Mechanical and Structural Properties of Zinc – Sodium - Phosphate Glasses Doped with Cu$_2$O

E. Nabhan$^{1,*}$, A. Nabhan$^2$, N. Abd El Aal$^3$

$^1$Physics Dept., Faculty of Science (Girls), Al Azhar University, Cairo, Egypt
$^2$Mechanical Production Dept. Faculty of Engineering, Al Minia University, Al Menia, Egypt
$^3$Ultrasonic Laboratory, National Institute of Standard, Giza, Egypt

Email address:
dr.emannabhan@yahoo.com (E. Nabhan)

*Corresponding author

To cite this article:

Received: November 5, 2016; Accepted: December 2, 2016; Published: December 20, 2016

Abstract: Ternary Zinc-Sodium-Phosphate glasses doped with copper of the composition 40ZnO-(20-x) Na$_2$O-40P$_2$O$_5$ xCu$_2$O where x =0, 2, 4, 6, 8 mol % were prepared by the tradition quenching method. The effect of Cu ions on density, molar volume and microhardness has been investigated. FTIR was measured in the range (400-1600) cm$^{-1}$ to investigate the effect of Cu ion on the structure of the studied glass. Longitudinal and shear velocities were measured for the studied glass using pulse echo technique. Elastic properties such as longitudinal modulus, shear modulus, bulk modulus, and Young’s modulus, Poisson’s ratio) and some physical parameters such as softening temperature, hardness, Debye temperature have been calculated. The ultrasonic results and the other measured parameters indicate the Cu ion increase the cross-link density by the formation of P-O-Cu. All the measurements are measured at room temperature.

Keywords: Infrared, Infrared Deconvolution, Density, Molar Volume, Hardness, Ultrasonic Velocity, Elastic Moduli

1. Introduction

Due to the unique properties of phosphate glasses, such as high thermal expansion coefficient, low melting, softening and transition temperatures, high electrical conductivity (with the addition of transition metal ions), ultraviolet and far infrared transmission and other optical characteristics, make them of great scientific and technical interest for many applications [1-4]. However, the poor chemical durability is one of the disadvantages of which limit its use in many applications [5,6]. The addition of one or more of the transition metal oxide to phosphate glass has improved the chemical durability [7]. With the Addition of ZnO to phosphate glass has an effect on the chemical durability and other properties that, when it adds as a modifier, it increases the cross-link between phosphate anions, inhibiting hydration reaction [8, 9]. Additionally, ZnO improves the melting properties that, it is lowering the melting and transition temperatures, and also improve the opacity of glass, which make it is important for many applications such as glass filters and as sealing glass. Also adding copper to phosphate glasses maintains optical absorption band in the visible –near IR region makes it a candidate as band pass filter [10], and also Cu ions exhibiting a semiconducting properties [11]. In different glasses, copper can exist in two states, as divalent Cu$^{2+}$ which give the glass color from blue to green depending on its concentration or monovalent Cu$^+$ (Cuprous) which doesn’t produce color because its five d-orbital occupied or containing both states. Their ratio of Cu$^+$ and Cu$^{2+}$ depending on the type of glass former, composition and thermal history (such as environment, melting temperature, and melting time) [12]. Recently, Cu$^{2+}$ ions doped glasses have shown a great importance because of their optical stability and variable optical and electrical applications [13, 14]. The mechanical properties such as elastic moduli, and other mechanical properties are of great importance because it gives a good information concerning the forces that are operative between atoms of the solid and also it suitable for describing the compactness of the glass structure [15, 16].
The main objective of this work is to investigate FTIR, density, molar volume, hardness, and elastic properties of some Zinc-sodium-phosphate-glasses doped with different concentrations of copper oxide up to 8 mol%. It is amid to study the effect of Cu$_2$O on the different physical properties which makes it candidate for many applications, such as glass to metal seals.

2. Experimental Procedure

2.1. Preparation of Glasses

The glass samples with chemical 40ZnO-(20-x) Na$_2$O-40P$_2$O$_5$-xCu$_2$O in molar ratio x = 0, 2, 4, 6, and 8 were prepared by the conventional melt and quenching technique. Batches were prepared from appropriate mixtures of reagent grade NaCO$_3$, ZnO, NH$_4$H$_2$PO$_4$ and Cu$_2$O. The batches were mixed and grinding using porcelain mortar and then calcinated in porcelain crucible using muffle furnace for about 1h at 350°C, then it heated at 1050°C for 1h. The melt were removed from the furnace several times and shaken well to ensure homogeneity. The melting were poured in a preheated copper moldan and annealed at 300°C. The resulting IR spectra have been being calculated using the formula:

\[\rho = \frac{w_a}{w_a - w_b} \rho_b\]  

(1)

Where $w_a$ and $w_b$ the weights of sample in air and buoyant respectively, $\rho_b$ is the density of the buoyant which equal 1.593 gm/cm$^3$. The molar volume $V_m$ of each sample was being calculated using the formula:

\[V_m = \frac{EM_iN_i}{\rho}\]  

(2)

Where $M_i$ is the molecular weight of the constituent oxides, and $N_i$ is the percent composition of the constituent oxides and $\rho$ is the density.

