Synthesis and characterization of Li$_2$O modified sodium phosphate glasses

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Abstract

The transparent glasses 55 P$_2$O$_5$ - (45-x) Na$_2$O - xLi$_2$O where (x=0, 3, 10, 15, 30, 35) were prepared by conventional melt quenching technique. Structural and characterization have been investigated by using X-Ray diffraction (XRD) and the results show that all samples are amorphous structure. The glass transition ($T_g$) and crystallization temperature ($T_c$) are evaluated using the differential thermal analyzer (DTA), which indicate that 15 mol% Li$_2$O contained glasses exhibits maximum thermal stability $h'$ of glass samples. Density, molar volume and oxygen packing density insure that Li$_2$O incorporated in sodium phosphate glass by increasing Li$_2$O content. The ac and dc electrical conductivity and dielectric constants of the prepared glass samples have been investigated. The variation of dc conductivity with the concentration of Li$_2$O mol% passes through a maximum at 15 mol% Li$_2$O. Temperature dependence of the dc conductivity of these glasses is found to obey the Arrhenius law. It reveals that the values of activation energies $\Delta E_{dc1}$ and $\Delta E_{dc2}$ at low and high temperatures lie in the range 0.452-0.93 eV. Also it was found that the values of $\sigma_{dc}$ to be the same as the values obtained from the impedance study. Conductivity mechanism for grain resistance at room temperature was discussed using Cole-Cole plot. To determine the conduction mechanism, the ac conductivity and its frequency exponent have been analyzed by correlated barrier hoping model (CBH). It was found that the exponent ($s$) has values between 0.62-0.9; consequently the (CBH) seems to be the most interesting model related to the obtained results. The variation of dielectric constants $\varepsilon'$ and $\varepsilon''$ with the concentration of Li$_2$O mol% pass through a maximum at 15 mol% Li$_2$O and this result would be discussed by means of dielectric polarization mechanism of material. The maximum value of the maximum barrier height $W_m$ obtained from Guitini equation was found to increase with increasing of Li$_2$O mol%.

Keywords: Sodium Phosphate glass; Thermal analysis; Electrical conductivity.

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1- Introduction

The synthesis and physical properties of phosphate glasses have attracted much attention because of their potential application in technology. Phosphate glasses possess a series of interesting and unique physical properties better than other glasses such as hardness, transparency at room temperature, sufficient strength, low glass transition temperature, excellent corrosion resistance, high electrical conductivity, low melting and softening temperature and high thermal expansion [Yahia H. Elbashar et al. (2016), R. K. Brow (2000), Samir Y. Marzouk (2009), A. Bhide et al. (2007), R. K. Brow (2000), I. Abrahams et al. (2000)]. Among oxide glasses, sodium and lithium phosphate glasses / glass-ceramics are used as solid electrolytes for battery applications [Paramjyot Komarjha et al. (2015), A. Yamano et al. (2014)]. Phosphate glasses have been considered as a promising group of glasses for optical amplifiers, fibers, etc. [A V. Chandrasekhar et al. (2003), Nehal Aboulffotoh et al. (2014)] and also play various important roles in laser systems. For laser application glasses used as transmitting optical components, as modulators, for photonic switching and magneto-optic materials [D. D. Ramteke et al. (2017)]. By varying the glass composition, glasses with specific properties can be achieved. Dc electrical properties of lithium metal oxide containing phosphate glasses like Li₂O – CdO – P₂O₅, Li₂O – MnO – BeO₃ ….. etc, have been studied with the change of concentration of the modifier or glass former [M. Altaf et al. (2001), Peipei Chen et al. (2015), V. C. Veerana et al. (2005)]. Sodium phosphate glasses are in a great demand because of their strong glass forming nature, low crystallization and melting temperature. It is expected that the replacement of Na₂O by Li₂O in P₂O₅ based glasses exhibit better ionic conductivity due to smaller size of Li⁺ (0.76Å) as compared to Na⁺ (1.02Å). The conductivity is generally studied as a function of temperature, and it may also depend on structural changes in the glasses. Recently the structural and thermal properties of P₂O₅ – Na₂O – Li₂O and Li₂O – Na₂O – P₂O doped with La₂O₃ has been reported in literature [Paramjyot Komarjha et al. (2015), A. Yamana et al. (2014), Peipei Chen et al. (2015)]. It was found that the structural properties of P₂O₅ – Na₂O – Li₂O glasses strongly depend on Na₂O and Li₂O content.

