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Journal of Alloys and Compounds



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# Influence of Ag<sub>2</sub>O on some physical properties of LiF-TiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> glass system

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#### ARTICLE INFO

Article history: Received 11 December 2008 Received in revised form 23 December 2008 Accepted 30 December 2008 Available online 6 January 2009

*Keywords:* Amorphous materials Dielectric response Electron paramagnetic resonance

## ABSTRACT

LiF–TiO<sub>2</sub>–P<sub>2</sub>O<sub>5</sub> glasses mixed with different concentrations of Ag<sub>2</sub>O (ranging from 0 to 1.5 mol%) were prepared. The samples were characterized by X-ray diffraction, scanning electron microscopy. The optical absorption and ESR spectral studies of these glasses have indicated that the titanium ions exist in Ti<sup>3+</sup> state in addition to Ti<sup>4+</sup> state in these samples. The IR spectral studies exhibit bands due to TiO<sub>4</sub> and TiO<sub>6</sub> structural units in addition to the conventional bands due to various phosphate structural groups. From the studies it is observed that the degree of disorder in the glass network increases with the increase in the concentration of Ag<sub>2</sub>O from 0 to 1.0 mol%. Studies on dielectric properties of these glasses over a range of frequency and temperature have also been carried out. These studies have indicated that as the concentration of Ag<sub>2</sub>O is increased up to 1.0 mol%, the insulating strength of the glasses decreases where as the rigidity of the glasses seems to increase when the concentration of Ag<sub>2</sub>O is raised from 1.0 to 1.5 mol%. The a.c. conductivity seems to be predominantly ionic in nature in the glass samples containing Ag<sub>2</sub>O up to 1.0 mol%.

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#### 1. Introduction

In recent years, there has been an enormous amount of research on improving the physical properties and the chemical durability of phosphate glasses by introducing a number of glass formers and modifiers such as  $V_2O_5$ ,  $Cr_2O_3$ ,  $Fe_2O_3$ ,  $Al_2O_3$ ,  $Ga_2O_3$ ,  $Sb_2O_3$ , etc., into  $P_2O_5$  glass network [1–10]. Among various such metal oxides, TiO<sub>2</sub> is expected to be more effective in improving the chemical durability of the phosphate glasses. Normally, the ions of titanium, exist in the glass in Ti<sup>4+</sup> state and participate in the glass network forming with TiO<sub>4</sub>, TiO<sub>6</sub> and some times with TiO<sub>5</sub> (comprising of trigonal bipyramids) structural units [11,12]. However, there are reports suggesting that these ions may also exist in Ti<sup>3+</sup> valence state in some of the glass matrices [13,14]. Further, the inclusion of Ti<sup>4+</sup> ions into the phosphate network makes these glasses useful for optically operated devices, since the empty or unfilled d-shells of Ti ions contribute more strongly to the non-linear polarizabilities.

Silver oxide mixed lithium titanium phosphate glasses can be considered as super ionic solids. Mixed electronic and ionic, pure electronic or pure ionic conduction is expected in these glasses depending upon the composition of the glass constituents. The materials that exhibit mixed conduction mechanism find numerous applications such as cathodes in electro chemical cells, smart windows, etc. Electronic conduction in this type of materials is predicted due to polaron hopping where as the ionic conduction is expected due to the diffusion of alkali ions or any other dopant ions like silver.

Though, a considerable number of studies on certain silver phosphate glasses are available [15,16] still there is a lot of scope to investigate the role of silver ions (especially in the presence of transition metal ions like titanium in small quantities) on the conduction mechanism in lithium fluoro phosphate glasses. In view of such practical importance of these glasses, this paper is devoted to report the results of investigations on dielectric relaxation and a.c. conduction phenomena and to analyze the results of these studies with the aid of the data on spectroscopic studies (optical absorption, ESR, IR) of LiF–TiO<sub>2</sub>–P<sub>2</sub>O<sub>5</sub> glasses mixed with different concentrations of silver ions.

#### 2. Experimental methods

For the present study, a particular composition (39.5 - x)LiF-0.5TiO<sub>2</sub>-60P<sub>2</sub>O<sub>5</sub>:xAg<sub>2</sub>O with eight values of *x* ranging from 0 to 1.5 is chosen. The detailed compositions are as follows:

 $\begin{array}{l} \mathsf{A}_0\colon 39.5 LiF-0.5 TiO_2-60P_2O_5\\ \mathsf{A}_2\colon 39.3 LiF-0.5 TiO_2-60P_2O_5: 0.2 Ag_2O\\ \mathsf{A}_4\colon 39.1 LiF-0.5 TiO_2-60P_2O_5: 0.4 Ag_2O\\ \mathsf{A}_6\colon 38.9 LiF-0.5 TiO_2-60P_2O_5: 0.6 Ag_2O\\ \mathsf{A}_8\colon 38.7 LiF-0.5 TiO_2-60P_2O_5: 0.8 Ag_2O\\ \mathsf{A}_{10}\colon 38.5 LiF-0.5 TiO_2-60P_2O_5: 1.0 Ag_2O\\ \mathsf{A}_{12}\colon 38.3 LiF-0.5 TiO_2-60P_2O_5: 1.2 Ag_2O\\ \mathsf{A}_{15}\colon 38.0 LiF-0.5 TiO_2-60P_2O_5: 1.5 Ag_2O\\ \end{array}$ 

