Induced crystallization and structural aspects of PbO-As$_2$O$_3$ glass system doped with Fe$_2$O$_3$

Y. Saritha Kumari

Department of Physics, St. Martin’s Engineering College, Dhumapally, Secunderabad, INDIA, A.P.

Abstract: PbO-As$_2$O$_3$ glasses mixed with different concentrations of Fe$_2$O$_3$ (ranging from 0 to 0.5 mol%) were crystallized. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS) techniques. Studies were extended to optical absorption. The X-ray diffraction and scanning electron microscopic studies reveal the presence of PbFe$_2$(As$_2$O$_5$)$_2$, Fe$_2$PbAs$_2$O$_6$ crystal phases. The optical absorption studies together with ESR measurements indicated the dominant presence of iron ions in the trivalent state when the concentration of nucleating agent Fe$_2$O$_3$ is less than 0.3 mol%.

I. Introduction

The transitional metal ions such as iron ions, dissolved in PbO-As$_2$O$_3$ glass matrix even in very small quantities, influence the insulating character of these glasses very strongly. The addition of iron to lead niobium phosphate glasses is anticipated to increase the chemical durability and to decrease the corrosion rate in aqueous environments [1]. 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 glass systems viz., silicate, borate, phosphate, germinate glasses [2-11] and also in certain tellurite glass systems [12, 13]. These ions exist in different valence states with different coordinations in glass matrices, for example as Fe$^{3+}$, with both tetrahedral and octahedral and as Fe$^{2+}$ with octahedral environment [14, 15]. Both Fe$^{3+}$ and Fe$^{2+}$ ions are well known paramagnetic ions. Fe$^{3+}$ ion has a large magnetic anisotropy due to its strong spin-orbit interaction of the 3d orbital where as such anisotropy energy of Fe$^{2+}$ ions is small because its orbital angular momentum is zero.

Fe$^{3+}$ has a d$^6$ electronic configuration, and octahedral complexes with weak field ligands have a high spin arrangement with four unpaired electrons. Fe$^{2+}$ has a d$^7$ electronic configuration and the ground state is $^5$S$_{1/2}$ in free atom and possesses zero orbital angular momentum. Hence, any magnetic behaviour of Fe$^{2+}$ ion is due to its spin only. Thus, complexes with weak field ligands have a high spin arrangement with five unpaired electrons [16]. In a cubic crystalline field at low to moderate strength, these five d electrons are distributed with three in the t$_{2g}$ and two in the e$_g$ orbitals.

The ground state configuration gives rise to electronic states $^4$A$_{1g}$, $^4$T$_{2g}$, $^4$E$_g$, $^4$T$_{1g}$, $^4$T$_{2g}$ and $^4$A$_{2g}$ and to a number of doublet states of which $^4$A$_{1g}$ lies lowest according to Hund’s rule. The optical absorption spectrum is expected to exhibit bands from the ground state $^4$A$_{1g}$ to some quartet states and these are both spin and parity forbidden. Generally, the optical absorption bands of Fe$^{3+}$ complexes can be seen in the visible and ultraviolet regions. In general, $^4$A$_{1g}$(G) $^4$E$_g$(G), $^4$A$_{1g}$(G) $^4$T$_{1g}$(G) and $^4$A$_{1g}$(G) $^4$E$_g$(D) bands are sharp as they arise from intraconfigurational transitions. The transitions $^4$A$_{1g}$(S) $^4$T$_{1g}$(G) and $^4$A$_{1g}$(S) $^4$T$_{2g}$(G) involve a change of configuration from (t$_{2g}$)$^3$(e$_g$)$^2$ to (t$_{2g}$)$^2$(e$_g$)$^3$ and are therefore observed to be broad.

