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## DETERMINATION OF ELASTIC PROPERTIES OF HOLMIUM PHOSPHATE GLASSES VIA ULTRASONIC TECHNIQUE

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### ABSTRACT

The elastic properties of holmium phosphate  $x\text{Ho}_2\text{O}_3 (1-x)\text{P}_2\text{O}_5$  glasses with different compositions containing from 10 to 25 mole%  $\text{Ho}_2\text{O}_3$  has been determined via ultrasonic technique as functions of temperature from 270 K to 303 K. By using ultrasonic measurement system, the velocities of ultrasonic propagate wave could be used to estimate the elastic properties of glasses. Hence, it could determine the elastic modulus  $C_{11}$  and  $C_{44}$ , Young's modulus (E), bulk modulus (B) and Poisson ratio ( $\sigma$ ). From the results, it shows that an addition of  $\text{Ho}_2\text{O}_3$  into phosphate glass system produced the variation of wave velocities thus effected the elastic properties of glass sample. The mechanism of chain entanglement effects of  $\text{PO}_2$  groups and the reduction of non-bridging oxygens by the modified rare earth cations seem to play significant roles to enhance the strength of our glasses as presented in our experimental observations of high values of elastic moduli.

### INTRODUCTION

Phosphate glasses have very interesting molecular structures and offer some unique physical properties [1] such as high thermal expansion coefficients, low transition and softening temperatures and low preparation temperature. These properties have made them ideal materials for fundamental studies of the glass transition and devitrification effects. However, their poor chemical durability limits their use and an improved chemical durability is often accompanied by a substantial decrease in thermal expansion coefficient.

Incorporation of rare-earth in modifiers into glass networks produces the energy level structure necessary for the manufacture of non linear magneto-optical devices, such as magnetically tunable lasers and amplifiers for the telecommunication industry[2,3]. Novel magnetic and magneto-optic phenomena occur in the rare-earth phosphate glasses of general formula in the vicinity of metaphosphate composition  $(\text{R}_2\text{O}_3)_{0.25} (\text{P}_2\text{O}_5)_{0.75}$  because they contain very large concentrations of magnetic ions. These materials exhibit the largest magnetic contributions to low temperature specific heats known in oxide glasses[4].

Ultrasonic technique is a versatile tool for investigating the changes in microstructure, deformation process and mechanical properties of material and components [5]. It is

due to the fact that, the ultrasonic waves are closely related with the elastic and inelastic availability of different frequency ranges and many modes of vibration of the ultrasonic waves to probe into the macro, micro and submicroscopic levels.

In an amorphous solid (such as glass), elastic strain produced by a small stress can be described by two independent elastic constants,  $C_{11}$ , longitudinal elastic constant and  $C_{44}$ , shear elastic constant. The Cauchy relation  $C_{44}=C_{11}-C_{12}$  allows one to determine  $C_{12}$ . For pure longitudinal waves  $C_{11}=\rho V_L^2$ , and for pure transverse waves  $C_{44}=\rho V_S^2$ . The sound velocities also allow the determination of Young's modulus,  $E$ , Shear modulus,  $S$ , and bulk modulus,  $B$ , by the following equations:

$$S = C_{44} = \rho V_S^2 \quad (1)$$

$$E = \rho V_S^2 [\{3V_L^2 - 4V_S^2\} / \{V_L^2 - V_S^2\}] \quad (2)$$

$$B = \rho [\{3V_L^2 - 4V_S^2\} / 3] \quad (3)$$

To obtain more complete and accurate information about the elastic constant of  $(x)\text{Ho}_2\text{O}_3$   $(1-x)\text{P}_2\text{O}_5$  glass, we measured, and report herein, the results of measurements of transit times of both longitudinal and shear ultrasonic waves at various temperatures. From the results we deduce the elastic stiffness moduli of each type of wave and use then to calculate the bulk modulus. The behavior of the ultrasonic velocity as a function of temperature includes an excess contribution; over that expected from the vibrational anharmonicity and thermally activated relaxation. As part of an extensive plan to study the properties of rare earth phosphate glasses, ultrasonic study as function of temperature has been undertaken on the holmium doped glasses. The aim has been to provide additional information of the elastic properties of these glasses.

