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FORMATION AND ELASTIC PROPERTIES OF LITHIUM CHLOROPHOSPHATE GLASSES

H.A.A. Sidek, S.P. Chow, Z.A. Talib and S.A. Halim
Ultrasonic Research Laboratory, Department of Physics, Universiti Putra Malaysia, 43400, Serdang, Selangor, Malaysia.
sidek@upm.edu.my

ABSTRACT

Two series of glasses, $(Li_2O)_x(P_2O_5)_{1-x}$ and $(LiCl)_y((Li_2O)_{0.4}(P_2O_5)_{0.6})_{1-y}$ were prepared by ordinary melt-quench technique. The range of x is from 0.1 to 0.5 with interval of 0.05 and the range of y is from 0.1 to 0.5 with interval of 0.1. The ultrasonic velocities for both series of glasses were measured at room temperature by using pulse echo technique at 10 MHz. The velocity data have been used to estimate the elastic modulus and Debye temperature for each composition. The density of Li_2O-P_2O_5 glasses increases with the addition of Li_2O but LiCl-Li_2O-P_2O_5 glasses shows the trend of decrement when the mole fraction of LiCl increases. The longitudinal, shear, bulk and Young's modulus for lithium phosphate glasses are found to increase with the addition of Li_2O whereas the elastic moduli for lithium chlorophosphate glasses are found to decrease with the concentration of LiCl; these kind of characteristics are due to the variation of ultrasonic waves in different glass structures.

INTRODUCTION

The studies of elastic properties on phosphate glasses thus far have not gained much interest from researchers, as very few papers regarding elastic properties of phosphate glasses were published. Most of the publications were limited to silicate or borosilicate glasses and the chalcogenides [1]. So far, it is believed that the elastic properties of Li_2O-P_2O_5 and LiCl-Li_2O-P_2O_5 glasses have not been studied nor any papers been published. However, some researchers have studied the structure and electrical properties of these two glasses [2 - 4]. The main objective of this work is to report the ultrasonics studies of these two series of phosphate glasses.

GLASS FORMATION

The Li_2O-P_2O_5 glasses were prepared by mixing calculated amount P_2O_5 (99.0% purity) with Li_2CO_3 (99.999% purity) in porcelain crucible. The mixtures were first heated to about 300^{o}C for 30 minutes to evaporate whatever moisture content inside the mixtures. The crucible was then transferred to a second furnace of 1000^{o}C. The mixtures melted completely and the melt was cast to a stainless steel cylindrical split mould after having been heated in the furnace for an hour. The glass samples were then annealed at 300^{o}C for an hour before they were left to cool down gradually to room temperature. The process of preparing LiCl-Li_2O-P_2O_5 glasses was practically the same with Li_2O-P_2O_5 glasses by the addition of one more chemical LiCl (99.8% purity).

Binary glasses $(Li_2O)_x(P_2O_5)_{1-x}$ were prepared with the range x = 0.1 to 0.5. The maximum mole fraction of the modifier Li_2O in the binary phosphate glasses was expected to be 60% for good glass formation [5]. Ternary glasses $(LiCl)_x((Li_2O)_{0.4}(P_2O_5)_{0.6})_{1-x}$ were also successfully prepared from range x = 0.1 to 0.5.

The samples were then cut to about 0.35 to 0.45 cm in height and were polished by using sand papers to obtain two parallel and smooth surfaces. The density was measured by Archimedes's method, using acetone as an immersion liquid, and it is accurate to ±0.002 gcm^{-3}. The thickness of the samples was measured to the accuracy of 0.01 mm. The ultrasonic longitudinal and shear velocities were measured by the pulse echo technique at frequency of 10 MHz by a fully computer interfaced measurement system (MBS8000 by Matec Instrument Inc.) [6].

