Physical Properties of \((\text{Li}_2\text{O})_{0.40}(\text{Fe}_2\text{O}_3)_{0.05-x}(\text{P}_2\text{O}_5)_{0.55-}\times(\text{Ag}_2\text{O})_x\) Glasses

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Abstract

\(\text{Li}_2\text{O}–\text{Fe}_2\text{O}_3–\text{P}_2\text{O}_5\) glasses containing small concentrations of \(\text{Ag}_2\text{O}\) from 0 to 2 mol\% were prepared. Samples are characterized by X-ray diffraction and scanning electron microscope techniques. A number of studies viz., chemical durability, dielectric studies (constant \(\varepsilon’\), loss tan \(\delta\), a.c. conductivity \(\sigma_{ac}\) over a range of frequency and temperature), spectroscopic (infrared, optical absorption ESR spectra) and magnetic susceptibility studies of these glasses, have been carried out. The interesting variations observed in all these properties with the concentration of Ag\(^+\) ions have been analyzed in the light of different oxidation states and environment of iron ions in the glass network.

Key Words: Glasses, dielectrics, optical materials and properties.

1. Introduction

Iron phosphate glasses are known for their high chemical durability and for their application in vitrifying nuclear waste \([1, 2]\). With the addition of lighter alkali ion-like lithium, iron phosphate glasses becomes suitable for a variety of technological applications such as solid electrolytes, and in electrochemical devices such as high energy density batteries \([3]\). Mixing of silver oxide in small quantity to phosphate glasses presents an added advantage allowing these glasses to be used as super ionic solids \([4]\). Mixed electronic and ionic, pure electronic or pure ionic conduction is expected in these glasses, depending upon the constituent composition of the glass. The materials that exhibit mixed conduction mechanism find numerous applications, such as cathodes in electro chemical cells, in smart windows etc. \([5]\). Electronic conduction in such materials is predicted due to polaron hopping, where the ionic conduction is expected due to the diffusion of alkali or other dopant ions such as silver. Phosphorous pentoxide is a strong glass network forming oxide, participating in the network with \(\text{PO}_4\) structural units. One of the four oxygen atoms in \(\text{PO}_4\) tetrahedron is doubly bonded to the phosphorus atom with the substantial \(\pi\)-bond character to account for pentavalency of phosphorous. The \(\text{PO}_4\) tetrahedrons are linked together with covalent bonding in chains or rings by bridging oxygens. Neighbouring phosphate chains are linked together by cross bonding between the metal cation and two non-bridging oxygen atoms of each \(\text{PO}_4\) tetrahedron in general, the P–O–P bond between \(\text{PO}_4\) tetrahedra is much stronger than the cross bond between chains via the metal cations \([6]\). Iron ions are expected to exist mainly in Fe\(^{3+}\) state in \(\text{Li}_2\text{O}–\text{Fe}_2\text{O}_3–\text{P}_2\text{O}_5\) glass network.

However, regardless of the oxidation state of the iron in the starting glass batch, the final glass contains both Fe\(^{3+}\) and Fe\(^{2+}\) ions \([7]\). The concentration of Fe\(^{2+}\) (or Fe\(^{3+}\)) in these iron phosphate glasses depends
primarily upon the melting temperature, and to some extent on the melting time. Majority of the studies available on iron phosphate glasses are on Mossbauer spectra [8, 9]. The studies on dielectric properties viz., dielectric constant, loss and a.c. conductivity (over a wide range of frequency and temperature) not only help understand the a.c. conduction mechanism but also contribute additional information on structural aspects of the glasses. Work along these lines has been carried out in recent years on a variety of inorganic glass systems yielding valuable information [10, 11]. However, such type of studies on iron phosphate glasses, especially those mixed with silver ions, are very few.

The intent of the present study is to report the results of a systematic study on dielectric properties, e.g. dielectric constant, loss and a.c. conductivity (over a wide range of frequency and temperature) and breakdown strength in air medium at room temperature of Li₂O–Fe₂O₃–P₂O₅ glasses doped with small concentrations of Ag₂O, and to throw some light on the influence of Ag⁺ ion on structural properties these glasses using the results of these studies with the aid of the data on IR, ESR and optical absorption and magnetic susceptibility. Studies on chemical durability are also included.

2. Experimental Methods

Within the glass forming region of Li₂O–Fe₂O₃–P₂O₅ glass system, the following compositions with a gradual increase in the concentration of Ag₂O, are chosen for the present study:

FA₀: (Li₂O)₀.40(Fe₂O₃)₀.050(P₂O₅)₀.55
FA₂: (Li₂O)₀.40(Fe₂O₃)₀.046(P₂O₅)₀.55: (Ag₂O)₀.002,
FA₄: (Li₂O)₀.40(Fe₂O₃)₀.046(P₂O₅)₀.55: (Ag₂O)₀.004,
FA₆: (Li₂O)₀.40(Fe₂O₃)₀.044(P₂O₅)₀.55: (Ag₂O)₀.006,
FA₈: (Li₂O)₀.40(Fe₂O₃)₀.042(P₂O₅)₀.55: (Ag₂O)₀.008,
FA₁₀: (Li₂O)₀.40(Fe₂O₃)₀.040(P₂O₅)₀.55: (Ag₂O)₀.010,
FA₁₅: (Li₂O)₀.40(Fe₂O₃)₀.035(P₂O₅)₀.55: (Ag₂O)₀.015,
FA₂₀: (Li₂O)₀.40(Fe₂O₃)₀.030(P₂O₅)₀.55: (Ag₂O)₀.020.

Appropriate amounts of “analar” grade reagents of Li₂CO₃, (NH₄)H₂PO₄, Fe₂O₃ and Ag₂O were thoroughly mixed in an agate mortar and melted in a thick walled platinum crucible at 1100 ± 10 °C for about 1 h until a bubble-free liquid was formed. The resultant melt was then cast in a brass mould and subsequently annealed at 350 °C. X-ray diffraction (Figure 1) and scanning electron microscopy studies were used to confirm that the samples prepared were vitreous. The results of these studies clearly indicated that the samples prepared are free from crystalline phases.

