

EPR and magnetic investigation of calcium – phosphate glasses containing iron ions

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The structural and magnetic properties of $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{P}_2\text{O}_5 \cdot \text{CaO}]$ with $0.5 \leq x \leq 50$ mol % were investigated. Information about the structural units involving iron ions, their valence state, the strengths and type of interactions involving them was obtained using EPR spectroscopy and magnetic susceptibility measurements. The Fe^{3+} ions in sites of distorted octahedral symmetry and clustered formations containing both Fe^{3+} and Fe^{2+} ionic species were evidenced. Dipolar and superexchange interactions involving iron ions were revealed depending on the iron content of the sample. For the glasses with $x > 35$ mol % the evaluated values of the μ_{eff} indicate the possible presence of Fe^{3+} ions or the coordination influence on the magnetic moment of iron ions, but the presence of small quantities of the antiferromagnetic or ferrimagnetic interactions between iron ions in studied temperature range cannot be excluded.

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1. Introduction

Iron ions have strong bearing on electrical, optical and magnetic properties of glasses. A large number of interesting studies are available on the environment of iron ion in various inorganic phosphate, silicate, borate and germanate glasses [1-7]. These ions exist in different valence states with different local symmetry in glass matrices, for example as Fe^{3+} with both tetrahedral and octahedral and as Fe^{2+} with octahedral environment [8-11]. The content of iron in different valence states with different local symmetry depends on nature and ratio of modifiers and formers in glass matrix, proportion, disposition of the iron in glass structure and their field strength. The valence states and distribution of iron ions determine the modification of the properties of glasses. Both Fe^{3+} and Fe^{2+} ions are well known paramagnetic ions, but only Fe^{3+} ($3d^5$, $^6S_{5/2}$) show EPR absorptions at room temperature. EPR of Fe^{3+} ions in vitreous matrices may provide useful information about the short range order around the paramagnetic ion due to the fact that in the EPR spectra occur distinct absorption lines for the ions involved in structural units with different symmetry and these lines are modify in function of nature of interactions which is manifest between paramagnetic ions. Data were reported for a great variety of glasses as phosphate [12, 13], borate [8, 14-19], bismuthate [20, 21], tellurite [22, 23], silicate [24, 25] and germanate [26], where Fe^{3+} species were detected as isolated in strongly distorted vicinities, options for the rhombic or tetragonal symmetries subjected to strong ligand field effects and interacting by dipolar or superexchange coupled pairs, depending on the Fe_2O_3 content in glasses.

Magnetic susceptibility measurements revealed as very useful to determine the valence states of transition metal ions and the type of interactions involving them over various composition ranges. Their magnetic properties depend on the concentration of the 3d element and the valence states ratio as well as on the structure of the vitreous matrix and implicitly on the conditions of sample preparation. The superexchange interaction of the iron ions in the oxide glasses was most frequently attributed to an antiferromagnetic coupling within the pairs Fe^{3+} - Fe^{3+} , Fe^{3+} - Fe^{2+} and Fe^{2+} - Fe^{2+} [22,27]. An antiferromagnetic coupling between iron ions was reported in borate [1,8], phosphate [27,28], tellurite [23,29] and bismuthate [20,21] oxide glasses.

This work aims to present the results obtained by means of EPR and magnetic susceptibility measurements performed on P_2O_5 -CaO glass matrix gradually doped with the iron ions.

2. Experimental

Glasses of the $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{P}_2\text{O}_5 \cdot \text{CaO}]$ system were prepared. The starting materials used in the present investigation were $(\text{NH}_4)_2\text{HPO}_4$, CaCO_3 and Fe_2O_3 of reagent grade purity. The samples were prepared by weighing suitable proportions of components, powder mixing and mixture melting in sintered corundum crucibles at 1250 °C for 5 minutes. The mixtures were put into the furnace directly at this temperature. The melts were poured onto 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 of the samples were performed using a Portable Adani PS8400 spectrometer, in X frequency band, at room temperature. To avoid the alteration of the glass structure due to the ambient condition, especially humidity, samples were poured immediately after preparation and enclosed in tubular holders of the same caliber. Equal quantities of samples were studied.

The magnetic susceptibility measurements were performed with a Faraday-type balance in the temperature range 80-300 K. Correction due to the diamagnetism of the P_2O_5 , CaO and Fe_2O_3 were taken into account in order to obtain the real magnetic susceptibility of iron ions in the studied glasses.