Analytical grade reagents of P<sub>2</sub>O<sub>5</sub>, LiF, Ag<sub>2</sub>O and TiO<sub>2</sub> powders in appropriate amounts (all in mol%) were thoroughly mixed in an agate mortar and melted in a platinum crucible at  $650 \pm 10$  °C in a PID temperature controlled furnace for about

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Table 1						
Summary	of data on	physical	parameters	of LiF-TiO <sub>2</sub>	-P205-Ag20	glasses.

Glass	Density (g/cm <sup>3</sup> )	Average molecular weight	Concentration of Ag <sup>+</sup> ions $N_i$ (×10 <sup>21</sup> ions/cm <sup>3</sup> )	Inter ionic distance of Ag <sup>+</sup> ions $r_i$ (Å)	Polaron radius, r <sub>p</sub> (Å)
A <sub>0</sub>	2.323	95.80	_	_	-
A <sub>2</sub>	2.338	96.22	2.93	6.99	2.82
$A_4$	2.340	96.6	5.83	5.55	2.24
A <sub>6</sub>	2.344	97.05	8.73	4.86	1.96
A <sub>8</sub>	2.346	97.46	11.59	4.418	1.78
A <sub>10</sub>	2.354	97.87	14.48	4.10	1.65
A <sub>12</sub>	2.359	98.28	17.32	3.87	1.56

1 h. The resultant bubble free melt was then poured in a brass mould and subsequently annealed at 250 °C. The amorphous nature of the samples was verified by X-ray diffraction technique (using Xpert's PRO analytical X-ray diffractometer with Cu K $\alpha$  radiation) and scanning electron microscopy studies using HITACHI S-3400N Scanning Electron Microscope.

The density of the glasses was determined to an accuracy of  $\pm 0.0001$ , by the standard principle of Archimedes' using o-xylene (99.99% pure) as the buoyant liquid. For evaluating the density, the mass of the samples was measured to an accuracy of 0.1 mg using Ohaus digital balance Model AR2140. Infrared transmission spectra were recorded on a JASCO-FT/IR-5300 spectrophotometer to a resolution of 0.1 cm<sup>-1</sup> in the spectral range 400-2000 cm<sup>-1</sup> using potassium bromide pellets (300 mg) containing pulverized sample (1.5 mg). These pellets were pressed in a vacuum die at  $\sim$ 680 MPa. The optical absorption spectra of the glasses were recorded at room temperature in the spectral wavelength range covering 300-900 nm to a resolution of 0.1 nm using JASCO Model V-670 UV-vis-NIR spectrophotometer. The electron spin resonance (ESR) spectra of the fine powders of the samples were recorded at liquid nitrogen temperature on IEOL IES-TES100 X-band EPR spectrometer. The dielectric measurements were carried out on LCR Meter (Hewlett-Packard Model-4263 B) in the frequency range 10<sup>2</sup>-10<sup>5</sup> Hz and in the temperature range 30-300 °C. The accuracy in the measurement of dielectric constant is ~0.001 and that of loss is  $\sim 10^{-4}$ 

#### 3. Results

From the measured values of density d and calculated average molecular weight  $\overline{M}$ , various physical parameters such as silver ion concentration  $N_i$  and mean silver ion separation  $r_i$  of these glasses are evaluated using the conventional formulae and are presented in Table 1.

Fig. 1 represents and X-ray diffraction pattern for some of the LiF-TiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>:Ag<sub>2</sub>O glass samples, respectively. We have also recorded SEM pictures of these samples. Both the studies indicate virtually no crystallinity in the samples. Fig. 2 represents the optical absorption spectra of LiF-TiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>:Ag<sub>2</sub>O glasses recorded at room temperature in the wavelength region 300–900 nm. The absorption edge observed at 313 nm for glass  $A_0$  (silver free glass) is shifted towards slightly higher wavelength side with increase in the concentration of Ag<sub>2</sub>O up to 1.0 mol %. The spectrum of glass A<sub>0</sub> exhibited two clearly resolved absorption bands at about 515 and 673 nm due to  $^2B_{2g} \rightarrow ^2B_{1g}$  and  $^2B_{2g} \rightarrow ^2A_{1g}$  transitions of Ti^{3+} ions, respectively [17]; with gradual increase in the concentration of Ag<sub>2</sub>O up to 1.0 mol%, the half width and intensity of these bands are observed to increase with the shifting of meta centers towards slightly higher wavelength (Table 2). However, when the concentration of Ag<sub>2</sub>O is raised beyond 1.0 mol%, a considerable decrease in the intensity of absorption of these bands is observed.