![Figure 1. XRD patterns of Li₂O–P₂O₅–Fe₂O₃ glasses containing different concentrations of Ag₂O.](image-url)
The density $d$ of the glasses was determined to an accuracy of $(\pm 0.001)$ by the standard principle of Archimedes' using o-xylene (99.99% pure) as the buoyant liquid. The mass of the samples was measured to an accuracy of 0.1 mg using a Denver balance, model APX-200. For evaluating the chemical durability, the bulk glasses were suspended by a weightless strand in about 100 ml of water of pH 7 for about 4 h at 90 °C for about 12, 24, 48 hours. At each time interval the weight loss ($\Delta W$) is evaluated and the dissolution rate $DR$ for the bulk glasses were calculated using the relation $DR = \Delta W / (St)$ g/cm$^2$/min, where $S$ is the surface area of the sample and $t$ is the time of immersion.

The glasses were then ground and optically polished. The final dimensions of the glasses used for electrical and optical absorption measurements were about $1 \times 1 \times 0.2$ cm$^3$. The glass transition temperature of these glasses were determined by differential scanning calorimetric studies using a TA instruments model DSC-2010 with a programmed heating rate of 10 °C·min$^{-1}$, in the temperature range 30–550 °C.

The optical absorption spectra of the glasses were recorded at room temperature in the wavelength range 300–800 nm up to a resolution of 0.1 nm using Cary-5000 spectrophotometer. The electron spin resonance (ESR) spectra of the fine powders of the samples were recorded at liquid nitrogen temperature on Jeol JES-TES100 X-band EPR spectrometer.

Infrared transmission spectra were recorded on a Jasco FT/IR–5300 spectrophotometer with a resolution of 0.1 cm$^{-1}$ in the range 400–2000 cm$^{-1}$ using potassium bromide pellets (300 mg) containing pulverized sample (1.5 mg). These pellets were pressed in a vacuum die at ~680 MPa. A thin layer of silver paint was applied on either side of the large-faces of the samples, in order to serve as electrodes for dielectric measurements. The dielectric measurements were made on LCR Meter (Hewlett-Packard Model-4263 B) in the frequency range $10^2$–$10^5$ Hz and in the temperature range 30–250 °C. The accuracy in the measurement of dielectric constant is $\sim 0.001$ and that of loss is $\sim 10^{-4}$. The dielectric breakdown strength of all the glasses was determined at room temperature in air medium using a high a.c. voltage breakdown tester (ITL Model AAH-55, Hyderabad) operated with an input voltage of 250 V at a frequency of 50 Hz; it was ensured that all the glasses used for this study were of nearly identical thicknesses. The magnetic susceptibility measurements were made by Guoy’s method to an accuracy of $10^{-4}$ emu.

3. Results

The samples prepared were free from visible inhomogeneities, such as inclusions, cracks or bubbles. Based upon the visual examination, the absence of peaks in the X-ray diffraction pattern, SEM images, the existence of glass transition temperature $T_g$, we could come to the conclusion that the samples prepared were amorphous in nature. From the measured values of density $d$ and calculated average molecular weight $\overline{M}$, various physical parameters such as silver ion concentration $N_i$, mean silver ion separation $r_i$, polaron radius $r_p$, which are useful for understanding the physical properties of these glasses are evaluated and presented in Table 1. The density of the glass is observed to increase with increase in the concentration of Ag$_2$O. The increase in the density although small is believed to be due to the replacement of lighter iron ions with the heavier silver ions in the glass matrix.

The dissolution rate of the lithium-iron phosphate glasses in distilled water solution (of pH 7) at 90 °C varied significantly with Fe$_2$O$_3$/Ag$_2$O content, as shown in Figure 2 and Table 1. The dissolution rate, decreased from $5 \times 10^{-7}$ to $10^{-9}$ g·cm$^{-2}$·min$^{-1}$ with an upward kink at 1.0 mol% of Ag$_2$O. The pH of the distilled water solution after corrosion testing shows a slow increase with increase in the concentration of Ag$_2$O from 0 to 0.6 mol% and from 1 to 1.5 mol%; however, a considerable decrease within the concentration range 0.8 to 1.0 mol% of Ag$_2$O and 4.2 to 4 mol% Fe$_2$O$_3$ (Figure 3) has been observed. Nevertheless, no significant change is observed, in pH of the liquid in contact with glasses containing 1.5 to 2.0 mol% of Ag$_2$O. The reduction in pH of the liquid in contact with glasses AF$_8$ and AF$_{10}$ is consistent with the dissolution of phosphate species from these glasses and the subsequent formation of phosphoric acid.
Figure 2. Dissolution rate of the lithium-iron phosphate glasses in distilled water solution at 90 °C.

Table 1. Various physical parameters of Li$_2$O–Fe$_2$O$_3$–P$_2$O$_5$ glasses doped with Ag$_2$O.

<table>
<thead>
<tr>
<th>Glass</th>
<th>Density g·cm$^{-3}$</th>
<th>Average molecular weight</th>
<th>Conc. Ag$^+$ ions $N_i$ (×10$^{21}$ ion·cm$^{-3}$)</th>
<th>Inter ionic distance $r_i$ of Ag$^+$ ions (Å)</th>
<th>Polaron Radius $r_p$ (Å)</th>
<th>Average Dissolution Rate ($\times10^{-7}$ g·cm$^{-2}$·min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF$_0$</td>
<td>2.3817</td>
<td>98.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.36</td>
</tr>
<tr>
<td>AF$_2$</td>
<td>2.3855</td>
<td>98.14</td>
<td>2.93</td>
<td>6.99</td>
<td>2.82</td>
<td>2.17</td>
</tr>
<tr>
<td>AF$_4$</td>
<td>2.3893</td>
<td>98.29</td>
<td>5.86</td>
<td>5.55</td>
<td>2.44</td>
<td>1.12</td>
</tr>
<tr>
<td>AF$_6$</td>
<td>2.3931</td>
<td>98.43</td>
<td>8.79</td>
<td>4.85</td>
<td>1.95</td>
<td>0.16</td>
</tr>
<tr>
<td>AF$_8$</td>
<td>2.3969</td>
<td>98.58</td>
<td>11.72</td>
<td>4.41</td>
<td>1.77</td>
<td>2.58</td>
</tr>
<tr>
<td>AF$_{10}$</td>
<td>2.4007</td>
<td>98.72</td>
<td>14.65</td>
<td>4.09</td>
<td>1.65</td>
<td>3.02</td>
</tr>
<tr>
<td>AF$_{15}$</td>
<td>2.4102</td>
<td>99.08</td>
<td>21.98</td>
<td>3.57</td>
<td>1.44</td>
<td>0.14</td>
</tr>
<tr>
<td>AF$_{20}$</td>
<td>2.4197</td>
<td>99.44</td>
<td>29.31</td>
<td>3.24</td>
<td>1.31</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Figure 3. Variation of solution pH with the concentration of Ag$_2$O, after corrosion testing.

