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Induced crystallization and structural aspects of PbO-As_2O_3 glass system doped with Fe_2O_3

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Abstract: *PbO–As_2O_3 glasses mixed with different concentrations of Fe_2O_3 (ranging from 0 to 0.5mol%) 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 $PbFe_4(As_5O_{11})_2$, $Fe_2PbAs_2O_6$ 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_2O_3 is less than 0.3mol%.*

I. Introduction

The transitional metal ions such as iron ions, dissolved in PbO-As_2O_5 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^{2+} ion has a large magnetic anisotropy due to its strong spin-orbit interaction of the 3d orbital where as such anisotropy energy of Fe^{3+} ions is small because its orbital angular momentum is zero.

Fe^{2+} has a d^6 electronic configuration, and octahedral complexes with weak field ligands have a high spin arrangement with four unpaired electrons. Fe^{3+} has a d^5 electronic configuration and the ground state is $^6S_{1/2}$ in free atom and possesses zero orbital angular momentum. Hence, any magnetic behaviour of Fe^{3+} 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 $^6A_{1g}$, $^4A_{1g}$, ^4E_g, $^4T_{1g}$, $^4T_{2g}$, $^4A_{2g}$ and to a number of doublet states of which $^6A_{1g}$ lies lowest according to Hunds' rule. The optical absorption spectrum is expected to exhibit bands from the ground state $^6A_{1g}$ 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, $^6A_{1g}(S)$ $^4E_g(G)$, $^6A_{1g}(S)$ $^4A_{1g}(G)$ and $^6A_{1g}(S)$ $^4E_g(D)$ bands are sharp as they arise from intraconfigurational transitions. The transitions $^6A_{1g}(S)$ $^4T_{1g}(G)$ and $^6A_{1g}(S)$ $^4T_{2g}(G)$ involve a change of configuration from $(t_{2g})^3(e_g)^2$ to $(t_{2g})^4(e_g)^1$ and are therefore observed to be broad.

The current investigation is aimed at an understanding the catalyst action of the iron ion on the crystallization of PbO–As_2O_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_2O_3
F_1: 39.9 PbO-60 As_2O_3: 0.1 Fe_2O_3
F_2: 39.8 PbO-60 As_2O_3: 0.2 Fe_2O_3
F_3: 39.7 PbO-60 As_2O_3: 0.3 Fe_2O_3
F_4: 39.6 PbO-60 As_2O_3: 0.4 Fe_2O_3
F_5: 39.5 PbO-60 As_2O_3: 0.5 Fe_2O_3

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

Ardelean et al [17] have studied the magnetic susceptibility of xFe2O3 · (100 - x)[3B2O3 · 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 Fe3+ 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 Fe3+ and Fe2+ valence states that participate in antiferromagnetic interactions. El-Samanoudy et al [12] have studied optical absorption and infrared spectra of Fe2O3 containing TeO2-GeO2 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 disilicate 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 Fe_2O_3-Bi_2O_3 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 studied structural and physical properties of Fe_2O_3 doped lead vanadate glasses; they have concluded that there is a strong role of iron both in the glass network and in the conduction mechanism of the glasses.

Brow et.al [26] have studied the Mossbauer and IR investigations of iron ultraphosphate glasses. Milankovic et.al [27, 28] have reported the spectroscopic and electrical investigations on iron phosphate glasses. Murawski et.al [29] have investigated the electronic conductivity of Na_2O-FeO-P_2O_5 glasses. Marasinghe et.al [30] have carried out a study on the investigation of 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. Hafid et.al [34] have carried out a study on the thermal and infrared characterization of new barum-iron-metaphosphate glasses. Romero-Perez et.al [35] have investigated the magnetic properties of glasses with high iron oxide content. Desoky et.al [36] have studied the conductivity and dielectric behaviour of iron sodium phosphate glases. Congiu et. al [37] have reported the Mossbauer spectroscopic investigation of some iron-containing 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.

III. Results

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.

