

Elastic properties of lanthanum gallogermanate glasses

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Room temperature ultrasonic velocities of eight lanthanum gallogermanate glasses were determined by pulse-echo technique. The results indicate that both longitudinal and transverse velocities of these glasses are composition dependent. The density and index of refraction of the samples were also studied. The experimental results were used to obtain elastic constants. The measured values of Young's modulus and bulk modulus for our glasses show good agreement with the theoretically calculated results based on the model of Makishima and Mackenzie. © 1999 Kluwer Academic Publishers

1. Introduction

Glasses containing heavy metal oxides are of interest for infrared transmission application due to their long IR cut-off wavelength relative to phosphate, borate and silicate glasses. Dumbaugh found that with addition of Ga_2O_3 to $\text{PbO-Bi}_2\text{O}_3$ and $\text{CdO-Bi}_2\text{O}_3$ dramatically improves glass stability and that these glasses have high optical transmission up to about $7\ \mu\text{m}$ [1]. Kokubo *et al.* found that alkali- and alkaline-earth $\text{Ta}_2\text{O-Ga}_2\text{O}_3$ or $\text{Nb}_2\text{O-Ga}_2\text{O}_3$ glasses also have high optical transmission up to about $7\ \mu\text{m}$ [2, 3]. GeO_2 -doped glasses make favorable fiber core material because of their longer wavelength cut-off at which the GeO_2 stretching vibration occurs. A study of barium gallogermanate glasses has demonstrated their potential for both infrared optical waveguide and bulk optic components at 3 to $5\ \mu\text{m}$ [4]. Lindquist and Shelby studied the properties of rare earth gallogermanate glasses which have an infrared cut-off at $6.05\ \mu\text{m}$ and show excellent chemical durability in water [5]. These glasses also have very high Verdet constants due to their high rare earth ion concentration, making them suitable for use in Faraday rotation devices.

Previous studies on the structural, physical, thermal and optical properties of lanthanum gallogermanate glasses [6, 7] concluded that (i) These glasses are transparent over frequencies ranging from the near UV to the mid-IR ($\sim 8\ \mu\text{m}$) and have ionic bond properties in their structure [6] and (ii) The Raman spectra indicate that the majority of Ge and Ga are four-coordinated in the glass-network, and the role of La^{3+} ion acts either as charge-compensator for GaO_4^- or as glass modifier for non-bridging oxygen [7].

Since the strength of materials increases with their elastic moduli, therefore it is easier to assess strength

indirectly from their elastic properties. Studies of the elastic constants of glassy materials give considerable information about the structure of non-crystalline solids since they are directly related to the interatomic forces and potentials [8–16]. In this paper the elastic properties of two series of the lanthanum gallogermanate glasses ($x\text{La}_2\text{O}_3\text{-GeO}_2\text{-}0.33\text{Ga}_2\text{O}_3$ and $x\text{La}_2\text{O}_3\text{-GeO}_2\text{-}0.50\text{Ga}_2\text{O}_3$ with $x = 0.20, 0.25, 0.33,$ and 0.50) are investigated with the help of the ultrasonic pulse-echo and density measurements. While the experimental results are used to obtain the elastic constants of the materials, and the measured results of the elastic moduli are compared with those calculated values based on the Makishima and Mackenzie's model [9, 10].

2. Experimental aspect

Eight samples with the formula: $x\text{La}_2\text{O}_3\text{-GeO}_2\text{-}y\text{Ga}_2\text{O}_3$, where $x = \text{La}_2\text{O}_3\ \text{mol}\%/\text{GeO}_2\ \text{mol}\%$ and $y = \text{Ga}_2\text{O}_3\ \text{mol}\%/\text{GeO}_2\ \text{mol}\%$ were prepared by melting appropriate amounts of La_2O_3 (Aldrich 99.9%), GeO_2 (Aldrich 99.9%), Ga_2O_3 (Aldrich 99.9%) in an open atmosphere at temperatures between 1550 and $1650\ ^\circ\text{C}$, for one to one hour and a half in a platinum crucible. The melts were quenched by placing the bottom of the crucible in water. The glassy samples were identified by X-ray diffraction. In order to produce samples large enough for the experimental requirements, samples were batched to obtain 10 g. The glass-forming tendency was discussed elsewhere [7].

Ultrasonic measurements were performed by a pulse-echo method with a Panametrics model 5800 pulser/receiver instrument with quartz transducer. X-cut transducers with 20 MHz frequency were employed for longitudinal modes and Y-cut for shear modes (also

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20 MHz frequency). The pulse transit time was measured with a Hewlett-Packard model 54502A oscilloscope. Several effects influence the accuracy of ultrasonic velocity measurements, such as multiple internal reflections within the transducer, sample thickness, and the acoustic impedance mismatch between glass sample and transducer. The uncertainty is estimated to be about $\pm 1\%$.

The density was determined by an Archimedes technique for which *n*-hexadecane was the working fluid. The accuracy of the measurement was about $\pm 0.001 \text{ g/cm}^3$. The reflective indexes of the sample were measured by J. Woolam Co. variable angle spectroscopic ellipsometer model VB-200 with a WVASE32 software (version 2.38), and the indexes were found to be accurate within ± 0.001 .

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

$$E = \rho V_T^2 \frac{3V_L^2 - 4V_T^2}{V_L^2 - V_T^2} \quad (1)$$

$$B = \rho \frac{3V_L^2 - 4V_T^2}{3} \quad (2)$$

$$\sigma = \frac{V_L^2 - 2V_T^2}{2(V_L^2 - V_T^2)} \quad (3)$$

3. Results and discussion

The density (ρ), index of refraction (n) at 514.5 nm, longitudinal (V_L) and transverse (V_T) sound velocities of eight lanthanum gallogermanate glasses and the pure GeO_2 glass are given in Table I. The data for the pure GeO_2 glass were obtained from Refs. [12, 17]. In both $x\text{La}_2\text{O}_3\text{-GeO}_2\text{-}0.33\text{Ga}_2\text{O}_3$ and $x\text{La}_2\text{O}_3\text{-GeO}_2\text{-}0.50\text{Ga}_2\text{O}_3$ series, the density and index of refraction increase with increasing La_2O_3 content, although the

TABLE I The refractive index, density, longitudinal and transverse sound velocities of eight lanthanum gallogermanate glasses and pure GeO_2 glass

Sample	n (514.5 nm)	ρ (g/cm^3)	V_L (m/s)	V_T (m/s)
0.20 $\text{La}_2\text{O}_3\text{-GeO}_2\text{-}0.33\text{Ga}_2\text{O}_3$	1.847	5.180	5201	2714
0.25 $\text{La}_2\text{O}_3\text{-GeO}_2\text{-}0.33\text{Ga}_2\text{O}_3$	1.851	5.266	5161	2704
0.33 $\text{La}_2\text{O}_3\text{-GeO}_2\text{-}0.33\text{Ga}_2\text{O}_3$	1.853	5.342	5149	2682
0.50 $\text{La}_2\text{O}_3\text{-GeO}_2\text{-}0.33\text{Ga}_2\text{O}_3$	1.889	5.561	5068	2632
0.20 $\text{La}_2\text{O}_3\text{-GeO}_2\text{-}0.50\text{Ga}_2\text{O}_3$	1.854	5.205	5340	2791
0.25 $\text{La}_2\text{O}_3\text{-GeO}_2\text{-}0.50\text{Ga}_2\text{O}_3$	1.860	5.255	5294	2777
0.33 $\text{La}_2\text{O}_3\text{-GeO}_2\text{-}0.50\text{Ga}_2\text{O}_3$	1.875	5.393	5230	2706
0.50 $\text{La}_2\text{O}_3\text{-GeO}_2\text{-}0.50\text{Ga}_2\text{O}_3$	1.923	5.522	5182	2669
GeO_2	1.601	3.629	3636	2233

longitudinal and transverse sound velocities decrease. The observed increase in density is expected since the atomic weight of La_2O_3 is larger than that of the GeO_2 and Ga_2O_3 . However, the detected decrease in the longitudinal and transverse sound velocities imply that the acoustic modes soften with increasing La_2O_3 content.

Table II gives the calculated elastic constants (C_{11} , C_{44} and C_{12}), the C_{44}/C_{12} ratio, Young's modulus, bulk modulus and Poisson's ratio from experimental sound velocities for lanthanum gallogermanate glasses and for pure GeO_2 glass. The overall uncertainty for above calculated quantities is estimated about $\pm 2\%$. The calculated longitudinal and transverse elastic constants (C_{11} and C_{44}) of the lanthanum gallogermanate glasses are about three times and two times larger than that of pure GeO_2 glass, respectively. This implies that lanthanum gallogermanate glasses have a very rigid lattice structure. The C_{44}/C_{12} ratio is an indicator of the character of the force field: central forces if $C_{44}/C_{12} = 1$ and non-central forces if $C_{44}/C_{12} \neq 1$. As the ratio of C_{44}/C_{12} approaches unity, the central force field may lead to the least broken bonds in the glass structure. Poisson's ratio for the lanthanum gallogermanate glasses is in the range of 0.31 to 0.32, where GeO_2 shows this ratio to be 0.192. The higher Poisson's ratio may be because most of the bonds are ionic, in comparison with GeO_2 , which is predominantly covalent [12, 18–20]. Bridge *et al.* suggested a close correlation between Poisson's ratio and the crosslink density of the glass structure [12]. Since the network-forming groups have lower connectivity, this gives rise to the higher Poisson's ratio. The higher Poisson's ratio of present glasses leads to the formation of disconnected structural units and indicates a smaller dimension of the glass network [14].

Makishima and Mackenzie [9, 10] proposed a theoretical model to calculate the elastic moduli of oxide glasses in terms of the packing density of chemical compositions and the dissociation energy of oxide constituents per unit volume by the following equations:

$$E_{\text{cal}} = 83.6V_i \sum_i G_i X_i \quad (4)$$

$$B_{\text{cal}} = 100V_i^2 \sum_i G_i X_i \quad (5)$$

$$\sigma_{\text{cal}} = 0.5 - \frac{1}{7.2V_i} \quad (6)$$

where G_i and X_i are the dissociation energy per unit volume and the mole fraction of the oxide component i , respectively.

In order to calculate the packing density (V_i) of oxide glasses in the form of $A_m O_n$, we must first calculate the packing factor (V_i) of the i th oxide component from the following equation:

$$V_i = 6.023 \times 10^{23} \frac{4\pi}{3} (mR_A^3 + nR_O^3) \quad (7)$$

where R_A and R_O are the respective Pauling's ionic radius of metal and oxygen. Therefore, the packing density for multi-component glasses is given as

$$V_i = (\rho/M) \sum_i V_i X_i \quad (8)$$

TABLE II The elastic constants (C_{11} , C_{44} and C_{12}), the ratio of C_{44}/C_{12} , Young's modulus, bulk modulus and Poisson's ratio for lanthanum gallogermanate glasses and pure GeO_2 glass

Sample	C_{11} (Gpa)	C_{44} (Gpa)	C_{12} (Gpa)	C_{44}/C_{12}	E (Gpa)	B (Gpa)	σ
0.20 La_2O_3 - GeO_2 -0.33 Ga_2O_3	140.1	38.2	63.7	0.60	100.3	89.2	0.31
0.25 La_2O_3 - GeO_2 -0.33 Ga_2O_3	140.3	38.5	63.3	0.61	101.2	88.9	0.31
0.33 La_2O_3 - GeO_2 -0.33 Ga_2O_3	141.6	38.4	64.8	0.59	100.9	90.4	0.31
0.50 La_2O_3 - GeO_2 -0.33 Ga_2O_3	142.8	38.5	65.8	0.56	101.3	91.5	0.32
0.20 La_2O_3 - GeO_2 -0.50 Ga_2O_3	148.4	40.5	67.4	0.60	106.3	96.4	0.31
0.25 La_2O_3 - GeO_2 -0.50 Ga_2O_3	147.3	40.5	66.3	0.61	106.1	93.2	0.31
0.33 La_2O_3 - GeO_2 -0.50 Ga_2O_3	147.5	39.5	68.5	0.58	104.1	94.9	0.32
0.50 La_2O_3 - GeO_2 -0.50 Ga_2O_3	148.3	39.3	69.7	0.56	103.7	95.8	0.32
GeO_2	48.0	18.1	11.8	1.534	43.3	23.9	0.192

TABLE III The dissociation energy per unit volume G_i , the packing factor V_i , the density ρ and the effective molecular weight M of each oxide component present in the lanthanum gallogermanate glass systems

Oxide	La_2O_3	GeO_2	Ga_2O_3
G_i (Kcal/cm ³)	16.2	27.4	17.1
V_i (cm ³)	28.4	14.2	21.9
ρ (g/cm ³)	6.50	3.629	6.00
M (g/mole)	325.8	104.6	187.4

where M is the effective molecular weight and X_i is the mole fraction of component i .

The dissociation energy per unit volume G_i , the packing factor V_i , the effective molecular weight M , and the density ρ of each oxide component present in the lanthanum gallogermanate glass systems are found in Refs [9, 12, 21] and are given in Table III. For the studied glass samples, Table IV gives the theoretically calculated packing density V_t , as well as the elastic moduli and the Poisson ratio based on the model of Makishima and Mackenzie. From Tables II and IV as well as Fig. 1a and b, the observed Young's and bulk moduli of these glasses show good agreement with theoretically calculated results and the high values of the

TABLE IV The theoretically calculated packing density V_t , elastic moduli and Poisson ratio based on the Makishima and Mackenzie's model for lanthanum gallogermanate glasses

Sample	V_t	E_{theory} (Gpa)	B_{theory} (Gpa)	σ_{theory}
0.20 La_2O_3 - GeO_2 -0.33 Ga_2O_3	0.61	120.19	87.17	0.27
0.25 La_2O_3 - GeO_2 -0.33 Ga_2O_3	0.61	118.93	86.21	0.27
0.33 La_2O_3 - GeO_2 -0.33 Ga_2O_3	0.60	116.11	83.41	0.27
0.50 La_2O_3 - GeO_2 -0.33 Ga_2O_3	0.60	113.06	81.36	0.27
0.20 La_2O_3 - GeO_2 -0.50 Ga_2O_3	0.61	117.38	85.52	0.27
0.25 La_2O_3 - GeO_2 -0.50 Ga_2O_3	0.61	115.76	83.88	0.27
0.33 La_2O_3 - GeO_2 -0.50 Ga_2O_3	0.61	114.85	83.63	0.27
0.50 La_2O_3 - GeO_2 -0.50 Ga_2O_3	0.60	110.76	79.70	0.27

elastic moduli are mainly due to the high packing density of the atoms in the present glasses (~ 0.61), in comparison with most common glasses, which have values of 0.51 to 0.57 [11, 15].

For Poisson's ratio as seen in Tables II and IV, the calculated values are consistently lower than the experimental results. The non-central or angular character of the force fields resulting from ion overlapping and covalent bonding may be the reason for this discrepancy of Poisson's ratio for the glasses in this study.

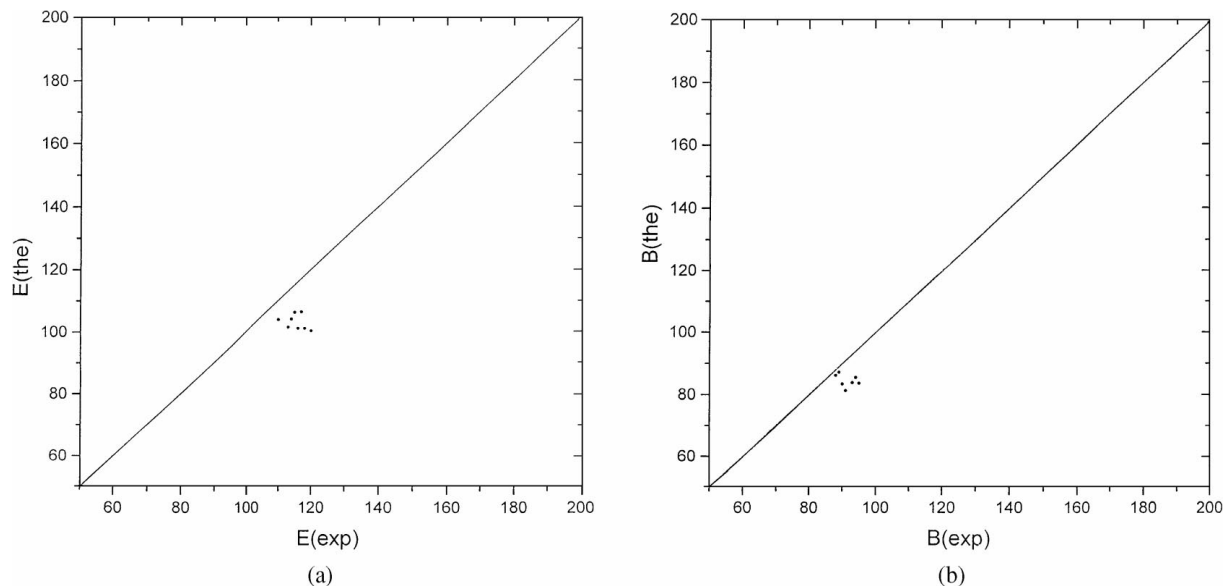


Figure 1 (a) Agreement between measured values of Young's modulus and those calculated from Makishima and Mackenzie's theory. (b) Agreement between measured values of bulk modulus and those calculated from Makishima and Mackenzie's theory.

4. Conclusion

We have measured the sound velocities of two series of lanthanum gallogermanate glasses. These glasses exhibit high values for Young's modulus and bulk modulus due to high packing density of each individual atom.

The general bonding picture was understood from our study on the elastic properties of the present glasses indicating that lanthanum gallogermanate glasses show an ionic bond behavior in their structure. In further research, experiments on the temperature and pressure dependence of the sound velocities may give a deeper insight into the elastic properties of these glasses.

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Received 17 December 1998
and accepted 6 May 1999