In the literature, we find that the dc and ac electrical conductivity of P₂O₅ – Na₂O – Li₂O glasses have not been studied extensively for this reason, the present work gives the preparation method and deals with the dc and ac electrical conductivity and structure properties of P₂O₅ – Na₂O – Li₂O glasses over a wide range of composition, temperature and frequency to determine the possible conduction mechanisms and to determine the activation energy and also to propose the crystallization mechanism of the prepared glasses.
2- Experimental

The transparent 55 P₂O₅ – (45-x) Na₂O – x Li₂O, (x = 0, 3, 10, 15, 30, 35) glasses used in the present study were prepared from high purity analytical grade chemicals (NH₄)₂HPO₄, Na₂CO₃ and LiCl by conventional melt quenching technique. The appropriate quantities of these chemicals were weighed and mixed in agate mortar and were hand ground for about one hour. The batches were initially kept at 400 °C in porcelain crucibles to release volatile products coming from the starting materials and then melted in an electric furnace with intermediate stirring at 1000 °C for one hour to ensure homogeneity of the glasses. Samples of the desired shape were obtained by quenching the melt at 350 °C between two preheated stainless steel plates for two hours to eliminate the mechanical and thermal stresses produced during casting and collected the next day. The prepared glass samples were polished by silicon carbide water proof abrasive papers of various grades ranging between 320 and 1000 to achieve a good optical transparency samples.

Glass transition temperature (T闪过) and crystallization temperature (Tсход) were determined using deferential thermal analysis (DTA) at heating rate 10 K/min.

Density measurements of the prepared samples were determined at room temperature using Archimedes principle. The mass of the glass samples were measured with a Precisa 205A balance sensitive to 0.1 mg. Toluene (ρₜ =0.85455 gm/cm³) was used as an immersion liquid.

The equation used for density calculation is given by

\[ \rho_{\text{sample}} = \frac{W_a}{(W_a - W_T)} \rho_T \]  

Where \( \rho_{\text{sample}} \) is the density of the sample, \( W_a \) is the weight of sample in air, \( W_T \) is the weight of sample in toluene and \( \rho_T \) is the density of toluene. The relative error in these measurements was about 1 mg/cm³.

The amorphous nature of synthesized glass samples was confirmed by (PANalytical PRO X’Pert Data) diffractometer which was operated at 40 KV and 45 mA and using CuKα radiation source of wavelength 1.5406 Å with Ni filter at room temperature.

X-Ray diffraction patterns were recorded in 2θ range between 4 and 90 degree with scanning rate 2 degree/min.

For dc and ac electrical conductivity a glass samples, coated with silver paint on both sides were used for the measurements and using a special designed holder.
The dc and ac electrical resistance $R$ for the prepared samples was carried out in the temperature range (300-512K). The sample temperature was measured and controlled by using a calibrated Chromel-Alumel thermocouple connected to (TCN4M-24R Aulonics-Korea) temperature controller. For AC electrical conductivity measurements a programmable automatic LCR bridge (Hioki, 3532-50) was used in a wide frequency range (50 Hz to 5 MHz).

3- Results and discussion

3.1 X-Ray Diffraction (XRD)

![XRD patterns](image)

Fig.1. XRD diffraction patterns of 55 $P_2O_5 - (45-x) Na_2O - x Li_2O$ glass samples at different composition of $Li_2O$ (mol.%).

Fig.1 shows XRD patterns of the prepared glass samples 55 $P_2O_5 - (45-x) Na_2O - x Li_2O$ (x=0 – 35 mol% $Li_2O$) at room temperature. The presence of one broad hump in the range of 15 – 35 for all the investigated samples indicated their amorphous nature and the absence of phase separation.

3-2 Differential thermal analysis (DTA)
Fig.2. DTA patterns of 55 P$_2$O$_5$ – (45-x) Na$_2$O – x Li$_2$O glass samples at different composition of Li$_2$O (mol.%).

Fig.2 shows the DTA patterns of 55 P$_2$O$_5$ – (45-x) Na$_2$O – x Li$_2$O glass samples (x = 0, 3, 10, 15, 30, 35). The DTA patterns are used to determine the glass transition temperature $T_g$, the crystallization temperature $T_c$ and the glass thermal stability $h' = (T_c - T_g) / T_g$. The determined data is given in Table 1.

