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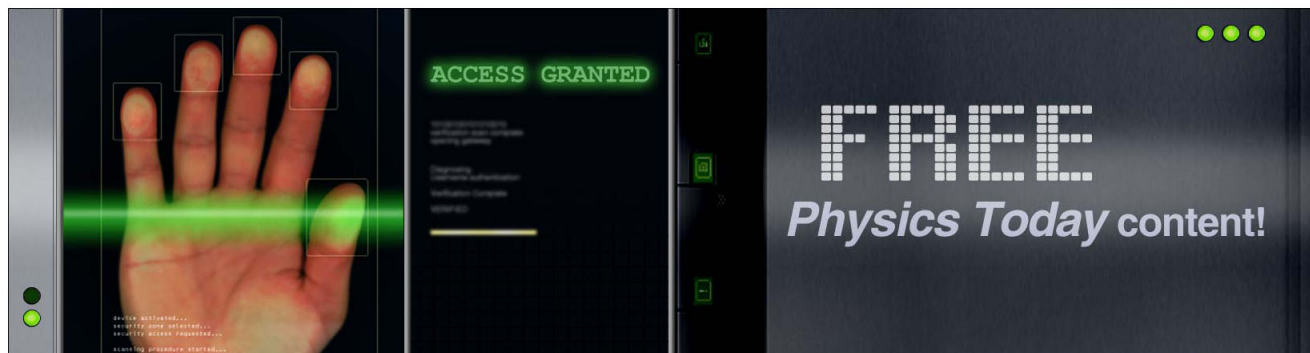
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## ADVERTISEMENT



## Inversion in the temperature coefficient of the optical path length close to the glass transition temperature in tellurite glasses

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In this study, thermal lens spectrometry was applied to determine the thermo-optical properties of fragile tellurite glasses as a function of temperature, close to the glass transition region. The results showed an inversion from positive to negative values in the temperature coefficient of the optical path length occurring after the glass transition temperature, which is the region where structural changes from the TeO<sub>4</sub> trigonal bipyramidal unit to a TeO<sub>3</sub> trigonal pyramid containing nonbridging oxygen take place. In addition, the thermal diffusivity values as a function of temperature exhibited behaviors that were related to thermodynamic and kinetic structural changes in the glass. © 2009 American Institute of Physics. [DOI: 10.1063/1.3155210]

Tellurite (TeO<sub>2</sub>-based) glasses are of scientific and technological interest because of their low melting temperatures, good optical transmission in the visible and infrared regions (up to about 7 μm), high refractive index, high dielectric constant, and large third-order nonlinear susceptibility. These properties suggest that those materials are suitable for applications involving third-harmonic generation or optical Kerr effects.<sup>1-5</sup> Tellurite glasses are also strong candidates for superhigh-speed optical switches or shutters, as well as promising materials for fiber-optic applications.<sup>6</sup> An interesting aspect of these glasses is their thermodynamic and fragile behaviors close to the glass transition temperature,<sup>1-3</sup> which are not yet well understood, despite their direct relationship to the structural changes.<sup>7,8</sup>

The magnitude of the thermal diffusivity ( $D$ ) and the temperature coefficient of the optical path length ( $ds/dT$ ) define whether an optical material can be used in optical systems, for instance, in laser windows, second- and third-harmonic generation, and high-power laser-active medium.<sup>9</sup> Another important aspect is that in many applications, the nonradiative relaxation processes induce significant temperature variation in the optical devices, which indicates that it is important to know the behavior of the thermo-optical parameters over a wide temperature range, up to the glass transition temperature ( $T_g$ ). For tellurite glasses, which exhibit structural changes even below  $T_g$ , the determination of these properties as a function of temperature may contribute to better understanding of the figure of merit of this material in terms of its application in the optoelectronic area.<sup>1-3</sup>

The two-beam mode-mismatched thermal-lens (TL) method has been used to determine the thermo-optical properties of several optical materials as a function of temperature.<sup>10,11</sup> The remote character may make the TL

technique a valuable tool for the complete characterization of transparent materials as a function of temperature. Therefore, in this study, the TL method was applied to determine the thermo-optical properties of three different tellurite glasses as a function of temperature. The nominal compositions of the glasses studied were, in mol%: 80TeO<sub>2</sub>-20Li<sub>2</sub>O (TeLi), 80TeO<sub>2</sub>-15Li<sub>2</sub>O-5TiO<sub>2</sub> (TeLiTi-5), and 80TeO<sub>2</sub>-10Li<sub>2</sub>O-10TiO<sub>2</sub> (TeLiTi-10). The focus of the study was to investigate the tellurite glass fragility close to  $T_g$  by analyzing the thermo-optical parameters along the glass transition region. The influence of TiO<sub>2</sub> on the thermo-optical properties close to  $T_g$  is also discussed. Measurements with thermal relaxation calorimetry (TRC), optical interferometry (OI), and infrared absorption spectroscopy were also performed.