3. Results

3.1. EPR data

The $xFe_2O_3 \cdot (100-x)[P_2O_5 \cdot CaO]$ glass samples were investigated by means of EPR for x varying in the range $0.5 \leq x \leq 50$ mol%. The features of the recorded spectra are detailed in Figure 1. As can be seen from the figure, there is a strong dependence of the absorption spectra structure and parameters on the Fe_2O_3 content of the samples. The spectra structure mainly consists in absorptions centered at $g \approx 4.3$ and $g \approx 2.0$ their prevalence depending on x concentrations. The evolution of the resonance lines with increasing of iron ions content was followed in the dependence of the EPR parameters, i.e. the intensity (J) and the line-width (ΔB). The corresponding variations of these parameters are plotted in Fig. 2 for the absorption lines at $g \approx 2.0$.

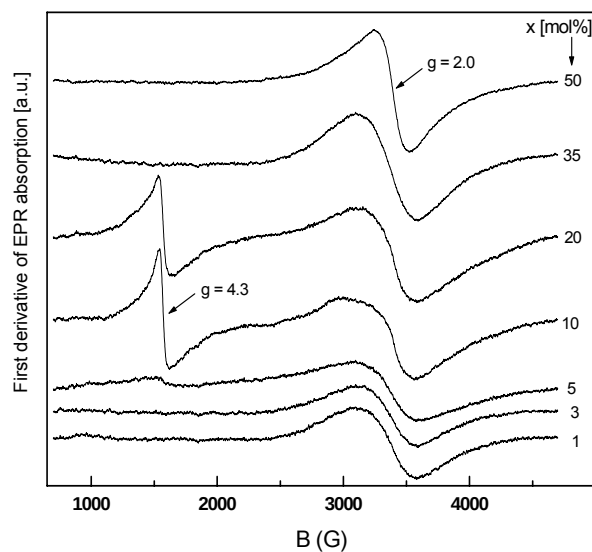


Fig. 1. EPR absorption spectra of Fe^{3+} ions in $xFe_2O_3 \cdot (100-x)[P_2O_5 \cdot CaO]$ glasses.

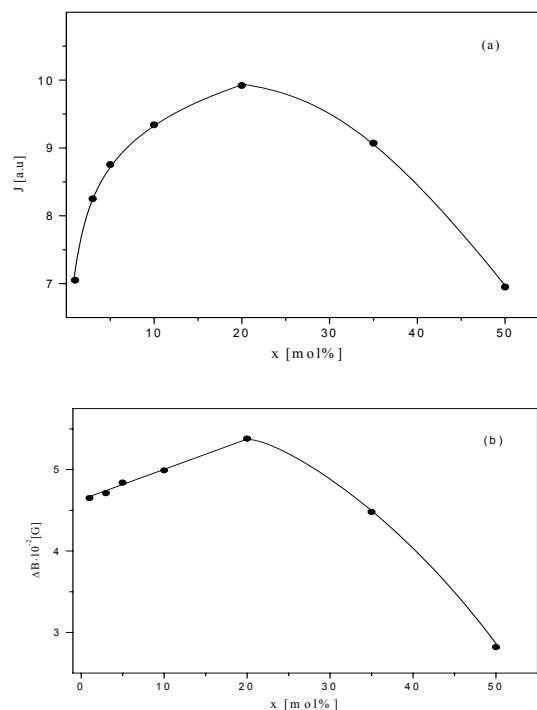
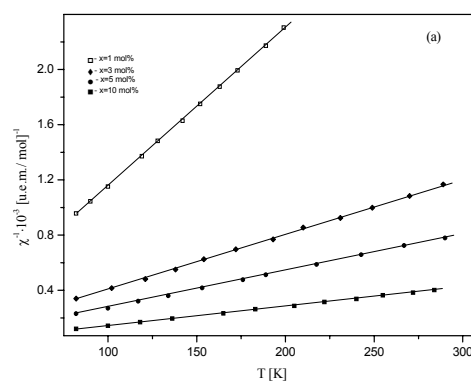


Fig. 2. Composition dependences of the line-intensity (a) and line-width (b) of resonance absorptions at $g \approx 2.0$.