**Table 1: Glass transition temperature ($T_g$), crystallization Temperature ($T_c$) and glass stability ($h'$) of different glass compositions.**

<table>
<thead>
<tr>
<th>Composition of 55 P$_2$O$_5$ – (45-x) Na$_2$O – x Li$_2$O (x mol %)</th>
<th>$T_g$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>ΔT (°C)</th>
<th>$h' = ΔT/T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>234.42</td>
<td>283.56</td>
<td>49.14</td>
<td>0.20962</td>
</tr>
<tr>
<td>3</td>
<td>262.13</td>
<td>317.79</td>
<td>55.66</td>
<td>0.21234</td>
</tr>
<tr>
<td>10</td>
<td>252.65</td>
<td>310.28</td>
<td>57.63</td>
<td>0.2281</td>
</tr>
<tr>
<td>15</td>
<td>285.88</td>
<td>391.05</td>
<td>105.17</td>
<td>0.36788</td>
</tr>
<tr>
<td>30</td>
<td>247.52</td>
<td>308.69</td>
<td>61.17</td>
<td>0.24713</td>
</tr>
<tr>
<td>35</td>
<td>243.69</td>
<td>305.59</td>
<td>61.9</td>
<td>0.25401</td>
</tr>
</tbody>
</table>

The value of $h'$ is indicative of the thermal stability of the glass samples [Yang Lia et al. (2017)]. From Table 1 it is observed that as the concentration of Li$_2$O increases from 3 to 10 mol % Li$_2$O and from 15 to 35 mol % Li$_2$O $T_g$ and $T_c$ are found to decrease. In this case Li$_2$O is acting as a strong network modifier, which creates non-bridging oxygen. The non-bridging disrupt the long chains and break the chemical bonds causing a decrease in $T_g$ and $T_c$. It is also observed that with increasing the concentration of Li$_2$O from 10 to 15 mol % $T_g$ and $T_c$ increases, this can be explained on the basis of nature of bonding present in the glass system [Paramjyot Komarjha et al. (2015)]. Lithium has electronegativity (0.98) which is higher than sodium (0.93). As a result P-O-Li and Li-O bonds, formed within the glass system might exhibit higher covalent character than P-O-Na and Na-O Bonds [S. Rani et al. (2008)]. The value of glass thermal stability $h'$ for the glass sample with Li$_2$O content 15% mol% is found to be maximum, which indicates its highest thermal stability than other glasses.
3-3 Density, molar volume and oxygen packing densities

Transparent and bubble free glasses were obtained for the compositional series of 55 P_2O_5 – (45-x) Na_2O – x Li_2O (x=0 – 35 mol% Li_2O). The values of the experimental density (ρ_{exp}) and the theoretical density (ρ_{th}) molar volume (V_m) and oxygen packing density (OPD) are listed in Table 2 and graphically presented in Fig.3 and Fig.4.

Table 2: Experimental (ρ_{exp}) and theoretical (ρ_{the}) density, molar volume (V_m) and oxygen packing density (OPD) of different glass compositions.

<table>
<thead>
<tr>
<th>Composition of 55 P_2O_5 – (45-x) Na_2O – x Li_2O (x mol %)</th>
<th>ρ_{exp} (gm/cm^3)</th>
<th>ρ_{the} (gm/cm^3)</th>
<th>V_m (cm^3/mol)</th>
<th>OPD (mol/litre)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.962</td>
<td>2.81</td>
<td>36.224</td>
<td>88.3391</td>
</tr>
<tr>
<td>3</td>
<td>2.668</td>
<td>2.57</td>
<td>39.821</td>
<td>80.3559</td>
</tr>
<tr>
<td>10</td>
<td>2.419</td>
<td>2.3</td>
<td>42.911</td>
<td>74.5735</td>
</tr>
<tr>
<td>15</td>
<td>2.37</td>
<td>2.27</td>
<td>43.061</td>
<td>74.3139</td>
</tr>
<tr>
<td>30</td>
<td>2.364</td>
<td>2.268</td>
<td>40.171</td>
<td>79.66</td>
</tr>
<tr>
<td>35</td>
<td>2.361</td>
<td>2.267</td>
<td>39.397</td>
<td>81.2253</td>
</tr>
</tbody>
</table>