The infrared transmission spectra of Li$_2$O–Fe$_2$O$_3$–P$_2$O$_5$ glasses (Figure 4) exhibit vibrational bands around 1300 cm$^{-1}$, (identified due to anti-symmetrical vibrations of PO$_2^-$ groups, this region may also consist of bands due to P=O stretching vibrations); 1050 cm$^{-1}$ (arising out of symmetric stretching vibrations of
PO\textsuperscript{2−} and the bands due to symmetric stretching normal vibrational mode in PO\textsubscript{3}\textsuperscript{−} may also lie in this region); and two prominent bands at 780 cm\textsuperscript{−1} due to P–O–P symmetric stretching vibrations. This region may also consist of bands due to pyrophosphate groups (P\textsubscript{2}O\textsubscript{7}\textsuperscript{−}); and at 900 cm\textsuperscript{−1}, due to P–O–P asymmetric stretching vibrations [12–14]. With the gradual introduction of Ag\textsubscript{2}O up to 0.6 mol%, the following changes in the vibrational bands of phosphate groups have been observed: (i) a progressive increase in the intensity of the bands due to PO\textsubscript{2} and PO\textsubscript{3}\textsuperscript{−} vibrational groups, accompanied by a shift towards slightly lower wave number has been observed. (ii) The band due to P–O–P asymmetric stretching vibrations is shifted towards higher wavenumber with a considerable decrease in the intensity. When the concentration of Ag\textsubscript{2}O is raised from 1.0 to 2.0 mol%, a gradual decrease in the intensity of the bands due to symmetrical stretching vibrational bands of phosphate groups is observed. Additionally, the spectra of these glasses have exhibited two FeO\textsubscript{6} octahedral bands due to $\nu_1$ and $\nu_3$ vibrations at 580 and 470 cm\textsuperscript{−1}, respectively [15, 16]. The spectra of these glasses have also exhibited a band at about 630 cm\textsuperscript{−1} identified due to the vibrations of FeO\textsubscript{4} tetrahedra. As the concentration of Ag\textsubscript{2}O is increased up to 0.6 mol%, the intensity of the octahedral bands is observed to decrease gradually where as that of the FeO\textsubscript{4} tetrahedral units, is observed to increase. However, in the concentration range of 0.8 to 1.0 mol% of Ag\textsubscript{2}O, the octahedral bands seem to be dominant over the octahedral bands; and beyond this concentration range, the occupation of iron ions in tetrahedral positions seems to prevail over octahedral positions. The summary of the data on the positions of various bands of IR spectra is presented in Table 2.

Figure 4. IR Spectra of Li\textsubscript{2}O–P\textsubscript{2}O\textsubscript{5}–Fe\textsubscript{2}O\textsubscript{3} :Ag\textsubscript{2}O glasses.
Table 2. Summary of the data on positions (cm\(^{-1}\)) of various absorption bands in the IR spectra of Li\(_2\)O–Fe\(_2\)O\(_3\)–P\(_2\)O\(_5\)–Ag\(_2\)O glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>Glass AF(_10)</th>
<th>Glass AF(_15)</th>
<th>Glass AF(_20)</th>
<th>Glass AF(_3)</th>
<th>Glass AF(_4)</th>
<th>Glass AF(_5)</th>
<th>Glass AF(_6)</th>
<th>Glass AF(_7)</th>
<th>Glass AF(_8)</th>
<th>Glass AF(_9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO(_2^+) asymmetric groups (P=O stretching)</td>
<td>1290</td>
<td>1285</td>
<td>1283</td>
<td>1280</td>
<td>1284</td>
<td>1287</td>
<td>1279</td>
<td>1275</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PO(_4^{3-}) groups</td>
<td>1060</td>
<td>1055</td>
<td>1050</td>
<td>1046</td>
<td>1052</td>
<td>1056</td>
<td>1044</td>
<td>1040</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P=O=P Asymmetric stretching</td>
<td>880</td>
<td>885</td>
<td>888</td>
<td>890</td>
<td>883</td>
<td>880</td>
<td>882</td>
<td>896</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P=O=P symmetric stretching</td>
<td>798</td>
<td>794</td>
<td>791</td>
<td>788</td>
<td>792</td>
<td>796</td>
<td>788</td>
<td>785</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PO(_2^+)O symmetric stretching</td>
<td>638</td>
<td>635</td>
<td>632</td>
<td>630</td>
<td>634</td>
<td>637</td>
<td>629</td>
<td>627</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ν(_1)-mode of FeO(_4) tetrahedra</td>
<td>560</td>
<td>564</td>
<td>567</td>
<td>570</td>
<td>565</td>
<td>561</td>
<td>562</td>
<td>566</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ν(_g)-mode of FeO(_6) octahedra</td>
<td>455</td>
<td>59</td>
<td>461</td>
<td>463</td>
<td>458</td>
<td>455</td>
<td>465</td>
<td>468</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The optical absorption spectra of Li\(_2\)O–Fe\(_2\)O\(_3\)–P\(_2\)O\(_5\)–Ag\(_2\)O glasses recorded in the wavelength region 300–1200 nm are shown in Figure 5a. The absorption edge observed at 343 nm for silver free glass is found to be shifted to slightly lower wavelength with increase in concentration of Ag\(_2\)O up to 0.6 mol%; whereas in the concentration range 0.8 to 1.0 mol% the edge is observed to shift towards higher wavelength. The absorption edge is observed at the lowest wavelength for the glass AF\(_{20}\). From the observed absorption edges, we have evaluated the optical band gap \(E_\text{g}\) for each of these glasses by drawing a Urbach plot between \((\alpha h\omega)^{1/2}\) and \(h\omega\). Figure 5b shows the Urbach plots of all these glasses in which a considerable part of each curve is observed to be linear. From the extrapolation of the linear portion of these curves, the values of optical band gap \(E_\text{g}\) are determined and presented in Table 3. The value of optical band gap is found to be the lowest for the glass AF\(_{10}\) and highest for the glass AF\(_{20}\).
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Figure 5b. Optical absorption spectra of Li$_2$O–P$_2$O$_5$–Fe$_2$O$_3$:Ag$_2$O glasses.