Table 2 Summary of data on optical absorption spectra of LiF-TiO\_2-P\_2O\_5:Ag\_2O glasses.



Fig. 1. XRD patterns of LiF-TiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>:Ag<sub>2</sub>O glasses.



Fig. 2. Optical absorption spectra of LiF–TiO $_2-P_2O_5$  glasses doped with different concentrations of Ag $_2O.$ 

From the observed absorption edges, we have evaluated the optical band gaps ( $E_0$ ) of these glasses by drawing Urbach plot between  $(\alpha h \omega)^{1/2}$  and  $h \omega$  as per the equation:

$$\alpha(\omega)\hbar\omega = C(\hbar\omega - E_0)^2 \tag{1}$$

Fig. 3 represents the Urbach plots of all these glasses in which a considerable part of each curve is observed to be linear. The values of optical band gap ( $E_0$ ) obtained from the extrapolation of

Glass	Cut-off wavelength (nm)	$^{2}B_{2} \rightarrow {}^{2}E\left(nm\right)$	$^2B_2 \rightarrow {}^2B_1 \ (nm)$	Optical band gap (eV)	Crystal field strength $D_q$ (cm <sup>-1</sup> )
A <sub>0</sub>	313	673	516	3.66	1712
A <sub>2</sub>	322	675	522	3.50	1699
A <sub>4</sub>	334	676	531	3.34	1681
A <sub>6</sub>	348	678	536	3.18	1672
A <sub>8</sub>	365	680	539	3.00	1669
A <sub>10</sub>	381	684	547	2.82	1645
A <sub>12</sub>	372	680	541	3.06	1656
A <sub>15</sub>	355	676	536	3.22	1670



Fig. 3. Urbach plots to evaluate energy band gaps for LiF–TiO $_2$ –P $_2O_5$ :Ag $_2O$  glasses.



Fig. 4. ESR spectra of LiF–TiO<sub>2</sub>–P<sub>2</sub>O<sub>5</sub>:Ag<sub>2</sub>O glasses recorded at room temperature.

these curves are presented in Table 2; the value of  $E_0$  is found to decrease with increase in the concentration of Ag<sub>2</sub>O up to 1.0 mol%; for further increase of Ag<sub>2</sub>O, the value of  $E_0$  is observed increase.

Fig. 4 represents the ESR spectra of LiF–TiO<sub>2</sub>–P<sub>2</sub>O<sub>5</sub>:Ag<sub>2</sub>O glasses recorded at room temperature. The spectrum of each sample consists of a triplet pattern with an intense spectral line centered at about g = 1.935 followed by two small satellites at g = 1.961 and 1.973. The signal of the sample A<sub>10</sub> is observed to be more intense with larger half width.



Fig. 5. IR spectra of LiF-TiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>:Ag<sub>2</sub>O glasses.

The infrared transmission spectrum of silver free LiF–TiO<sub>2</sub>–P<sub>2</sub>O<sub>5</sub> glasses (Fig. 5) exhibits vibrational bands at 1294 cm<sup>-1</sup> (identified due to anti-symmetrical vibrations of PO<sub>4</sub><sup>-</sup> groups; this region may also consist of bands due to P=O stretching vibrations), 1040 cm<sup>-1</sup> (a normal vibrational mode in PO<sub>4</sub><sup>3-</sup> group arising out of  $\nu_3$ -symmetric stretching), 901 cm<sup>-1</sup> (due to P–O–P asymmetric bending vibrations) and another band at 785 cm<sup>-1</sup> due to P–O–P symmetric stretching vibrations, this region may also consist of bands due to pyrophosphate groups (P<sub>2</sub>O<sub>7</sub><sup>4-</sup>) [18-20]. Additionally, the spectra have exhibited two prominent bands one at 726 cm<sup>-1</sup> due to Ti–O–Ti symmetric stretching vibrations of TiO<sub>4</sub> units and another at 636 cm<sup>-1</sup> due to the vibrations of TiO<sub>6</sub> structural units [21,22]. The summary of the data on the positions of various bands of IR spectra is presented in Table 3.