RESULTS AND DISCUSSION

As shown in Figure 1, the density of Li_2O-P_2O_5 glasses increases with the addition of Li_2O but LiCl-Li_2O-P_2O_5 glasses shows the trend of decrement when the mole fraction of LiCl increases. The longitudinal velocities and shear velocities of lithium phosphate glasses increase with the concentration of alkali oxide Li_2O whereas the longitudinal and shear velocities for lithium chlorophosphate glasses decrease with the concentration of doping salt LiCl as depicted in Figure 2. The longitudinal, shear, bulk and Young's modulus show the same trend as the ultrasonic wave velocities (Figure 3 and 4). In the interpretation of compositional dependence of ultrasonic velocities and elastic moduli as well as transition temperature of glasses, the effects of bond strength, packing density, coordination number and crosslinking in the glasses [1,7] must be cput in consideration. Thus we may relate them to the glass structure for more informative explanations.

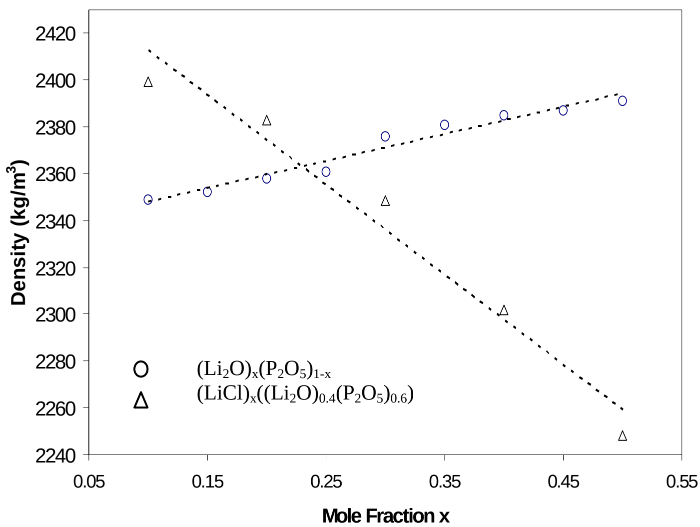

Figure 1: Composition dependence of density for Li_2O-P_2O_5 and LiCl-Li_2O-P_2O_5 glasses.

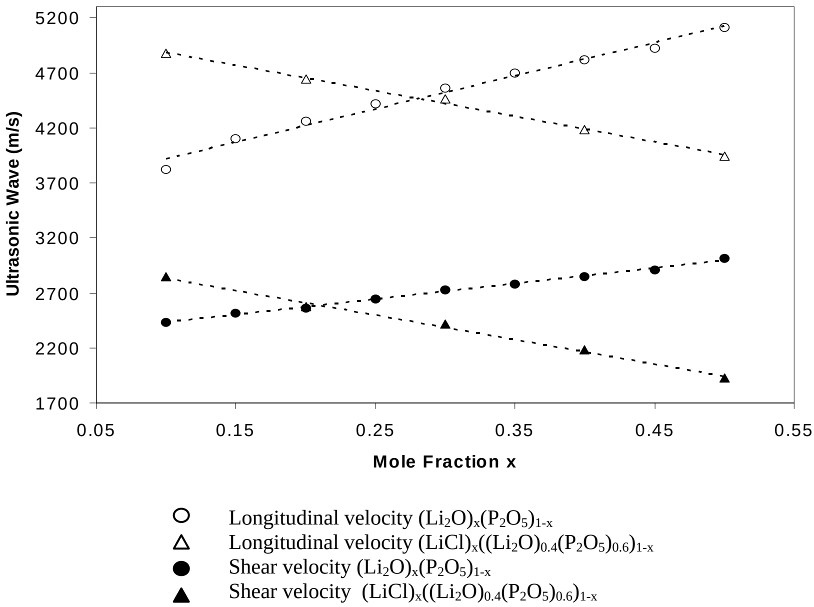

Figure 2: Composition dependence of longitudinal and shear wave velocities for Li_2O-P_2O_5 and LiCl-Li_2O-P_2O_5 glasses.

