Formation and Elastic Behavior of Lead-Magnesium Chlorophosphate Glasses

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Abstract

A series of ternary lead-magnesium chlorophosphate glasses, $(PbCl_2)_x(MgO)_{1-x}(P_2O_5)_{0.4}$, of various compositions with $0.3 \leq x \leq 0.45$ have been successfully prepared and their elastic properties have been characterized at room temperature. Results from the studies show that both the longitudinal and shear wave velocities decrease with increase of $PbCl_2$ composition. The elastic constants C_{11}, C_{44} and Young's modulus show a decreasing trend while the elastic constant C_{12}, bulk modulus and Poisson's ratio show an increasing trend as the fraction of $PbCl_2$ increases. This behavior of the elastic properties is related to the change in the structure of glasses as well as the interatomic bonding.

Key Words: Chlorophosphate glasses, Wave velocities, Elastic constants.

1. Introduction

Ternary lead-magnesium chlorophosphate glasses have a variety of important technological applications due to their useful and special properties such as optical transparency, the refractive and dispersive behavior, resistance to chemical attack, mechanical stability and stability in vacuum [1–3]. Lead glasses processed mainly by extrusion, casting, pressing, and molding, show high electrical resistivity and refractive index. They are used in optical components, radiation shielding, decorative applications, and for a range of technical glasses. The $MgOP_2O_5$ glass as an ionic conductive material has been used in electrochemical applications, i.e. batteries, sensors, etc. The magnesium oxide phosphate glass is also used in glass-to-metal seals because of its low transportation temperature and their relatively high thermal expansion coefficients [4–7].

For the present work, six selected chlorophosphate glasses based on $(P_2O_5)_x(PbCl_2)_{1-x}(ZnCl_2)_{0.4}$, x = 0.3, 0.35, 0.375, 0.4, 0.425, 0.45, were prepared and their physical, thermal and optical properties were investigated. The glasses exhibited relatively low density. Both the longitudinal and transverse velocities increased monotonically with decreasing temperature. The combined effect of relaxation and anharmonicity is considered to explain the variation of velocity with temperature.

The objective of this work is to investigate the elastic properties of ternary lead-magnesium chlorophosphate, $PbCl_2MgOP_2O_5$, glasses. A Matec MBS 8020 ultrasonic data acquisition system was used to measure the ultrasonic wave velocities of the glass samples over various compositions to further characterize the elastic property of the glasses.

2.   Basics Theory of Elasticity

The physical properties of each glass sample can be determined by measuring the velocities of ultrasonic waves propagating in a sample.

The longitudinal wave velocity ν_l can be computed as

$$\nu_l = \left(\frac{\lambda + 2\mu}{\rho}\right)^{1/2} \tag{1}$$

and the shear wave velocityν_s can be computed as

$$\nu_s = \left(\frac{\mu}{\rho}\right)^{1/2}, \tag{2}$$

where ρ is the volume density, and λ and μ are Lame's constant.

The elastic constants for isotropic materials are closely related to the density and ultrasonic wave velocity and are related to the following constants:

$$C_{12} = C_{11} - 2C_{44}, C_{11} = \rho\nu_l^2, C_{44} = \rho\nu_s^2. \tag{3}$$

C_{11} and $C_{44}$are known as the longitudinal modulus and shear modulus, respectively. Lame's elastic constants can be written as

$$\lambda = \rho(\nu_1^2 - 2\nu_s^2), \mu = \rho\nu_s^2. \tag{4}$$

The bulk modulus B is defined as the ratio of hydrostatic pressure to the fractional change in volume. This pressure is produced when it is applied to an isotropic body. It can be shown that

$$B = \lambda + 2/3\mu = \rho(\nu_l^2 - 4/3\nu_s^2). \tag{5}$$

Young's modulus E is defined as the ratio of longitudinal stress to longitudinal strain, so that

$$E = \frac{\rho\nu_l^2(3\nu_l^2 - 4\nu_s^2)}{\nu_l^2 - \nu_S^2}. \tag{6}$$

3.   Experimental Techniques

Ternary lead-magnesium chlorophosphate glass samples of selected compositions were prepared. Chemical reagents phosphorous pentoxide P_2O_5 (98.5% purity), magnesium oxide MgO (99.0% purity), and lead chloride $PbCl_2$(98.0% purity) were used in the glass preparation. Batches of approximately 20 g to 25 g of the calculated amount of chemical reagents based on the mole fraction of the constituent were weighed into a porcelain crucible using an electronic digital weighing machine providing an accuracy of $\pm$0.0001 g. Since the chemical reagents used are hazardous, especially P_2O_5, which is very corrosive, a mouth dust protector and rubber gloves were worn for safety during the weighing of the chemicals.