2.2. Infrared Measurements

The infrared absorption spectra of the studied glasses were measured at room temperature using Beckman 4250 IR spectrometer in the range (400-4000) cm$^{-1}$, using the KBr pellet technique. The resulting IR spectra have been deconvoluted in order to know further information about the structural groups and their changes.

2.3. Density Measurements

Densities of all studied glass samples were measured at room temperature by applying Archimedes Principle using carbon tetrachloride as buoyant liquid using the relation:

\[\rho = \frac{w_a}{w_a - w_b} \rho_b\]  

(1)

Where $w_a$ and $w_b$ the weights of sample in air and buoyant respectively, $\rho_b$ is the density of the buoyant which equal 1.593 gm/cm$^3$. The molar volume $V_m$ of each sample was being calculated using the formula:

\[V_m = \frac{EM_iN_i}{\rho}\]  

(2)

Where $M_i$ is the molecular weight of the constituent oxides, and $N_i$ is the percent composition of the constituent oxides and $\rho$ is the density.

2.4. Microhardness Measurements

The microhardness of the samples were determined using a microhardness tester of the type Shimadzu (Japan). High polishing was necessary for obtaining smooth, flat parallel surfaces before indentation testing. Ten indentations were measured for each sample. The appropriate loading of the studied samples is 200 gm for 15 sec. The microhardness value was calculated automatically.

2.5. Ultrasonic Measurements

The longitudinal and shear ultrasonic wave velocity $V_l$ and $V_s$, respectively, were measured at room temperature using pulse-echo method. X cut and Y cut transducers operated at a fundamental frequency of 4MHz and a digital flaw detector (USIP 20, Krauthramer, Germany) were used, the velocity was calculated using the relation

\[V = \frac{2d}{\Delta t}\]  

(3)

Where $d$ is the sample thickness, $\Delta t$ is the time interval.

3. Determination of Elastic Moduli

The longitudinal and shear ultrasonic wave velocity $V_l$ and $V_s$ were calculated using equation (3). Then the elastic strains produced by a small stress can be described by the longitudinal modulus ($L$) and shear modulus ($S$) given by

\[L = \rho V_l^2\]  

\[S = \rho V_s^2\]  

(4)

Where $\rho$ is the density of the studied glass samples. Young’s modulus ($E$), the bulk modulus ($K$), Poisson’s ratio ($\sigma$) and the microhardness ($H_u$) can be calculated using the following equations [17]

\[K = L - \frac{4S}{3}\]  

\[E = (1+\sigma)2S\]  

\[\sigma = \frac{(V_l^2 - 2V_s^2)}{2(V_l^2 - V_s^2)}\]  

\[H_u = \frac{(1-2\sigma)E}{6(1+\sigma)}\]  

(5)

Other parameters can be calculated using the ultrasonic velocities and the experimental density, Debye temperature $\Theta_D$, the mean velocity and the softening temperature. The mean sound velocity $V_{mean}$ has the expression

\[V_{mean} = \left[\frac{1}{3} \left(\frac{1}{V_l} + \frac{2}{V_s}\right)\right]^{\frac{1}{2}}\]  

(6)

Then the Debye temperature can be expressed interims of the mean velocity

\[\Theta_D = \left(\frac{\hbar}{k_B}\right) \left(\frac{3N_i \Psi}{4\pi V_{mean}}\right)^{\frac{1}{2}}\]  

(7)
Where, \( h \) is Plank’s constant, \( k_B \) is Boltzman constant, \( N_A \) is Avogadro’s number, \( \Psi \) is the number of atoms in the chemical formula, \( V_M \) is the molar volume.

Softening temperature \( T_s \) can also be calculated using the shear ultrasonic velocity by the equation:

\[
T_s = \frac{V_s^2 M}{C^2 \Psi}
\]

Where \( M \) is the molecular weight, and \( C \) is a constant of value 507.4 m s\(^{-1}\) k\(^{-1}\) for alumina-silicate glasses and assumed to be the same for all glasses.