The current investigation is aimed at understanding the catalyst action of the iron ion on the crystallization of PbO–As$_2$O$_3$ glass system by means of different analytical techniques. The details of the compositions chosen for the present study are:

- F$_0$: 40 PbO-60 As$_2$O$_3$
- F$_1$: 39.9 PbO-60 As$_2$O$_3$: 0.1 Fe$_2$O$_3$
- F$_2$: 39.8 PbO-60 As$_2$O$_3$: 0.2 Fe$_2$O$_3$
- F$_3$: 39.7 PbO-60 As$_2$O$_3$: 0.3 Fe$_2$O$_3$
- F$_4$: 39.6 PbO-60 As$_2$O$_3$: 0.4 Fe$_2$O$_3$
- F$_5$: 39.5 PbO-60 As$_2$O$_3$: 0.5 Fe$_2$O$_3$

II. Brief review of the previous work on the glasses containing iron ions

Ardelean et al [17] have studied the magnetic susceptibility of xFe$_2$O$_3$·(100-x)[3BZ03·BaO] glasses with 0 < x < 50 mol%. For x < 10 mol% they have shown that these glasses to obey Curie law and iron ions exist only in Fe$^{3+}$ state, but for higher concentrations, the magnetic susceptibility of these glasses is described by Curie-Weiss law and iron ions are found to exist in both Fe$^{3+}$ and Fe$^{2+}$ valence states that participate in antiferromagnetic interactions. El-Samanoudy et al [12] have studied optical absorption and infrared spectra of Fe$_2$O$_3$ containing TeO$_2$-GeO$_2$ glasses; they showed that the fundamental absorption edge is a...
function of composition and the validity of the Urbach rule is investigated. Tanaka et al [18] have investigated the local structure around iron ions in the Bi2O3-Fe2O3 glasses by means of ESR studies. They have ascribed the ESR lines centered at $g = 4.3$ and $g = 2.0$ to isolated Fe3+ in the orthorhombic crystal field and Fe3+-O-Fe3+ spin pair respectively. The electrochemical behaviour of Fe2+/Fe3+ redox couple in sodium silicate glasses has been studied by Maric et al [19]; from the results they have concluded that Fe3+ acts both as network former and network modifier while Fe2+ acts as network modifier. Sanad et al [20] have reported structural and magnetic properties of Fe2O3 containing CaO-P2O5 glasses. They have concluded that iron exists in both Fe2+ and Fe3+ states and the infrared measurements showed that the increase in the iron content of glass matrix caused a change in the coordination of iron from FeO6 to FeO4.

Chaudhuri et al [21] have reported the frequency dependent a.c. conductivity of amorphous Fe2O3- Bi2O3 glasses in the frequency range $10^2$-$10^5$ Hz and in the temperature range of 77 to 450 K. They have analyzed the experimental data based on various theoretical models and showed that the correlated barrier hoping model as the most appropriate. Dance et al [22] have investigated ESR of Fe$^{3+}$ ions in fluoroaluminate glasses and attributed the single line centered at $g = 4.3$ in the ESR spectrum to the presence of Fe$^{3+}$ ions in sites of fully rhombic symmetry. Baiocchi et al [23] have studied the optical and magnetic properties of iron ions in lead silicate glasses; they have assigned the bands observed in the optical absorption spectrum to the corresponding transitions by taking into account the selection rules and on the basis of ligand field energy calculations. They have also concluded that the four-fold coordination of Fe$^{3+}$ ions is more common than the six fold in silicate glasses. Stefan et al [24] have reported EPR of Fe$^{3+}$ ions doped in bismuth borate glasses and the studies indicate various sites for Fe$^{3+}$ ions in environments characterized by different crystalline field intensities. Mandal and Hazra [25] have reported the conductivity and dielectric behaviour of iron sodium phosphate glasses. Congiu et al [37] have reported the magnetic properties of glasses with high iron ox compounds. Murawski et al [29] have investigated the electronic conductivity of Na$_2$O-FeO-P$_2$O$_5$ glasses. Hafid et al [34] have carried out a study on the local iron environment in iron phosphate glasses. Martinelli et al [31] have studied the structural features of lead iron phosphate glasses. Santic et al [32] have investigated the dc electrical conductivity of iron phosphate glasses. Resi et al [33] have reported the chemical durability and structure of zinc-iron phosphate glasses. Desoky et al [36] have studied the conductivity and dielectric behaviour of iron sodium phosphate glasses. Ray et al [38] have carried out a study on the effect of melting temperature and time on iron valency and crystallization of iron phosphate glasses.