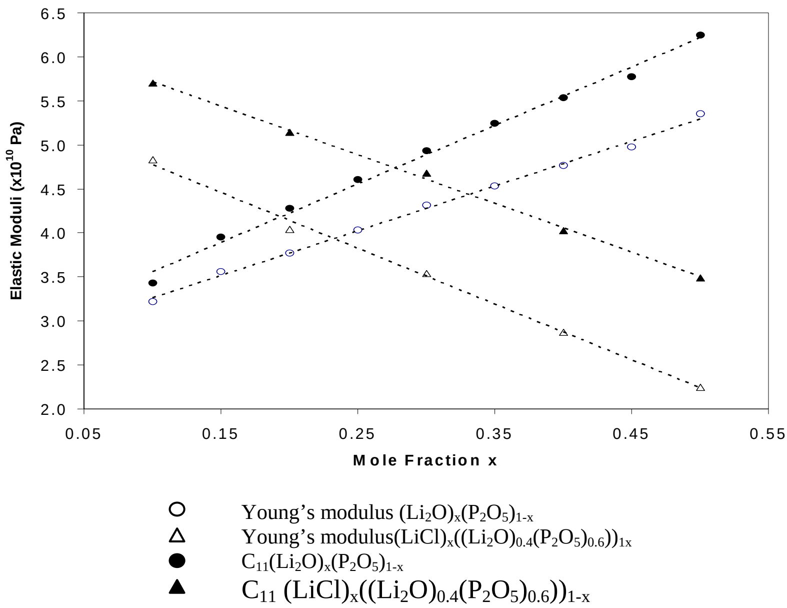

Figure 3: Variation of Young's modulus for Li_2O-P_2O_5 and LiCl-Li_2O-P_2O_5 glasses.

The elastic constant C_{11}, C_{44}, bulk modulus and Young's modulus, for lithium phosphate glasses all increase with the concentration of Li_2O, whereas the lithium chlorophosphate glasses show a decreasing trend with increasing LiCl. As considered from the structural views of the glasses, the Young's modulus and bulk modulus are related to the crosslinking density with large influence on the propagation of the ultrasound velocities.

The Young's modulus is not only dependent on the interatomic bond strength of constituent atoms, but also depends on the packing state [7,8]. The increasing of Young's modulus for lithium phosphate glasses suggests that the addition of Li_2O into the network strengthens the overall atomic bond strength. This well agreed with the density of the glasses and the results reported by Hudgens [9], in which the glass transition temperature of lithium phosphate glasses increases after 20-25 mol% of Li_2O implying the increase of bonding strength. However, the decreasing Young's modulus in lithium chlorophosphate glasses implies the weakening of the overall bonding strength. By looking at its structure, which is swelled up and causes the average atomic ring size to increase with the addition of LiCl, the bonding strength will decrease as more crosslinking disappears. The decrease in bonding strength of this glasses is also in accord with the decrease in glass transition temperature [10] and density.

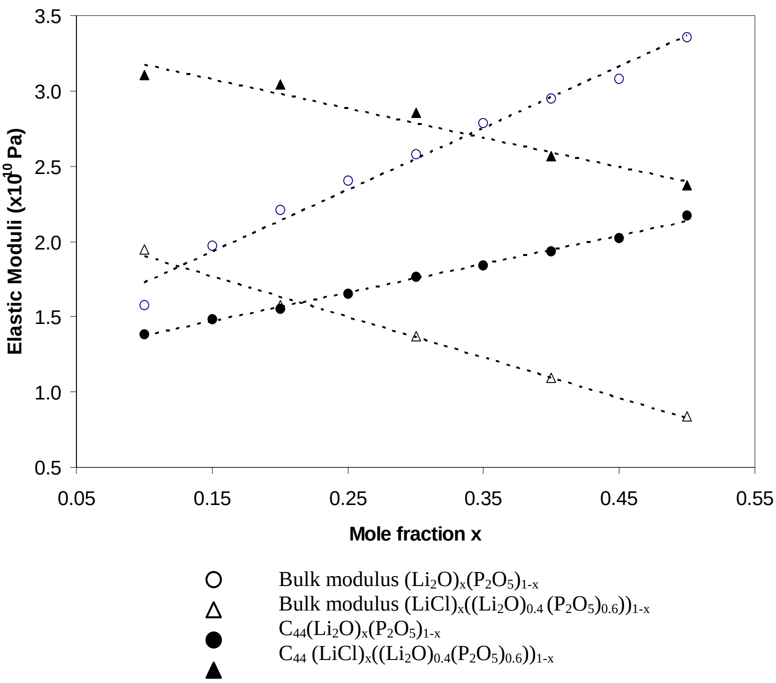

Figure 4: Composition dependence of Bulk modulus for Li_2O-P_2O_5 and LiCl-Li_2O-P_2O_5 glasses.