Summary of data on various physical parameters of PbO -As_2O_3: Fe_2O_3 glass ceramics.

property	glass F	glass F_1	glass F_2	glass F_3	glass F_4	glass F_5
Density d (g/cm^3)	5.1255	5.4115	5.4379	5.4878	5.4896	5.4959
Avg. mol. wt	207.98	207.92	207.86	207.79	207.73	207.67
Iron ion conc. N_i ($x10^{21}$, ions/cm^3)	-	1.57	3.21	4.78	6.38	7.95
Inter ionic distance of iron ions R_i (Å)	-	8.608	6.821	5.940	5.393	5.011
Polran radius R_p(Å)			2.75	2.40	2.17	2.02

3.2 XRD analysis

The X-ray diffraction pattern (Fig. 3.1) of the PbO-As_2O_3 samples crystallized at 400 °C with different concentrations of nucleating agent Fe_2O_3 indicated that these ceramic samples contain $PbFe_4(As_5O_{11})_2$, $Fe_2PbAs_2O_6$ crystal phases along with the lead arsenate crystal phases. These results show that in these glass ceramics, iron ions exist in Fe^{3+} and Fe^{2+} states.

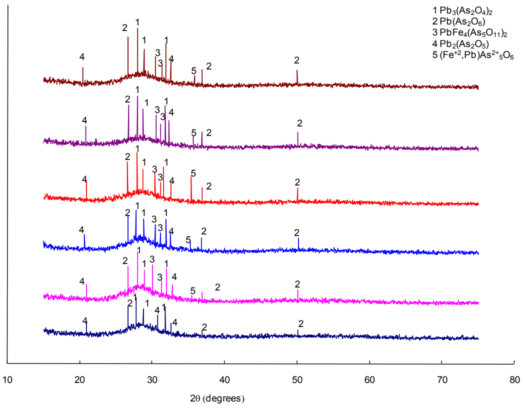

Fig. 3.1 XRD patterns of PbO-As_2O_3: Fe_2O_3 Glasses

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.

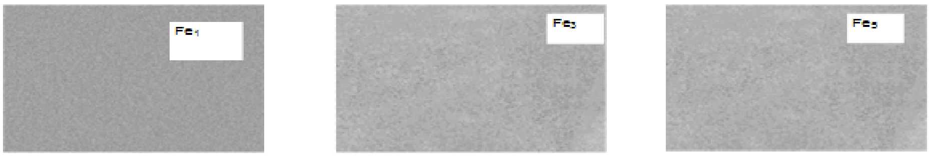

Fig. 3.2 (a) SEM photographs of some of the pre heated PbO-As_2O_3: Fe_2O_3 glasses