### 3.1 Physical Parameters

From the measured values of density $d$ and calculated average molecular weight, various physical parameters such as iron ion concentration $N_i$ and mean iron ion separation $R_i$ of these glass ceramics are evaluated using the conventional formulae [6] and are presented in Table 3.1.

<table>
<thead>
<tr>
<th>property</th>
<th>glass F1</th>
<th>glass F2</th>
<th>glass F3</th>
<th>glass F4</th>
<th>glass F5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density $d$ ( g/cm$^3$ )</td>
<td>5.4353</td>
<td>5.4115</td>
<td>5.4379</td>
<td>5.4878</td>
<td>5.4896</td>
</tr>
<tr>
<td>Avg. mol. wt</td>
<td>207.98</td>
<td>207.92</td>
<td>207.86</td>
<td>207.79</td>
<td>207.73</td>
</tr>
<tr>
<td>Iron ion conc. $N_i$ x10$^{21}$</td>
<td>-</td>
<td>1.57</td>
<td>3.21</td>
<td>4.78</td>
<td>6.38</td>
</tr>
<tr>
<td>Inter ionic distance of $R_i$ (Å)</td>
<td>-</td>
<td>8.608</td>
<td>6.821</td>
<td>5.940</td>
<td>5.393</td>
</tr>
<tr>
<td>Polyanion radius $R_p$ (Å)</td>
<td>2.75</td>
<td>2.40</td>
<td>2.17</td>
<td>2.02</td>
<td></td>
</tr>
</tbody>
</table>

### 3.2 XRD analysis

The X-ray diffraction pattern (Fig. 3.1) of the PbO-As$_2$O$_3$ samples crystallized at 400 °C with different concentrations of nucleating agent Fe$_2$O$_3$ indicated that these ceramic samples contain PbFe$_2$(As$_2$O$_3$)$_2$: Fe$_2$PbAs$_5$O$_9$ crystal phases along with the lead arsenate crystal phases. These results show that in these glass ceramics, iron ions exist in Fe$^{2+}$ and Fe$^{3+}$ states.
3.3 SEM and EDS

The scanning electron microscopic (SEM) pictures of some of the crystallized samples are shown in Figs. 3.2. The scanning electron microscopic (SEM) pictures of the crystallized samples exhibit well defined and randomly distributed crystals entrenched in glassy matrix. The chemical makeup of the phases characterized by energy dispersive spectroscopy (EDS) for some of the samples is shown in Fig. 3.3. The EDS analysis of the glass ceramic materials exhibits Pb, As and Fe elements in various crystalline phases. Fig. 3.4 shows X-ray maps of the glass ceramics for Fe ion for some of the glass ceramic samples. The maps indicate the reasonably uniform distribution of iron ions in the entire glass ceramic material.
Induced crystallization and structural aspects of PbO-As₂O₃ glass system doped with Fe₂O₃

