Ultrasonic Properties of Zinc-Lithium Phosphate Glass: Effect of Strontium

Nur Fatihah N., Nurhafizah H. *, Ahmad N.H.
1 Advanced Optical Material Research Group (AOMRG), Department of Physics, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia

E-mail: nurhafizah.h@utm.my

Abstract. Glasses of the general formula (50–x)P_2O_5 – 30ZnO – 20Li_2O – (x)SrCO_3, where (0.00 ≤ x ≤ 5.00 mol%) were prepared via the melt-quench technique. The mechanical properties of the glass are utilized by using ultrasonic testing. The absence of distinct and Bragg peaks in XRD spectra, confirming the amorphous nature of samples. The glass densities are found increases as well as the packing densities with respect to SrCO_3 concentration, which leading to the decrease in molar volume values, indicating the rigidity of the glasses. The ultrasonic results and other measured parameters attribute to the Sr ion increase in the cross-link density by the formation of P-O-Sr due to the value of Poisson’s ratio obtained are between range of 0.1 to 0.2.

Keywords. Phosphate-based glass; Mechanical Analysis; Ultrasonic Testing.

1 Introduction

Phosphate glasses are known for its technological interest for electrochemical devices, which has been explored mainly for biomedical applications (i.e. bone tissue repair and fixation) as well as for wide ranging applications such as optical and nuclear waste storage. It also can easily be doped with a wide variety of ions. The phosphate glass role (network former) is used in different applications. The short-range order of phosphate glasses can be explained by the type and concentration of [PO_4]. The addition of any multivalent oxide to P_2O_5 can improves the chemical durability but mostly keep the unique physical properties of the phosphate glasses. They are generally possessing high thermal expansion coefficients, low glass transition temperatures, low softening temperatures beside low preparation temperatures and high transmission [1,2].

The addition of alkaline and alkaline earth metal ions can alter the glass structures by opening up a modified network and to reduce the bond strength. Therefore, it will disrupt the glass structure through creation of a terminal oxygen (P–O–M) bond by breaking the bridging oxygen (P–O–P) bonds resulting in depolymerisation of the phosphate glass network. The alkaline earth metals are known as shiny, silvery-white, and quite reactive metals at standard temperature and pressure. While not as reactive as the alkali metals, this family knows how to make bonds very easily. Moreover, by introducing other oxide elements such as zinc oxide (ZnO) and lithium oxide (Li_2O) as a glass modifier, a good quality of glass can be formed. This study is to find an optimum composition of P_2O_5 – ZnO – Li_2O – SrCO_3 in order to produce strontium doped phosphate glass. Throughout this study, the nature of the glass can be determined as well as the physical and mechanical properties for industrial purpose.
2 Methodology

2.1 Melt Quench Technique

The melt quenching technique is the common way of obtaining a glass, especially for the production of bioactive glass. The required amounts of all the precursors were weighed, mixed, and heated in different types of crucibles depending on the glass composition. The materials are weighed using an electronic weighing balance, Precisa XT 220A. Then, the materials are grinded into powdered form by a ball mill to obtain more homogenous particle size in 15 minutes. The mixed quantities of these chemicals were put in alumina crucibles and placed in an electric furnace open to the atmosphere and held at 300 °C for one hour. The ground mixture is then melted in a furnace at 950 °C. Finally, the melted material is immediately transferred to an annealing furnace and poured into moulds, which held at 300 °C for three hours. This procedure was repeated for all glass samples with different mol% concentration as listed in Table 1.

Table 1: The composition of 
(50 − x)P₂O₅ − 30ZnO − 20Li₂O − (x)SrCO₃ where (0 ≤ x ≤ 5 mol%).

| Samples | Composition (mol%) |
|---------|-------------------|
|         | P₂O₅  | ZnO  | Li₂O | SrCO₃ |
| S1      | 50    | 30   | 20   | 0    |
| S2      | 49    | 30   | 20   | 1    |
| S3      | 48    | 30   | 20   | 2    |
| S4      | 47    | 30   | 20   | 3    |
| S5      | 46    | 30   | 20   | 4    |
| S6      | 45    | 30   | 20   | 5    |

2.2 X-Ray Diffraction

The amorphous state of the sample is confirmed by X-ray diffraction (XRD) measurement on Rigaku Model of Siemens Diffractometer D500 with Cu-Kα radiation, operated at 40 kV and the glass samples are in fine powder form in 2θ range of 10-80°.