In the TL experiment, the change in intensity of the probe beam is proportional to the TL-induced phase shift, which is given by<sup>11,4</sup>

$$\theta = -\frac{P_{\text{abs}}}{K\lambda_p} \varphi \frac{ds}{dT}, \quad (1)$$

where  $\lambda_p$  is the probe beam wavelength,  $P_{\text{abs}} = PAL_{\text{eff}}$  is the absorbed power of the excitation beam,  $P$  is the excitation power,  $A$  is the optical absorption coefficient at the excitation wavelength,  $L_{\text{eff}} = [1 - \exp(-AL)]/A$  is the effective sample thickness,  $L$  is the sample thickness,  $K = \rho C_p D$  is the thermal conductivity,  $\rho$  is the density,  $C_p$  is the specific heat, and  $\varphi$  is the fraction of the absorbed energy converted into heat. For samples with no fluorescent characteristics, such as tellurite glasses,  $\varphi = 1$ .

In our measurements, an Ar<sup>+</sup> laser at 514 nm was used to excite the samples and consequently to create the TL effect, and a HeNe laser at  $\lambda_p = 632.8$  nm was used to probe this effect. Figure 1(a) shows a typical curve for TeLi glass at 270 °C, which is very similar to that obtained at room temperature. The observed increase in the intensity of the probe

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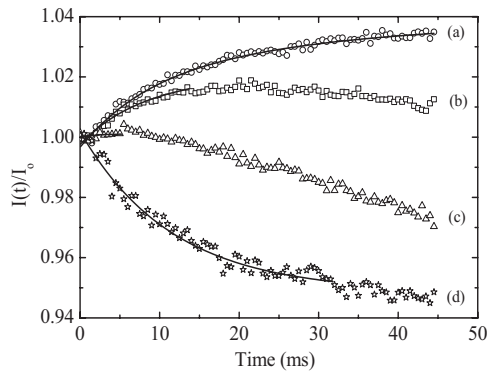


FIG. 1. TL signal for TeLi glass at 270 °C (a), 280 °C (b), 290 °C (c), and 311 °C (d). The error for each experimental point was lower than 0.5%. The solid lines represent the curve fittings with the TL analytical equation, as described in Ref. 12. We used  $P_e=48.6$  mW.

beam means that  $ds/dT > 0$ . By fitting the experimental curve with the TL time-resolved analytical equation given in Ref. 10, both  $\theta$  and the characteristic time response,  $t_c = w_{oe}^2/4D$ , were obtained. Here,  $w_{oe}$  is the excitation beam spot size (radius) at the sample position, at  $L/2$ . Consequently, the  $D$  values were calculated. We used  $w_{oe} = 48.5$   $\mu\text{m}$ . The three tellurite glasses exhibited similar values at room temperature,  $D = (2.9 \pm 0.1) \times 10^{-3}$   $\text{cm}^2/\text{s}$ , indicating that no significant changes are observed when the glass structure is modified by replacing  $\text{TiO}_2$  with  $\text{Li}_2\text{O}$ . Comparing with other glasses, tellurite has a  $D$  value around 10% higher than that of chalcogenide ( $2.6 \times 10^{-3}$   $\text{cm}^2/\text{s}$ ) (Ref. 12) and approximately half the value of aluminosilicates ( $\sim 5.7 \times 10^{-3}$   $\text{cm}^2/\text{s}$ ).<sup>13</sup> To determine the thermal conductivity, we measured the specific heat using the TRC method.<sup>14</sup> The value ( $0.47 \pm 0.02$ ) J/g K at room temperature was not dependent on the glass composition. Assuming that the tellurite glasses studied have the same density ( $\rho = 4.825$   $\text{g}/\text{cm}^3$ ),  $K = (6.6 \pm 0.5) \times 10^{-3}$  W/K cm was determined. This value is much lower than that of aluminosilicates ( $\sim 15 \times 10^{-3}$  W/K cm).<sup>13</sup> As defined in Eq. (1),  $ds/dT$  can be determined by normalizing the obtained  $\theta$  parameter by the absorbed excitation power ( $P_{\text{abs}}$ ) and using the  $K$  and  $\lambda_p$  values. Thus, the value of  $ds/dT$  for the three glasses was  $12.3 \times 10^{-6}$   $\text{K}^{-1}$ , which is similar to that of aluminosilicates.<sup>13</sup>

