

EPR Study of some lead-phosphate glasses

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The $x\text{Fe}_2\text{O}_3(1-x)[2\text{P}_2\text{O}_5 \cdot \text{PbO}]$ glass system with $0.5 \leq x \leq 50$ mol% was prepared and investigated by means of EPR spectroscopy in order to evidence the structural changes induced by the iron ions in different ratios. The isolated Fe^{3+} ions are situated in sites of distorted octahedral symmetries (rhombic or tetragonal). The dipolar and superexchange interactions were also revealed among iron ions in function of Fe_2O_3 content of the samples.

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1. Introduction

Phosphate glasses containing transition metal ions have unique properties which offer their many technical applications in electrochemical, electronic and electro-optical devices [1, 2]. However, these glasses have a relatively poor chemical durability that often limits their usefulness [3]. Several studies have shown that chemical durability of phosphate glasses can be improved by the addition of various oxides such as PbO and Fe_2O_3 [4, 5] which lead to the formation of P-O-Pb and P-O-Fe bonds and thus to the increasing of durability [6, 7].

The local order in diamagnetic vitreous matrices may be revealed by the 3d paramagnetic ions used as probes in EPR experiments. It is well known that EPR supply valuable information about the local site symmetry, the fine structures parameters of the EPR absorption spectra being very sensitive to locale structure.

In the study of Fe^{3+} ions, it was obtained effective g parameter at 2; 4.29 and 6. Loveridge and Parke [8] reported the occurrence of resonance fitting in amber glasses containing both iron and sulfur and ventured the explanation that the strong axial field term in this case must arise from a single sulfur atom substituting for one of the oxygen ligands.

For ESR of Fe^{3+} in glasses the obtained g values are also at 3.3 and 2 [9]. The appearance of these signals seems to be free from the effect due to the randomness of the glass structure.

In the EPR study of $\text{Fe}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3$ as a function of the thermal treatment length applied, there were obtained spectra with different absorbance for different g values through which a value at 7.52; this value was obtained in the case of some vicinities having a strong axial symmetry [10,11].

It can be said that iron ions were often used to investigate the structure of the vitreous materials by means

of EPR [12-16].

In order to obtain further information on the local symmetry and interaction between metallic 3d ions in oxide glasses the lead-phosphate glasses with iron ions are investigated by EPR spectroscopy.

2. Experimental

The starting materials for obtain the $x\text{Fe}_2\text{O}_3(1-x)[2\text{P}_2\text{O}_5 \cdot \text{PbO}]$ glass system with $\text{P}_2\text{O}_5/\text{PbO}$ ratio constant were $(\text{NH}_4)_2\text{HPO}_4$, PbO and Fe_2O_3 of reagent grade purity. The samples were prepared by weighing suitable proportions of the components, powder mixing and mixture melting in sintered corundum crucibles at 1250°C for five minutes. The obtained glass- samples, were quenched by pouring the molten glass 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 50 mol% Fe_2O_3 .

EPR measurements were performed at 9.35GHz (X-band) and a field modulation of 100 KHz at room temperature using an Adani Portable EPR PS 8400 spectrometer equipment.

3. Results and discussion

The EPR spectra of the $x\text{Fe}_2\text{O}_3(100-x)[2\text{P}_2\text{O}_5 \cdot \text{PbO}]$ glass system attest the presence of the iron ions in (3+) valence state for all the investigated samples. The shape of the spectra strongly depend on the Fe_2O_3 content in the glasses (Fig. 1). Thus, for $x \leq 3$ mol% the spectra consist in the three absorption lines centered at $g_1 \approx 6.91$, $g_2 \approx 4.24$ and $g_3 \approx 2$. These suggest the presence of isolated Fe^{3+} ions

situated in tetragonally or octahedral - sites subjected to strong crystal fields effects and are due to the transitions between the lowest Kramers doublet lines [16-18]. Characteristic EPR tetragonally parameters of these glasses are given in Table 1.

In the case of the increasing the Fe_2O_3 content at $10 \leq x \leq 20$ mol%, the spectra contain only two signals characteristic for isolated Fe^{3+} ions at $g_2 \cong 4.27$ and $g_3 \cong 2$. These are characteristic for a rhombic symmetry of the oxygen coordination polyhedra around the iron ions and are the result of the induced transitions between median Kramers doublet lines [8, 19].

Both local vicinities of the isolated iron ions, octahedral-tetragonally and rhombic distorted symmetries coexist in the studied glasses, but with the increase of Fe_2O_3 content, the rhombic sites prevail. Generally, the intensity of these signals increase with the number of EPR active species which are involved in resonance absorption, so the decrease of the intensity of these lines suggest the fact that the number of the isolated Fe^{3+} ions decreases with the iron oxide concentration.