Table 3. Summary of data on optical absorption spectra of Li$_2$O–Fe$_2$O$_3$–P$_2$O$_5$:Ag$_2$O glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>Cut-off wavelength (nm)</th>
<th>Optical band gap $E_0$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF$_0$</td>
<td>343</td>
<td>2.90</td>
</tr>
<tr>
<td>AF$_2$</td>
<td>330</td>
<td>2.94</td>
</tr>
<tr>
<td>AF$_4$</td>
<td>323</td>
<td>3.16</td>
</tr>
<tr>
<td>AF$_6$</td>
<td>317</td>
<td>3.22</td>
</tr>
<tr>
<td>AF$_8$</td>
<td>350</td>
<td>3.06</td>
</tr>
<tr>
<td>AF$_{10}$</td>
<td>359</td>
<td>2.84</td>
</tr>
<tr>
<td>AF$_{15}$</td>
<td>306</td>
<td>3.32</td>
</tr>
<tr>
<td>AF$_{20}$</td>
<td>295</td>
<td>3.45</td>
</tr>
</tbody>
</table>

Furthermore, the spectra of all these glasses exhibited three absorption bands at 785, 580 and 540 nm, identified as due to transitions of Fe$^{3+}$ ions [17]. Additionally, a band at 980 nm, identified as due to the transition of Fe$^{2+}$ (d$^6$) ions [18], is also located in the spectra of all the glasses. With increase in the concentration of Ag$_2$O up to 0.6 mol%, the intensity of bands due to Fe$^{3+}$ ions has been observed to increase; when the concentration of Ag$_2$O is raised beyond 0.6 mol%, a gradual decrease in the intensity of the bands due to Fe$^{3+}$ ions could clearly be observed, while that of band due to Fe$^{2+}$ ions is observed to increase; this trend continued to 1.0 mol%. Further increase of Fe$_2$O$_3$ was accompanied with an increase in intensity of the band due to Fe$^{3+}$ ions. However, variation of Ag$_2$O concentration did not affect the band positions of iron ion transitions.

Magnetic susceptibility of Li$_2$O–Fe$_2$O$_3$–P$_2$O$_5$:Ag$_2$O glasses measured at room temperature is observed to increase with Fe$_2$O$_3$ content in the glass composition. From the values of magnetic susceptibilities, the effective magnetic moments $\mu_{eff}$ are evaluated and presented in Table 4. The value of $\mu_{eff}$ is found to lie in the region 5.6$\mu_B$ to 5.7$\mu_B$ for glasses AF$_2$ to AF$_6$, and AF$_{15}$ to AF$_{20}$ and decreases to within the range 4.3$\mu_B$ to 4.4$\mu_B$ for glasses AF$_8$ to AF$_{10}$.

ESR spectra for Li$_2$O–Fe$_2$O$_3$–P$_2$O$_5$:Ag$_2$O glasses were recorded at room temperature and are shown in Figure 6. The intense spectral line centred at about $g = 2.0$ can be clearly seen in the spectra of all the glasses. The intensity of this signal is observed to increase with the concentration of Ag$_2$O from 0.2 to 0.6 mol% and from 1.5 to 2.0 mol%; the signal however seemed to be weak in glasses AF$_8$ and AF$_{10}$. The value of $g$ is found to be slightly higher for glasses AF$_{15}$ and AF$_{20}$ (see Table 4). Additionally, a weak signal at about $g = 4.3$ could be detected in the spectra of all the glasses.

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Table 4. Data on magnetic susceptibility of Li$_2$O–Fe$_2$O$_3$–P$_2$O$_5$:Ag$_2$O glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>Magnetic susceptibility $\chi$ (×10$^{-6}$ emu)</th>
<th>$\mu$ (µB)</th>
<th>$g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF$_0$</td>
<td>5.7</td>
<td>16.19</td>
<td>1.99</td>
</tr>
<tr>
<td>AF$_2$</td>
<td>5.65</td>
<td>15.28</td>
<td>1.99</td>
</tr>
<tr>
<td>AF$_4$</td>
<td>5.6</td>
<td>14.38</td>
<td>1.99</td>
</tr>
<tr>
<td>AF$_6$</td>
<td>5.58</td>
<td>13.66</td>
<td>1.99</td>
</tr>
<tr>
<td>AF$_8$</td>
<td>4.4</td>
<td>8.11</td>
<td>1.99</td>
</tr>
<tr>
<td>AF$_{10}$</td>
<td>4.3</td>
<td>7.38</td>
<td>1.99</td>
</tr>
<tr>
<td>AF$_{15}$</td>
<td>5.71</td>
<td>11.39</td>
<td>2.02</td>
</tr>
<tr>
<td>AF$_{20}$</td>
<td>5.72</td>
<td>9.80</td>
<td>2.04</td>
</tr>
</tbody>
</table>

Dielectric constant $\varepsilon'$ and loss tan $\delta$ at room temperature (≈30 °C) of pure Li$_2$O–Fe$_2$O$_3$–P$_2$O$_5$ glasses at 100 kHz are measured to be 10.99 and 0.011, respectively. The values of these parameters are found to increase considerably with decrease in frequency. Figure 7 shows the variation of dielectric constant and loss of Li$_2$O–Fe$_2$O$_3$–P$_2$O$_5$ glasses containing different concentrations of Ag$_2$O with frequency, measured at room temperature. The values of $\varepsilon'$ and tan $\delta$ are observed to slowly decrease with increasing concentration of Ag$_2$O, up to 0.6 mol%; and beyond this concentration (up to 1.0 mol%), these values are found to increase.

Figure 6. ESR spectra of Li$_2$O–P$_2$O$_5$–Fe$_2$O$_3$:Ag$_2$O glasses recorded at liquid nitrogen temperature.
The temperature dependence of $\varepsilon'$, for glasses containing different concentrations of Ag$_2$O at 1 kHz, is shown in Figure 8; and in the inset is shown $\varepsilon'$ at different frequencies for glass AF$_4$. The value of $\varepsilon'$ is found to exhibit a considerable increase at higher temperatures, especially at lower frequencies. However, the rate of increase of $\varepsilon'$ with temperature is found lowest for the glass containing 2.0 mol% of Ag$_2$O, AF$_{20}$, and highest for the glass containing 1.0 mol%, AF$_{10}$. 