4. Results and Discussions

4.1. IR Results and Discussion

The IR spectra of the studied glass samples are represented in Figure (1) as the Cu\(_2\)O content increases from 0.0 up to 8.0 mol%, these values being reported in the following as the G0, G1...G8. Inspection of the spectra shows that these spectra are almost similar without any significant differences except in a slight shift of band positions and sometimes changes in the relative intensities of the main bands. Based on information predicted from previous studies [18, 19] leads to the following assignments:

- The band at 500 cm\(^{-1}\) which can be assigned as the deformation vibration of PO\(_4^{3-}\) group is slightly shifted to higher as Cu\(_2\)O increase from glass G0 to G8.
- The band at 750 cm\(^{-1}\) which is attributed to P-O-P symmetric band is slightly shifted to higher wavenumber as Cu\(_2\)O content increase from glass G0 to G8.
- The band at about 900 cm\(^{-1}\) which is assigned to P-O-P asymmetric, is slightly shifted to higher wave number as Cu\(_2\)O content increase from glass G0 to G8.
- The two absorption bands at 1000 and 1100 cm\(^{-1}\) are attributed to P-O symmetric and P-O asymmetric, the phosphate non bridging oxygen portion in PO\(_4\) tetrahedra in a chain structure respectively. The symmetric band P-O\(_{sym}\) doesn’t affect by Cu\(_2\)O content while the P-O\(_{asy}\) there is a decrease in the intensity and the band become more broadening and its center slightly shifted to higher wavenumber as Cu\(_2\)O increase.
- The shoulder which observed at 1270 cm\(^{-1}\) is assigned to asymmetric stretching modes of the two non bridging oxygens bonded to phosphorus atoms-O-P-O units in the phosphate tetrahedral[20,21]. It is noticed that its intensity decrease and seems to overlap with the P-O\(_{asy}\) as Cu\(_2\)O content increase. From the spectra, it is clear that the IR spectra are free from any characteristic absorption bands of ZnO or Cu\(_2\)O as network formers which means that both of them play the role of network modifiers and so it occupy the interstices.

From the results of the IR, the shift of the two bands at 740 and 900 cm\(^{-1}\) of the P-O-P\(_{sym}\) and P-O-P\(_{asy}\) respectively to higher wavenumber may be due the increase of the covalence character of these bands indicates that the bonds are strengthened as Na\(_2\)O is replaced by Cu\(_2\)O in agreement with Shin et al.[22] and Chahine et al [23]. The decrease in intensity of the band at 1000 cm\(^{-1}\) assigned to P-O\(_{sym}\) reveals a decrease in the non-bridging oxygen and increase in the cross-link density as Na\(_2\)O is replaced by Cu\(_2\)O. This suggestion is in agreement with the results of Gresh et al [24], who suggested that M\(^{2+}\) cations increase the cross-link density without breaking P-O-P chains. In other words Cu cations decrease the non-bridging oxygen and increase the cross-link density by the formation of P-O-Cu bonds which increase the cross-link density. A deconvolution process, as described elsewhere [25], should be performed to get further information about the characteristic parameters such as the band centers (C), which is related to some type of vibration specific structural groups, its width (W) and relative area (A), which is proportional to the concentration ratio of this structural group. The deconvolution parameters of the band for the investigated glasses are given in Table [1]. Figure (2) illustrates the deconvoluted spectra of sample G2 as an example.
4.2. Density and Molar Volume

From the deconvolution data, of the studied glass system, represented in Figure (3), the band centered at 754 cm$^{-1}$, which due to P-O-P $^{as}$, its center shifted to higher wavenumber as Na$_2$O is replaced by Cu$_2$O. While its relative intensity remains constant. The band centered at 907 cm$^{-1}$ which is due to P-O-P $^{as}$, shifted to higher wavenumber and its relative intensity increases as Cu$_2$O increases. The results of the two bands reveal that as Na$_2$O is replaced by Cu$_2$O the cross-link density increase due to the formation of P-O-Cu which indicated from the increase of the relative intensity of P-O-P $^{as}$. There is also increasing in the bond strength of both the P-O-P $^{as}$ and P-O-P $^{sy}$ due to the shift to higher wavenumber.

![Figure 2. Band deconvolution of IR spectrum for glass sample G2. The red line shows the fit of IR spectra of G2.](image)

The band at 987 cm$^{-1}$, which is related to the non-bridging oxygen atoms P-O, shifted to higher wavenumber and its relative intensity decrease as Na$_2$O is replaced by Cu$_2$O, which means the increase in the cross-link density and decreasing in the non-bridging oxygen atoms.