With the introduction of  $Ag_2O$  up to 1.0 mol%, the intensity of the bands due to  $PO_4{}^{3-}$  groups, P–O–P symmetric stretching and TiO<sub>4</sub> units, is observed to decrease with a shift in the band positions towards slightly higher wavenumber; the intensity and the position of P–O–P asymmetric bending vibrational band and the bands due

#### Table 3

 $Summary of the data on band positions (cm^{-1}) of various absorption bands in the IR spectra of LiF-TiO_2-P_2O_5: Ag_2O glasses.$ 

Structural unit (nm)	Glass A <sub>0</sub>	Glass A <sub>2</sub>	Glass A <sub>4</sub>	Glass A <sub>6</sub>	Glass A <sub>8</sub>	Glass A <sub>10</sub>	Glass A <sub>12</sub>	Glass A <sub>15</sub>
PO <sub>2</sub> <sup>-</sup> asymmetric groups/P=O stretching	1294	1290	1287	1282	1278	1274	1277	1280
PO <sub>4</sub> <sup>3–</sup> groups	1040	1044	1046	1045	1051	1055	1053	1048
P–O–P asymmetric bending	901	897	893	890	886	882	885	889
P–O–P symmetric stretching	785	787	789	792	796	798	796	794
TiO <sub>4</sub>	726	731	736	738	741	744	742	739
TiO <sub>6</sub>	636	629	622	615	611	605	608	613



Fig. 6. Variation of dielectric constant and dielectric loss with frequency at room temperature for LiF–TiO<sub>2</sub>–P<sub>2</sub>O<sub>5</sub>:Ag<sub>2</sub>O glasses.

to P=O stretching vibrations and  $\text{TiO}_6$  structural units exhibited an increasing trend in this concentration range of Ag<sub>2</sub>O. Nevertheless, when the concentration of dopant is increased beyond 1.0 mol% a reversal trend in the intensity of these bands has been observed. It may be noted here that the band positions of various phosphate structural groups observed for the present glass samples are found to be well within the ranges reported in the literature [23,24].

The dielectric constant  $\varepsilon'$  and loss tan  $\delta$  at room temperature (30 °C) of silver free glass at 100 kHz are measured to be 5.4 and 0.004, respectively. The values of  $\varepsilon'$  and tan  $\delta$  of all the samples are found to increase considerably with decrease in frequency. Fig. 6 represents the variation of dielectric constant and loss of LiF–TiO<sub>2</sub>–P<sub>2</sub>O<sub>5</sub> glasses doped with different concentrations of Ag<sub>2</sub>O with frequency, measured at room temperature; the parameters,  $\varepsilon'$  and tan  $\delta$  are observed to increase with the concentration of Ag<sub>2</sub>O up to 1.0 mol% and for further increase of Ag<sub>2</sub>O the vales of these parameters observed to decrease.

The temperature dependence of  $\varepsilon'$  at different frequencies for one of the glasses, viz., A<sub>6</sub>, and that of the glasses doped with different concentrations of Ag<sub>2</sub>O at 1 kHz are shown in Fig. 7. The value of  $\varepsilon'$  is found to exhibit a considerable increase at higher temperatures especially at lower frequencies; the rate of increase of  $\varepsilon'$  with temperature is found to be the highest for the glass containing 1.0 mol% of Ag<sub>2</sub>O.

The temperature dependence of  $\tan \delta$  of glass A<sub>8</sub> (glass containing 0.8 mol% of Ag<sub>2</sub>O) at different frequencies (as an inset) and a comparison plot of variation of  $\tan \delta$  with temperature, measured at a frequency of 10 kHz are presented in Fig. 8. The curves have exhibited distinct maxima; with increasing frequency the temperature maximum shifts towards higher temperature and with increasing temperature the frequency maximum shifts towards higher fre-



**Fig. 7.** Comparison plot of variation of dielectric constant with temperature measured at 1 kHz for LiF–TiO<sub>2</sub>–P<sub>2</sub>O<sub>5</sub>:Ag<sub>2</sub>O glasses. Inset shows the variation of dielectric constant with temperature for the glass  $A_6$  at different frequencies.

quency, indicating the dielectric relaxation character of dielectric losses of these glasses. Further, the observations on dielectric loss variation with temperature indicate an increase in the broadness and  $(\tan \delta)_{max}$  of relaxation curves with a shift of  $\tan \delta_{max}$  towards lower temperature with increase in the concentration of Ag<sub>2</sub>O up to 1.0 mol%.

The effective activation energy  $W_d$ , for the dipoles is evaluated for all the glasses using the relation:

$$f = f_0 \,\mathrm{e}^{-W_{\mathrm{d}}/kT},\tag{2}$$

and furnished in Table 4 along with other pertinent data on dielectric loss. The activation energy is found to be the lowest for the glass  $A_{10}$ .

The ac conductivity  $\sigma_{ac}$  is calculated at different temperatures using the equation:

$$\sigma_{\rm ac} = \omega \varepsilon_0 \, \varepsilon' \, \tan \delta \tag{3}$$

Table 4

Summary of data on dielectric loss of LiF-TiO<sub>2</sub>- $P_2O_5$ :Ag<sub>2</sub>O glasses.

