

# Time-resolved thermal lens measurements of the thermo-optical properties of glasses at low temperature down to 20 K

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In this work the time resolved thermal lens spectrometry was applied to measure the absolute values of the thermo-optical properties of low silica calcium aluminosilicate and soda lime glasses at low temperatures, in the range between 20 and 300 K. The thermal relaxation calorimetry was used as a complementary technique to determine the specific heat. The results showed a marked decrease of the thermal diffusivity with the temperature rise, with a dependence similar to that of the mean free path ( $\sim T^{-1}$ ) in the interval between 20 and 70 K, while in the range between 70 and 300 K the dependence was  $T^{-(0.33 \pm 0.02)}$ . The marked variation of the temperature coefficient of the optical path length change with the temperature rise was attributed to the increase in the coefficient of the electronic polarizability. The results also showed that for the aluminosilicate glass the excess in the specific heat correlated to the so-called boson peak occurred at about 17 K, higher than that of soda lime, which occurs at about 12 K. In conclusion, our results showed the ability of the time resolved thermal lens to determine the thermo-optical properties of glasses at low temperatures, bringing possibilities for experiments in a wide range of optical materials.

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## I. INTRODUCTION

There has been an increasing interest in the development of modified materials for a broad range of optoelectronic applications. The thermo-optical properties—thermal conductivity ( $K$ ) or thermal diffusivity ( $D$ ), specific heat ( $c_p$ ), and the temperature dependence of the optical path length ( $ds/dT$ ) are important parameters which are necessary to model, design, and operate the considered systems.<sup>1–6</sup> Thermal diffusivity and thermal conductivity give quantitative information about the thermalization time, heat flow, and heat dissipation,<sup>1</sup> while  $ds/dT$  is related to the optical distortions induced by both the sample thickness change and the refractive index variation when the sample temperature is modified.<sup>2–4</sup> Since such properties may be strongly dependent on temperature, it is desirable to measure their absolute values as a function of temperature. The precise determination of material properties at low temperatures is always a challenging task. In the case of thermal properties there is always a rapid variation in their measured values as the sample temperature decreases, demanding therefore, both appropriate excitations and devices to obtain the data.<sup>7</sup> Certainly the possibility of using noncontacting and sensitive methods is an advantageous route to perform measurements at low temperature condition.

In the last few years the thermal lens spectrometry (TLS) has been explored as a highly sensitive photothermal technique with attractive characteristics. It is remote, nondestructive, and fast, demanding a transient of a few milliseconds with excitations of the order of  $10^{-2}$  °C to provide the data.<sup>8–10</sup> When operated in the transient mode the method permits us to reduce the heat transfer as compared to steady state techniques. Indeed, it has been used recently to obtain optical and thermal properties during phase modification of a wide range of materials, including glasses,<sup>5,10</sup> polymers,<sup>11</sup> and liquid crystals.<sup>12</sup> In those works the thermo-optical properties of the samples were investigated as a function of temperature in the region above room temperatures, up to 580 K.

In the present paper we extended the capability of the thermal lens spectrometry to quantify the thermal diffusivity, thermal conductivity, and temperature coefficient of the optical path length of two different oxide glasses, the low silica calcium aluminosilicate (LSCAS) and the soda lime, as a function of temperature, in the range between 20 and 300 K. In order to perform the experiments a low temperature device was used. As a complementary method a thermal relaxation calorimeter was used to obtain the specific heat of the low silica calcium aluminosilicate glass in a similar temperature interval.