### Table 1. Deconvolution parameters of the infrared spectra of the studied glasses.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Composition in mol %</th>
<th>Exp. Density g/cm$^3$</th>
<th>Exp. Molar volume</th>
<th>Hardness kg/mm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>G0</td>
<td>ZnO 40 Na$_2$O 20 P$_2$O$_5$ Cu$_2$O 0</td>
<td>3.027</td>
<td>33.61</td>
<td>344</td>
</tr>
<tr>
<td>G1</td>
<td>ZnO 40 Na$_2$O 18 P$_2$O$_5$ Cu$_2$O 2</td>
<td>3.084</td>
<td>33.51</td>
<td>355</td>
</tr>
<tr>
<td>G2</td>
<td>ZnO 40 Na$_2$O 16 P$_2$O$_5$ Cu$_2$O 4</td>
<td>3.161</td>
<td>33.38</td>
<td>366</td>
</tr>
<tr>
<td>G3</td>
<td>ZnO 40 Na$_2$O 14 P$_2$O$_5$ Cu$_2$O 6</td>
<td>3.204</td>
<td>33.27</td>
<td>375</td>
</tr>
<tr>
<td>G4</td>
<td>ZnO 40 Na$_2$O 12 P$_2$O$_5$ Cu$_2$O 8</td>
<td>3.281</td>
<td>32.98</td>
<td>387</td>
</tr>
</tbody>
</table>

Table 2 display the composition of the studied glass samples and their experimental density $\rho$, molar volume $V_m$ and the Vickers microhardness $H$. The data of both density and molar volume as a function of Cu$_2$O content have been represented in Figure (3). From the figure density increase as Cu$_2$O content while the molar volume decreases.

![Figure 3. The relation between Cu$_2$O mol % and both the density and molar volume of the studied glasses.](image)

The increase of the density as Cu$_2$O increase is related to the difference in atomic mass of Cu ion and Na ion [26] while the decrease of the molar volume may be due to the less ionic character of Cu-O than that of Na-O (0.53 and 0.82 respectively) as calculated from Pauling [27]. This means that the increase in the covalence character of the system as Cu$_2$O increase on the expense of Na$_2$O. The results of the density and molar volume reveals that as Na$_2$O is replaced by Cu$_2$O the glass structure becomes more compacted. Such compaction can be realized through any of the following changes:

- Shortening of the bond length as indicated by the observed shift of P-O-P symmetric and asymmetric stretching vibrations at 750 and 900 cm$^{-1}$ respectively towards higher wavenumber.
- The role of Cu$_2$O cation in crosses linking the phosphate groups.
- Occupation of interstices as also concluded from IR results.
4.3. Microhardness

Figure (4) shows that the hardness of the studied glass samples as a function of Cu$_2$O content and the data are represented in [2]. From the figure the value of the hardness is found to increase as Cu$_2$O content increase. It is known that the hardness increases as the flow mobility of the matrix element decrease. This was supported by the conclusion obtained from the viscosity studies of Fen et. al. [28]. He suggested that an increase in the hardness number of different oxides is attributed to the decrease in the flow mechanism in a glass containing oxides. Decrease in the flow mobility is expected to occur in replacing Na$_2$O by Cu$_2$O due to the decrease in the non-bridging oxygen atoms resulting from the increasing of the cross-link density as well as the remarkable difference of Na atomic mass and the atomic mass of Cu and consequently the hardness increase.

The effect of replacing progressive mol ratio of Na$_2$O by Cu$_2$O of the studied glass samples on the different parameters is represented in Figure (5, 6, 7, 8 and 9).

![Figure 4. The relation between Cu$_2$O mole % and the experimental Vicker's microhardness of the studied glasses.](image)