Glass	Temperature region of relaxation (°C)	$(\tan \delta_{\max})_{avg}$	Activation energy for dipoles (eV)
A <sub>0</sub>	119–140	0.0074	3.86
A <sub>2</sub>	114–130	0.0091	3.50
A <sub>4</sub>	99–122	0.0112	3.34
A <sub>6</sub>	87-110	0.0134	3.26
A <sub>8</sub>	80-106	0.0156	3.14
A <sub>10</sub>	60-90	0.0183	2.98
A <sub>12</sub>	70–95	0.0165	3.25
A <sub>15</sub>	85-107	0.0143	3.38



**Fig. 8.** A comparison plot of variation of dielectric loss with temperature measured at 10 kHz for LiF–TiO<sub>2</sub>–P<sub>2</sub>O<sub>5</sub>:Ag<sub>2</sub>O glasses. Inset shows the variation of dielectric loss with temperature at different frequencies for the glass A<sub>8</sub>.

(where  $\varepsilon_0$  is the vacuum dielectric constant) for different frequencies and the plot of  $\log \sigma_{\rm ac}$  against 1/T for all the glasses at 100 kHz is shown in Fig. 9 and at different frequencies for one of the glasses (glass A<sub>4</sub>) is shown as inset (a) of the same figure, the conductivity is found to increase considerably with increase in the concentration of Ag<sub>2</sub>O up to 1.0 mol% at any given frequency and temperature. From these plots, the activation energy for the conduction in the high temperature region over which a near linear dependence of  $\log \sigma_{\rm ac}$  with 1/T could be observed is evaluated and presented in Table 5; the activation energy is found to decrease with increase of Ag<sub>2</sub>O content up to 1.0 mol% in the glass matrix.

### 4. Discussion

LiF–TiO<sub>2</sub>–P<sub>2</sub>O<sub>5</sub>:Ag<sub>2</sub>O glasses have a complex composition and are admixtures of network formers and modifiers. Normally, the structure of the simple phosphate glasses is dependent on O/P ratios and the fraction of Q phosphate tetrahedra. For single P<sub>2</sub>O<sub>5</sub> glass O/P=2.5 and the glass network is build up of Q<sup>3</sup> tetrahedra

# Table 5Summary of data on a.c. conductivity of LiF-TiO2-P2O5:Ag2O glasses.

Glass	$N(E_{\rm F})$ in $10^{21}$	eV <sup>-1</sup> /cm <sup>3</sup>		Activation energy	
	Austin	Butcher	Pollack	for conduction (eV)	
A <sub>0</sub>	0.728	0.303	0.740	0.47	
A <sub>2</sub>	0.871	0.363	0.885	0.44	
A <sub>4</sub>	1.043	0.435	1.059	0.32	
A <sub>6</sub>	1.225	0.511	1.245	0.31	
A <sub>8</sub>	1.437	0.599	1.460	0.30	
A <sub>10</sub>	1.636	0.682	1.662	0.29	
A <sub>12</sub>	1.540	0.642	1.564	0.31	
A <sub>15</sub>	1.342	0.560	1.363	0.33	



**Fig. 9.** Variation of  $\sigma_{ac}$  with 1/T for LiF–TiO<sub>2</sub>–P<sub>2</sub>O<sub>5</sub>:Ag<sub>2</sub>O glasses at the frequency of 100 kHz. Inset (a) shows variation of  $\sigma_{ac}$  with 1/T at different frequencies for the glass A<sub>4</sub> and inset (b) shows variation of  $\sigma_{ac}$  with the activation energy for conduction.

with the bridging oxygens; and with the fourth oxygen doubly bonded to the phosphorus atom. With the addition of titanium oxide, an ultraphosphate network consisting of  $Q^2$  and  $Q^3$  tetrahedra may form [25]. LiF and Ag<sub>2</sub>O are well known modifier oxides and enter the glass network either by rupturing or by breaking up the P–O–P structures. In turn, the break-up of the P–O–P structures introduces coordinated defects, known as dangling bonds, along with non-bridging oxygen ions. It is also quite likely that Ag<sup>+</sup> ions cause a change from the pure covalent bonds of PO<sub>4</sub> cluster to the substantial admixture of the ionic component similar to Li–F [16].

Titanium ions are expected to exist mainly in  $Ti^{4+}$  state in LiF–TiO<sub>2</sub>–P<sub>2</sub>O<sub>5</sub>:Ag<sub>2</sub>O glass network. However, the reduction of  $Ti^{4+}$  to  $Ti^{3+}$  appears to be viable during melting, annealing and crystallization processes of the glasses. Earlier reports on some other glass systems containing  $TiO_2$  suggested that upon heating at about 700 °C, there is a possibility for the reduction of  $Ti^{4+}$  ions to  $Ti^{3+}$  ions [26]. Further, the reduction,  $Ti^{4+} + e^- = Ti^{3+}$ , takes place only with energy  $E^0 = 0.2$  V. The speciation of titanium ions in these glasses is controlled by the reversible reaction:

$$4\mathrm{Ti}_{\mathrm{atm}}^{4+} + 2\mathrm{O}_{\mathrm{melt}}^{2+} \rightleftharpoons 4\mathrm{Ti}_{\mathrm{melt}}^{3+} + 2\mathrm{O}_{2\,\mathrm{melt}\,\mathrm{atm}}$$