The chemical reagents were well-mixed in the crucible before being melted in an electric furnace. Two furnaces were used to ensure the efficiency of glass preparation. The first furnace, set at the temperature of 450 °C, allowed any water component to evaporate and caused the phosphorous pentoxide to decompose and

react with the other components of the admixture. After 30 min, the crucible was then transferred into the second furnace, the temperature set at 1000 °C, using a pair of modified metal tongs. The purpose of the second furnace was to ensure rapid melting and reaction between the chemicals so that the loss of chemicals by way of evaporation could be minimized. The crucible was left in the second furnace for 60 minutes, after which the melt in the crucible was cast into a preheated mould.

Some mass was lost to evaporation while the crucible was in the second furnace, but no action was taken to compensate for the loss because the amount of loss was difficult to estimate. So, the fraction indicated in the glass samples was actually based on the mole fraction of the initial chemicals used.

The mould was a stainless steel cylinder of 20 mm height and 10 mm diameter. Prior to the melt being cast into the split-mould, the mould was cleaned of dust and impurities with acetone. The mould was preheated to 450 °C in the first furnace to reduce thermal shock of the samples during the first casting process. Glasses with high thermal stress are unstable and may be shattered easily.

After the melting process, the melt in the crucible was assumed to be homogenous molten liquid. The lid was removed from the crucible and the melt was poured quickly into the mould to avoid solidification before reaching the split mould. After the melt was firm enough, after a few seconds, the ring surrounding the split mould was removed.

The glass sample was then transferred into the first furnace and annealed at 400 °C for one hour immediately after casting, to relieve the stress and to prevent the sample from cracking. The first furnace was switched off after one hour and the sample was left inside for another hour before being removed. The glass sample was then packed into a small plastic bag and was labeled; it was then kept inside a desicator to isolate it from moisture.

To prepare the samples for ultrasonic measurements, the samples were cut with a diamond cutter to remove cavities that had formed on the surface. Since the samples were brittle, the diamond cutter was adjusted to low speed to prevent the samples from cracking.

For ultrasonic measurement, the samples were cut approximately 8–10 mm in length to improve precision of measurement. The glass samples were then polished with successive grades of sandpapers, grade 80 to grade 1500, to produce flat and parallel surfaces. The polishing process is very crucial and necessary to ensure the smoothness of the glass surfaces in order to achieve clear ultrasonic signals. Following polishing the samples were then ready for characterization via non-destructive ultrasonic measurement.

The sample were then characterized using a Matec Instruments (USA) MBS 8020 ultrasonic data acquisition system, to measure the ultrasonic wave velocities of the glass samples, and the elastic properties of glasses. This system is fully computer automated and therefore enables determination of the final data for transit time and wave velocities. Figure 1 shows a block diagram of the MBS-8020 system and its operation is detailed elsewhere [8].

Thickness of each glass sample was measured prior to any ultrasonic measurements. The frequency of the ultrasonic pulse is set to 5 MHz. Ultrasonic transducer was attached to the surface of the glass sample before being loaded into a sample holder. Burnt honey was used as bonding agent to ensure good contact between the transducer and the sample. Furthermore, it is to minimize the loss of acoustic energy due to unwanted reflection.

Longitudinal velocities were obtained using an X-cut transducer plate, and the shear velocities were obtained with a Y-cut transducer plate. The velocities obtained were then used to calculate the elastic constants C_{11}, C_{44}, C_{12}; Young's modulus E, bulk modulus B, Poisson's ratio σ and Debye temperature. The mean velocity reported by the computer is the computed average of 10 consecutive measurements.
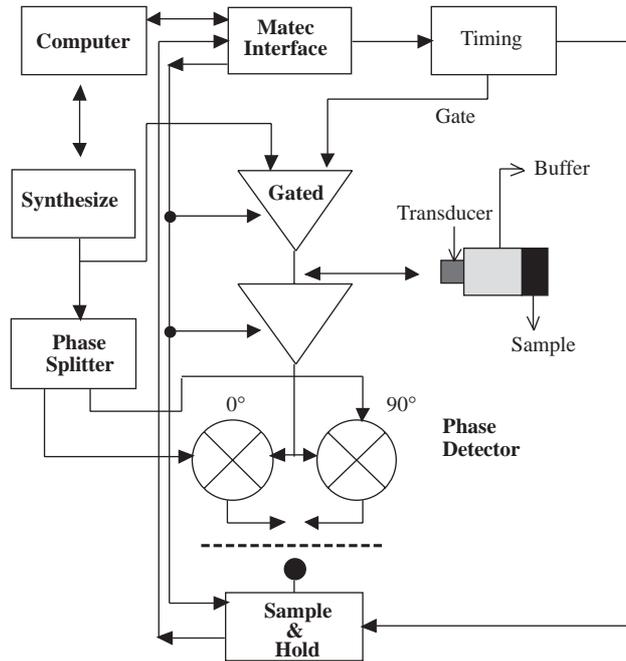
Figure 1. MBS-8020 measurement system block diagram (Matec Instruments).