Fig.3. The variation of theoretical, experimental densities and molar volume with composition of Li_2O (mol%).
It is found from Fig. 3 that the theoretical and experimental values of density decrease with increasing concentration of Li$_2$O and the molar volume pass through maximum at 15 mol% Li$_2$O. The density decreases because the molar mass of Li$_2$O (29.28 g/mol) is lower than that of molecular mass of Na$_2$O (61.97 g/mol). The experimental density values decreases from 2.962 g/cm$^3$ to 2.361 g/cm$^3$ for the prepared glass with increasing $x$ from zero to 35 which are in well agreement with reported values [L. Bih et al. (2008)]. This could be also explained by considering the fact that a high density Na$_2$O (2.2 gm/cm$^3$) is replaced by low density Li$_2$O (2.01 g/cm$^3$) which caused the decrease in mass density of the glass. Lithium oxide is a known glass modifier. The addition of glass modifier (Li$_2$O) do not contribute in glass formation but cleaves the structure of glass network and causes an increase in the molar volume of the glass [Kirk Othmar (1963)].

Oxygen packing density which is a measure of the tightness of packing of the oxide network can be used to explain the decreasing of $T_g$ with the increase of Li$_2$O content. It can be seen from Fig. 4 that OPD decreases from 88.3 to 74.3 mole/liter as the concentration of Li$_2$O increases from zero to 15 mol%. This indicates that the structure becomes loosely packed with increase in the concentration of Li$_2$O and the formation of a more open macromolecular chain in the prepared glass samples leading to decrease in $T_g$. By increasing the concentration of Li$_2$O from 15 to 35 mol% it was found that the
oxygen packing density increases from 74.3 to 81.2 mole/liter as the concentration of Li$_2$O increases from 15 to 35 mol%.

3-4 Electrical conductivity

3-4-1 dc electrical conductivity

Fig.5 shows the temperature dependence of dc electrical conductivity of 55 P$_2$O$_5$ – (45-x) Na$_2$O – x Li$_2$O (0 ≤ x ≤ 35) at different concentrations of Li$_2$O (mol%). The electrical conductivity $\sigma_{dc}$ is a thermally activated process and important to describe electrical behavior of a material. The data fit the Arhenius equation $\sigma_{dc} = \sigma_o \exp (-E_a / kT)$, $\sigma_o$ is the pre-exponential factor which including the charge carrier mobility and density of states, $E_a$ is the thermal activation energy for conduction and $k$ is the Boltzmann constant.

![Graph showing the variation of Ln $\sigma_{dc}$ versus 1000/T for different concentrations of Li$_2$O (mol%).](image)

Fig.5. The variation of Ln $\sigma_{dc}$ versus 1000/T for 55 P$_2$O$_5$ – (45-x) Na$_2$O – x Li$_2$O glass samples at different composition of Li$_2$O (mol.%).
Fig. 6. The variation of activation energies $\Delta E_{dc1}$ and $\Delta E_{dc2}$ and $\sigma_{dc}$ at room temperature with the composition of $\text{Li}_2\text{O}$ (mol%).

As shown in Fig. 5 there are two linear regions of conductivity that gave two activation energies $\Delta E_{dc1}$ and $\Delta E_{dc2}$ which indicating the conduction mechanism in the investigated temperature range (303K – 413K). The activation energies $\Delta E_{dc1}$ and $\Delta E_{dc2}$ arise from impurity scattering. Fig. 6 represents the variation of $\sigma_{dc}$ at room temperature and the activation energies $\Delta E_{dc1}$ and $\Delta E_{dc2}$ with the concentration of $\text{Li}_2\text{O}$ (mol%). It is clear from Fig. 6 that $\sigma_{dc}$ decreases from $3.3 \times 10^{-5}$ to $1 \times 10^{-5}$ (\Omega.cm)$^{-1}$ with increasing of $\text{Li}_2\text{O}$ concentration from zero to 35 mol% $\text{Li}_2\text{O}$ and the plot is found to exhibit a maximum for $x = 15$ mol% of $\text{Li}_2\text{O}$. In order to explain this behavior one must note that these ternary glasses were fabricated by adding different amount of $\text{Li}_2\text{O}$ to binary sodium-phosphate glass. The sodium ions were gradually replaced by lithium ions because the amount of glass former $\text{P}_2\text{O}_5$ was fixed at 55 mol%. Further addition of $\text{Li}_2\text{O}$ concentration from 10 to 15 mol% leads to increase in $\sigma_{dc}$ up to $7 \times 10^{-5}$ (\Omega.cm)$^{-1}$. Such behavior is likely to arise due to the structural changes accusing in phosphate network then decrease again up to $2.1 \times 10^{-6}$ (\Omega.cm)$^{-1}$ at $\text{Li}_2\text{O}$ concentration 35 mol%. The activation energies calculated from analysis of Ln $\sigma_{dc}$ versus 1000 / T plots is found to increase with increasing $\text{Li}_2\text{O}$ content to 10 mol% and then decrease with increasing $\text{Li}_2\text{O}$ content to 15 mol% and increase again.
3-4-2 ac electrical conductivity