For the TL measurements as a function of temperature, the glasses were placed in a furnace so that the sample temperature could be increased to cross  $T_g$ . The TL curves were obtained by scanning the temperature with a ramp rate of 0.5 °C/min. The time interval between each consecutive laser shot was about 30 s, which was the appropriate condition to obtain a complete TL relaxation between the events. In addition, it should be stressed that the laser-induced temperature rise in the sample necessary to obtain a detectable TL signal is very low, on the order of  $10^{-2}$  K. Therefore, the furnace temperature monitored very close to the sample position can be assumed to be the respective sample temperature for each TL datum shown. The TL transients were fitted in the same way as described above, so that  $D(T)$  and  $ds/dT(T)$  could be determined. The curves (a), (b), (c), and (d) in Fig. 1 show the TL experimental transients obtained for TeLi glass at 270, 280, 290, and 311 °C, respectively, with the same excitation power ( $\sim 48.6$  mW). The solid lines represent the theoretical fittings. An inversion in the TL

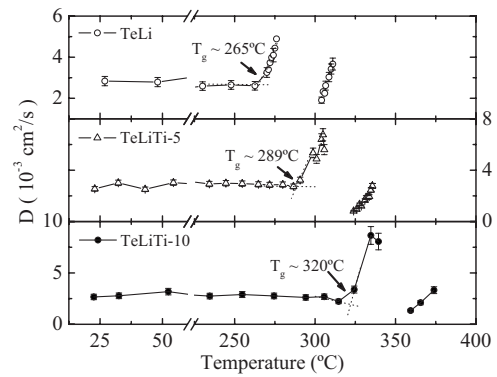


FIG. 2. Thermal diffusivity values,  $D(T)$ , for TeLi, TeLiTi-5, and TeLiTi-10 glasses.

curve behavior [from  $ds/dT > 0$ , curve (a), to  $ds/dT < 0$ , curve (d)], occurred around  $T_g$ . This inversion was also observed in the TeLiTi-5 and TeLiTi-10 glasses, but at different temperatures, so  $T_g$  was different for each sample. The explanation for this effect is that tellurite glasses combine  $ds/dT > 0$  and  $dn/dT < 0$  because of their high values of both the thermal expansion coefficient and the refractive index around  $T_g$ .

Figure 2 shows the  $D(T)$  values for the three glasses studied. The lack of data between 280 and 300 °C for TeLi, between 305 and 325 °C for TeLiTi-5, and between 335 and 360 °C for TeLiTi-10 is due to the fact that over these temperature intervals, the TL effect goes to zero as a consequence of the inversion of  $ds/dT$  values, as shown in Fig. 1, curves (b) and (c). Note that in Fig. 2 there are three distinct regions for the thermal diffusivity behavior: (i) a monotonic trend from room temperature up to the region close to  $T_g$ ; (ii) a significant increase after  $T_g$ ; and (iii) a subsequent increase after passing through a minimum in the region of the inversion of  $ds/dT$ . The thermal diffusivity behavior from room temperature up to  $T_g$  is similar to the differential scanning calorimetry (DSC) curves, independently of the tellurite glass studied, so they do not exhibit either endothermic or exothermic trends in this temperature range. A similar observation was reported for fluoride glasses.<sup>10,11</sup> The  $T_g$  values can be determined by  $D(T)$  curves, as indicated in Fig. 2, and were 264, 288, and 318 °C for the TeLi, TeLiTi-5, and TeLiTi-10 glasses, respectively. These values are in agreement with those determined by the DSC method, which were 264, 285, and 312 °C, respectively.

The observed increase in  $D(T)$  values for temperatures above  $T_g$  may be related to the structural change from the  $\text{TeO}_4$  trigonal bipyramid (TBP) unit to the  $\text{TeO}_3$  trigonal pyramid (TP) containing nonbridging oxygen. The occurrence of this structural change in tellurite glass was previously confirmed by high-temperature Raman measurements, which showed a decrease in the TBP Raman peak intensity of around 770  $\text{cm}^{-1}$  and a corresponding increase in the TP Raman peak intensity near 670  $\text{cm}^{-1}$ .<sup>2</sup> The structural alteration above  $T_g$  increases the glass viscosity,<sup>2</sup> producing an increase in both  $D$  and heat capacity  $\Delta C_p = C_{pe} - C_{pg}$  values, in which  $C_{pe}$  and  $C_{pg}$  are the heat capacities of supercooled liquids and glasses, respectively.<sup>1-3</sup> The  $\Delta C_p$  was measured with the TRC, and the result obtained was  $C_{pe}/C_{pg} = 1.55$ , which is similar to the value of  $\sim 1.6$  for fragile glasses found in the literature.<sup>1-3</sup> This parameter was used by some