2.3 Physical Properties

Archimedes principle is used to measure the density of prepared glass by using Mettler Toledo electronic weighing balance. The physical parameters such as the density, molar volume density and ionic packing density of the glass sample are calculated by using different mathematical expression shown in Equation (1) to (4):

\[ \rho = \left[ \frac{A}{A-B} \times (\rho_o - d) \right] + d \]  

(1)
where \( A \) represents the weight of the glass sample in air and \( B \) is the weight of the sample in immersed liquid. While \( \rho_o \) is the density of immersed liquid (distilled water = 1 g cm\(^{-3}\)) and \( d \) is the density of air (0.001 g cm\(^{-3}\)). Moreover, the molar volume can be solved by using Equation (2):

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

(2)

where \( V_m \) is the molar volume, \( \rho \) is the density and \( M \) is the molecular weight of the sample. The measurement of rigidity of the oxide system can be determined by packing density, \( V_d \) which may be obtained from the Equation (3):

\[
V_d = \frac{1}{V_m} \sum V_i X_i
\]

(3)

where \( V_i \) and \( X_i \) represent the packing factor and mole fraction of the composition, respectively. Thus, packing factor of any oxide \( D_xO_y \) having \( D \) and \( O \) ions with ionic radii \( r_m \) and \( r_o \) may be solved by Equation (4):

\[
V_i = \frac{4\pi N_A}{3} \left( X r_m^3 + Y r_o^3 \right)
\]

(4)

2.4 Ultrasonic Measurement (Pulse echo Technique)

The glass samples with diameter between 3.62 mm to 5.19 mm were measured by using vernier callipers. Before undergoes ultrasonic scanning, the essential oil is applied to the surface of sample (scan area) as well as the ultrasonic probe to ensure that ultrasonic waves were transmitted to the sample without reflection. The pulse, which generated by the pulse oscillator were depending on the transmitting transducer. It transforms them into acoustic pulses. These acoustic pulses generated through the glass sample, then converted into electrical signals, which receive by the transducer. Hence, the output signal (amplified) from the sample is displayed on the oscilloscope. A high-power ultrasonic process control system Pulser-Receiver Panametrics NDT, a digital storage oscilloscope RIGOL DS2203E and KB-Aerotech straight beam contact transducer of diameter 0.5 mm and the central frequency of 2.25 MHz were employed for measuring the ultrasonic signals. The angle wedges KB - Aerotech made of perspex with refraction angle of 45\(^\circ\) was used and the wedges attached to the KB - Aerotech straight beam contact transducer of diameter 0.5 mm and the central frequency of 2.25 MHz.
In pulse-echo ultrasonic test, an incident ultrasound wave emitted from a transducer on the surface of the specimen and its echo, i.e., a reflection from another surface, is detected by the same transducer at a later time, after the wave has passed through the specimen and returned [3,4]. The pulse, which generated by the pulse oscillator were depending on the transmitting transducer. It transforms them into acoustic pulses. These acoustic pulses generated through the glass sample, then converted into electrical signals, which receive by the transducer. Hence, the output signal (amplified) from the sample is displayed on the oscilloscope. The information displayed was taken to calculate the elastic constant measurements, which can be evaluated by using Equation (5) to (8).

Longitudinal Modulus: \( L = \rho V_L^2 \) \hspace{1cm} (5)

Shear Modulus: \( G = \rho V_s^2 \) \hspace{1cm} (6)

Bulk Modulus: \( K = L - \left(\frac{4}{3}\right)G \) \hspace{1cm} (7)

Young’s Modulus: \( E = 2G(1+\sigma) \) \hspace{1cm} (8)

Poisson’s Ratio: \( \sigma = \frac{(L-2G)}{2(L-G)} \) \hspace{1cm} (9)

Microhardness: \( H = \frac{(1-2\sigma)E}{[6(1+\sigma)]} \) \hspace{1cm} (10)

3 Results and Discussion

3.1 XRD Analysis

The existence of a broad hump in S6 revealed that, there is no significant or Bragg’s peak in glass spectra. Therefore, it has been confirmed that the plane is glass. This is most likely due to the fact that density is very sensitive to both the ionic size and atomic weight of the alkaline rare earth [5]. These results revealed that addition of alkaline earth elements leads to the formation of NBOs and expands (opens up) the structure [5]. Thus, the obtained data reveals the amorphous nature of the prepared glasses and the presence of random strontium phosphate network in the samples.
3.2 Physical Analysis

The physical analysis, which calculated by using Equation (1) to (4) then tabulated in Table 2. Therefore, Figure 1(a) and 2(b) present the change in density, molar volume and packing density that occurred with the addition of SrCO₃. The increase in Sr content directly correlated with an increase in glass density [6].

| Mol% of SrCO₃ | Density, ρ (g cm⁻³) | Molar Volume, Vₘ (cm³ mol⁻¹) | Packing Density, Vᵣ |
|---------------|---------------------|----------------------------|--------------------|
| 0             | 1.8910              | 53.6044                    | 0.3861             |
| 1             | 2.3020              | 44.0588                    | 0.4681             |
| 2             | 2.3796              | 42.6457                    | 0.4818             |
| 3             | 2.4524              | 41.4031                    | 0.4946             |
| 4             | 2.1548              | 47.1473                    | 0.4325             |
| 5             | 2.1415              | 47.4672                    | 0.4280             |

Table 2: Density, molar volume and packing density of the glass.