The measured total conductivity $\sigma_t$, can be considered a summation of $\sigma_{dc}$, and ac conductivity, $\sigma_{ac}$. At very low frequency region $\sigma_{dc}$ is independent of frequency and appears as a flat dc plateau in this region of frequency. The ac conductivity is approximately independent of the frequency at lower frequencies, but more frequency dependent in high frequency region. The total conductivity follows the relation:

$$\sigma_t = \sigma_{dc}(\omega=0) + \sigma_{ac}(\omega) \quad (2)$$

In this relation, the dc conductivity is taken to represent the ac conductivity at $\omega$ tends to zero. The ac conductivity has been analyzed used Almond-West type power law with single exponent [D. P. Almond et al. (1984)].

$$\sigma_{ac} = A \cdot \omega^s \quad (3)$$

Where $A$ is a temperature dependent constant, $\omega = 2\pi f$ is the angular frequency and $s$ is the frequency exponent which depend on temperature. Such a dependence on temperature determines the ac conduction mechanism and has been found to be material dependant.

3-4-2-1 Complex impedance analysis

Complex impedance is a powerful technique for the characterization of electrical properties of polycrystalline sample such as conductivity, dielectric behavior ..... etc. It may be used to explain the dynamics of mobile or bound charges in the grain or grain boundaries. The expression of real ($Z'$) and imaginary ($Z''$) components of the impedance ($Z$) can be expressed by the following relationships:

$$Z = Z' - jZ'' \quad (4)$$

$$Z' = Z \cos Q \quad (5)$$

$$Z'' = Z \sin Q \quad (6)$$

Where $Q = 1 / [ C \cdot Z \cdot (2\Pi f) ]$
Fig. 7 (a). Cole-Cole plots of $Z'$ and $Z''$ at 3 MHz of 55 P$_2$O$_5$ – (45-x) Na$_2$O – x Li$_2$O glasses containing 15 mol% Li$_2$O at different temperatures

Fig. 7 (b). Cole-Cole plots at 3 MHz and 453 K for different concentrations of Li$_2$O mol%

Fig. 7-a shows the plot of $Z'$ versus $Z''$ (Cole-Cole plot) at 3 MHz for glass sample (with x = 15 mol% Li$_2$O) at different temperature, Fig. 7-b Cole-Cole plots of $Z'$ and $Z''$ for glass samples with different compositions of Li$_2$O mol%. The impedance plots of all the samples were found to exhibit good single semicircle starting from the origin over the entire range of temperature and the composition studied. The absence of
second semicircle in the complex impedance plots indicates that the glass samples have only grain effect to the conductivity mechanism at room temperature.

The values of dc conductivity were calculated by taking the intersection points of semicircles on the Z’ axis [M. J. Miah et al. (2016)]. From Fig.7-a it was found that the diameter of the semicircle decreasing and the intersection points of the semicircles shifted to lower Z’ values with increasing temperature which suggests that the value of grain resistance is decreasing and $\sigma_{dc}$ increasing with increasing temperatures. It is obvious from Fig.7-b that the diameter of the semicircle decreasing and the intersection points of semicircles shifted to lower Z’ values with decreasing Li$_2$O content in glass samples and the value of grain resistance is decreasing to minimum. For glass sample 15 mol% of Li$_2$O content it was found that it has the smallest diameter of semicircles which indicating the least value of grain resistance.

To compare the obtained data of $\sigma_{dc}$ calculated from Cole-Cole and $\sigma_{dc}$ calculated from $\sigma_t$ versus frequency are listed in Table 3. It is clear from the Table 3 that $\sigma_{dc}$ (Cole-Cole) and $\sigma_{dc}$ ($\sigma_t$ Vs f) approximately have same values.