The Poisson's ratio for both series of glasses vary from 0.24 to 0.34 and 0.16 to 0.23 for lithium phosphate and lithium chlorophosphate glasses respectively. The Poisson's ratio tends to level out after 15 mol% of Li_2O. We know that the structure of lithium phosphate glasses consists of 1-dimensional long chains after the 3-dimenasional network is degraded by the addition of alkali oxides, Li_2O. From the increasing Poisson's ratio we can say that if we apply the same amount stress over the whole range of the glass compositions, the lateral strain will increase gradually. We may suggest that the chain-like structures of the glasses are able to balance out the lateral strain over the longitudinal stress.As for the case of lithium chlorophosphate glasses, the model proposed by Bridge [1] is somewhat applicable as the Poisson's ratio increase with the addition of LiCl, which will swell up the structure and eventually causes the crosslinking to decrease.

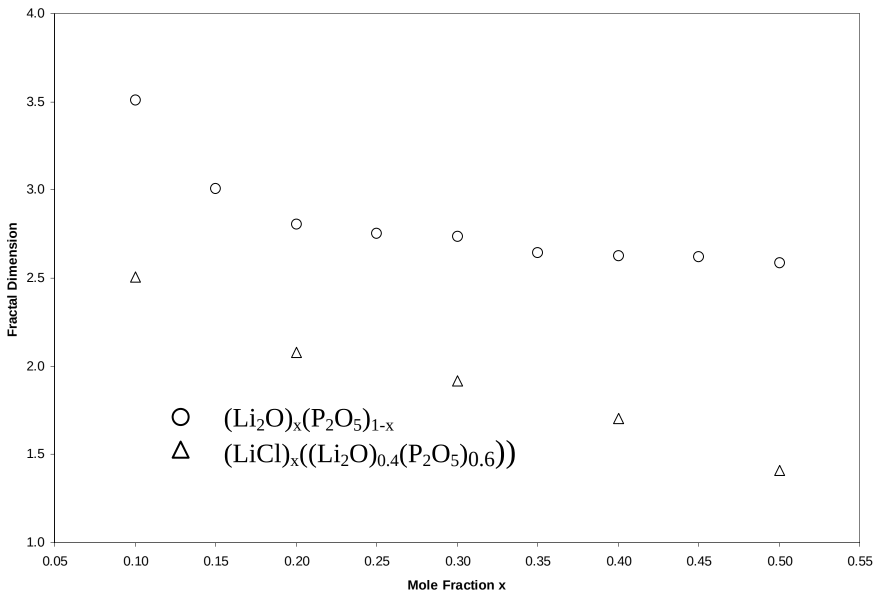

Figure 5: Variation of Debye temperature for Li_2O-P_2O_5 and LiCl-Li_2O-P_2O_5 glasses.

The Debye temperatures calculated from the sound velocities for both lithium phosphate and lithium chlorophosphate glasses are shown in Figure 5. The former glasses shows an increasing trend with concentration of Li_2O and the latter glasses show a decreasing trend with addition of LiCl. Debye temperature, θ_a represents the temperature at which nearly all modes of vibrations in a solid are excited, and its increase implies an increase in the rigidity of the glass. The increasing trend in lithium phosphate glasses means that the glasses have become more rigid as more Li_2O is added and this agrees well with the internal structures that we have discussed. As for the lithium chlorophosphate glasses, decreasing trend is expected as suggested by their internal structure.

As a conclusion, the longitudinal, shear, bulk and Young's modulus for lithium phosphate glasses are found to increase with the addition of Li_2O whereas the elastic moduli for lithium chlorophosphate glasses are found to decrease with the concentration of LiCl; these kind of characteristics are due to the variation of ultrasonic waves in different glass structures. However, Poisson's ratios are a bit out of our explanation in lithium phosphate glasses and we think that more information on the structure will be needed in order to have a clearer picture of its behaviour. In all the consideration, one also has to take into account of the effect of water content for a more reasonable explanation of the glass characteristics.

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