Fe$^{3+}$ as the Main form of Iron Ions in Iron-Lead-Phosphate Glasses

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Electron Paramagnetic Resonance EPR, hydrostatic density ($\rho$), molar volume ($V$), differential thermal analysis (DTA) and infrared spectroscopy measurements have been employed to investigate the effect of Fe$_2$O$_3$ content on the physical properties of a series of iron-lead-phosphate glasses in the system (100-2x)Fe$_2$O$_3$-xPbO-xP$_2$O$_5$ with x = 12.5, 15, 17.5 and 20 mol%. The samples have been prepared by melting the mixtures under normal atmosphere at $1300 \pm 20$° C. The EPR spectra, for all samples, reveal the presence of an intensive resonance peak at $g \sim 2$ which is attributed to Fe$^{3+}$ ion located in a site with high symmetry. A monotonic increase in ($\rho$) value and a corresponding decrease of the ($V$) value are also detected with increasing Fe$_2$O$_3$. The increasing value of the glass transition temperature $T_g$ with Fe$_2$O$_3$ content as detected by DTA indicates the increase of the degree of bridging. The increased ($T_{c}$-$T_g$) value reveals the stability of iron-rich phosphate glasses. The experimental IR absorption bands have been identified. The data have been discussed in terms of the formation of Fe$^{3+}$ as the main form of iron ions in iron-lead-phosphate glasses.

1. Introduction:

Electron paramagnetic resonance spectroscopy is a powerful experimental technique which can be used to get information about the structural and dynamic phenomena of materials. EPR studies of glasses containing transition metal ions (TMI) have been used to obtain information regarding the glassy network and to identify the site symmetry around the TMI. Several studies have been made on the EPR spectra of TMI in oxide glasses [1-6]. Sales and Boatner [7] found that iron-lead-phosphate glasses were more durable than many borosilicate glasses and they suggested the use of these glasses for vitrifying nuclear waste. Shih as well as others [8-13] suggested that the addition of one or more of SnO, PbO, ZnO, Al$_2$O$_3$ and Fe$_2$O$_3$ oxides to phosphate glasses resulted in the formation of Sn-O-P, Pb-O-P, Zn-O-P, Al-O-P
and Fe-O-P bonds, which lead to an improvement in the chemical durability of the modified phosphate glasses. Of all additions to phosphate glasses, PbO is the only one which reduces the dissolution rate and softening temperature at the same time [14-16]. On the other hand, the structural role of PbO in many oxide glasses is unique since PbO is known to play a dual structural role, both as a network modifier [17], and as a network former [18]. The objective of the present work is to report the effect of the Fe$_2$O$_3$ content on the physical properties of a series of iron rich glasses containing equimolar ratio of PbO and P$_2$O$_5$.

2. Experimental:

The glass samples were prepared by mixing the appropriate amounts of analar grade chemicals Fe$_2$O$_3$, PbO, P$_2$O$_5$ in the ratio (100-2x) Fe$_2$O$_3$–x PbO–xP$_2$O$_5$ (x=12.5, 15, 17.5 and 20 mol %). The mixture was melted in a silica crucible at normal atmosphere at 1300 ± 20°C for 3 hours. The melt was cast in iron preheated moulds on iron plate, and was immediately transferred to an annealing furnace held at 250°C for 15 minutes. Gradual self cooling to room temperature was then achieved. Part of the prepared samples was grinded into fine powder and sieved using 200 mesh sieve to be used for different purposes. The amorphous state of the prepared samples was checked by x-ray diffraction. Electron paramagnetic resonance spectra were made at room temperature using a Varian X-band spectrometer with a modulation frequency of 100 KHz. The infrared spectra were recorded over the range 200-2000 cm$^{-1}$ at room temperature using FTIR spectrometer (Beckman 4220). Differential thermal analysis was carried out from room temperature up to 750°C with heating rate of 10°C/min using Perkin Elmer DTA apparatus. The density measurement of the samples was determined experimentally using xylene as the buoyancy liquid, while the theoretical density was calculated according to the relation:

$$\rho_{th} = \frac{1}{\Sigma \left( a_i / \rho_i \right)}$$

where $a_i$ is the weight fraction of the $i^{th}$ oxide and $\rho_i$ is the density of the $i^{th}$ oxide.