The temperature dependence of tan $\delta$ of all glasses measured at the frequency 10 kHz is presented in Figure 9. In the inset of the same figure is shown the variation of tan $\delta$ for glass AF$_8$, containing 0.8 mol% of Ag$_2$O, at different frequencies. The curves of both silver oxide-free and Ag$_2$O-doped glasses exhibited
distinct maxima, with the characteristic that, with increasing frequency, the temperature maximum shifts towards higher temperature and with increasing temperature the frequency maximum shifts towards higher frequency, indicating the dielectric relaxation character of dielectric losses of these glasses. Further, the observations on dielectric loss variation with temperature for different concentrations of Ag$_2$O show that the highest value of $(\tan \delta)_{\text{max}}$ of relaxation curves for the glass AF$_{10}$ and the lowest for the glass AF$_{20}$.

**Figure 9.** Plots comparing variation in dielectric loss with temperature for Li$_2$O–P$_2$O$_5$–Fe$_2$O$_3$:Ag$_2$O glasses at 10 kHz. Figure inset gives the variation of dielectric loss with temperature for glass AF$_8$ at different frequencies.

Using the relation

$$f = f_0 \exp(-W_d/KT),$$  \hspace{1cm} (1)

the effective activation energy $W_d$ for the dipoles is calculated for different concentrations of Ag$_2$O and is presented in Table 5. The activation energy is found to increase with increase in the concentration of Ag$_2$O up to 0.6 mol%, and beyond this, up to 1.0 mol% of Ag$_2$O, the value of activation energy is found to decrease.

The a.c. conductivity as a function of frequency $\sigma_{ac}$ is calculated using the equation

$$\sigma_{ac} = \omega \varepsilon' \varepsilon_0 \tan \delta,$$ \hspace{1cm} (2)

where $\varepsilon_0$ is the vacuum dielectric constant. In Figure 10, log $\sigma_{ac}$ is plotted against $1/T$ for glass AF$_{10}$, and log $\sigma(1/T)$ is plotted for all glasses, at 10 kHz, in Figure 11. The conductivity is found to decrease considerably with increase in concentration of Ag$_2$O at any given frequency and temperature from 0 to 0.6 mol% (characterized in Figure 12). Note between 0.6 to 1.0 mol% the clear presence of a hike in the conductivity. From these plots, the activation energy for the conduction in the high temperature region over
which a near linear dependence of \( \log \sigma_{ac} \) with \( 1/T \) could be observed is evaluated and its variation with the concentration of \( \text{Ag}_2\text{O} \) is shown in inset (a) of Figure 12.

Table 5. Data on dielectric loss of \( \text{Li}_2\text{O}-\text{Fe}_2\text{O}_3-\text{P}_2\text{O}_5:\text{Ag}_2\text{O} \) glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>Average ( \tan \delta_{\text{max}} )</th>
<th>Temperature region of relaxation (°C)</th>
<th>Dipole Activation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF_0</td>
<td>0.0542</td>
<td>64–90</td>
<td>2.51</td>
</tr>
<tr>
<td>AF_2</td>
<td>0.0496</td>
<td>76–100</td>
<td>2.65</td>
</tr>
<tr>
<td>AF_4</td>
<td>0.0409</td>
<td>95–122</td>
<td>2.95</td>
</tr>
<tr>
<td>AF_6</td>
<td>0.0377</td>
<td>108–131</td>
<td>3.10</td>
</tr>
<tr>
<td>AF_8</td>
<td>0.0457</td>
<td>85–112</td>
<td>2.80</td>
</tr>
<tr>
<td>AF_{10}</td>
<td>0.0611</td>
<td>62–84</td>
<td>2.37</td>
</tr>
<tr>
<td>AF_{15}</td>
<td>0.0344</td>
<td>120–150</td>
<td>3.26</td>
</tr>
<tr>
<td>AF_{20}</td>
<td>0.0319</td>
<td>132–152</td>
<td>3.42</td>
</tr>
</tbody>
</table>

Figure 10. Variation of \( \sigma_{ac} \) with \( 1/T \) for glass AF_{10} at different frequencies.
4. Discussion

Li$_2$O–P$_2$O$_5$–Fe$_2$O$_3$:Ag$_2$O glasses have a complex composition and are an admixture 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$_2$O$_5$ glass O/P = 2.5 and the glass network is build up of Q$^3$ tetrahedra with the bridging oxygens; and with the fourth oxygen, is doubly bonded to the phosphorus atom. With the addition of iron oxide an ultraphosphate network consisting of Q$^2$ and Q$^3$ tetrahedra may form with O/P $<$ 3.0 [19].

Li$_2$O and Ag$_2$O are well known modifier oxides and enter the glass network either by rupturing or by breaking up the P–O–P structures. (Normally, the oxygens of M$_2$O break the local symmetry, while the M$^+$ ions occupy interstitial positions.) In turn, the breakup of the P–O–P structures introduce coordinated defects, known as dangling bonds, along with non-bridging oxygen ions. Iron may exist both in Fe$^{2+}$ and Fe$^{3+}$ states.

The speciation of iron in these glasses is controlled by the reversible reaction

$$4Fe^{3+}_{\text{melt}} + 2O^{2-}_{\text{melt}} \rightleftharpoons 4Fe^{2+}_{\text{melt}} + 2O_2_{\text{melt, atm}}$$

where ‘melt atm’ stands for melting in a reducing atmosphere.

Fe$^{3+}$ ions are expected to occupy both tetrahedral and octahedral positions in the glass network. However, the four-fold coordination of Fe$^{3+}$ is observed to be more common than the six fold coordination in many of the glasses [20]. Both of these Fe$^{3+}$ sites can be considered as substitutional and subjected to strong
interaction between its external orbitals and the p-orbitals of the neighbouring oxygens [21] and form the linkages of the type P–O–Fe. Basing on the above discussion, the anticipated structure of Li$_2$O–Fe$_2$O$_3$–P$_2$O$_5$:Ag$_2$O glass network is illustrated in Figure 13.

**Figure 12.** A.C. conductivity isotherms, at 10 kHz, of Li$_2$O–P$_2$O$_5$–Fe$_2$O$_3$ glasses, as a function of Ag$_2$O concentration. Inset (a) shows the variation of activation energy for conduction, as a function of Ag$_2$O concentration; and inset (b) gives the variation of conductivity as a function of activation energy.