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Density Kg/m$^3$</th>
<th>$V_l$ m/sec</th>
<th>$V_s$ m/sec</th>
<th>$S$ GPa</th>
<th>$L$ GPa</th>
<th>$K$ GPa</th>
<th>$E$ GPa</th>
<th>$σ$</th>
<th>$H_u$ Kg/mm$^2$</th>
<th>$T_s$ k</th>
<th>$Θ_D$k</th>
</tr>
</thead>
<tbody>
<tr>
<td>G0</td>
<td>3027</td>
<td>4716</td>
<td>2543</td>
<td>19.58</td>
<td>67.32</td>
<td>41.22</td>
<td>50.70</td>
<td>0.295</td>
<td>267</td>
<td>537</td>
<td>371</td>
</tr>
<tr>
<td>G2</td>
<td>3084</td>
<td>4800</td>
<td>2586</td>
<td>20.62</td>
<td>71.06</td>
<td>43.55</td>
<td>53.44</td>
<td>0.296</td>
<td>281</td>
<td>565</td>
<td>378</td>
</tr>
<tr>
<td>G4</td>
<td>3144</td>
<td>4856</td>
<td>2595</td>
<td>21.17</td>
<td>74.13</td>
<td>45.90</td>
<td>55.30</td>
<td>0.300</td>
<td>282</td>
<td>578</td>
<td>380</td>
</tr>
<tr>
<td>G6</td>
<td>3204</td>
<td>4919</td>
<td>2609</td>
<td>21.82</td>
<td>77.52</td>
<td>48.44</td>
<td>56.90</td>
<td>0.300</td>
<td>284</td>
<td>593</td>
<td>383</td>
</tr>
<tr>
<td>G8</td>
<td>3281</td>
<td>4935</td>
<td>2637</td>
<td>22.81</td>
<td>79.00</td>
<td>49.48</td>
<td>59.33</td>
<td>0.300</td>
<td>303</td>
<td>615</td>
<td>388</td>
</tr>
</tbody>
</table>

The values of the density $ρ$, longitudinal velocity $V_l$, shear velocity $V_s$, shear modulus $S$, Longitudinal modulus $L$, bulk modulus $K$, Young's modulus $E$, Poisson's ratio $σ$, Hardness $H_u$, softening temperature $T_s$, Debye temperature $Θ_D$ are given in Table [3].

![Figure 5. The relation between Cu$_2$O content and the longitudinal and shear velocity $V_l$ and $V_s$, respectively](image)

Inspection of these relations reveals that, Form Figure (5), each of the longitudinal velocity $V_l$, transverse velocity $V_s$ are progressively increased as Na$_2$O is replaced by Cu$_2$O. It is obvious that the increase in the cross link density and the decrease in the non bridging oxygen and so the increase in connectivity will reflect on the ultrasonic velocities to increase in agreement with the results obtained from the above result (IR, density, molar volume, and hardness) by the formation of P-O-Cu which decrease the non bridging oxygen atoms and increase both of the cross-link density and the covalency of the bonds. This also will reflect on the chemical durability and enhance it to increase with increasing Cu$_2$O.

Figure (6) represented the relation between Cu$_2$O content and the different elastic moduli ($L$, $E$, $K$, and $S$). From the figure all the elastic moduli increase with increasing Cu$_2$O content for the same reasons that reflect on the shear and longitudinal velocities and in agreement with results obtained from the other results.

![Figure 6. The relation between the elastic moduli ($S$, $L$, $K$ and $E$) with the Cu$_2$O content.](image)

The variation of Debye temperature $Θ_D$ softening temperature $T_s$ with Cu$_2$O content is represented in Figure (7). The Debye temperature at which nearly all mode of vibrations in the solid are excited and it is increasing as the
rigidity of the system. From the figure it is clear that $\Theta_D$ increase with the increase of Cu$_2$O content, which means that the rigidity of the glass system increase as Cu$_2$O increase.

The softening temperature and hardness which represented in Figure (7), Figure (8) are also affected by the rigidity of the system, the rigidity increases as the non bridging oxygen decreases, the cross-link density increases, and with the strengthening of the bonds, all of these increased as Cu$_2$O increase in agreement with Marzouk[18].

Poisson's ratio $\sigma$ with Cu$_2$O content is represented in Figure (8). The value of $\sigma$ is varied from 0.295 to 0.300 as Cu$_2$O content increase from 0 to 8 mol % is almost negligible in agreement with Rajendran et.al.[29] who neglect the variation of $\sigma$ in the range from about 0.27to about 0.29 as SiO$_2$ increase.

5. Conclusions

Studies of IR, density, molar volume, hardness, ultrasonic velocities, elastic moduli and other parameters such Debye temperature, softening temperature, hardness and poisson's ratio as Na$_2$O is replaced by Cu$_2$O in zinc sodium phosphate glasses were carried out. Infrared absorption spectra indicate that the cross-link density of the glassy system increase by the decrease in the number of non-bridging oxygen atoms, the formation of P-O-Cu bonds, and the increase of the covalence character of bonds. Which also causes strengthening of the bonds as Cu$_2$O content increase. The IR results have been ascertained by the deconvolution of the IR spectra of the samples. Both the density and hardness increase with increasing Cu$_2$O content, while the molar volume decreases. The increases in the longitudinal and shear velocities, Debye temperature, softening temperature, hardness, and elastic moduli, are attributed to the increase of the connectivity of the system.

References