4. Results and Discussion

A series of lead magnesium chlorophosphate glasses were successfully prepared and all the samples were transparent and free from bubbles. Figure 2 shows the glass forming range for $(PbCl_2)_x(MgO)_{1-x}(P_2O_5)_{0.4}$ system with the glass preparation method used in this work. The series of ternary glass samples were prepared for $x = 0.3$, $x = 0.35$, $x = 0.375$, $x = 0.4$, $x = 0.425$ and $x = 0.45$. Preparation of glass samples with mole fraction higher than 0.45 had been attempted but was not successful.
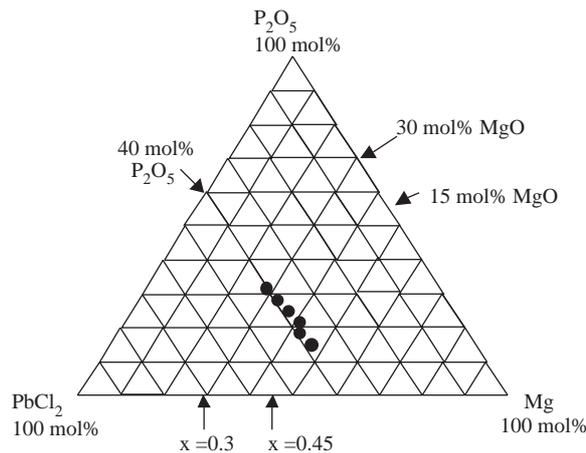
Figure 2. Glass forming region of $(PbCl_2)_x \cdot (MgO)_{1-x} \cdot (P_2O_5)_{0.4}$ system.

Table 1 shows the density of lead-magnesium chlorophosphate glasses as a function of $PbCl_2$. The increase in density with the increase in the amount of $PbCl_2$ (corresponding with the decrease in the concentration of MgO) is shown. Sample with 40 mol% $PbCl_2$ shows a high increase in density compared to the others and is out of the trend.

Table 1. Elastic properties of $(PbCl_2)_x \cdot (MgO)_{1-x} \cdot (P_2O_5)_{0.4}$ glasses at room remperature.

Sample mole fraction, x	0.300	0.350	0.375	0.400	0.425	0.450
Density, ρ (kgm^{-3})	3739	3849	3878	4045	3971	4077
Number of atoms per volume, N/V (m^{-3})	6.352	6.136	6.001	6.082	5.809	5.808
Molar Volume (cm^3/mole)	40.7	42.6	43.9	43.5	45.8	46.1
Longitudinal Velocity, ν_l (ms^{-1})	3921	3770	3707	3687	3664	3608 3608
Shear Velocity, ν_s(ms^{-1})	2568	2199	2219	2122	2116	1946
C_{11} (GPa)	57.5	54.7	53.3	55.0	53.3	53.1
C_{44} (GPa)	24.7	18.6	19.1	18.2	17.8	15.4
C_{12} (GPa)	8.2	17.5	15.1	18.6	17.8	22.2
Young's modulus, E (GPa)	55.5	46.2	46.6	45.6	44.4	40.0
Bulk modulus, B (GPa)	24.6	29.9	27.8	30.7	29.6	32.5
Poisson's ratio	0.124	0.242	0.221	0.252	0.250	0.295
Debye Temperature, θ (K)	335	287	287	276	271	251

In this glass system, $PbCl_2$ acts as network former and network modifier, depending on the glass composition. Pb^{2+} ion in $PbCl_2$ is the network modifier which breaks up the continuous network and the divalent cation Pb^{2+} can produce two non-bridging oxygen ions each. The degree of crosslinking in these glasses is progressively degraded as the mole fraction of $PbCl_2$ increases. As a result of the non-directed bonding to cations, the structural skeleton collapses into closer packing and hence the density increases.