Fig 3.3(b) EDS Spectra of glass ceramic sample F₁

Fig 3.3(c) EDS Spectra of glass ceramic sample F₂

Fig 3.3(d) EDS Spectra of glass ceramic sample F₃

Fig 3.3(e) EDS Spectra of glass ceramic sample F₄
3.4 Optical Absorption Studies

The optical absorption spectra (fig 3.4) of all these glasses recorded at room temperature have exhibited three absorption bands at about 660, 570 nm; these bands are identified due to Fe$^{3+}$ ion transitions. Additionally a band at 900 nm, identified due to transition of Fe$^{2+}$ (d$^6$) ions [39] is also located in the spectra of all the glasses. With increase in the concentration of Fe$_2$O$_3$ up to 0.3 mol %, the intensity of bands due to Fe$^{2+}$ ions is observed to increase; when the concentration of Fe$_2$O$_3$ is raised beyond 0.3 mol %, a gradual decrease in the intensity of the bands due to Fe$^{2+}$ ions could clearly be observed while that of band due to Fe$^{3+}$ ions is observed to increase. The summary of data on spectral positions of various bands of iron ions in PbO-As$_2$O$_3$ glass ceramics is presented in Table 3.2

<table>
<thead>
<tr>
<th>Glass</th>
<th>Position of Fe$^{3+}$ transitions (nm)</th>
<th>Position of Fe$^{2+}$ transition (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^6A_1(T^2_e^g)$ $^2T_1(T^4_e^g)$</td>
<td>$^5T_2g$ $^5E_g$</td>
</tr>
<tr>
<td>F$_1$</td>
<td>570</td>
<td>680</td>
</tr>
<tr>
<td>F$_2$</td>
<td>570</td>
<td>680</td>
</tr>
<tr>
<td>F$_3$</td>
<td>570</td>
<td>680</td>
</tr>
<tr>
<td>F$_4$</td>
<td>570</td>
<td>680</td>
</tr>
<tr>
<td>F$_5$</td>
<td>570</td>
<td>680</td>
</tr>
</tbody>
</table>

PbO-As$_2$O$_3$ glasses have a complex composition and are the admixtures of network formers and modifiers. As$_2$O$_3$ is a strong network former with corner sharing AsO$_3$ pyramidal units. Normal bond lengths of As-O lie in the range 1.72-1.81 Å and O-As-O and As-O-As bond angles lie in the range 90-103° and 123-135°, respectively [40-43]. PbO in general is a glass modifier and enters the glass network by breaking up the As-O-As bonds (normally the oxygens of PbO break the local symmetry while Pb$^{2+}$ ions occupy interstitial positions) and introduces coordinate defects known as dangling bonds along with non-bridging oxygen ions. In this case the lead ions are octahedrally positioned. However, PbO may also participate in the glass network with PbO$_4$.
The observed gradual increase in the intensity of the bands due to Fe$^{2+}$ ions at the expense of the bands due to Fe$^{3+}$ ions up to 0.3 mol% of Fe$_2$O$_3$ indicates that in this concentration range, iron ions exist largely in divalent state. When the concentration of Fe$_2$O$_3$ is raised from 0.3 to 0.5 mol%, the $5T_2g$-$5E_g$ transition seems to be faded away slowly whereas, the Fe$^{3+}$ ions grew at the expense of $5T_2g$-$5E_g$ band indicating in this concentration range, the iron ions predominantly exist in trivalent state. Further, these Fe$^{3+}$ ions are expected to occupy only interstitial positions since the ratio of cation-oxygen radii is 0.63 for Fe$^{2+}$ ion, which is far from the value of 0.19 to be possessed by an ion to occupy tetrahedral or substitutional sites [45].

The increase in the concentration of modifying ions (Fe$^{3+}$ ions) that participate in the depolymerisation of the glass network, leads to an increase in the concentration of bonding defects and non-bridging oxygens (NBO’s). The higher the concentration of such modifiers, the higher is the concentration of NBO’s in the glass matrix. This leads to a increase in the degree of localization of electrons there by increasing the donor centers in the glass matrix. The increasing presence of these donor centers, may decreases the optical band gap and shifts the absorption edge towards higher wavelength side. Hence we may expect lower band gap for the glass ceramic F3 and higher band gap for the sample F5.
Induced crystallization and structural aspects of PbO-As$_2$O$_3$ glass system doped with Fe$_2$O$_3$

References