The Ti<sup>4+</sup> ions occupy both tetrahedral and substitutional octahedral sites as corner-sharing  $[TiO_6]^{2-}$  units where as Ti<sup>3+</sup> ions occupy only modifying positions in the glass network. TiO<sub>4</sub> and TiO<sub>6</sub> units of Ti<sup>4+</sup> ions enter the glass network, may alternate with PO<sub>4</sub> structural units and form linkages of P–O–Ti type. The entry of TiO<sub>2</sub> into lithium fluoro phosphate glass network as was reported in other

alkali phosphate glasses may be visualized as follows:

Entry of TiO<sub>6</sub> octahedral in to LiF-TiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>:Ag<sub>2</sub>O glass network may twist or distort the interconnected chains of PO<sub>4</sub> units and increase the randomness of the glass network.

The ingress of Ag<sup>+</sup> ions are expected to modify P-O-Ti and Ti-O-Ti linkages as

$$P\text{-}O\text{-}Ti \,+\, Ag_2O \,\rightarrow\, P\text{-}O\text{-}Ag^+ \,+\, Ti\text{-}O \,-\, Ag^+$$

or



As a consequence a disruption in the PO<sub>4</sub> and TiO<sub>4</sub> tetrahedra with the creation of a number of bonding defects are expected.

Using Tanabe–Sugano diagrams for d<sup>1</sup> ions, the bands observed in the optical absorption spectra in the regions 510-550 nm and 670–685 nm are assigned to  $^2B_{2g} \rightarrow {}^2B_{1g}$  and  $^2B_{2g} \rightarrow {}^2A_{1g}$  transitions of 3d<sup>1</sup> electron of the Ti<sup>3+</sup> ions, respectively. With the gradual increase in the concentration of dopant Ag<sub>2</sub>O up to 1.0 mol% in the sample, these bands have exhibited red shift with increasing intensity. So one can conclude that: (i) an increase in the concentration of Ti<sup>3+</sup> ions or decrease in the concentration of Ti<sup>4+</sup> ions and (ii) weaker ligand field of existing Ti<sup>3+</sup> ions in these samples. The ligand field parameter  $D_q$  (crystal field strength) is evaluated using energies of these transitions and the values obtained are furnished in Table 2. The variation of the parameter  $D_q$  with the concentration of Ag<sub>2</sub>O exhibited the lowest value for the glass A<sub>10</sub>. This dependence is just similar to optical band gap.

As mentioned earlier, Ag<sup>+</sup> ions and the octahedrally coordinated Ti<sup>3+</sup> ions act as modifiers similar to lithium ions and induce non-bridging oxygens (NBOs) in the glass network. The higher the concentration of these modifier ions, the higher is the concentration of NBOs in the glass matrix. Because of these reasons an increase in the degree of localization of electrons there by an increase in the donor centers in the glass network is expected. The gradual increase in the concentration of Ag<sup>+</sup> ions and Ti<sup>3+</sup> ions causes a creation of large number of donor centers; subsequently, the excited states of localized electrons originally trapped on Ti<sup>3+</sup> sites begin to overlap with the empty 3d states on the neighboring Ti<sup>4+</sup> sites. As a result, the impurity band becomes more extended into the main band gap. This development might have shifted the absorption edge to the lower energy (Table 2) which leads up to a significant shrinkage in the band gap as observed.

The higher concentration of Ti<sup>4+</sup> ions that participate in the glass network, the lower is the concentration of NBOs in the glass matrix. Because of this reason a decrease in the degree of localization of electrons or a decrease in the donor centers in the glass-ceramic network is expected. The presence of smaller concentration of these donor centers increases the optical band gap and shifts the absorption edge towards lower wavelength side as observed for the glasses A12 and A15

spectrum the central line at g = 1.94 is due to tetragossed octahedral sites of Ti<sup>3+</sup> ions with  $|xy\rangle$  ground state

$$[TiO_{6/2}]^{2-} + 2[PO_{4/2}]^{+}$$

[27,28] where as the auxiliary components are due to the hyperfine interaction of an unpaired electron with two equivalent I = 1/2nuclear spins. Based up on the earlier reports [29,30], it seems reasonable to attribute the observed triplet to TiF<sup>2+</sup> molecular ion. The relatively highest intensity and half-width of the signal observed for the spectrum of the sample A<sub>10</sub> suggests a larger concentration of reduced Ti<sup>4+</sup> ions in to Ti<sup>3+</sup> ions in this sample.

The IR spectra of these glasses appears to be dominated by orthophosphate structural units; however, the band due to pyrophosphate structural units lies around 1090 cm<sup>-1</sup>, which is not too far from the band position of PO<sub>4</sub><sup>3–</sup> units. Hence the observed band at about 1050 cm<sup>-1</sup> in the spectra of these glasses may be considered as the superposition of these two bands, especially in the spectrum of more disordered glass. The same is true for metaphosphate groups also, because the band due to these groups is expected at about  $1280 \,\mathrm{cm}^{-1}$  [31].