Figure 1: Density and molar volume (a) while (b) is packing density of (50–x)P₂O₅ – 30ZnO – 20Li₂O – (x)SrCO₃ glass system.

3.3 Ultrasonic Measurement (Pulse echo Technique)

The ultrasonic wave velocities obtained from existing samples are found to be sensitive to the glass system as shown in Table 3 and Table 4. It is observed as SrCO₃ content increases, both Vᵣ and Vₘ also increase. The decreasing trend of σ in Figure 4, indicates the glass network weakens. It is well reported that as Poisson’s ratio decreases, the rigidity increases in glasses [18]. The de-polymerization of phosphate group increases the mechanical strength. The rigidity is generally dependent upon the bond strength and cross-link density [9]. Modi et al. [19] and Manupriya et al. [20] have also reported that a low cross-link density contained glass has higher σ i.e. 0.2 to 0.5 whilst the high cross-link density has σ between 0.1 and 0.2. Thus, it certainly shows that the present glass samples contain high-cross
link density with addition of SrCO₃ to the glass system attributed to the compactness in the packing structure of the glass due to the reduction of NBO’s. Elastic moduli are particularly helpful in correlating structural changes in glasses which are expected to occur as a function of composition [35]. The ultrasonic wave velocities obtained from existing samples are found to be sensitive to the glass system as shown in Table 3. It is observed from the Table 3 as SrCO₃ content increases, both longitudinal and shear velocity also increase. Figure 3 with aid of Table 3 display the divergence of elastic moduli with addition of SrCO₃ content. Longitudinal modulus, L obtained increases from 35.372 to 82.273 GPa with the increasing concentration of SrCO₃ up to 2 mol%. The increase in velocities has been attributed to the increase of glass network rigidity. The presence of SrCO₃ in zinc-lithium phosphate increased the formation of bridging oxygens (BO), resulting in high rigidity. However, addition of SrCO₃ up to 5 mol%, decreases the value of L from 82.273 to 21.697 GPa. It can be seen, from Table 3, all the elastic moduli values decreased with increasing of SrCO₃. This nonlinear variation also happens to shear, bulk as well as Young’s modulus, which follow the same trend of variation as density.

Table 3: The velocities and elastic moduli of the glass system.

| Mol % of SrCO₃ | Longitudinal Velocity, v₁ (ms⁻¹) | Shear Velocity, v₃ (ms⁻¹) | Longitudinal Modulus, L (GPa) | Shear Modulus, G (GPa) | Bulk Modulus, K (GPa) | Young’s Modulus, E (GPa) |
|---------------|----------------------------------|---------------------------|-------------------------------|-----------------------|-----------------------|------------------------|
| 0             | 4325                             | 3191                      | 35.372                        | 19.255                | 9.699                 | 3.7591                 |
| 1             | 5190                             | 3336                      | 62.007                        | 25.619                | 27.848                | 58.8212                |
| 2             | 5880                             | 3373                      | 82.273                        | 27.073                | 46.176                | 67.9424                |
| 3             | 4827                             | 2694                      | 57.141                        | 17.799                | 33.409                | 45.3447                |
| 4             | 4091                             | 2651                      | 36.063                        | 15.143                | 15.872                | 34.4685                |
| 5             | 3183                             | 2573                      | 21.697                        | 14.177                | 2.794                 | 15.8045                |

Table 4: The Poisson’s ratio and microhardness of the glass system.

| Mol % of SrCO₃ | Poisson’s Ratio, σ | Microhardness, H (GPa) |
|---------------|-------------------|-----------------------|
| 0             | -0.0974           | 0.8293                |
| 1             | 0.148             | 6.0119                |
| 2             | 0.2548            | 4.4255                |
| 3             | 0.2738            | 2.6841                |
| 4             | 0.1381            | 3.6535                |
| 5             | -0.4426           | 8.9088                |
4 Conclusions

The physical and mechanical properties as P$_2$O$_5$ is replaced by SrCO$_3$ in zinc-lithium phosphate glasses were carried out. The existence of broad hump in XRD reveals that there is no significant or Bragg’s peak in glass spectra. The ultrasonic results and other measured parameters attribute to the Sr ion increase in the cross-link density by the formation of P-O-Sr. The Poisson’s ratio obtained is between 0.1 and 0.2, which certainly shows that the present glass samples contain high-cross link density with addition of SrCO$_3$ to the glass system attributed to the compactness in the packing structure of the glass due to the reduction of NBO’s.

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