## EXPERIMENTAL TECHNIQUES

### *Sample Preparation*

The binary holmium phosphate glass  $(x)\text{Ho}_2\text{O}_3$   $(1-x)\text{P}_2\text{O}_5$  were prepared, by varying the  $\text{Ho}_2\text{O}_3$  content in the range  $0.05 \leq x \leq 0.25$ . Mixed batches of 20 g each were placed in platinum crucibles and heated at  $500^\circ\text{C}$  to remove the water for an hour, and then the mixtures were melted at  $1500^\circ\text{C}$  for an hour and half in an electric furnace. To ensure proper mixing and homogeneity, the molten liquid was shaken frequently and vigorously using stirrer. The melt was then poured into a steel split mould to quench to form a glass. The glass was immediately transferred to an annealing furnace at  $500^\circ\text{C}$  and kept at that temperature for 3 hours, after which the furnace was switched off and the glasses left to cool down to room temperature, at cooling rate  $0.5^\circ\text{C}/\text{min}$ . The samples containing up to 25 mol %  $\text{Ho}_2\text{O}_3$  were transparent and free from crack and bubbles, yellow, good optical quality glass. After preparation, sample were stored in plastic dessicator. The measurement of velocity of longitudinal and shear ultrasonic wave was performed at frequencies 10 MHz and within the temperature range of 273 to 328 K. Longitudinal and shear waves velocity ( $V_L$  and  $V_S$ , respectively) were determined from the transit times of ultrasonic waves using the pulse-echo-overlap technique. Density was determined at room temperature by Archimedes principle using toluene as the immersant.

## RESULT AND DISCUSSION

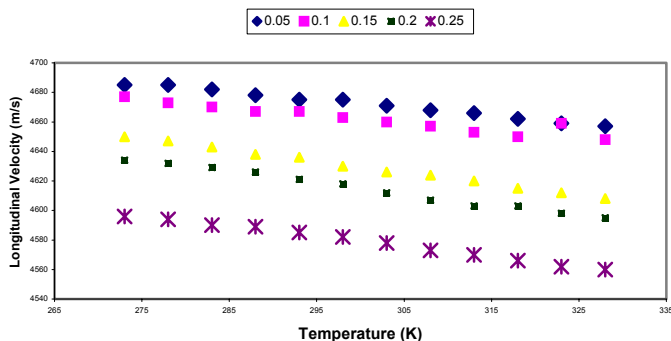


Figure 1: The temperature dependences of the longitudinal velocity of various mol % Ho phosphate glass

The temperature dependence from 273 K to 328 K of the ultrasonic wave velocity of the  $x \text{ Ho}_2\text{O}_3$   $(1-x) \text{ P}_2\text{O}_5$  glass is shown in Fig.1-2, it is showed that the longitudinal and shear ultrasonic waves velocity change monotonically with temperature. The measurements of ultrasonic velocity in holmium phosphate glasses clearly indicate a dependence of ultrasonic wave velocities properties on temperature which differs from those of crystal. The low temperature properties have been attributed to low energy

excitations which are present in amorphous materials. As would be expected for vitreous materials, the temperature dependences of the ultrasonic wave velocities do not conform to the behaviour usually observed in crystalline materials (corresponding to the effects of vibrational anharmonicity, namely, a linear increase of the ultrasonic wave velocity with decreasing temperature, terminating in zero slope at low temperatures). The measurements within the range of 273K to 328K do not give any indication of a minimum in the variation of sound velocity with temperature. Thus, it appears that the variation of sound velocity with temperature in holmium phosphate glasses does not resemble the behaviour observed in many other glasses having tetrahedrally coordinated structures for which such a minimum always exist. Studies on temperature dependence of the elastic moduli and acoustic velocity in phosphate glasses containing high concentration of samarium ions [6,7]  $\text{Nd}_2\text{O}_3\text{-P}_2\text{O}_5$  glass [8] and  $\text{Zn}(\text{PO}_3)_2$  glass [9] clearly show such anomalies. The acoustic velocity as function of temperature in  $\text{Zn}(\text{PO}_3)_2$  glass has a minimum at about 200 K, while in the case of  $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$  glass such minimum has not been observed at least within the range from 77 to 300 K and the temperature coefficient of sound velocity is found to be negative throughout this range [10].

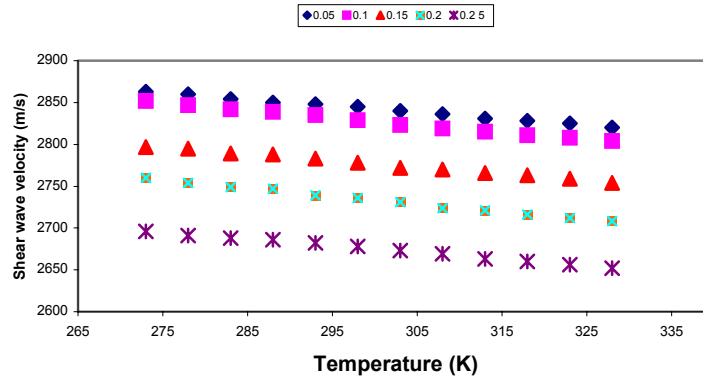


Figure 2: The temperature dependences of the shear wave velocities of various mol % Ho phosphate glass

Temperature dependence of the acoustic velocity for both longitudinal and transverse ultrasonic wave propagation within the temperature range 80-300 K has been interpreted in term of thermally activated relaxation process [11]. This relaxations process comes into play when the ultrasonic wave disturbs the equilibrium of an atom moving in double-well potential. The result of both velocities were used to determine the elastic stiffness moduli  $C_{11}$  and  $C_{44}$  of  $x$   $\text{Ho}_2\text{O}_3$   $(1-x)$   $\text{P}_2\text{O}_5$  glasses with various  $\text{Ho}_2\text{O}_3$  concentrations at temperature range 273 K to 328 K. The result show correlate well with those of other rare-earth phosphate glasses determine previously [7,8] as might be expected from their similar structural configuration.

