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 TeO₄ trigonal bipyramidal unit to a TeO₃ 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 (TeO₂-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.1–4 Tellurite glasses are also strong candidates for superhigh-speed optical switches or shutters, as well as promising materials for fiber-optic applications.6 An interesting aspect of these glasses is their thermodynamic and fragile behaviors close to the glass transition temperature,1–3 which are not yet well understood, despite their direct relationship to the structural changes.7,8

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.9

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 (Tg). For tellurite glasses, which exhibit structural changes even below Tg, 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.1–3

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.10,11 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 %: 80TeO₂–20Li₂O (TeLi), 80TeO₂–15Li₂O–5TiO₂ (TeLiTi-5), and 80TeO₂–10Li₂O–10TiO₂ (TeLiTi-10). The focus of the study was to investigate the tellurite glass fragility close to Tg by analyzing the thermo-optical parameters along the glass transition region. The influence of TiO₂ on the thermo-optical properties close to Tg 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

\[ \theta = -\frac{P_{\text{abs}}}{K \lambda_p} \frac{ds}{dT}, \]  

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, \( K = \rho C_p \) 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, \( \varphi \approx 1 \).

In our measurements, an Ar⁺ 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...
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, $t_c = w_{oc}^2/4D$, were obtained. Here, $w_{oc}$ is the excitation beam spot size (radius) at the sample position, at $L/2$. Consequently, the $D$ values were calculated. We used $w_{oc} = 48.5 \mu m$. 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 TiO$_2$ with Li$_2$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 $(~5.7 \times 10^{-3} \text{cm}^2/\text{s})$. To determine the thermal conductivity, we measured the specific heat using the TRC method. The value $(0.47 \pm 0.02) J/g \text{K}$ at room temperature was not dependent on the glass composition. Assuming that the tellurite glasses studied have the same density ($\rho = 4.825 \text{g/cm}^3$), $K = (6.6 \pm 0.5) \times 10^{-3} \text{W/K cm}$ was determined. This value is much lower than that of aluminosilicates $(~15 \times 10^{-3} \text{W/K cm})$. As defined in Eq. (1), $ds/dT$ can be determined by normalizing the obtained $\theta$ parameter by the absorbed excitation power ($P_{abs}$), 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.

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 ($\sim 48.6 \text{mW}$). The solid lines represent the theoretical fittings. An inversion in the TL 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. 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 TeO$_4$ trigonal bipyramid (TBP) unit to the 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 cm$^{-1}$ and a corresponding increase in the TP Raman peak intensity near 670 cm$^{-1}$. The structural alteration above $T_g$ increases the glass viscosity, 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. $\Delta C_p$ 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. This parameter was used by some
TeLiTi-5, and TeLiTi-10 glasses. The inset shows
observations reported by Prod’homme\cite{16} for oxide glasses.
Tellurite glasses have structural units of TeO4 and TeO3 that
tend to have smaller changes in heat capacity at
room temperature to
higher temperatures, $T_g$. For instance, a typical fluoride glass has
$C_p^f/C_p^g$ on the order of 1.1.\cite{7,8} 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: $ds/dQ(T)=\left(\frac{\rho C_p}{\rho C_p}\right)^d ds/dT(T)$. This is under-
stood as the sample characteristic response denoting how the
optical path changes with the laser-induced heat deposited
per unit of volume.\cite{10} 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 fol-
lowed 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-
oclastic (dn/dT) by\cite{15}
\[
\frac{ds}{dT} = (n-1)(1 + \nu)\alpha + \frac{dn}{dT},
\]
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 $dn/dT=(\varphi-\beta)$, in which $\varphi$ is the temperature coefficient
of the electronic polarizability and $\beta=\Delta \alpha$ 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\cite{16} for oxide glasses.
Tellurite glasses have structural units of TeO4 and TeO3 that
are connected weakly with each other, and thus the interme-
diate structure varies easily with increasing temperature,
which can change the electronic polarizability of the glasses.\cite{2} Another interesting observation is that $\varphi$ exhibits a
stronger temperature dependence for the glasses containing
TiO2, indicating that this metal produces significant changes
in the glass structure.

Above $T_g$, the structural change (from TeO4 TBP units to
TeO3 TP units containing nonbridging oxygen) is more
pronounced, resulting in a considerable increase in the volumet-
ric thermal expansion coefficient (as observed by the temper-
ature 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 interfer-
ence fringes inverted their dislocation direction for tempera-
tures 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 pro-
vided $T_g$ 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 coeffi-
cient and the structural change from TeO4 TBP units to a
TeO3 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 TiO2 in their composi-
tion, undergo a higher beam deformation than that of the
TeLi glass.

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