**Figure 13.** An illustration of Li$_2$O–Fe$_2$O$_3$–P$_2$O$_5$: Ag$_2$O glass network with Fe$^{3+}$ ions in both tetrahedral and octahedral substitutional positions and Fe$^{2+}$ in octahedral positions. Arrow indicates the entry of modifier ions (Li$^+$, Ag$^+$).
Fe$^{2+}$ ions are expected to occupy only interstitial positions since the ratio of cation-oxygen radii is 0.63 for Fe$^{3+}$ ion, which is far from the value of 0.19 possessed by an ion to occupy tetrahedral or substitutional sites [21] and act as modifiers similar to Li$^+$ and Ag$^+$ ions.

The ingress of Ag$^+$ ions may result in the following changes in the glass network. The P–O–Fe linkages are expected to form from P–O–P and Fe–O–Fe complexes. After the entry of Ag$^+$ ions, these linkages may be modified as per the following relations:

\[
\text{Ag}_2\text{O} + \text{P–O–Fe} \rightarrow \text{P–O}
\]

or,

\[
\text{P–O–Fe} + \text{Ag}_2\text{O} \rightarrow \text{P–O}^\text{–Ag}^+ + \text{Fe–O}^\text{–Ag}^+.
\]

As a consequence there is a disruption in the PO$_4$ and FeO$_4$ tetrahedral with the creation of number of non-bridging oxygens.

The dissolution rate of Li$_2$O–Fe$_2$O$_3$–P$_2$O$_5$–Ag$_2$O glasses in water at 90 °C varied considerably with the change in the concentration of Fe$_2$O$_3$ or Ag$_2$O in the glass matrix. Glasses containing 0.6 to 1.0 mol% Ag$_2$O have a significant dissolution rate when compared with that of other glasses; further, the external surface of these glasses was observed to be rough and heavily pitted after corrosion testing. On the other hand, glasses AF$_{15}$ and AF$_{20}$ showed a remarkable improvement of chemical durability; surfaces of these samples after the testing are observed to be smooth, with the corners and the edges retaining original sharpness. The pH of the residual water solution also correlates notable improvement of the durability of glasses AF$_{15}$ and AF$_{20}$. The observed decrease in the average dissolution rate (DR) of the glasses with increase in the concentration of Ag$_2$O indicates that the concentration of undisturbed P–O–P and P–O–Fe bonds is higher in the glasses containing 0.6 mol% and 2.0 mol% of Ag$_2$O. This is also an indication of a high Fe:P ratio (yet with value <1, for substitutionally positioned Fe) in these glasses. The presence of such unruffled bonds at higher concentrations makes the glasses more corrosion resistant. Additionally, the length and orientation distribution of PO$_4$ chains also play a major role in deciding the chemical durability of these glasses. Previous empirical studies showed that the shortened PO$_4$ chains in the glass network are responsible to some extent for the high corrosion resistance of the glasses [22]. This conclusion obviously suggests in this concentration ranges (4.4–5.0 and 3.0 to 3.5 mol%), the iron ions prefer to go in to the network forming positions rather than acting as modifiers and the role of Ag$^+$ ions as modifiers in this concentration range seems to be minimal. The considerable decrease observed in the pH value of the residual water solution with in the concentration range 0.8 to 1.0 mol% of Ag$_2$O or 4.2 to 4 mol% Fe$_2$O$_3$ (Figure 3b) clearly indicates that corrosion resistance in these glasses is comparatively low.

The optical absorption spectra of these glasses have exhibited four absorption bands at 408, 540, 580 and 785 nm. Using Tanabe-Sugano diagrams for d$^5$ ion, the spectra have been analyzed and the bands are assigned to $^6\text{A}_1(\text{S})t_0 \rightarrow ^4\text{T}_2$ (D), $^6\text{A}_1(t_{2g}^3e_g^2) \rightarrow ^4\text{T}_1(t^4_{2g}e^2)$, $^6\text{A}_1(t_{2g}^2e^4_g) \rightarrow ^4\text{T}_2(t^4_{2g}e^2)$, $^6\text{A}_1(e^{2}t^2_{2g}) \rightarrow ^4\text{T}_1(e^4_{2g}t^2_{2g})$ (spin forbidden) transitions of Fe$^{3+}$ ions, respectively [24] with LF parameters, D$_q$ (crystal field splitting energy $=1282$ cm$^{-1}$ and Racah inter electronic repulsion parameters B $= 840$ cm$^{-1}$). More precisely, basing on selection rules and ligand field calculations, the band $^6\text{A}_1(\text{e}^2t^2_{2g}) \rightarrow ^4\text{T}_1(\text{e}^4_{2g}t^2_{2g})$ is identified due to FeO$_4$ groups, and the remainder due to FeO$_6$ groups. The band observed at 977 nm is identified due to $^5\text{T}_{2g} \rightarrow ^5\text{E}_g$ transition of Fe$^{3+}$ (d$^6$) ions [23].

The observed increase in the intensity of Fe$^{3+}$ ion bands up to 0.6 mol%, and from 0.8 mol% of Ag$_2$O, indicates that in this concentration range the silver ions facilitate Fe$^{3+}$ ions to occupy substitutional positions. When the concentration of Fe$_2$O$_3$ is raised from 0.6 to 1.0 mol%, the $^5\text{T}_{2g} \rightarrow ^5\text{E}_g$ transition of Fe$^{3+}$ ions
(d\(^6\)) seems to be dominant over the transitions from \(^6\)A\(_1\) ground state, indicating that in this concentration range, the iron ions predominantly exist in divalent state and occupy only interstitial positions [23].

Increase in concentration of modifying ions that participate in the depolymerisation of the glass network leads to a decrease in the concentration of bonding defects and non-bridging oxygens (NBO). Higher the concentration of such modifiers, higher is the concentration of NBOs in the glass matrix. This leads to an increase in degree of localization of electrons by increasing the donor centres in the glass matrix. The increasing presence of these donor centres decreases the optical band gap and shifts the absorption edge towards higher wavelengths. The decrease in the optical band gap \(E_o\) with increase in the concentration of \(\text{Ag}_2\text{O}\) from 0.6 to 1.0 mol\% (Table 3) obviously indicates an increasing degree of depolymerisation of the glass network, where as higher values of \(E_o\) for the glasses \(\text{AF}_{15}\) and \(\text{AF}_{20}\) suggest high rigidity of these glasses. It may be worth mentioning that the IR spectra of these glasses appear dominated by orthophosphate structural units; however, the band due to pyrophosphate structural units lies around 1090 cm\(^{-1}\), which is not too far from the band position of \(\text{PO}_4^{3-}\) units. Hence the observed band at about 1090 cm\(^{-1}\) in the spectra of these glasses may indicate 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 cm\(^{-1}\) [24].