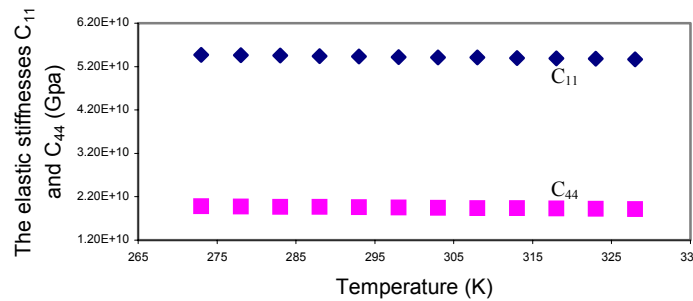


Figure 3: The temperature dependences of the elastic stiffnesses  $C_{11}$  and  $C_{44}$  of 15 mol% Ho phosphate glass

Fig. 3 shows the elastic stiffness moduli  $C_{11}$  and  $C_{44}$  decreased almost linearly with increasing  $\text{Ho}_2\text{O}_3$  content with the value of elastic constant  $C_{44}$  is smaller than the value of elastic constant  $C_{11}$ , even though the density increases with  $\text{Ho}_2\text{O}_3$  content except for 25 mol% of  $\text{Ho}_2\text{O}_3$ . The elastic stiffness depend upon the bonding in the glass and can be used to provide useful information about the connectivity of the network.

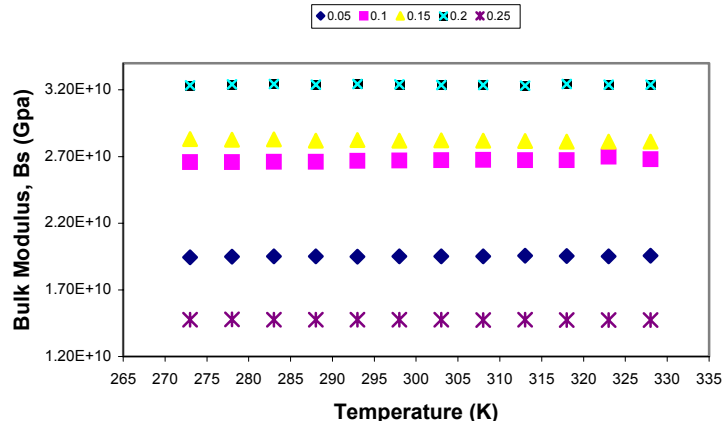


Figure 4. The temperature dependences of the bulk modulus of various mol % Ho phosphate glass

From Figure 4 the bulk modulus show that the elasticity of the glass decreases with the increase in mol % of  $\text{Ho}_2\text{O}_3$ . It is apparently that the stiffness of binary glasses decreases with the increase of content of  $\text{Ho}_2\text{O}_3$ .

The elastic constants ( $C_{11}$  and  $C_{44}$ ) and bulk modulus B of the pure  $\text{P}_2\text{O}_5$  glass are 41.4, 12.1 and 25.3 GPa respectively [12]. The measured elastic properties for the molybdenum phosphate glass are 40.12 and 22 GPa respectively [13]. Comparison of these data with those of holmium phosphate glasses shows that the values of elastic modulus is much higher. In order to explain the high value of elastic constants in holmium phosphate glasses, the chain entanglement mechanism in alkali phosphate glasses with the structural modification by alkaline earth ions was used [13]. We attempt to correlate the number of non-bridging oxygens with the charge of the modifier cations. To preserve the electric neutrality locally, holmium ions are paired with two non-bridging oxygens. Consequently, it leads to an enhancement in the strength of the structure and to an increase in the elastic moduli of the present glasses.

## CONCLUSIONS

The elastic properties of holmium phosphate glass with composition of  $x \text{Ho}_2\text{O}_3 (1-x) \text{P}_2\text{O}_5$ , where  $x$  from 5 to 25 mole % has been measured using ultrasonic technique as functions of temperature from 273 K to 328 K. The mechanism of chain entanglement effects of  $\text{PO}_2$  groups and the reduction of non-bridging oxygens by the modified rare earth cations seem to play significant roles to enhance the strength of our glasses as presented in our experimental observations of high values of elastic moduli.

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