The composition dependence of longitudinal and shear wave velocities is shown in Figure 3. Both the longitudinal and shear wave velocities (ν_l and ν_s, respectively) decrease gradually with the concentration of $PbCl_2$. It can be seen that the values of ν_l are higher than ν_s. For most materials, ultrasonic wave velocities will increase as the density increases. But the lead-magnesium chlorophosphate glasses show the opposite phenomena, where the ultrasonic velocities decrease as the density increases. This happens because the Pb^{2+} ion in $PbCl_2$ and the Mg^{2+} ion in MgO reduce the degree of crosslinking and give rise to the non-bridging oxygen bond (single bonded oxygen ion). Polarizability of the glasses increases and the anharmonicity of the lattice vibrations increases as well. The glass network is therefore weakened or disrupted. The presence of Mg^{2+} ion induces more Pb^{2+} ion from $PbCl_2$ into the network. The increase in concentration of $PbCl_2$causes more random distributed network in the glass structure. The elasticity data are dependent on the microstructure and the interatomic bonding.
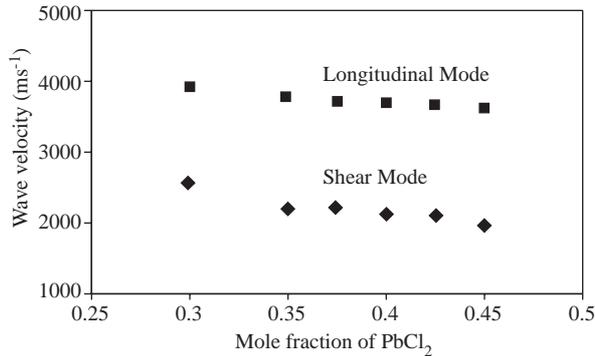
Figure 3. Ultrasonic wave velocities versus mole fraction of $PbCl_2$.

As shown in Table 1, the values of C_{11} and C_{44} decrease as the mole fraction of $PbCl_2$ increases, while the values of C_{12} increase generally as the mole fraction of $PbCl_2$ increases. In comparison, the longitudinal modulus is always higher than the shear modulus. This means that the glasses can withstand longitudinal stress better than shear stress. Young's modulus is the ratio of the linear stress to the linear strain. The

decreasing Young's modulus implies the weakening of the overall bonding strength, as more crosslinking are degraded. As the mole fraction of $PbCl_2$ increases, the bulk modulus increases too. Comparing the bulk modulus to the Young's modulus, the values of bulk modulus are relatively lower. This concludes that the glass samples can tolerate stress in one direction better than stress acting in all directions; they are tougher at certain axes.

Poisson's ratio σ is defined as the ratio of lateral contraction per unit length to longitudinal extension per unit length [9]. In terms of wave velocities, this can be expressed as

$$\sigma = \frac{\nu_l^2 - 2\nu_s^2}{2(\nu_l^2 - \nu_s^2)} \tag{7}$$

As shown in Table 1, σ increases generally with the mole fraction of $PbCl_2$. The increasing trend of Poisson's ratio suggests that if the same amount of stress is applied over the whole range of the glass composition, the lateral strain will gradually level out.

The thermal loss mechanisms (temperature dependence) of a material are most suitably described in terms of the Debye temperature θ. The Debye temperature may be calculated with the help of shear and longitudinal wave velocities, for an infinite medium [10–11]. The mean integrated velocity is calculated for the isotropic material and fed into an equation containing Planck's constant h, Boltzmann's constant k, number of atoms N, of the material. The mean integrated velocity ν_m is given by

$$\nu_m = \left[\frac{1}{3} \left(\frac{1}{\nu_l^2} + \frac{2}{\nu_s^2} \right) \right]^{-1/3} \tag{8}$$

and the Debye temperature θ is

$$\theta = \frac{h}{k} \left(\frac{3N}{4\pi} \right)^{1/3} \nu_m \tag{9}$$

The acoustic Debye temperature (see Table 1), calculated from the sound wave velocities, decreases with the increase in mole fraction of $PbCl_2$. MgO substituted by $PbCl_2$ results in a monotonic decrease in the total vibrational energy of the system. This is because any of the conceivable vibrational units resulting from the substitution will be of lower energy.

5. Conclusion

For lead-magnesium chlorophosphate glasses, one can observe an increasing trend in the density, molar volume, elastic constant C_{12}, bulk modulus and Poisson's Ratio as the mole fraction of $PbCl_2$ increases. On the other hand, one can observe a decreasing trend in the number of atom per unit volume, elastic constants C_{11} and C_{44}, Young's modulus σ and Debye temperature. Exhibition of these behaviors are mainly due to the non-bridging oxygen ions, weak interatomic and crosslinking degradation. Glass structure becomes more randomly distributed over the entire network and hence the glass network becomes softer. The elastic moduli give an indication of the strength of the glass structure. The most influential ion, Pb^{2+} ion from $PbCl_2$, is believed to have taken part in the glass network as both network former and network modifier.

Acknowledgements

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