3 content. Also, in the case of system S_2 are present the g ≈ 6.0 resonance absorption, even exhibits weak intensity. Following, depending on Fe_2O_3 content, the glass structure from system S_1 permits to a number of Fe^{3+} ions to be disposed in sites with neighbourhoods which ensures their magnetic isolation, dipole-dipole and, respectively, superexchange magnetic interactions.

The analyzed results indicate the fact that vitreous matrix status (in this the case presence of Ag_2O in the matrix) is decisive for distribution of iron ions in different structural sites that determine specific EPR absorptions.

4. Conclusions

Glasses of the system $xFe_2O_3\cdot(100-x)[3B_2O_3\cdot0.5PbO\cdot0.5Ag_2O]$ were obtained over the $0 \leq x \leq 20$ mol% concentration range.

EPR absorption spectra due to Fe^{3+} ions were detected within $0.5 \leq x \leq 20$ mol%. The structure of the spectra and the values of the EPR parameters of resonance lines depend on the Fe_2O_3 concentration. The isolated Fe^{3+} ions situated in the sites of distorted octahedral symmetry subjected to strong crystalline field effects were detected over a relatively broad concentration range, confirming the structural stability of the vitreous matrix when these ions are received.

The EPR measurements revealed both dipolar and superexchange type interactions involving iron ions.

The principal difference observed between systems S_1 and S_2 consists in diminishing the concentration range in which the homogeneous glasses are formed, in the case of system S_1, due to the introduction of Ag_2O in $3B_2O_3\cdot PbO$ glass matrix. The partial substitution of PbO by Ag_2O in S_1 leads to a relative different evolution for EPR characteristics parameters, comparative to S_2.

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