3.2. Magnetic susceptibility data

The temperature dependence of the reciprocal magnetic susceptibility of some glasses from the investigated glass system is presented in Figure 3. The concentration dependence of the paramagnetic Curie temperature (θ_p) is given in Figure 4. The values of the effective magnetic moment of iron ions in the studied samples were estimated as $\mu_{eff} = 2.827 \cdot [C_M/2x]^{1/2}$. These results and the molar Curie constant values, C_M , are given in Table 1.



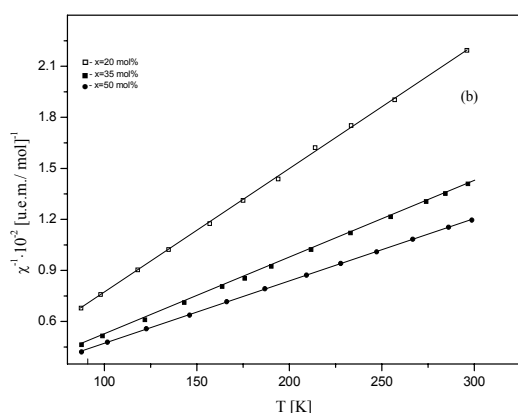


Fig. 3. Temperature dependence of the reciprocal magnetic susceptibility for $x\text{Fe}_2\text{O}_3 \cdot (100-x) [\text{P}_2\text{O}_5 \cdot \text{CaO}]$ glasses with $1 \leq x \leq 10$ mol % (a) and with $20 \leq x \leq 50$ mol % (b).

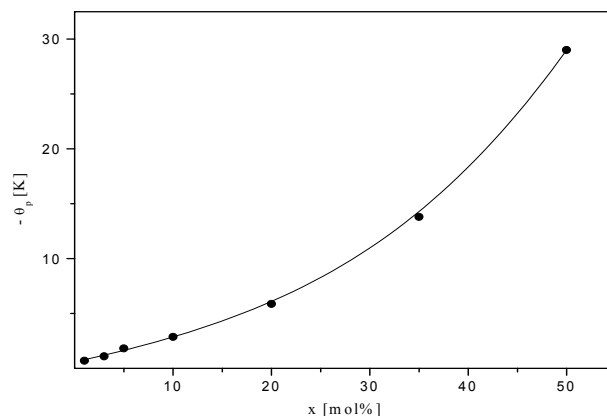


Fig. 4. Composition dependence of the paramagnetic Curie temperature.

Table 1. Molar Curie constant, experimental values of μ_{eff} and molar fraction of Fe^{3+} (x_1) and Fe^{2+} (x_2) ions for $x\text{Fe}_2\text{O}_3 \cdot (100-x) [\text{P}_2\text{O}_5 \cdot \text{CaO}]$ glasses.

x [mol %]	C_M [emu/mol]	μ_{eff} [μ_B]	x_1 [mol % $\text{Fe}_2^{3+}\text{O}_3$]	x_2 [mol % $\text{Fe}_2^{2+}\text{O}_3$]
1	0.08713	5.90	1	0
3	0.25001	5.77	2.5	0.5
5	0.37311	5.46	2.6	2.4
10	0.71646	5.35	4.2	5.8
20	1.37460	5.24	6.2	13.8
35	2.20619	5.01	3.5	31.5
50	2.7268	4.66	—	—

4. Discussion

EPR spectra typical for Fe^{3+} ($3d^5$, $^6S_{5/2}$) ions were obtained (Fig. 1). They attest the presence of the iron ions in the (3+) valence state for all the investigation samples. The resonance spectra mainly consist in absorption lines centered at $g \approx 4.3$ for samples with $5 \leq x \leq 20$ mol % and $g \approx 2.0$ for all investigated concentration range respectively. Their prevalence in the spectrum depends on the Fe_2O_3 content of the samples (Fig. 1). The EPR parameters of the absorption line centered at $g \approx 2.0$ also depend on iron concentration (Fig. 2).