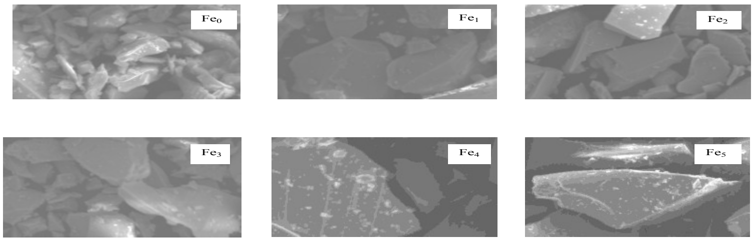

Fig. 3.2 (b) SEM photographs of PbO-As_2O_3: Fe_2O_3 glass ceramics

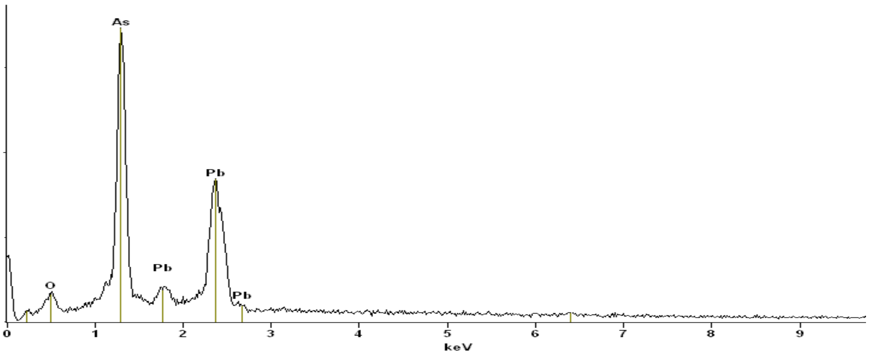

Fig 3.3(a) EDS Spectra of glass ceramic sample F_0

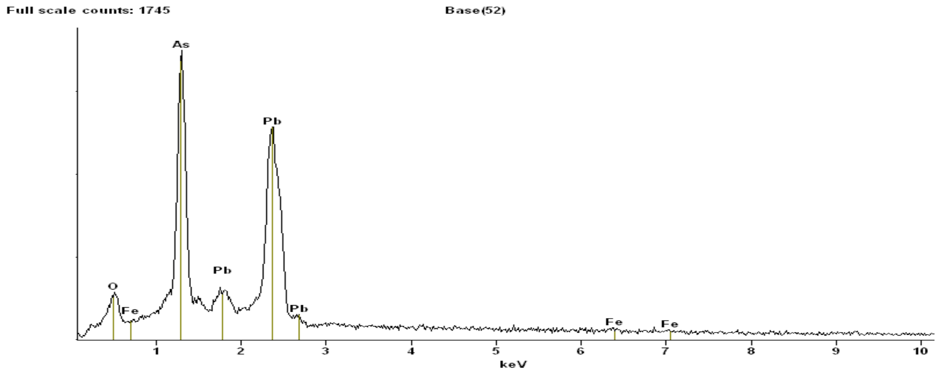

Fig 3.3(b) EDS Spectra of glass ceramic sample F_1

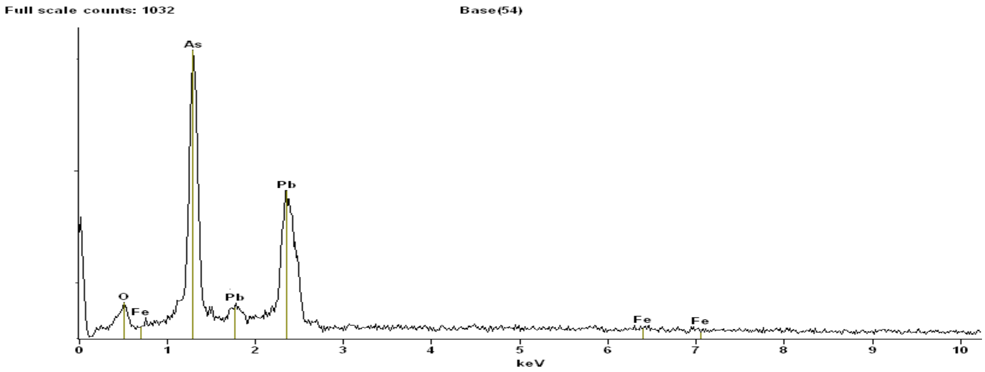

Fig 3.3(c) EDS Spectra of glass ceramic sample F_2

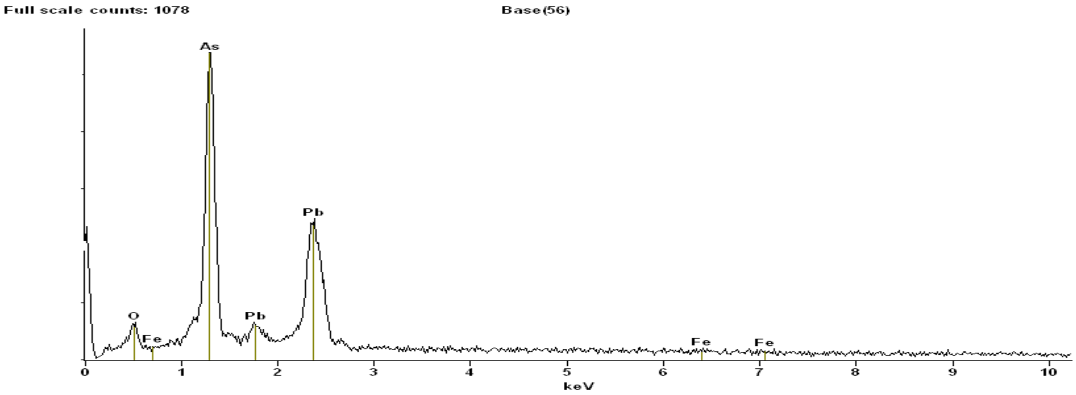

Fig 3.3(d) EDS Spectra of glass ceramic sample F_3

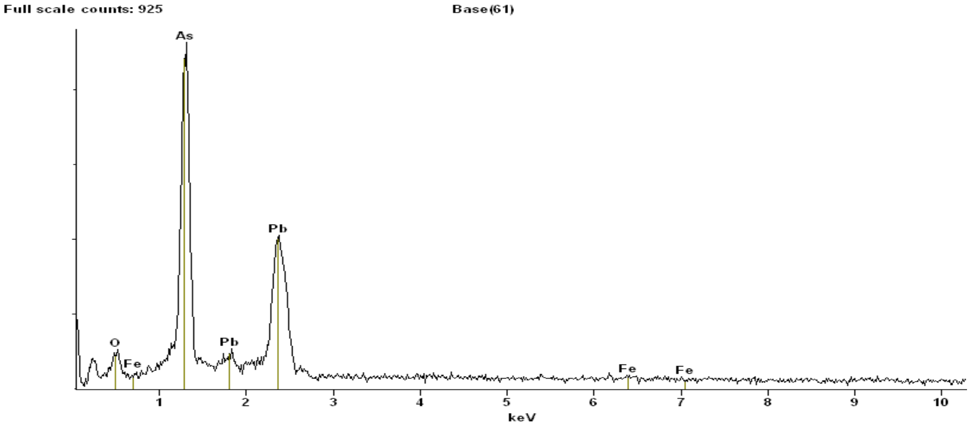

Fig 3.3(e) EDS Spectra of glass ceramic sample F_4

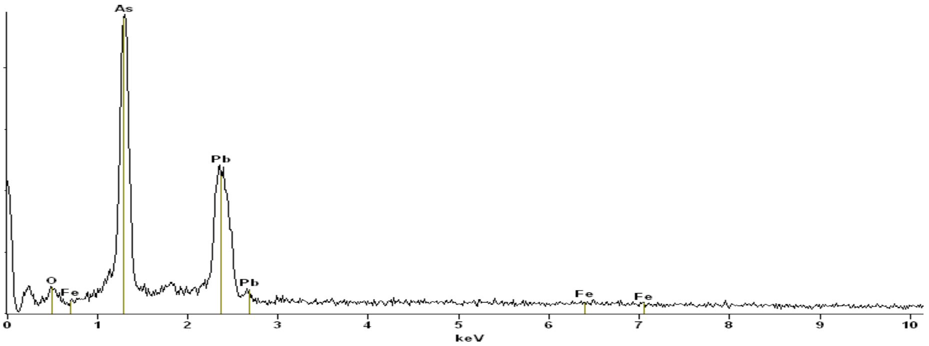

Fig 3.3(f) EDS Spectra of glass ceramic sample F_5