If silver and trivalent titanium ions act as modifiers, the  $\pi$ -bond of P=O may be ruptured, creating new non-bridging oxygens. Even if Ti<sup>4+</sup> ions enter substitutional positions with octahedral units in the glass network, the PO<sub>4</sub> 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, PO<sub>4</sub> structural units undergo structural distortions involving changes in bond lengths and angles of P-O bonds. For these reasons we expect decrease in the intensity, PO<sub>4</sub><sup>3–</sup> symmetric stretching and a band due to P-O-P symmetric/Ti-O-P stretching vibrations in the IR spectra. The observed gradual decrease in the intensity of these bands in the spectra of the glasses  $A_0-A_{10}$  may be ascribed to these reasons. The observed increase in the intensity of these symmetrical bands and simultaneous decrease in the intensity of the bands due to P–O–P asymmetric vibrations in the spectra of the glasses A<sub>10</sub>-A<sub>15</sub> suggests that, in the networks of these glasses, the titanium ions mostly occupy tetrahedral positions and their positions are less disturbed by silver ions.

In general, the dielectric constant of a material is due to electronic, ionic, dipolar and space charge polarizations. Out of these, the space charge contribution depends on the perfection of the glasses. Recollecting the data, on dielectric properties, for LiF-TiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>:Ag<sub>2</sub>O glasses, the slight increase in the dielectric constant and loss at room temperature, particularly at low frequencies can be ascribed to the defects produced in the glass network that contribute to the space charge polarization. With the gradual increase of Ag<sub>2</sub>O up to 1.0 mol% in the glass network, the values of  $\varepsilon'$ , tan  $\delta$  and  $\sigma_{ac}$  are found to increase at any frequency and temperature and the activation energy for a.c. conduction is observed to decrease; such variations of these parameters are obviously due to larger space charge polarization owing to the enhanced degree of disorder in the glass network.

To be more specific, the concentration of Ag<sub>2</sub>O is increased up to 1.0 mol% in the glass network, there is a growing presence of Ti<sup>3+</sup> ions in the glass network; these ions similar to Li<sup>+</sup> and Ag+ ions disrupt the glass network as mentioned earlier. The defects thus



**Fig. 10.** Comparison plot of  $\varepsilon'$  and  $\varepsilon''$  with 1/T for the sample A<sub>10</sub> measured at 1 kHz for LiF–TiO<sub>2</sub>–P<sub>2</sub>O<sub>5</sub>:Ag<sub>2</sub>O glasses.

produced create easy path ways for the migration of charges that would build up space charge polarization leading to an increase in the dielectric parameters as observed. The data on the dielectric properties of LiF–TiO<sub>2</sub>–P<sub>2</sub>O<sub>5</sub>:Ag<sub>2</sub>O glasses further, indicate a gradual decrease in the dielectric parameters with increase in the concentration of Ag<sub>2</sub>O from 1.0 to 1.5 mol%; these results suggest that there is a decrease in the concentration of free charge carriers that build up space–charge polarization [32,33] and support the view point that there is a growing presence of titanium ions that participate in the network forming with TiO<sub>4</sub> structural units.

Conventionally, the dielectric relaxation effects are described with the variable frequency at a fixed temperature. However, similar information can also be obtained by analyzing these results at a fixed frequency at variable temperature as suggested by Bottcher and Bordewijk [34]. Substituting Eq. (2) in the standard Debye dielectric relaxation relations, one obtains:

$$\varepsilon'(\omega, T) = \varepsilon_{\infty} + \frac{1}{2}(\varepsilon_{s} - \varepsilon_{\infty}) \left\{ 1 - tgh\left[\frac{E_{a}(1/T - 1/T_{m}(\omega))}{k}\right] \right\}$$
(4)

$$\varepsilon''(\omega,T) = \frac{(1/2)(\varepsilon_s - \varepsilon_\infty)}{\cosh[E_a(1/T - 1/T_m(\omega))/k]}$$
(5)

In these equations  $T_{\rm m}(\omega)$  is the temperature at  $(\varepsilon')_{\rm max}$ . Thus, as per Eqs. (4) and (5), the plots of  $\varepsilon'(\omega, T)$  and  $\varepsilon''(\omega, T)$  against 1/Tshould be centro symmetric and symmetric curves, respectively in the dielectric relaxation region. As an example for one of the glass samples (viz., A<sub>10</sub>) under investigation, the variation of  $\varepsilon'(\omega, T)$  and  $\varepsilon''(\omega, T)$  with 1/T are shown in Fig. 10. The shape of these curves is well in accordance with Eqs. (4) and (5) and clearly confirms the relaxation character of dielectric properties of these glasses. Earlier studies on the glasses containing d<sup>1</sup> ions like W<sup>5+</sup>, Cr<sup>5+</sup>, V<sup>4+</sup>, Mo<sup>5+</sup>



**Fig. 11.** Isotherms of ac conductivity as a function of  $Ag_2O$  in the high temperature region for LiF–TiO<sub>2</sub>–P<sub>2</sub>O<sub>5</sub>:Ag<sub>2</sub>O glasses. Inset shows the variation of activation energy with the concentration of Ag<sub>2</sub>O.

showed that these ions contribute to the dielectric relaxation effects [35–38]; hence, the observed relaxation effects in the present glass samples can safely be attributed to  $Ti^{3+}$  ions. The increase in the breadth and the intensity of the relaxation peaks and the decrease in the activation energy for dipoles is the manifestation of increase in the concentration of  $Ti^{3+}$  ions with increase in Ag<sub>2</sub>O content in the glass matrix.