The resonance line at $g \approx 4.3$ is due to Fe^{3+} ions which are isolated and situated in sites of distorted octahedral symmetry (rhombic or tetragonal) subjected to strong crystal field effects. The absorption may induce transitions between the medians Kramers doublet lines when the site symmetry is rhombic [24, 30, 31] or between the lines of the lowest doublet, in the case of tetragonally [32] or cubic tetragonally distorted sites [33]. In our glasses there is a concentration, $5 \leq x \leq 20$ mol % (Fig. 1), where the structural states involving Fe^{3+} ions may be revealed these configurations. It is interesting to remark that in the case of studied glasses do not appear isolated Fe^{3+} ions (with $g \approx 4.3$) at small concentration of Fe_2O_3 ($x < 5$ mol %), fact

remarked in the case of other oxide glasses [8, 12-26]. From this it can conclude that at small content of Fe_2O_3 , the Fe^{3+} ions are not disposed in the vitreous network of matrix ($\text{P}_2\text{O}_5 \cdot \text{CaO}$) by playing the role of the network former or modifier, but they are disposed in sites easier to occupy, offered by the matrix. As results from EPR data, these sites are higher large and they allow the association of Fe^{3+} ions even at small content of Fe_2O_3 . For $x \geq 5$ mol % these sites are exhausted from a part of Fe^{3+} ions, the others being disposed in the matrix network, in sites which assure their isolation. At higher concentration ($x > 20$ mol %) all Fe^{3+} ions participate at magnetic interactions.

The $g \approx 2.0$ line may be attributed either to Fe^{3+} species interacting by dipole-dipole interaction in sites of less distorted octahedral (tetrahedral) field or to superexchange coupled pairs [22, 25]. The composition dependence of the $g \approx 2.0$ absorption line intensity shows an increasing up to $x = 20$ mol % and for higher concentrations decrease (Fig. 3a). Generally the signal intensity is proportional to the number of EPR active species involved in the resonance absorption, so the decrease of the $g \approx 2.0$ line intensity suggests probable another valence states of iron ions which co-exist with Fe^{3+} species in matrix when iron ions is accumulated. Without giving rise to EPR absorption these ions may

influence the Fe^{3+} ions absorption spectra when they are involved in interactions. The progressive accumulation of these ions in the system during the increase of iron content in samples, could explain the $J = f(x)$ dependence (Fig. 3a). The line-width of the $g \approx 2.0$ absorption depends also on the Fe_2O_3 concentration (Fig. 3b) revealing different possibility of interaction of the iron ions in the investigated matrix. The $\Delta B = f(x)$ dependence suggests the competition between the broadening mechanisms as the dipol-dipol interactions, the increased disordering of the matrix structure, the interactions between ions in multivalent states 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. Thus, the line-width from $g \approx 2.0$ increasing due to dipole-dipole interactions between Fe^{3+} ions, which are put in evidence for $x \leq 20$ mol %. However, the higher values of ΔB (even for $x = 1$ mol%) for $x \leq 20$ mol% suggest that in this concentration range the Fe^{3+} ions participates at dipol-dipol as well as at superexchange interactions. For $x \geq 20$ mol% the absorption line from $g \approx 2$ is narrowing, so in this concentration range Fe^{3+} ions participate at superexchange interactions.

The magnetic susceptibility data correlate well with the EPR result and also complete them. The temperature dependence of the reciprocal magnetic susceptibility show a Curie-Weiss-type behaviour, with negative paramagnetic Curie temperature for all studied glasses (Fig. 4). This fact suggests the participation of iron ions (their proportion depends on x) at superexchange magnetic interactions, of antiferromagnetic type, in all concentration range studied. Due to the disordered structure of glasses, the magnetic order takes place at short range making possible a mictomagnetic-type order [34]. Therefore, in the $\text{P}_2\text{O}_5\text{-CaO}$ glass matrix, in the studied concentration range, the iron ions behave magnetically similarly as in other oxide glasses [20,28,29,35,36], but concentration of Fe_2O_3 over which magnetic superexchange interactions occur is lower. This is in agreement with experimental remarks according which the concentration range of transition metal ions over which these interactions occur depend of the nature of the glass matrix [9].

The absolute magnitude of θ_p values increases when content of Fe_2O_3 is increased (Fig. 5). The exchange integral increases as the content of the magnetic ions are increased in the glass and as a result the magnitude of the θ_p increases [35].