If silver and divalent iron ions act as modifiers, the \(\pi\)-bond of P=O may be ruptured, creating new non-bridging oxygens. Even if \(\text{Fe}^{3+}\) ions enter substitutional positions with octahedral units in the glass network, the \(\text{PO}_4\) 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, \(\text{PO}_4\) 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 of the bands due to \(\text{PO}_4^{3-}\) stretching vibration, \(\text{PO}_4^{3-}\) symmetric stretching and a band due to P-O-P symmetric/ Fe–O–P stretching vibrations in the IR spectra. The observed gradual decrease in the intensity of these bands in the spectra of these glasses may indicate 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 cm\(^{-1}\) [24].

The magnetic properties of these glasses arise from the 3d\(^5\) and 3d\(^6\) electrons of \(\text{Fe}^{3+}\) and \(\text{Fe}^{2+}\) ions, respectively. The value of the effective magnetic moment (\(~5.6\) to \(5.7\) \(\mu_B\)) obtained for glasses \(\text{AF}_{15}\) to \(\text{AF}_{20}\) confirms the highest concentration of \(\text{Fe}^{3+}\) ions in these glasses. The decrease in the value of \(\mu_{\text{eff}}\) from 5.7\(\mu_B\) to 4.3\(\mu_B\) (for the glasses \(\text{AF}_8\) and \(\text{AF}_{10}\)) indicates a gradual conversion of iron ions from \(\text{Fe}^{3+}\) state to \(\text{Fe}^{2+}\) state, that takes modifying positions and increase the degree of disorder in the glass network.

The ESR spectra of these glasses have exhibited two signals centered at \(g = 4.3\) and 2.0. These two resonance lines have been discussed at length by many investigators [25, 26]. The absorption at \(g = 4.2\) arises from tetrahedral environment and the line at \(g = 2.0\) is predicted due on the \(\text{Fe}^{3+}–\text{O}–\text{Fe}^{3+}\) spin pair [27]. However, there are reports suggesting that the \(g = 4.3\) line arises due to rhombic sites of either tetrahedral or octahedral coordination [28]. Since, it is also evident from the IR spectra that the band due to \(\text{FeO}_4\) units is more intense for glass \(\text{AF}_{20}\), the relatively high intensity of the ESR signal observed for the same glass reinforces the view that the majority of the iron ions in the glass \(\text{AF}_{20}\) occupy tetrahedral positions.

Since \(\text{Fe}^{3+}\) ion belongs to \(d^5\) configuration with \(^6\)S ground state there is no spin-orbit coupling. As a result we expect that the value of \(g\) very near to free ion \(g\) value, i.e. 2.0023. However for the present glasses, we have observed values of \(g\) greater than 2.0 for glasses \(\text{AF}_{15}\) and \(\text{AF}_{20}\). Such higher values of \(g\) arise when certain symmetry elements are present. The spin Hamiltonian associated with such higher values of \(g\) is usually expressed as [29]

\[
H = g\beta BS + D[S_z^2 - \{S(S + 1)/3\}] + E(S_x^2 - S_y^2), \tag{3}
\]

where \(S = 5/2\). Here, \(D\) and \(E\) are the axial and rhombic structure parameters and \(\lambda = E/D\) lies within the limits 0 \(\leq \lambda \leq 6/5\).

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The $^6S_{5/2}$ ground state of Fe$^{3+}$ ($d^5$) free ion is expected to split in to three Kramers doublets $| \pm 5/2 \rangle$, $| \pm 3/2 \rangle$ and $| \pm 1/2 \rangle$ with separation normally greater than the microwave quantum. The symmetric and isotropic line observed at $g = 4.3$ in the present glasses is due to the middle Kramers doublets containing an admixture of different $| \pm m_j \rangle$ which are identified due to the low symmetry term $E(S^2_g - S^2_i)$ in the Hamiltonian, the signal with $g = 2.0$ is due to EPR transitions in the $| \pm 1/2 \rangle$ doublet [30].

The effective value of $g$ obtained from ESR spectra show a gradual increase from 1.99 (Table 5) with increase in the concentration of Ag$_2$O in the glass matrix from 1.0 to 2.0 mol%. This is partly ascribable to the contribution of orbital angular momentum to the magnetic moment of Fe$^{3+}$ ions. The fraction of the magnetic moment due to the orbital angular momentum $I_x$ (spin), to that due to spin angular momentum, $I_y$ (orbit), may be expressed as [31]

$$I_x/I_o = (g/2) - 1. \quad (4)$$

Such an interesting feature may be understood in terms of the dipolar interactions, which are more predominant in the glass with the content of Fe$_2$O$_3$; these interactions cause a localized magnetic field at the site of Fe$^{3+}$ ion and increase the effective $g$ value, as observed [32].

The observed low intensity of the ESR signal in the concentration range of 0.8 to 1.0 mol% of Ag$_2$O (Fig. 6), may be due to both the destruction of more Fe$^{3+}$-O-Fe$^{3+}$ pairs than are formed Fe$^-$O$^-$Ag$^+$ complexes; and the reduction of Fe$^{3+}$ iron ions to Fe$^{2+}$. This is also evidenced from optical absorption spectra (Fig. 5a); the spectra show a gradual growth of the band due to Fe$^{2+}$ ions (i.e., $^5T_{2g} \rightarrow ^5E_g$ band) at the expense of the bands due to Fe$^{3+}$ ions with in this concentration range of Fe$_2$O$_3$.

Usually, electronic, ionic, dipolar and space charge polarizations contribute to the dielectric constant; among these, the space charge polarization depends on the perfection of the glass network. Normally, the modifying ions generate bonding defects in the glass network; these defects create easy path ways for the migration of charges that would build up space charge polarization and lead to an increase in the dielectric parameters [33–35].

The data on the dielectric properties of Li$_2$O-Fe$_2$O$_3$-P$_2$O$_5$:Ag$_2$O glasses show a gradual decrease in the parameters dielectric constant $\varepsilon'$, loss tan $\delta$ and a.c. conductivity $\sigma_{ac}$, with increase in the concentration of Ag$_2$O in the glass network, from 1.0 to 2.0 mol%. These results suggest that there is a decrease in the concentration of free charge carriers that build up space-charge polarization [36, 37]. This observation supports the view point that in the glasses AF$_{15}$ to AF$_{20}$, iron ions participate in the network forming with FeO$_4$ tetrahedral units. The gradual increase of these parameters with increasing content of Ag$_2$O from 0.6 to 1.0 mol%, suggests a greater degree of disorder in the glass network that enhances space charge polarization. In other words, in this concentration range the iron ions mostly occupy octahedral positions and disrupt the glass network similar to Li$^+$ and Ag$^+$ ions.