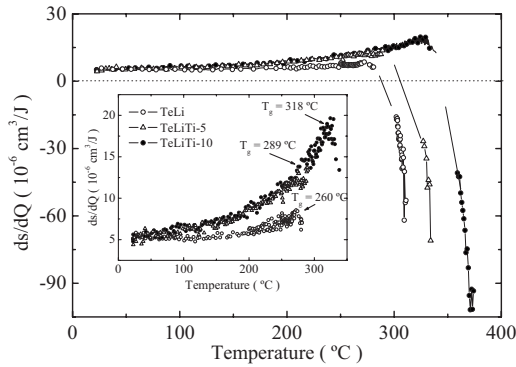


FIG. 3. Temperature dependence of  $ds/dQ$ . The error for each experimental point is around 7%. The inset shows the region between room temperature and  $T_g$ .

authors to define a fragile character of the tellurite glass.<sup>1-3</sup> On the contrary, the so-called strong liquids, as pointed out by Angell,<sup>7,8</sup> tend to have smaller changes in heat capacity at  $T_g$ . For instance, a typical fluoride glass has  $C_{pe}/C_{pg}$  on the order of 1.1.<sup>1-3</sup> For higher temperatures,  $D(T)$  values increased from a minimum to a maximum, from where we were not able to go further because of the deterioration of the optical quality of the sample. This behavior may also be related to the structural changes with a strong increase in the viscosity of the glass.

In order to discuss  $ds/dT(T)$ , we wrote it in terms of  $ds/dQ(T)$  as:  $ds/dQ(T) = (\rho C_p)^{-1} ds/dT(T)$ . This is understood as the sample characteristic response denoting how the optical path changes with the laser-induced heat deposited per unit of volume.<sup>10</sup> Figure 3 shows  $ds/dQ(T)$  for the TeLi, TeLiTi-5, and TeLiTi-10 glasses. The inset shows  $ds/dQ(T)$  from room temperature up to the maximum, corresponding to  $T_g$  values. These are compared with those obtained by the  $D(T)$  and DSC methods. The increase in  $ds/dQ(T)$  is followed by a decrease, crossing the zero line and assuming negative values. In order to understand this behavior it is important to remember that  $ds/dT$  is related to the thermo-optical coefficient ( $dn/dT$ ) by<sup>15</sup>

$$\frac{ds}{dT} = (n-1)(1+\nu)\alpha + \frac{dn}{dT}, \quad (2)$$

where  $n$  is the refractive index,  $\nu$  is the Poisson's ratio, and  $\alpha$  is the linear thermal expansion coefficient. Because the first term on the right side of Eq. (3) is always positive, the term responsible for the signal of  $ds/dT$  is  $dn/dT$ . Remembering that  $dn/dT \propto (\varphi - \beta)$ , in which  $\varphi$  is the temperature coefficient of the electronic polarizability and  $\beta = 3\alpha$  is the volumetric thermal expansion coefficient, and also that  $\beta$  of tellurite glasses did not change when the temperature varied from room temperature to  $T_g$  (not shown), we conclude that the observed  $ds/dQ$  (or  $ds/dT$ ) behavior up to  $T_g$  is related to an increase in the electronic polarizability. This is similar to the observations reported by Prod'homme<sup>16</sup> for oxide glasses. Tellurite glasses have structural units of  $\text{TeO}_4$  and  $\text{TeO}_3$  that are connected weakly with each other, and thus the intermediate structure varies easily with increasing temperature,

which can change the electronic polarizability of the glasses.<sup>2</sup> Another interesting observation is that  $\varphi$  exhibits a stronger temperature dependence for the glasses containing  $\text{TiO}_2$ , indicating that this metal produces significant changes in the glass structure.

Above  $T_g$ , the structural change (from  $\text{TeO}_4$  TBP units to  $\text{TeO}_3$  TP units containing nonbridging oxygen) is more pronounced, resulting in a considerable increase in the volumetric thermal expansion coefficient (as observed by the temperature behavior of the specific heat), causing a negative increase in  $dn/dT$ . This explains the inversion from positive to negative in  $ds/dQ$  values, which was also observed in the OI measurements via visual inspection, in which the interference fringes inverted their dislocation direction for temperatures above  $T_g$ .

In conclusion, the TL method was successfully applied to measure the thermo-optical properties of fragile tellurite glasses as a function of temperature. The measurements provided  $T_g$  values in good agreement with those obtained by the DSC method. The observed inversion in the  $ds/dQ$  (or  $ds/dT$ ) parameter above  $T_g$  may be associated with both the strong variation in the volumetric thermal expansion coefficient and the structural change from  $\text{TeO}_4$  TBP units to a  $\text{TeO}_3$  TP containing nonbridging oxygen. A significant change in the thermal diffusivity occurred above  $T_g$  because of the increase in the glass viscosity. Our results also showed that when the sample is heated above room temperature, the TeLiTi-5 and TeLiTi-10 glasses, with  $\text{TiO}_2$  in their composition, undergo a higher beam deformation than that of the TeLi glass.

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