The composition dependence of the molar Curie constant is presented in Table 1. For the glass with $x = 1$ mol % the experimental value obtained for effective magnetic moment (μ_{eff}) is $5.90 \mu_B$ (Table 1) and is very close to the atomic magnetic moment of free Fe^{3+} ion: $\mu_{\text{Fe}^{3+}} = 5.92 \mu_B$. Therefore, we consider that in the glasses with $x \leq 1$ mol % only the Fe^{3+} ions are present. For the glasses with $3 \leq x \leq 35$ mol %, the C_M and consequently the μ_{eff} values (Table 1) are smaller than those corresponding to a Fe_2O_3 content having all iron ions as Fe^{3+} species but higher than those of Fe^{2+} ions. For this

reason, both Fe^{3+} and Fe^{2+} ions may be assumed to be present in these glasses. The presence of Fe^{3+} and Fe^{2+} ions has been evidenced in other oxide glasses [23,28,36]. Therefore, the molar fractions of these ions were estimated, in a first approximation, by using the relations:

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

and

$$x = x_1 + x_2, \quad (2)$$

where μ_{eff} represents the experimental effective magnetic moment value (Table 1) determined from the temperature variation of the magnetic susceptibility (Fig. 3), x_1 and x_2 are the molar fractions of Fe^{3+} and Fe^{2+} ions and $\mu_{\text{Fe}^{2+}} = 4.90 \mu_B$ is the value of the magnetic moment of the free Fe^{2+} ion. The results obtained are listed in Table 1. For the glass with $x = 50$ mol %, the experimental value obtained for μ_{eff} is $4.66 \mu_B$ (Table 1) and are lower than those which correspond to the value of $\mu_{\text{Fe}^{2+}}$. This value

of μ_{eff} reflects either the iron ions coordination effects upon the magnetic moment values of Fe^{3+} and Fe^{2+} ions or the simultaneous presence of Fe^{+} ($3d^7$) ions having a value $\mu_{\text{Fe}^{+}} = 3.87 \mu_B$ in free ion state. Up to now the Fe^{+} species was detected only in single crystals, at temperatures lower than 20 K [37]. But, if one supposes that in this glass the magnetic superexchange interactions are similar to those from the iron oxides (Fe_2O_3 , Fe_3O_4), which exhibit stable superexchange interactions until before high temperature ($T_N = 953$ K for Fe_2O_3 and $T_c = 585$ K for Fe_3O_4), results than they can persist, partially in glasses, too. Therefore, the presence of antiferromagnetic or ferromagnetic interactions between the iron ions in the studied glass and studied temperature range can determine the decreasing of μ_{eff} . Similar behaviour of iron ions was put in evidence in other vitreous matrices as $\text{Bi}_2\text{O}_3\text{-GeO}_2$ and $\text{B}_2\text{O}_3\text{-CaO}$, respectively [38,39].

The estimation of molar fraction of Fe^{2+} ions indicates that the content of these ions increase with Fe_2O_3 concentration and for $x \geq 10$ mol % are higher than those of Fe^{3+} ions. In case of Fe^{3+} ions, they content increase up to $x = 20$ mol % after decrease, result which are similar with the evolution of the $g \approx 2$ line intensity with the increasing of Fe_2O_3 content (Fig. 2a).

5. Conclusions

Glasses of the $x\text{Fe}_2\text{O}_3\text{-(100-x)[P}_2\text{O}_5\text{-CaO]}$ system were obtained within a large concentration range, i.e. $0 \leq x \leq 50$ mol %.

EPR absorption spectra due to Fe^{3+} ions were detected within $0.5 \leq x \leq 50$ 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 in sites of distorted octahedral symmetry subjected to strong crystalline field effects (resonance absorption at $g \approx 4.3$) were detected only in $5 \leq x \leq 20$ mol% Fe_2O_3 concentration range.

The EPR absorption at $g \approx 2.0$ and magnetic measurements revealed both dipolar and superexchange-type interactions involving iron ions for samples with $x \geq 1$ mol %.

For the glasses with $x \leq 1$ mol % only Fe^{3+} ions are evidenced. In $3 \leq x \leq 35$ mol % composition range, iron enters the $\text{P}_2\text{O}_5\text{-CaO}$ glass matrix in both Fe^{3+} and Fe^{2+} valence states, the Fe^{2+} ions concentration exceeding the Fe^{3+} one for glasses with $x \geq 10$ mol %. For the glasses with $x > 35$ mol %, the estimated values of the μ_{eff} reflect either the coordination influence on the magnetic moment of iron ions or the presence of Fe^+ ionic species simultaneously with the Fe^{2+} and Fe^{3+} ions, but is not excluded the presence in small quantities, in the given temperature range of the antiferromagnetic or ferrimagnetic interactions, which can determine the decrease of μ_{eff} .

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