The observed dielectric relaxation effects may be attributed to association of divalent iron, Fe$^{2+}$ ions, with a pair of PO$_2^-$ groups in analogy with the mechanism-association of divalent positive ion with a pair of cationic vacancies in conventional glasses, glass ceramics and crystals [38, 39]. The lower values of tan $\delta_{max}$ and the higher values of activation energy for dipoles for the glasses AF$_{15}$ and AF$_{20}$ suggests a decreasing degree of freedom for dipoles to orient in the field direction in the networks of these glasses. Indirectly, it leads to the conclusion that there is an increasing stiffness of the glass network as the concentration of Ag$_2$O is increased from 1.0 to 2.0 mol%.

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 Figure 12). This observation suggests that the conductivity enhancement is directly related to the thermally stimulated mobility of the charge carriers in the high temperature region [40].

The conductivity curve as a function of Ag$_2$O concentration passes through a maximum at $x = 1.0$ mol% (Figure 12). The activation energy for conduction as a function of the concentration of Ag$_2$O, exhibited
a minimum $x = 1.0$ mol% (see inset (a) of Figure 12). Thus Figure 12 and its insets suggest a kind of transition from predominantly electronic (zone-I, for $0.6 < x < 1.0$ mol%) to electric (zone-II for $x > 1.0$ mol%) conductivity [41]. The mobile electrons, or polarons, involved in the process of transfer from Fe$^{3+}$ to Fe$^{2+}$, are attracted by the oppositely charged Ag$^+$ and/or Li$^+$ 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. As a result, we expect a decrease in the conductivity, as observed in zone-II [42]. In other words, with the entry of Ag$^+$ ions into the glass network, the electronic paths are progressively blocked causing an inhibition of the electronic current with a simultaneous increase in the ionic transport of Ag$^+$.

The value of $N(E_F)$, the density of the defect energy states (in the nearly temperature independent part of the conductivity range), is evaluated using the equation [43-46]

$$\sigma \omega \rho g = g(\pi v z g) K T [ N(E_F) ]^2 \alpha^{-2} \omega \left[ \ln(v_{ph}/\omega) \right]^4,$$

at frequency $\omega = 10^4$ Hz at $T = 340$ K, taking $\alpha = 0.50$ A$^{-1}$ (electronic wave function decay constant, obtained by plotting $\log \sigma_{ac}$ against $R_i$) and $v_{ph} \sim 5 \times 10^{12}$ Hz; the results are presented in Table 6. The value of $N(E_F)$ is found to decrease with increasing concentration of Fe$_2$O$_3$ up to $x = 0.6$ mol% (indicating decreasing disorder in the glass network); and thereafter, $N(E_F)$ is observed to increase (see Table 6).

Table 6. The concentration of defective energy states and a.c. conductivity of Li$_2$O-CaF$_2$–P$_2$O$_5$:Ag$_2$O glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>$N(E_F)$ (×10$^{20}$ eV$^{-1}$·cm$^{-3}$)</th>
<th>Activation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF$_0$</td>
<td>7.83</td>
<td>0.15</td>
</tr>
<tr>
<td>AF$_2$</td>
<td>6.80</td>
<td>0.17</td>
</tr>
<tr>
<td>AF$_4$</td>
<td>5.30</td>
<td>0.19</td>
</tr>
<tr>
<td>AF$_6$</td>
<td>4.85</td>
<td>0.22</td>
</tr>
<tr>
<td>AF$_8$</td>
<td>5.98</td>
<td>0.169</td>
</tr>
<tr>
<td>AF$_{10}$</td>
<td>9.56</td>
<td>0.12</td>
</tr>
<tr>
<td>AF$_{15}$</td>
<td>4.34</td>
<td>0.26</td>
</tr>
<tr>
<td>AF$_{20}$</td>
<td>3.93</td>
<td>0.31</td>
</tr>
</tbody>
</table>

When the dielectric is placed in an electric field, the heat is liberated due to dielectric loss. If the applied field is an alternating field, the specific dielectric loss, i.e., the loss per unit volume of the dielectric is given by

$$r_1 = E^2 \varepsilon \varepsilon_0 \tan \delta \ W \cdot m^{-3}.$$

This equation indicates that, the lower the values of $\varepsilon \tan \delta$ for the glass at a given frequency, are the values of $r_1$. The dielectric breakdown strength, on the other hand, is in fact inversely proportional to the specific dielectric loss represented by equation (6). Our observations on dielectric parameters of Li$_2$O–Fe$_2$O$_3$–P$_2$O$_5$:Ag$_2$O glasses, as mentioned earlier, indicate, the rate of increase of $\varepsilon \tan \delta$ with temperature is the highest for glass AF$_{10}$ and the lowest for the glass AF$_{20}$. Thus the experiments on dielectric properties of Li$_2$O–Fe$_2$O$_3$–P$_2$O$_5$:Ag$_2$O glasses also reveal that there is an increase in the dielectric breakdown strength of the glasses with increase in the concentration of Ag$_2$O beyond 1.0 mol%. This revelation is also consistent with the view that, in the concentration range of 1.5 to 2.0 mol%, the iron ions mostly exists in trivalent state and occupy network forming positions with FeO$_4$ structural units and increase the rigidity of the glass network.
5. Conclusions

The summary of the results of various studies of Li$_2$O–Fe$_2$O$_3$–P$_2$O$_5$ glasses doped with different concentrations of Ag$_2$O is as follows. The present analysis of chemical durability suggests that glasses containing Ag$_2$O above 1.0 mol% are more corrosion resistant. Optical absorption and magnetic susceptibility studies indicated that iron ions in these glasses exist both in trivalent and divalent states. IR spectral studies indicated that iron ions exist in tetrahedral and octahedral substitutional positions and form P-O-Fe linkages. The entry of Ag$^+$ ions causes formation of P–O$^-$Ag$^+$ and Fe–O$^-$Ag$^+$ complexes in the glass network. The results of dielectric properties indicate that the a.c. conduction, with in the concentration range of 0.6 to 1.0 mol% of Ag$_2$O, is mainly electronic in nature, whereas in the samples containing more than 1.0 mol% Ag$_2$O, ionic conduction seems to prevail.

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