Table 3: values of $\sigma_{dc}$ (Cole-Cole) and $\sigma_{dc}$ ($\sigma_t$ Vs f) at different temperatures

<table>
<thead>
<tr>
<th>T(k)</th>
<th>$\sigma_{dc}$ (Cole-Cole)</th>
<th>$\sigma_{dc}$ ($\sigma_t$ Vs f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>453</td>
<td>0.0188</td>
<td>0.0186</td>
</tr>
<tr>
<td>483</td>
<td>0.084</td>
<td>0.089</td>
</tr>
<tr>
<td>513</td>
<td>0.214</td>
<td>0.23</td>
</tr>
</tbody>
</table>

3-4-2-2 Frequency and temperature dependence of ac electrical conductivity

Fig.8 shows the frequency dependence of ac electrical conductivity at different temperatures for 55 P$_2$O$_5$ – (45-x) Na$_2$O – x Li$_2$O (with x = 15 mol% Li$_2$O). The ac conductivity behavior of all the other glass samples (with x = 3, 10, 30, 35 mol% Li$_2$O) is qualitatively similar. It is shown from Fig.8 that the ac conductivities exhibit a change of slope to higher values as the frequency is increased.
Fig. 8. Frequency dependence of $\sigma_{dc}$ for 55 P$_2$O$_5$ – (45-x) Na$_2$O – x Li$_2$O glasses containing 15 mol% Li$_2$O at different temperatures.

The increase of $\sigma_{ac}$ with increasing frequency suggests that hoping conduction prevails and the increase of the applied frequency enhances the hopping of charge carriers between the localized states [A. Ben Rasem et al. (2009)].

Fig. 9. Temperature dependence of the frequency exponent S at different concentrations of Li$_2$O mol%.

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Values of the exponent $s$ were calculated from the slopes of these lines at different temperatures. The temperature dependence of $s$ for all the prepared glass samples with different concentrations is shown in Fig. 9 in which $s$ decreases with increasing temperature and the concentration of the modifier oxide (Li$_2$O). Also it was found that for all the prepared glass samples $s$ values are significantly lower than unity and lie between 0.62-0.9.

According the correlated barrier hopping (CBH) model values of $s$ decrease with increasing temperatures, this is in good agreement with the obtained results, as shown in Fig. 9. Accordingly the frequency dependence of $\sigma_{ac}$ can be explained in terms of CBH model. This model first developed by Pike [G. E. Pike (1972)] for single electron hoping and has been extended by Elliot and Chen [S. R. Elliot (1978), R. H. Chen et al. (2006)] for simultaneous two electron hoping.

![Fig. 10. Temperature dependence of ac conductivity for glasses containing 15 mol% Li$_2$O at different frequencies](image)

Fig. 10 shows the variation of $\ln \sigma_{ac}$ with the reciprocal of temperature $1000 / T$ in the investigated temperature range at different frequencies for 55 P$_2$O$_5$ – 30 Na$_2$O – 15 Li$_2$O glass sample. This dependence of ac conductivity on temperature suggests that the ac conductivity is a thermally activated process. The value of the activation energies $\Delta E_{ac1}$ and $\Delta E_{ac2}$ has been calculated from the slope of $\ln \sigma_{ac}$ versus $1000 / T$ curves.
Fig. 11 (a,b) shows the variation of the activation energies $\Delta E_{ac1}$ and $\Delta E_{ac2}$ with concentration of Li$_2$O mol% at different frequencies. It is found that the activation energies $\Delta E_{ac1}$ and $\Delta E_{ac2}$ increase with increase of Li$_2$O concentration and the plot is found to exhibit minimum at $X = 15$ mol% Li$_2$O, also it is observed that the behavior of both $\Delta E_{dc}$ and $\Delta E_{ac}$ are almost the same, Such increase can be attributed to the contribution of the applied frequency to the conduction mechanism, which confirms the hopping conduction to be dominant mechanism [Sh. A. Mansour et al. (2010)].