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. Additionaly 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_2O_3 up to 0.3 mol %, the intensity of bands due to Fe^{2+} ions is observed to increase; when the concentration of Fe_2O_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 intra central spectral maxima of iron ions is presented in Table 3.2

Summary of data on spectral positions of various bands of iron ions in PbO-As_2O_3 glass ceramics

Glass	Position of Fe^{3+} transitions (nm)		Position of Fe^{2+} transition (nm)
	$^6A_1(t^3_{2g}e^2_g)$ $a^4T_2(t^4_{2g}e_g)$	$^6A_1(e^2t^3_2)$ $a^4T_1(e^3t^2_2)$	$^5T_{2g}$ ^5E_g
F_1	570	680	889
F_2	570	680	889
F_3	570	680	890
F_4	570	680	890
F_5	570	680	890

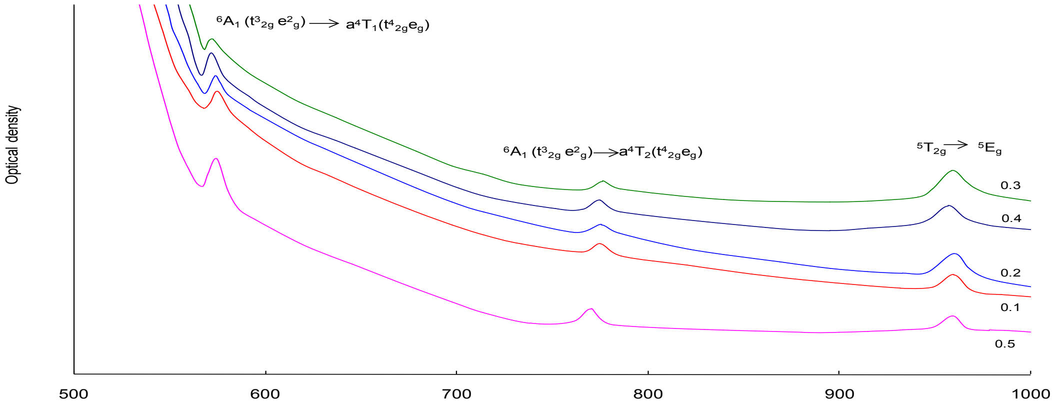

Fig.3.5 Optical absorption speectra of ZnO-Sb_2O_3: Fe_2O_3 glass ceramic samples.