Fe_2O_3 content is shown in figure 2. This increases with the iron oxide concentration due to the dipolar interactions between paramagnetic ions for $x \leq 30$ mol%. For $x > 30$ mol % this line becomes narrow because at high concentrations of Fe^{3+} ions, the superexchange interaction prevail between clustered ions. It is a competition between the broadening mechanisms such as dipole-dipole interactions and the narrowing ones that are the superexchange interactions within the pairs of iron ions. These mechanisms can act simultaneously but they are predominant in function of the Fe_2O_3 sample content [16].

Table 1. EPR parameters of Fe^{3+} ions in Fe_2O_3 - P_2O_5 - PbO glasses

x [mol%]	g_1	g_2	g_3
0.5	6.98	4.27	2.02
1	6.95	4.28	2.01
3	6.87	4.29	2.01
10	-	4.29	1.99

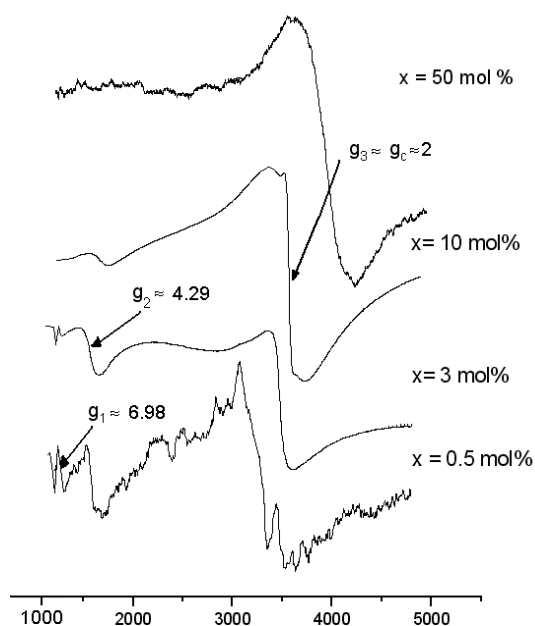


Fig. 1. EPR spectra of Fe^{3+} ions in $x\text{Fe}_2\text{O}_3(100-x)[2\text{P}_2\text{O}_5\text{PbO}]$ glasses

The decreases of the intensities of $g \approx 6.98$ and $g \approx 4.29$ lines with the addition of Fe_2O_3 content occur due to the structural configuration destruction from the iron ions neighborhood, which assures their magnetic isolation [14, 16].

Beside the isolated Fe^{3+} species, the coupled pairs of paramagnetic ions interacting by dipole-dipole or/and superexchange interactions exist [12-16]. These clustered ions are manifest in the EPR spectra by a broad absorption line at $g_c \approx 2.0$. The variation of its line-width (ΔB) with the

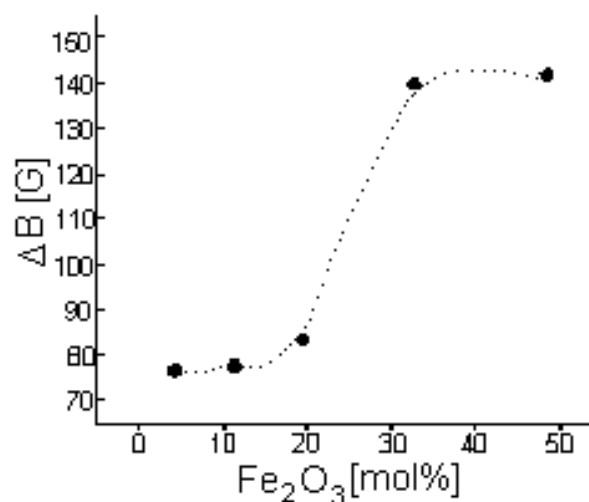


Fig. 2. Linewidth (ΔB) variations vs Fe_2O_3 content in $x\text{Fe}_2\text{O}_3(100-x)[2\text{P}_2\text{O}_5\text{PbO}]$ glasses.

4. Conclusions

The shape of the EPR spectra of the $x\text{Fe}_2\text{O}_3(100-x)[2\text{P}_2\text{O}_5\text{PbO}]$ glass system strongly depends on the Fe_2O_3 concentration. Thus, the isolated Fe^{3+} ions in sites of distorted octahedral symmetries (tetragonal and rhombic) subjected to strong crystalline field effects were detected up to $x = 10$ mol%, attesting the structural ability of the investigated vitreous matrix in receiving these ions.

For $x > 10\%$ the dipolar or/and superexchange coupled clustered Fe^{3+} ions prevail and their number increases with the Fe_2O_3 content.

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