3-4-2-3 Temperature and frequency dependence of dielectric constant $\varepsilon'$ and $\varepsilon''$

The complex dielectric constant of the investigated samples is formulated with two parts, $\varepsilon = \varepsilon' + i \varepsilon''$; where $\varepsilon'$ is the real part of dielectric constant and it is a measure of the energy, stored from the applied electric field in the material and identified the strength of alignment of dipoles in the dielectric. $\varepsilon''$ is the imaginary part of dielectric constant and it is the energy dissipated in the dielectric. $\varepsilon'$ and $\varepsilon''$ were evaluated using the following relations:

$$\varepsilon' = \frac{C L}{\varepsilon_o A}$$  \hspace{1cm} (7)

$$\varepsilon'' = \varepsilon' \tan \delta$$  \hspace{1cm} (8)
Where $C$ is the capacitance of the sample, $\varepsilon_0$ is the free space permittivity, $L$ is the sample thickness and $A$ is the area and $\tan \delta$ is the dissipation factor.

The real and imaginary parts of dielectric constant $\varepsilon'$ and $\varepsilon''$ of P$_2$O$_5$ – 30 Na$_2$O – 15 Li$_2$O glass samples with different concentration of Li$_2$O are measured over frequency range from 50 Hz to 5 MHz.

Fig.12. The temperature dependence of real part ($\varepsilon'$) of glass containing 15 mol% Li$_2$O at different frequencies

Fig.13. The temperature dependence of imaginary part ($\varepsilon''$) of glass containing 15 mol% Li$_2$O at different frequencies
The temperature dependence of the real $\varepsilon'$ and imaginary $\varepsilon''$ parts of dielectric constant at different frequencies for 55 P$_2$O$_5$ – 30 Na$_2$O –15 Li$_2$O glass are shown in Fig.12 and Fig.13 respectively. It is clear from Fig.12 that he obtained plots are straight and the values of $\varepsilon'$ increase with increasing temperature and also with decreasing frequency which is normal in oxide glasses and this cannot be taken as indication for spontaneous polarization [A. A. Bahgat et al. (2001)].

A similar behavior is observed in Fig.13 for the variation of $\varepsilon''$ with temperature. This can be explained by means of dielectric polarization mechanism of the material. Among various polarization, deformational polarization (electronic and ionic) and relaxation polarization (dipolar and space charge polarization) that contribute to the dielectric constant. Electronic and ionic polarizations are active in high frequency range, while the other two mechanisms prevail in the low frequency range [S. Kurien et al. (2006), I. Bunget et al. (1984)]. The increase of both $\varepsilon'$ and $\varepsilon''$ toward the low frequency region may be attributed to space charge polarization. As the frequency increases, the polarizability contribution from ionic source decreases and finally disappear [K. H. Mahmoud et al. (2011)].

Table.4 Shows the dependence of the real $\varepsilon'$ and imaginary $\varepsilon''$ parts of dielectric constant at room temperature and frequency 3 MHz on concentration of Li$_2$O mol%.

<table>
<thead>
<tr>
<th>Composition of 55 P$_2$O$_5$ – (45-x) Na$_2$O – x Li$_2$O mol %</th>
<th>Real part ($\varepsilon'$) of dielectric constants (cm)</th>
<th>Imaginary part ($\varepsilon''$) of dielectric constants (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>4.42455</td>
<td>6.12816</td>
</tr>
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<td>10</td>
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</tr>
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<td>15</td>
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<td>10.4</td>
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<td>30</td>
<td>9.61353</td>
<td>10.2387</td>
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</tbody>
</table>
Fig. 14 shows the variation of $\ln \varepsilon''$ with $\ln \omega$ for the investigated samples. It is clear from this figure that the obtained curves are straight lines at various temperatures. According to Guntini et al. [J. C. Guntini et al. (1981)] $\varepsilon''$ at a particular frequency in the temperature range where dielectric dispersion occurs, is given by:

$$\varepsilon'' = B \omega^m \quad (9)$$

The power $m$ of this equation was calculated from the negative slopes of the obtained straight lines of Fig. 14 at different temperatures.