IV. Discussion

PbO-As_2O_3 glasses have a complex composition and are the admixtures of network formers and modifiers. As_2O_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

structural units when lead ion is linked to four oxygens in a covalency bond configuration. In such a case the network structure is considered to build up of PbO_4 and AsO_3 pyramidal units, which are linked together by As-O-Pb bonds.

Iron ions are expected to exist mainly in Fe^{3+} state in the present PbO-As_2O_3 glass ceramic network. However, regardless of the oxidation state of the iron in the starting glass batch, the final glass ceramic may contain both Fe^{2+} and Fe^{3+} ions. The speciation of iron in these glasses is controlled by the following reversible reaction:

$$\mathbf{4Fe^{2+}_{melt} + O_{2\ melt\ atm.}\quad 4Fe^{3+}_{melt} + 2\ O^{2-}_{melt}}$$

A slight compositional dependence of density of PbO-As_2O_3: Fe_2O_3 glass-ceramics has been observed (Table 3.1). In general, the degree of structural compactness, the modification of the geometrical configuration of the glassy network, the change in the coordination of the glass forming ions and the fluctuations in the dimensions of the interstitial holes, are the factors that influence the density of the glass-ceramic material. The progressive introduction of crystallizing agent Fe_2O_3 causes a slight increase in the density; this is an indicative of growing structural compactness of the material.

If lead and iron oxides act as modifiers, As-O bond may be ruptured with the creation of new non-bridging oxygens. Even if Pb^{2+} ions go in to substitutional positions with tetrahedral units, in the glass network, the AsO_3 structural units are subjected to perturbations (like bonding, compression and chemical interactions) due to change in the environment and the incompatibility in ion size. As a result, AsO_3 structural units under go structural distortions involving changes in bond lengths and angles of As-O bonds.

X-ray diffraction patterns exhibit micro structural changes. Lead arsenate and lead iron arsenate crystal phases that are kinetically and thermodynamically feasible seemed to be the main products in the present samples. In iron rich glasses, the presence of $(Fe_2Pb)As_2O_6$ crystalline phases are also detected. These meta stable crystals are usually in solid-solution phases that contain the major constituents of the glass composition in the approximately same proportion as they were present in the original glass matrix. This type of separation of various phases may lead to a iron fortification of the droplet, leaving the glass matrix with a very low content of iron. The Fe rich areas in the glass may enhance the reactivity of Fe with the other oxides that precipitate as high density of fine Fe rich crystals. These tiny crystals act as heterogeneous nuclei for the crystallization of the remaining glass. Further, the diffraction pattern indicates the crystalline phases of Fe^{2+} ions are larger (peak 5) in F_3 sample indicating the presence of larger concentration of iron ions in divalent state in this sample. The low intensity of this diffraction peak observed for the glass ceramic sample (F_5) indicates the lower concentration of these ions in this sample. The scanning electron microscopic pictures of Fe_2O_3 doped glass-ceramics exhibit larger crystals than those visible in the Fe_2O_3 free samples. Further, a reasonably homogeneous distribution of these crystals can be seen. The residual glass phase may act as interconnecting zones among the crystallized areas making the samples free of voids and cracks.

The optical absorption spectra of these glasses have exhibited three absorption bands at 680, 570 nm. Using Tanabe-Sugano- diagrams for d^5 ion, the spectra have been analyzed and the bands are assigned to ${}^6A_1$ $a^4T_2$and ${}^6A_1$() a^4T_1() (spin forbidden) transitions of Fe^{3+} ions respectively [44] with LF parameters, Dq (crystal field splitting energy) =1270cm^{-1} and Racah inter electronic repulsion parameters $B = 840$ cm^{-1}. More precisely basing on selection rules and ligand field calculations the first band is identified due to FeO_6 group and the second band is due to FeO_4 group. The band observed at 980 nm is identified due to ${}^5T_{2g}$ ${}^5E_g$ transition of Fe^{2+} (d^6) ions [39].

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_2O_3 indicates that in this concentration range, iron ions exist largely in divalent state. When the concentration of Fe_2O_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+} ion bands 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^{2+} 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^{2+} 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 centres 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 F_3 and higher band gap for the sample F_5.

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