The molar volume was calculated from the experimentally determined density ($\rho$) according to the relation:

$$V = \Sigma (M_i N_i) / \rho$$

where $M_i$ and $N_i$ are the molecular weight and the mole fraction of the different constituent oxides respectively.
3. Results and discussion:

3.1. Electron paramagnetic resonance:

The EPR spectrum may be interpreted by the spin Hamiltonian

\[ H = B \ g \ H \ S + I \ A \ S \]  \hspace{1cm} (3)

where \( B \) is the Bohr magneton, \( g \) is the spectroscopy splitting factor, \( A \) is the hyperfine structure tensor, and \( H, I, S \) are the static magnetic field operator, the electron spin operator and the nuclear spin operator respectively. Fig.(1) is a typical EPR spectra for the samples under study measured at room temperature. As shown in the figure, an intense resonance peak at \( g \sim 2 \) is a characteristic feature for all the EPR recorded spectra. Absence of the resonance at \( g \sim 4.3 \) and \( g \sim 6 \) is noticed except for the sample with 60 mol % \( \text{Fe}_2\text{O}_3 \) which shows a weak resonance peak at \( g \sim 4.3 \). This may be due to the high concentration of iron included in the prepared samples. As the resonance from \( \text{Fe}^{2+} \) ion is undetectable at room temperature [19,20], one may suggest that the present observed resonance peaks are due to \( \text{Fe}^{3+} \) ions. On the other hand, the high intensity of the \( g \sim 2 \) resonance indicates that almost all the incorporated iron form clusters.

![EPR spectra](image)

Fig.(1): EPR spectra of \((100-2x) \text{Fe}_2\text{O}_3 - x \text{PbO} - x \text{P}_2\text{O}_5\) glasses Numbers in the figure represent glass numbers in table (1).
The features of the EPR spectra can be qualitatively explained as follows [21- 23]: the large resonance peak for Fe$^{3+}$ at $g \sim 2$ can only occur if the Fe$^{3+}$ is located in a site where the crystal field interaction energy is less than the magnetic Zeeman energy. This case would correspond to iron located in a site with a higher symmetry. On the other hand, the resonance at $g \sim 4.3$ is due to an environment, where the interaction energy between the surrounding crystal field and the Fe$^{3+}$ ion is larger than the Zeeman energy. This case would correspond to iron in a relatively low symmetry site in the glass structure. Fig.(1) clearly shows that with increasing iron content, the weak resonance at $g \sim 4.3$ is rapidly broadened out; presumably due to spin–spin interactions between neighboring iron ions. The $g \sim 2$ resonance peak is, on the contrary, not sensitive to this effect as its width becomes narrower with increasing the iron content. In fact, this peak is known to appear when the iron content is sufficiently large for the iron–iron distance to be small enough for the spin–spin interaction to be effective[24].

The integrated area is determined by the concentration of paramagnetic ions present in each glass. The area under the resonance peaks have been calculated using the approximation $A = W I (\Delta H)^2$ where $W$ is a weighting factor necessary for suitable correction for the weight of the sample, $I$ is the relative peak to peak intensity and $\Delta H$ is the line width in derivative plots. Table 1 and Fig.(2) represent the calculated areas as a function of Fe$_2$O$_3$ content. It is clear that, the area decreases rapidly as the PbO content increases in replacement of Fe$_2$O$_3$. This result can be explained as follows: Addition of PbO gives rise to the formation of non bridging oxygen attached to Fe$^{3+}$ ions.

![Fig.(2): Variation of area under the peak with iron content (mole %) in (100- 2x) Fe$_2$O$_3$ – x PbO – x P$_2$O$_5$ glasses.](image-url)
As a result the iron-iron distance increases due to the fact that now two non-bridging oxygen have to be accommodated instead of the bridging one which was present earlier [25]. This weakens the spin-spin interactions and hence decreases the area of the $g \sim 2$ resonance. If the formed non-bridging oxygen are attached to phosphorus ions, the iron-iron distance will not appreciably affected. It is therefore obvious that, the area under the peak is more likely to be controlled by the PbO content.

3.2. Hydrostatic density, molar volume and thermal analysis:

The variation of both the experimental and theoretical data of the hydrostatic density with iron content is given in Fig. (3). The figure shows a monotonic change in density with iron content. Such monotonic behavior indicates that the structure of the glass does not change with composition. In fact, a change in the structure would be reflected by a sharp change in the slope of the plot of density against composition [26]. The calculated density deviation ($\rho_{th} - \rho_{exp}$) is found to be always positive and increases with increasing Fe$_2$O$_3$ content for all the compositions under study. This is in agreement with the role of Pb$^{2+}$ in crosslinking the polymeric chains.

![Graph showing variation of density with iron content](image)

**Fig.(3):** Variation of density with iron content (mole %) in (100- 2x) Fe$_2$O$_3$ – xPbO – x P$_2$O$_5$ glasses. O experimental data Δ theoretical data

The molar volume (V) of the compositions under study is calculated according to Eqn. (2) and illustrated in Table 1. A decrease in the value of V is detected as increasing the Fe$_2$O$_3$ content. This decrease may be a result of a decreasing of the Fe$^{3+}$ - Fe$^{3+}$ distance, thereby enhancing the formation of
clusters. This agrees well with the increased area of the $g \sim 2$ resonance line as shown in Table (1).