Fig. 15. Temperature dependance of the investigated glasses for exponent $m$ at different concentrations of $\text{Li}_2\text{O}$ mol%
The variation of the obtained values of m with temperature for different concentration of Li2O is shown in Fig.15. Fig.15 shows that m decreases with increasing temperature. According to Guintini et al the exponent m can be related to the temperature and the maximum barrier height \( W_m \) through the following equation:

\[
m = -4K_B T/W_m
\]  

(10)

Table 5 Shows the variation of the obtained values of the maximum barrier height \( W_m \) at different concentrations of Li2O mol%:

<table>
<thead>
<tr>
<th>Composition of 55 P2O5 – (45-x) Na2O – x Li2O (mol %)</th>
<th>Maximum barrier height (( W_m )) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.61</td>
</tr>
<tr>
<td>3</td>
<td>0.68</td>
</tr>
<tr>
<td>10</td>
<td>0.71</td>
</tr>
<tr>
<td>15</td>
<td>0.59</td>
</tr>
<tr>
<td>30</td>
<td>0.702</td>
</tr>
<tr>
<td>35</td>
<td>0.728</td>
</tr>
</tbody>
</table>

4- Conclusion

Transparent glasses of 55 P2O5 - (45-x) Na2O - xLi2O (0 ≤ x ≤ 35) were prepared using the melt quenching technique. All prepared glasses are amorphous as confirmed by X-Ray diffraction. The increase of Li2O concentration decreases the glass transition temperature (\( T_g \)) and decreases crystallization temperature (\( T_c \)) except for glass contains 15 mol% Li2O which has the maximum value for \( T_g \) and \( T_c \) and this glass exhibits highest thermal stability. Density, molar volume and oxygen packing density insure that Li2O incorporated in sodium phosphate glass by increasing Li2O mol% concentration. The experimental and theoretical densities follow the similar trend. The dc and ac conductivity and their related conduction mechanisms of the investigated glasses were analyzed. Activation energies \( \Delta E_{dc1} \) & \( \Delta E_{ac1} \) and \( \Delta E_{dc2} \) & \( \Delta E_{ac2} \) at low and high temperatures are calculated. It was found the behavior of both \( \Delta E_{dc} \) and \( \Delta E_{ac} \) are the same.
The ac conductivity studies of investigated glasses have been carried out at different concentration of Li₂O mol% and the data has been analyzed by using Almond-West power law

\[ \sigma_{ac} = \sigma(0) + A \cdot \omega^s \]  (11)

The power law exponent S is found to decrease with increasing temperature and exhibits lower values in highly modified glasses. The correlated barrier hoping (CBH) seems to be the most interesting model related to the obtained results.

The dielectric parameters \( \varepsilon' \) and \( \varepsilon'' \) are found to increase with the increase in temperature and their variation with Li₂O mol% pass through a maximum at 15 mol% Li₂O (Table 2). These results would be discussed by means of dielectric polarization mechanism of material. The values of the maximum barrier height \( W_m \) obtained from Guillaume equation were found to increase with increasing of the concentration of Li₂O mol% except 15 mol% Li₂O glass.

References


تحضير و توصيف زجاجيات فوسفات الصوديوم العدلية بأكسيد الليثوم

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في هذا البحث تم تحضير زجاج شفاف من (x) Na2O - (45 - x) P2O5 - 55Li2O (x = 0, 3, 10, 15, 30, 35) باستخدام تقنية الصهر والتبريد المفاجيء. وقد تم فحص العينات باستخدام تقنية حيود أشعة أكس (XRD) و اثبطت النتائج ان جميع العينات ذات طبيعة أمورفية. وقد تم تعيين كلاً من درجة التحول للزجاج (Tg) و درجة التبلور (Tc) باستخدام تقنية (DTA) وقد أوضح ان النتائج ان الزجاج الذي يحتوي على 15 mol% Li2O حراري. وكذلك تم قياس كلاً من الكثافة والحجم المولاري للعينات المحمضرة. وتم دراسة الخواص الكهربيه لكل من التيار المستمر والتياير المتردد ومعاملات ثابت العزل و"ε" و من الدراسة تم تعيين طاقتي التشتيط عند درجات الحرارة المنخفضة و المتوسطة وكذلك Cole-Cole plot و تم شرح ميكانيكية لتعيين ميكانيكية التوصيل و تم دراسة الموصليه الكهربيه للتياير المتردد عند تردادات مختلفة و تم exponent (CBH) correlated barrier hopping تحليلاً على اساس (CBH) هو اتسب موديل منطق مع النتائج. وكذلك تم دراسة معاملات ثابت العزل و"ε" و مدي تغييرها مع التردادات المختلفة و تركيزات Li2O و تم شرح النتائج بواسطة dielectric polarization mechanism of material و تم حساب قيمة (Wm) ل(maximum barrier height (Wm) ليزداد بزيادة Li2O mol%.)