When  $\log \sigma(\omega)$  is plotted as a function of activation energy for conduction (in the high temperature region) a near linear relationship is observed (see inset (b) of Fig. 9). This observation suggests that the conductivity enhancement is directly related to the thermally stimulated mobility of the charge carriers in the high temperature region [39].

The conductivity curve as a function of Ag<sub>2</sub>O concentration passes through a maximum at  $x = 1.0 \mod \%$  (Fig. 11). The activation energy for conduction as a function of the concentration of Ag<sub>2</sub>O, exhibited a minimum x = 1.0 mol% (see inset (a) of Fig. 9). Thus Fig. 11 and its inset suggest a kind of transition from predominantly ionic (zone-I, for 0 < x < 1.0 mol%) to electronic (zone-II for x > 1.0 mol%) conductivity [40]. The gradual increasing contents of the modifier ions Ag<sup>+</sup> and Ti<sup>3+</sup> ions, the active centres for ionic conduction, the highly mobile lithium ions or the non-bridging oxygens become closer and the ionic transport progressively increases. On the other hand in the zone-II, the mobile electrons, or polarons, involved in the process of transfer from Ti<sup>3+</sup> to Ti<sup>4+</sup>, are attracted by the oppositely charged Ag<sup>+</sup> and/or Li<sup>+</sup> ions. This cation-polaron pair moves together as a neutral entity. As expected, the migration of this pair is not associated with any net displacement of the charge and thus does not contribute to electrical conductivity [41]; in consequence a decrease in the conductivity results, as observed.

The low temperature part of the conductivity (a near temperature independent part, as in the case of present glasses up to nearly 350 K) can be explained on the basis of quantum mechanical model [42]. The equation for a.c. conductivity due to quantum mechanical tunneling is given by [42]:

$$\sigma(\omega) = \eta e^2 KT [NE_{\rm F}]^2 \alpha^{-5} \omega \left[ \ln \frac{\nu_{\rm ph}}{\omega} \right]^4 \tag{6}$$

From Eq. (6), the value of  $N(E_{\rm F})$ , i.e. the density of the defect energy states near the Fermi level is evaluated, taking the value of  $\alpha$  (electronic wave function decay constant) as  $0.486 (\text{\AA})^{-1}$  (obtained by plotting log  $\sigma_{\rm ac}$  against  $R_{\rm i}$ ), e is the charge of the electron, k is the Boltzmann constant,  $\omega$  is the frequency and  $\nu_{\rm ph}$  the phonon frequency (5 × 10<sup>12</sup> Hz) and  $\eta$  is a constant and its value is given by

 $\eta = \pi/3$  [42], =3.66 $\pi^2/6$  [43], = $\pi^4/96$  [44] is computed for a frequency of 10<sup>5</sup> Hz at T=333 K and presented in Table 5. The value of  $N(E_{\rm F})$  is found to increase with increase in the concentration of Ag<sub>2</sub>O up to 1.0 mol%. Such increase also suggests an increasing disorder in the glass network with increase in the concentration of Ag<sub>2</sub>O up to this concentration.

#### 5. Conclusions

The summary of the results of various studies of LiF–TiO<sub>2</sub>–P<sub>2</sub>O<sub>5</sub> glasses doped with different concentrations of Ag<sub>2</sub>O is as follows: Optical absorption and ESR spectral studies indicated that titanium ions in these glasses exist in trivalent state in addition to and tetravalent state. These studies have also revealed that the concentration of Ti<sup>3+</sup> ions increases gradually with increases in the concentration of Ag<sub>2</sub>O. IR spectral studies indicated that titanium ions exist in tetrahedral and octahedral substitutional positions and form P–O–Ti linkages. The entry of Ag<sup>+</sup> ions causes formation of P–O<sup>–</sup>Ag<sup>+</sup> and Ti–O<sup>–</sup>Ag<sup>+</sup> complexes in the glass network. The results of dielectric studies exhibited dielectric relaxation effects and these effects are attributed to Ti<sup>3+</sup> ions. The analysis of a.c. conductivity in the high temperature region indicated that with in the concentration range of 0 to 1.0 mol% of Ag<sub>2</sub>O, the conductivity is mainly ionic in nature.

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