Figure (4) displays the experimental DTA thermograms of the compositions under study. The glass transition temperatures ($T_g$) as well as the crystallization temperatures ($T_c$) deduced from the thermograms are given in Table (1). We notice that the values of both $T_g$ and $T_c$ continuously shift to higher temperatures with increasing iron content. It is well known that $T_g$ value is closely correlated to the change in the coordination number of the glass forming atoms (network former) and with the formation of non-bridging oxygen, which correspond to the depolymerization of the glass skeleton [27]. In general, it is known that $T_g$ increases with increasing the degree of bridging and contrary to this, the formation of non-bridging oxygen decreases it. Therefore, one can conclude that the increase detected in $T_g$ value from 551 to 564°C (Table (1)) can be ascribed to a corresponding increase in the degree of bridging with increasing Fe$_2$O$_3$ content. It is to be also noted that the increased ($T_c - T_g$) difference value for the higher Fe$_2$O$_3$ sample reveals the stability of the iron-rich phosphate glasses.

Fig. (4): Thermograms of (100-2x) Fe$_2$O$_3 - x$ PbO - x P$_2$O$_5$ glasses. Numbers in the figure represent glass numbers in table (1)
3.3. Infrared study:

Figure (5) shows the infrared spectra of the samples under study. All the measured spectra show the same six bands at 230, 360, 460, 540, 620 and 920-1080 cm\(^{-1}\). Assignments of the observed bands are as follows:

![Figure 5: Infrared Spectra](image)

**Table (1):** Characterization data for (Fe\(_2\)O\(_3\) - PbO - P\(_2\)O\(_5\)) glasses

<table>
<thead>
<tr>
<th>Glass No.</th>
<th>P(_2)O(_5) (%)</th>
<th>PbO (%)</th>
<th>Fe(_2)O(_3) (%)</th>
<th>I (arb. Units)</th>
<th>(\Delta H) (Gauss)</th>
<th>Area ((\times 10^6))</th>
<th>g factor</th>
<th>Density ((\text{g cm}^-3))</th>
<th>(\Delta \rho)</th>
<th>Molar volume ((\text{cm}^3\text{mol}^-1))</th>
<th>(T_g) (^{(\text{oc})})</th>
<th>(T_c) (^{(\text{oc})})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>20</td>
<td>20</td>
<td>173</td>
<td>125</td>
<td>2.703</td>
<td>2.0121</td>
<td>4.375</td>
<td>0.179</td>
<td>41.289</td>
<td>550.79</td>
<td>624.81</td>
</tr>
<tr>
<td>2</td>
<td>65</td>
<td>17.5</td>
<td>17.5</td>
<td>189</td>
<td>122.5</td>
<td>2.836</td>
<td>2.0047</td>
<td>4.401</td>
<td>0.215</td>
<td>40.706</td>
<td>554.54</td>
<td>631.57</td>
</tr>
<tr>
<td>3</td>
<td>70</td>
<td>15</td>
<td>15</td>
<td>200</td>
<td>121.5</td>
<td>2.953</td>
<td>1.9974</td>
<td>4.429</td>
<td>0.247</td>
<td>40.077</td>
<td>559.68</td>
<td>638.49</td>
</tr>
<tr>
<td>4</td>
<td>75</td>
<td>12.5</td>
<td>12.5</td>
<td>340</td>
<td>100</td>
<td>3.400</td>
<td>2.0121</td>
<td>4.452</td>
<td>0.312</td>
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<td>564.54</td>
<td>649.63</td>
</tr>
</tbody>
</table>

**Fig.(5):** Variation of area under the peak with iron content (mole %) in \((100- 2x)\) Fe\(_2\)O\(_3\) – x PbO – x P\(_2\)O\(_5\) glasses. (Numbers represent glass numbers in Table (1)).
(i) Both the bands at 230 and 360 cm$^{-1}$ are due to stretching vibrations of Fe-O group with different bond lengths. The existence of Fe$^{3+}$ ions in octahedral structure was previously identified by the frequency bands appeared at 220, 365, 408, 460 and 610 cm$^{-1}$ [29].

(ii) The band at 460 cm$^{-1}$ observed in phosphate glasses was previously suggested to be due to FeO$_6$ and/or P$_2$O$_7$ groups [30].

(iii) The band in the range 920-1080 cm$^{-1}$ was suggested to be due to metal-(PO$_4$)-link vibration [31, 32].

From the infrared spectra, it is noticeable that an increase in Fe$_2$O$_3$ concentration does not affect the position of any vibration peak. The relative intensity I (460)/ I(1000) is detected to increase progressively with the increase of Fe$_2$O$_3$. This may reveal that on increasing Fe$_2$O$_3$ content the density of the Fe-O bonds increases on the expense of metal phosphate groups.

4. Conclusion:

1. An intense resonance peak at $g \sim 2$ is a characteristic feature of all the EPR spectra except that of the glass containing 60 mol % Fe$_2$O$_3$ which shows a weak band at $g \sim 4.3$.

2. The increasing value of the glass transition temperature with the Fe$_2$O$_3$ content indicates the increase of the degree of bridging, while the increased (T$_c$-T$_g$) value reflects the stability of these glasses.

3. It is noticeable that the presence of equimolar ratio of PbO and P$_2$O$_5$, within the range studied, not significantly affects the infrared spectra of iron-lead-phosphate glasses.

References:


