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Temperature dependence of elastic moduli of lanthanum gallogermanate glasses

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Temperature dependence of sound velocities of a series of Lanthanum Gallogermanate glasses have been determined from ultrasonic pulse-echo and Brillouin scattering measurements ranging from room temperature up to and through the glass transition temperature. 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 are used to obtain elastic moduli. The correlation of elastic stiffness, the crosslink density, and the fractal bond connectivity of the glass are discussed. The normal behavior of negative temperature dependence of elastic properties is observed in these glasses. A possible explanation of the observed discrepancy of high temperature sound velocity of these glasses from two different measurements is given.

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 the addition of Ga_2O_3 to PbO-Bi_2O_3 and CdO-Bi_2O_3 dramatically improves glass stability and that these glasses have high optical transmission up to about 7 μm [1]. Kokubo *et al.* found that alkali- and alkaline-earth Ta_2O-Ga_2O_3 or Nb_2O-Ga_2O_3 glasses also have high optical transmission up to about 7 μm [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 wave-guide and bulk optic components at 3 to 5 μm [4]. Lindquist and Shelby studied the properties of rare earth gallogermanate glasses, which have an infrared cut-off at 6.05 μm 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 device [5].

Previous studies on the structural, physical, elastic and optical properties of lanthanum gallogermanate glasses [6–9] concluded that (i) these glasses are transparent over frequencies ranging from the near UV to the mid-IR (~8 μm) and have ionic bond properties in their structure [6]. (ii) The Raman and Infrared spectra indicate that the majority of Ge and Ga are four-coordinated in the glass network. The role of La^{3+} ion acts either as charge-ompensator for GaO_4^- or as glass modifier for non-bridging oxygen [7, 8]. (iii) These glasses exhibit high values of Young's modulus, shear modulus and bulk modulus due to high packing density of each individual atom [9].

In this paper the temperature dependence of elastic properties of a series of the lanthanum gallogermanate glasses ($0.2La_2O_3$-GeO_2-yGa_2O_3 with $y = 0.20$, 0.25, 0.33, and 0.50) is investigated with the help of the ultrasonic pulse-echo and Brillouin scattering measurements at ultrasonic frequency and hypersonic frequency, respectively. The experimental results are used to obtain the elastic moduli of the materials. The temperature dependence of sound velocity determined by ultrasonic pulse-echo and Brillouin scattering measurements are compared.

2. Experimental aspect

Four samples in a series of $0.20La_2O_3$-GeO_2-yGa_2O_3, where $y = Ga_2O_3$ mol%/GeO_2 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°C, for 60–90 mins in a platinum crucible. The melts were quenched in water. In order to produce sample large enough for the experimental requirements, samples prepared in 10 g batches. The glassy samples were then identified by X-ray diffraction.

The density was determined by an Archimedes technique for which n-hexadecane was used as the working

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fluid. The accuracy of the measurement was about ± 0.001 g/cm^3. The refractive indexes of the samples 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.

High temperature ultrasonic measurements were performed by a pulse-echo method with a Panametrics model 5800 pulser/receiver instrument and with two specially designed high temperature PZT transducers with probable cooling system, for temperature up to 930°C at 20 MHz frequency. X-cut transducers were employed for longitudinal modes and Y-cut for shear modes. X-cut and Y-cut transducers have the delay time 13 μs and 22.9 μs, respectively. The pulse transit time was measured with a Hewlett-Packard model 54502A oscilloscope. Several effects, such as multiple internal reflections within the transducer, sample thickness, and the acoustic impedance mismatch between the glass sample and the transducer, influence the accuracy of ultrasonic velocity measurements. The uncertainty is estimated to be about $\pm 1\%$.

To obtain the Brillouin spectra of lanthanum gallogermanate glasses, we employed laser excitation (Argon-ion, Coherent Inova-90-3 with single-mode etalon) operating at 514.5 nm coupled to a stabilized multi-pass high contrast Fabry-Perot interferometer with a photon counting detection system and associated data handling electronics [10]. Both the quasi-elastic scattered Rayleigh line and the propagating inelastically scattered Brillouin lines were detected. The spectra were recorded in the 90° scattering configuration with VV polarization as a function of temperature up to and through the glass transition temperature (V denotes the polarization perpendicular to the scattering plane). The polished sample was placed on a glass plate and then positioned in a temperature controlled molybdenum furnace with temperature stability of about ± 1°C. The furnace has three optical windows, which makes it possible to collect 90° scattering light. The temperature of the sample in the furnace was monitored with a K-type thermocouple positioned just beneath the sample holder. A slow flow of nitrogen gas was maintained through the furnace in order to prevent surface oxidation and rapid surface crystallization below the melting temperature. The sound velocities can be calculated from the Brillouin equation given as [11]:

$$V_{\mathrm{L,T}} = \frac{C}{2\nu_0}\left(\frac{\Delta\nu_{\mathrm{L,T}}}{\sin\theta/2}\right)\frac{1}{n} \tag{1}$$

where $\Delta\nu_{\mathrm{L,T}}$ is the appropriate Brillouin splitting (either longitudinal or transverse) in Gigahertz, C is the velocity of light, ν_0 is the incident laser frequency, n is the index of refraction at 514.5 nm, and θ is the scattering angle. The VV polarization was used in our experiment to determine the longitudinal sound velocity.

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 four lanthanum gallo-germanate 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] and [13]. In $0.2La_2O_3$-GeO_2-yGa_2O_3 series, the density and index of refraction increase with increasing Ga_2O_3 content. Similar trend was observed for both longitudinal and transverse sound velocities, and this implies the acoustic modes stiffen with increasing Ga_2O_3 content in these glasses.

TABLE I The density, index of refraction, longitudinal and transverse sound velocities (with the experimental uncertainty of $\pm 1\%$) for lanthanum gallo-germanate glasses and GeO_2 glass

	Property			
Glass composition	ρ (g/cm^3)	n (514.5 nm)	V_{L} (m/s)	V_{T} (m/s)
$0.2La_2O_3$-GeO_2-$0.2Ga_2O_3$	5.16	1.834	5144	2701
$0.2La_2O_3$-GeO_2-$0.25Ga_2O_3$	5.16	1.838	5146	2701
$0.2La_2O_3$-GeO_2-$0.33Ga_2O_3$	5.18	1.847	5207	2718
$0.2La_2O_3$-GeO_2-$0.5Ga_2O_3$	5.21	1.854	5346	2790
GeO_2	3.63	1.601	3636	2233

TABLE II The calculated second order elastic constants C_{11} and C_{44}, Young's modulus, bulk modulus and the Poisson's ratio (with the uncertainty of $\pm 2\%$) for lanthanum gallo-germanate glasses and GeO_2 glass

	Property					
Glass composition	C_{11} (Gpa)	C_{44} (Gpa)	E (Gpa)	B (Gpa)	σ	$\frac{4C_{44}}{B}$
$0.2La_2O_3$-GeO_2-$0.2Ga_2O_3$	136.6	37.7	98.7	86.4	0.31	1.75
$0.2La_2O_3$-GeO_2-$0.25Ga_2O_3$	136.7	37.7	98.6	86.5	0.31	1.74
$0.2La_2O_3$-GeO_2-$0.33Ga_2O_3$	140.4	38.3	100.5	89.4	0.31	1.71
$0.2La_2O_3$-GeO_2-$0.5Ga_2O_3$	148.8	40.5	106.4	94.7	0.31	1.71
GeO_2	48.0	18.1	43.3	23.9	0.19	3.03

In a glassy material, the elastic strain produced by a small stress, which 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 $C_{11} = \rho V_{\mathrm{L}}^2$, 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), shear modulus (S), bulk modulus (B), and Poisson's ratio (σ), by the following equations:

$$E = \rho V_{\mathrm{T}}^2 \frac{3V_{\mathrm{L}}^2 - 4V_{\mathrm{T}}^2}{V_{\mathrm{L}}^2 - V_{\mathrm{T}}^2} \tag{2}$$

$$S = C_{44} = \rho V_{\mathrm{T}}^2 \tag{3}$$

$$B = \rho \frac{3V_{\mathrm{L}}^2 - 4V_{\mathrm{T}}^2}{3} \tag{4}$$

$$\sigma = \frac{V_{\mathrm{L}}^2 - 2V_{\mathrm{T}}^2}{2\left(V_{\mathrm{L}}^2 - V_{\mathrm{T}}^2\right)} \tag{5}$$

Table II gives the calculated elastic constants (C_{11} and C_{44}), Young's modulus, bulk modulus and Poisson's ratio from experimental sound velocities for lanthanum gallo-germanate 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. Poisson's ratio for the lanthanum gallogermanate glasses is about 0.31, 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, 14–16].

Bridge *et al.* suggested a close correlation between Poisson's ratio and the crosslink density (defined as the number of bridging bonds per cation) of the glass structure [12]. The crosslink density of two, one and zero are related to the value of Poisson's ratio of 0.15, 0.30 and 0.40, respectively. Consequently, Poisson's ratio for the lanthanum gallogermanate glasses is about 0.31, which implies a 2-D layer structure.

Bergman and Kantor [17] suggested an expression: $d = 4C_{44}/B$, which was derived for an inhomogeneous random mixture of fluid and a solid backbone near the percolation limit [17–19]. This new parameter "d", Bogue and Sladek [18] called the fractal bond connectivity, can give information on effective dimensionality of the materials: $d = 3$ for 3D tetrahedral coordination polyhedra; $d = 2$ for 2D layer structures; and $d = 1$ for 1D chains. The calculated d-values are also given in Table II. The fractal bond connectivity of lanthanum gallo-germanate glasses has a connectivity $d \sim 1.75$, where the pure GeO_2 glass shows this ratio to be 3.03.

The temperature dependence behavior of sound velocities for the studied glasses is similar. We present a particular example of a $0.2La_2O_3$-GeO_2-$0.25Ga_2O_3$ glass in Figs 1 and 2 for longitudinal and transverse sound velocities, respectively. The results indicate the ultrasonic velocities, both longitudinal and transverse, decrease slowly and monotonically with increasing temperature in the range of 25°C to 930°C. The variation of sound velocities has a small negative temperature coefficient. However, a large increase of sound velocity change is observed near the glass transition temperature.

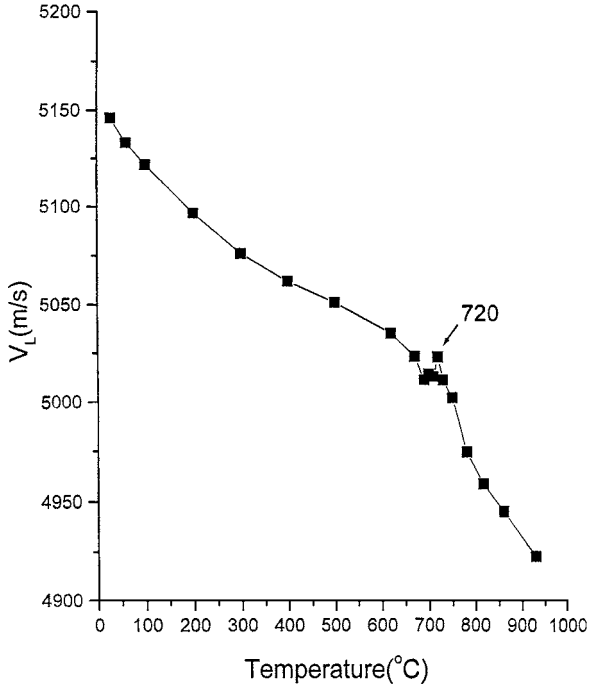

Figure 1 The temperature dependence of longitudinal sound velocity for a $0.2La_2O_3$-GeO_2-$0.25Ga_2O_3$ glass from ultrasonic measurement.

TABLE III The glass transition temperature (T_g), room temperature longitudinal sound velocity V_L, and the slope of sound variation with temperature below and above T_g from ultrasonic and Brillouin measurements for a $0.2La_2O_3$-GeO_2-$0.25Ga_2O_3$ glass

	Ultrasonic	Brillouin
T_g (°C)	740	701
V_L (m/s)	5146	5150
dV_L/dT below T_g	−0.18	−0.20
dV_L/dT above T_g	−0.42	−3.00

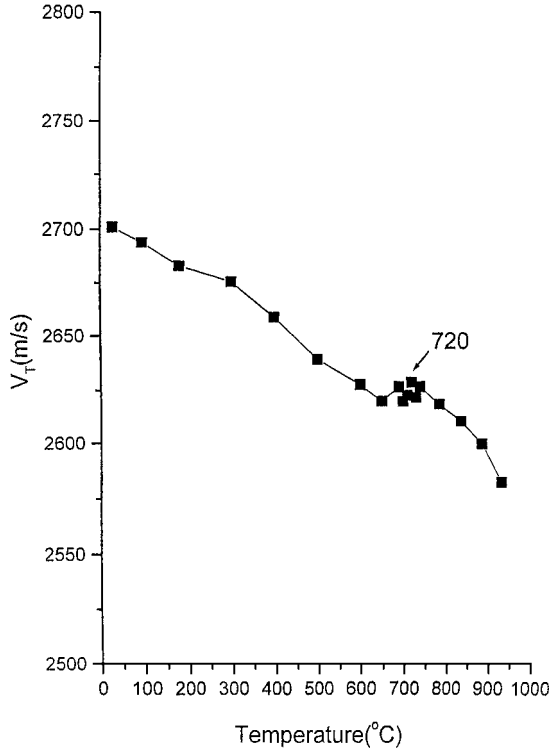

Figure 2 The temperature dependence of transverse sound velocity for a $0.2La_2O_3$-GeO_2-$0.25Ga_2O_3$ glass from ultrasonic measurement.

For most glasses, a sudden change is expected in their thermodynamic properties, such as heat capacity, thermal expansion coefficient, and compressibility near the glass transition temperature [20–24]. Consequently, we assign the temperature as the glass transition temperature T_g when the slope of sound velocities undergoes a sudden change. The glass transition temperature of a $0.2La_2O_3$-GeO_2-$0.25Ga_2O_3$ glass is about 720°C as indicate in Figs 1 and 2. Fig. 3 gives the temperature dependence of longitudinal sound velocity of a $0.2La_2O_3$-GeO_2-$0.25Ga_2O_3$ glass at hypersonic frequency from Brillouin scattering measurement. A marked break in the longitudinal sound velocity-temperature plot is observed at the glass transition temperature of 701°C. Table III gives a comparison between the Brillouin results and the ultrasonic data on the same glass in the temperature range of 25–740°C. Two measurements give a good agreement below T_g; however, above T_g the Brillouin data drop much faster than the ultrasonic

TABLE IV Temperature dependence of shear modulus ($\partial S/\partial T$) and bulk modulus ($\partial B/\partial T$), for a series of lanthanum gallogermanate, SiO_2 and GeO_2 glasses

Sample	Modulus $\frac{\partial B}{\partial T} \times 10^{-3}$ (GpaK^{-1})	Modulus $\frac{\partial S}{\partial T} \times 10^{-3}$ (GpaK^{-1})
$0.2La_2O_3$-GeO_2-$0.2Ga_2O_3$	−9.8	−5.5
$0.2La_2O_3$-GeO_2-$0.25Ga_2O_3$	−7.6	−4.9
$0.2La_2O_3$-GeO_2-$0.33Ga_2O_3$	−12.8	−5.8
$0.2La_2O_3$-GeO_2-$0.5Ga_2O_3$	−13.8	−2.9
GeO_2	2.32	0.69
SiO_2	15.04	4.41

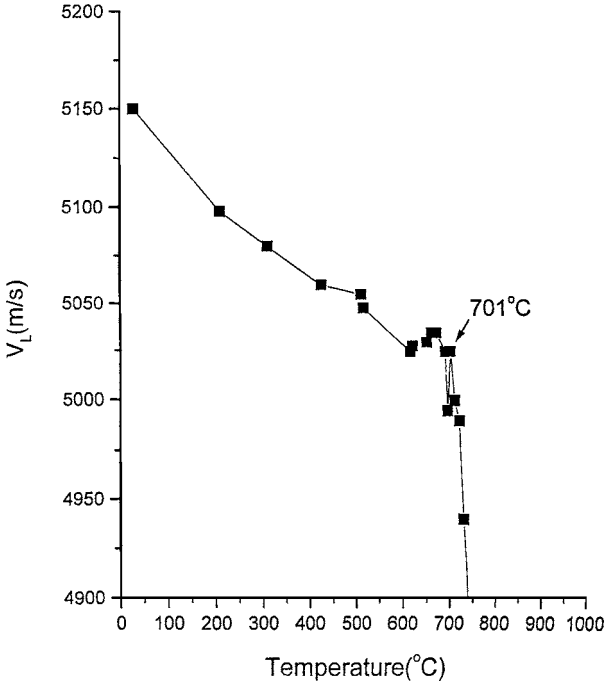

Figure 3 Longitudinal sound velocity as a function of temperature for a $0.2La_2O_3$-GeO_2-$0.25Ga_2O_3$ glass from Brillouin scattering.

data. This discrepancy is attributed to the frequency dependence of the visco-elastic properties of the glass and the different relaxation behavior of the glass plays an important role at ultrasonic and hypersonic frequencies [25, 26].

Similar negative temperature dependence is observed for shear modulus ($\partial S/\partial T$) and bulk modulus ($\partial B/\partial T$). This normal behavior agrees with most oxide glasses, ceramic and metallic materials [14, 19, 25, 27–31]; and in sharp contrast with most tetrahedral bonded glasses, such as SiO_2, BeF_2, and GeO_2, which show the anomalous positive temperature dependence of sound velocities [14, 32, 33]. Table IV gives the temperature dependence of shear modulus ($\partial S/\partial T$) and bulk modulus ($\partial B/\partial T$) for a series of lanthanum gallogermanate glasses, and the values of SiO_2 and GeO_2 glasses are also given for comparison purpose.

The temperature dependence of second order elastic constants can also give information on the fourth order elastic constants of the materials. However, this is beyond the scope of the present discussion. We are conducting further study on the temperature and pressure dependence of the sound velocities in our laboratory and this effort may give a deeper insight into the higher-order (non-linearity) elastic properties of these glasses in the future.

4. Conclusions

We have successfully measured the temperature dependence of sound velocities of a series of lanthanum gallogermanate glasses. These glasses exhibit a normal behavior of negative temperature dependence of elastic properties. Two different structural models, which are related to elastic moduli, suggest a 2-D layer structure for these glasses. Temperature dependence of sound velocity at above glass transition temperature shows a strong frequency dependence behavior.

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