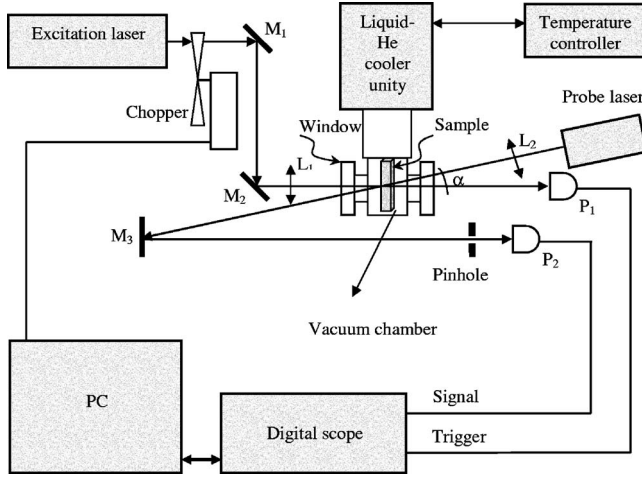


FIG. 1. Thermal lens experimental setup. The excitation and probe beams are provided by an Ar<sup>+</sup> ion laser ( $\lambda=488$  nm) and a He-Ne laser ( $\lambda=632.8$  nm) respectively.  $M_i$ ,  $L_i$ , and  $P_i$  correspond to mirrors, lenses, and photodiodes, respectively. The windows are made of quartz disks.

## II. EXPERIMENT

The samples used in this work have the following compositions in wt %: (a) LSCAS: 47.4 CaO-41.5Al<sub>2</sub>O<sub>3</sub>-7.0 SiO<sub>2</sub>-4.1 MgO and (b) Soda lime: 70.4SiO<sub>2</sub>-17.6Na<sub>2</sub>O-10CaO-2Fe<sub>2</sub>O<sub>3</sub>. The LSCAS sample was prepared under vacuum condition to minimize the presence of OH<sup>-</sup> in the glass structure as described in Ref. 13. The melting temperature was 1550 °C. The soda lime sample was prepared at room atmosphere and the melting temperature was 1300 °C.

The TL experiment was performed in the dual beam mode-mismatched configuration, as shown in Fig. 1, and described elsewhere.<sup>2,8</sup> Briefly, the TL effect is caused by the generation of heat by nonradiative decay processes after the laser energy is absorbed by the sample. As a consequence, a temperature gradient is established, inducing a lenslike optical element in the sample, resulting in what is called TL effect. When a probe laser beam propagates through this TL, there is a variation of its on-axis intensity  $I(t)$ , which can be detected both in the steady state and in the time resolved modes.<sup>2,14</sup> For the measurements as a function of temperature, the samples were cooled at 20 K by He exchange in a continuous flow cryostat (Janis, ST-100), and a temperature controller (LakeShore, 321-01) was used to stabilize the temperature. The measurements were performed in the range between 20 and 300 K. We used two highly transparent quartz disks to seal the Dewar chamber, as indicated in Fig. 1, in order to avoid the induction of thermal lens in the windows. The probe beam was a He-Ne laser operating at 632.8 nm, while the excitation laser was an Ar<sup>+</sup> laser at 488 nm.

The detection of the TL transient signal was performed by a silicon photodiode, connected to a digital scope in the millisecond scale. In order to obtain the TL signal in the time domain the chopper frequency was chosen according to the temperature region, in such a way that every consecutive shot was performed after the complete relaxation of the TL

generated in the previous event. We adopted this procedure because the thermal lens time constant increased almost two times when the sample temperature was varied from 20 to 300 K, as will be shown in the results. As examples, at  $T=20$  K the frequency used was 12 Hz (a transient of about 40 ms) and at 300 K the frequency was 4 Hz (a transient of 125 ms). For the adopted (cw) excitation mode, for each chosen temperature we used about 50 excitation beam shots to average the final transient.

In the cw excitation regime, the analytical expression for the probe beam intensity  $I(t)$  is given by<sup>2,8</sup>

$$I(t) = I(0) \left\{ 1 - \frac{\theta}{2} \tan^{-1} \left[ \frac{2mV}{[(1+2m)^2 + V^2]t_c/2t + 1 + 2m + V^2} \right] \right\}^2, \quad (1)$$

in which

$$m = \left( \frac{\omega_p}{\omega_e} \right)^2; \quad V = \frac{Z_1}{Z_c} \text{ with } Z_c \ll Z_2. \quad (2)$$

Here,  $Z_c$  is the confocal distance of the probe beam,  $Z_1$  is the distance between the probe beam waist and the sample,  $Z_2$  is the distance between the sample and the photodiode,  $\omega_p$  is the probe beam radius at the sample,  $\omega_e$  is the excitation laser beam radius at the sample, and  $I(0)=I(t)$  when the transient time  $t$  or  $\theta$  is zero. The used parameters for the TL configuration were  $V=1.73$  and  $m=33$ .

The temporal evolution of the TL signal depends on the characteristic TL signal time constant  $t_c$ , which is related with the thermal diffusivity ( $D$ ) by the expression:  $t_c = \omega_e^2/4D$ . The amplitude of the TL signal  $\theta$  is approximately the phase difference between the probe beam at  $r=0$  and  $r = \sqrt{2}\omega_e$ , induced by TL

$$\theta = - \frac{P_{\text{abs}} ds}{K\lambda_p dT}, \quad (3)$$

in which  $\lambda_p$  is the probe beam wavelength,  $K$  is the thermal conductivity,  $ds/dT$  is the temperature coefficient of the optical path length change of the sample at the probe beam wavelength and  $P_{\text{abs}}$  is the absorbed power, which can be determined by<sup>15</sup>

$$P_{\text{abs}} = \frac{P_{\text{in}}(1-R)[1 - \exp(-A_e L)]}{[1 - R \exp(-A_e L)]}, \quad (4)$$

with  $P_{\text{in}}$  as the input power of the excitation beam,  $R$  as the Fresnel reflectivity,  $A_e$  as the optical absorption coefficient at the excitation wavelength, and  $L$  as the sample thickness. The denominator of the  $P_{\text{abs}}$  equation accounts for the multiple internal reflections of the pump beam within the sample.<sup>15</sup> The values of  $A_e$  were obtained by measuring the transmittance of the samples as a function of temperature in the same TL setup, while the reflectivity as a function of temperature was determined from refractive index data obtained from the literature.<sup>16</sup>

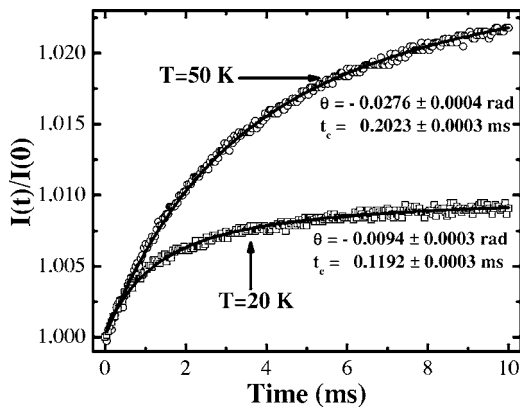


FIG. 2. Normalized thermal lens signal  $[I(t)/I(0)]$  for LSCAS glass at 20 and at 50 K.

The specific heat experiments were performed in Quantum design PPMS equipment between 2 and 150 K, and in a homemade thermal relaxation calorimeter between 150 and 470 K.<sup>17</sup>

### III. RESULTS AND DISCUSSION

Figure 2 shows two examples of normalized TL signal  $[I(t)/I(0)]$  for the LSCAS sample at 20 and 50 K using the same excitation beam power, 500 mW. It can be observed that the signal intensity is significantly higher at 50 K than at 20 K. In order to better demonstrate the difference between the buildups of the two transients, we showed only the data of the first 10 ms of the curves. The least-squares fit using Eq. (1), corresponding to the continuous lines, give the values of the thermal lens characteristic time response  $t_c$  as  $(0.1192 \pm 0.0003)$  ms at 20 K and  $(0.2023 \pm 0.0003)$  ms at 50K, and the probe beam phase shift  $\theta$  as  $(-0.0094 \pm 0.0003)$  rad at 20 K and  $(-0.0276 \pm 0.0004)$  rad at 50 K. The temperature dependence of such parameters is obtained by performing the acquisition of the curves  $I(t)$  for the temperature range from 20 to 300 K. The values of  $t_c$  give a direct measurement of the thermal diffusivity, while the phase shift  $\theta$  permits us to determine  $ds/dT$ , using Eq. (3). The thermal diffusivity values of the LSCAS sample as a function of temperature are shown in Fig. 3, curve *a*. It can be seen that there was a decrease in  $D$  values from  $22.9 \times 10^{-3}$  cm<sup>2</sup>/s at 20 K to  $5.1 \times 10^{-3}$  cm<sup>2</sup>/s at room temperature. As can be seen in Fig. 3, curve *b*, the temperature dependence of the thermal diffusivity of soda lime glass shows similar behavior. However, it should be noted that the power dependences in the region between 20 and 70 K, as shown in the inset of Fig. 3, were  $T^{(-1.03 \pm 0.05)}$  for LSCAS and  $T^{(-0.87 \pm 0.02)}$  for soda lime. This observation will be discussed later in this work. The values of the specific heat for the LSCAS as a function of temperature are shown in Fig. 4, curve *a*, together with those for soda lime obtained from the literature, curve *b*.<sup>18</sup> Both glasses show similar behavior as a function of temperature (note that the scale is  $c_p/T^3$ ). It can be seen that, similar to that observed for the thermal diffusivities above, they present different temperature dependences in the interval between 2 and about 70 K, evidencing

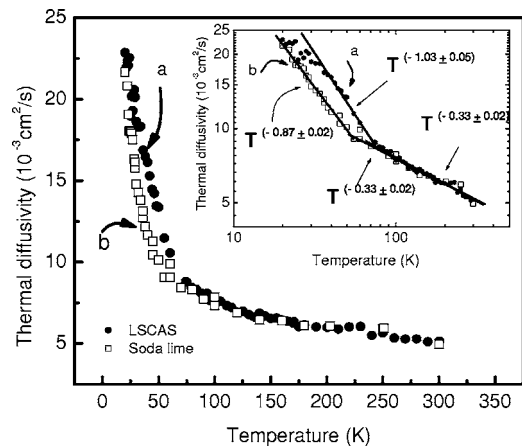


FIG. 3. Thermal diffusivity ( $D$ ) as a function of the sample temperature for LSCAS and soda lime glasses. The inset presents the same data in logarithmic scale.

a more pronounced variation of  $c_p$  of soda lime when the temperature decreased.

Having  $D(T)$  and  $c_p(T)$  for both glasses, to calculate the thermal conductivities as a function of the sample temperature  $K(T)$  using the relation  $K = D\rho c_p$ , with  $\rho$  as the mass density, the values of  $\rho(T)$  are needed. By considering that the volumetric thermal expansion coefficient  $\beta$  of both glasses are of the order of  $10^{-5}$  K<sup>-1</sup> at room temperature, and even smaller at lower temperature, the variation in the samples volume in the considered temperature interval are smaller than 1%. Then, the mass density  $\rho(T)$  can be considered as approximately constant in our calculations. Therefore, having  $D(T)$  and  $c_p(T)$ ,  $K(T)$  was calculated for both glasses and the results are shown in Fig. 5, curves *a* and *b*, as indicated. For comparison, curve *c* shows  $K(T)$  values for the silica vitreous obtained from Ref. 18. It can be noted that  $K$  increases one order of magnitude when the temperature varied from 20 K to room temperature, in good agreement to what is observed in the literature<sup>18,19</sup> for amorphous materials. It has been reported that all amorphous materials present very similar temperature dependence for the thermal conduc-

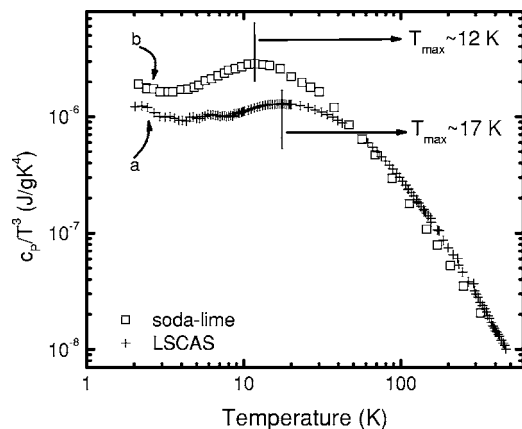


FIG. 4. Specific heat as a function of the sample temperature for LSCAS measured in this work and for soda lime glasses retrieved from Ref. 18.

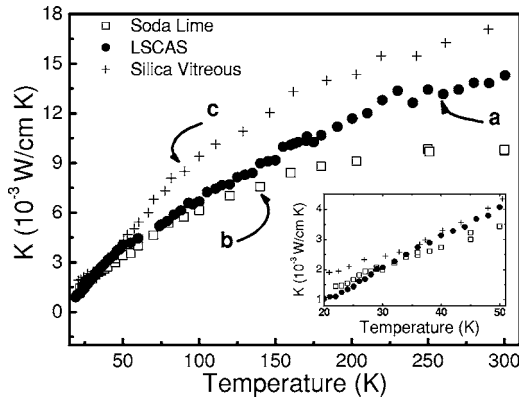


FIG. 5. Thermal conductivity as a function of the sample temperature for LSCAS (a) and soda lime (b), measured in this work, and for silica vitreous (c) obtained from Ref. 18. The inset shows the data at low temperature in an expanded scale.

tivity, suggesting a universal behavior, whose origin is not completely understood.<sup>20,21</sup> In fact, the temperature dependence of the thermal conductivity and the specific heat of noncrystalline solids differ markedly from those of crystalline ones, and despite the intensive investigation on the subject a satisfactory microscopic description of the origin of the mentioned difference has not yet been given. The Debye model states that the thermal conductivity is related to  $\rho c_p$  by

$$K = \frac{1}{3} v_s \ell \rho c_p, \quad (5)$$

in which  $v_s$  is the average sound velocity, and  $\ell$  is the phonon mean free path. Comparing Eq. (5) with the thermal diffusivity definition, namely,  $D = K / \rho c_p$ , it follows that Debye's model predicts that the thermal diffusivity is

$$D = \frac{1}{3} v_s \ell. \quad (6)$$

That is, the behavior of  $D$  as a function of temperature depends on  $v_s(T)$  and  $\ell(T)$ .

Our data show two well-defined regions for the thermal diffusivity, as illustrated in the inset of Fig. 3, using log-log plot. In the temperature range between 20 and about 70 K, the decrease of  $D$  varies as  $T^{(-1.03 \pm 0.05)}$  for LSCAS and  $T^{(-0.87 \pm 0.02)}$  for soda lime, while for higher temperatures both glasses present a  $T^{(-0.33 \pm 0.02)}$  dependence, tending to be constant as the limit of higher temperatures is reached. It is known that at moderate low temperature the number of phonons involved in anharmonic scattering is proportional to  $T$ , resulting in an increase in the mean free path as the temperature decreases, with a  $T^{-1}$  dependence.<sup>18</sup> Therefore, the results indicate that the observed decrease of the thermal diffusivity at the low temperature range is driven by the mean free path. On the other hand, for the temperature interval above 70 K the behavior of  $D$  reflects the variation of both the mean free path and the sound velocity. This happens due to the fact that at high temperatures the mean free path in amorphous materials coincides, in a first approximation,<sup>11</sup> with the mean distance between two neighboring atoms,

whereas the sound velocity is proportional to  $(k_e/m)^{1/2}$ , in which  $k_e$  is the characteristic elastic constant of the bonding forces between two neighboring atoms with effective mass  $m$ . In other words, our results show that at the temperature interval  $20 < T < 70$  K the change of the thermal diffusivity with temperature is basically dominated by the  $1/T$  variation of the mean free path, while at high temperatures, the change of the sound velocity also contributes to the slight variation of the thermal diffusivity.

Before moving to  $ds/dT$  results we go back to the differences in the values of  $D(T)$  and  $c_p(T)$ , and consequently  $K(T)$  observed between the two glasses in the region of low temperature. When  $c_p/T^3$  for LSCAS is plotted versus the absolute temperature (curve *a* of Fig. 4) it is possible to identify the peak temperature  $T_{\max}$  at about 17 K. This maximum in  $c_p/T^3$  in glasses is correlated to what is called in the literature as the *boson peak*.<sup>22,23</sup> The term *boson peak* for glasses is currently used to nominate the broad, asymmetric to the high energy side and almost universal behavior of the intensities of incoherent neutron scattering and light scattering (the dispersion spectra) observed in these materials.<sup>22</sup> This denomination comes from the similarity between the mentioned shape of the dispersion spectra intensities scaled with temperature and that obtained for systems that obey the Bose-Einstein statistics.<sup>22</sup> There is a current debate on the possible explanation for the excitation given rise to the so-called *boson peak*, since disordered systems, such as glasses, in principle do not allow us to derive some kind of quasiparticle and its excitation spectrum. For further details we refer to Refs. 20–22. In addition and relevant for the analysis of our results, as it is known from the literature, the boson peak occurs at the temperature region where the product between the specific heat and the mean free path becomes independent of temperature.<sup>18</sup> Therefore, the observation of  $T_{\max}$  at about 17 K in  $c_p/T^3$  may be associated with the almost unnoticeable plateau for the thermal conductivity data in our LSCAS glass. In the case of the soda lime, as already shown in the literature, the plateau is more pronounced and  $T_{\max}$  occurs around 12 K.<sup>23</sup> Therefore, our results indicate that  $T_{\max}$  observed at higher temperatures (about 17 K) for LSCAS as compared to the soda lime (12 K) may be the possible explanation for the differences in the temperature dependence of  $D(T)$  between the two glasses. Another information that can be retrieved from these results is the ratio between  $T_{\max}$  and the Debye temperature  $\Theta_D$  of the material, which some authors have used to try to connect the glass properties at low temperatures to its structural fragility.<sup>23–25</sup> Accordingly to Granato,<sup>24,25</sup> the dynamic and thermodynamic properties of a glass are governed by a few percent of interstitial-like defects in the material. With this hypothesis the author predicted that the low temperature specific heat of glasses should have a maximum in  $c_p/T^3$  peaked at temperatures of about  $\Theta_D/35$ . This correlation was associated to the shift of certain vibration states to lower frequencies induced by the structural disorders of the materials, which have been used to explain the specific heat maxima in  $c_p/T^3$ . Considering our LSCAS glass  $T_{\max}$  at 17 K and using Granato's model we obtained  $\Theta_D$  as 595 K, which is above the measured value of the Debye temperature of the crystalline phase of this glass, which is about 455 K. In the case of soda lime,



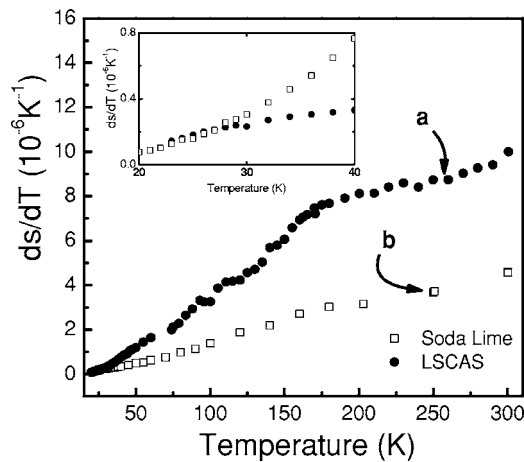


FIG. 6. The values of  $ds/dT$  as a function of temperature for LSCAS (a) and soda lime (b) glasses. The inset shows the data at low temperature in an expanded scale.

$\Theta_D/T_{\max}$  was about 36 in agreement with the mentioned model. We should stress that this is a controversial issue in the literature,<sup>20,23</sup> since other materials such as metallic glasses and some polymers also present such discrepancies.<sup>23</sup> Therefore further studies are necessary to better understand these results.

Figure 6, curves *a* and *b*, show the behavior of  $ds/dT$  as a function of temperature for the LSCAS and soda lime samples, respectively, which were calculated with Eq. (3) using the measured values of  $\theta(T)$ ,  $P_{\text{abs}}(T)$ , and  $K(T)$ . Our measurements showed that the phase shift  $\theta$  was negative in the whole temperature interval, and therefore  $ds/dT$  is always positive. To obtain  $P_{\text{abs}}(T)$  using Eq. (4) we measured the transmittance of the samples at 488 nm in the same temperature range adopted for the TL experiments. The result showed that the transmitted intensity for each glass was constant in the whole temperature interval. Therefore, considering that the variation of the values of the refractive index, determined by R. M. Waxler and G. W. Cleek<sup>16</sup> in a similar temperature range, was smaller than 0.2%, we considered  $A_e(T)$  and  $R(T)$  as their respective values at room temperature and then calculated the values for  $P_{\text{abs}}(T)$  for both glasses.

It can be noted that  $ds/dT$  increases about two orders of magnitude as the temperature goes from 20 to 300 K. For example, for LSCAS it varied from  $(0.08 \times 10^{-6} \text{ K}^{-1})$  at 20 K to  $(10 \times 10^{-6} \text{ K}^{-1})$  at 300 K. In order to analyze this variation it is important to remember that  $ds/dT$  measured by thermal lens technique can be written as<sup>2</sup>

$$\frac{ds}{dT} = (n-1)(1+v)\alpha + \frac{dn}{dT}, \quad (7)$$

in which  $n$  is the refractive index,  $dn/dT$  is the temperature coefficient of the refractive index change,  $v$  is the Poisson's ratio, and  $\alpha$  is the linear thermal expansion coefficient. The first term in Eq. (7) is associated to the sample bulging induced by the excitation beam during the TL formation. According to Prod'homme,<sup>26</sup>  $dn/dT$  is given by

$$\frac{dn}{dT} = \frac{(n^2-1)(n^2+2)}{6n}(\Phi-3\alpha). \quad (8)$$

Here,  $\Phi$  is the temperature coefficient of the electronic polarizability. When the electronic polarizability term is dominant, as in silicate glasses,<sup>2</sup>  $dn/dT$  becomes positive, and the refractive index  $n$  increases with temperature. On the other hand,  $dn/dT$  is negative when the thermal expansion term is dominant, like it is observed in fluoride glasses.<sup>5</sup> Rearranging the contributions for  $ds/dT$  [Eqs. (7) and (8)] we have

$$\frac{ds}{dT} = \left[ \left( \frac{(n^2-1)(n^2+2)}{6n} \right) \Phi + \left( (n-1)(1+v) - \frac{(n^2-1)(n^2+2)}{2n} \right) \alpha \right]. \quad (9)$$

Then, considering  $n=1.65$  for LSCAS and 1.52 for soda lime and the Poisson's ratio as 0.29 for LSCAS and 0.21 for soda lime and the very small variation of the refractive index with temperature as mentioned above,<sup>16</sup> it can be seen that  $(ds/dT)(T)$  is mainly dependent on  $\Phi$  and  $\alpha$  values.

It is known that the material thermal expansion coefficient originates from vibrational anharmonicity in the potential energy and it is usually measured by the Grüneisen parameter.<sup>27</sup> As the temperature is reduced, vibrational modes in the higher-energy states freeze out and their contribution to the thermal expansion decreases. At high temperatures, there are additional occupants of other vibrational states that contribute to the thermal expansion. Some typical values at room temperature are  $\alpha=7 \times 10^{-6} \text{ K}^{-1}$  in metaphosphate glasses,  $\alpha=7 \times 10^{-5} \text{ K}^{-1}$  for  $\text{SiO}_2$ , and  $\alpha=7.5 \times 10^{-6} \text{ K}^{-1}$  for LSCAS.

In the case of  $\Phi$ , Campbell and Suratwala<sup>28</sup> have shown that this parameter can be considered as an additive contribution from each glass component. Moreover, Izumitani and Toratoni<sup>29</sup> after analyzing several glasses' composition observed that  $\Phi$  is related to the electronic polarizing power of the network forming ions, described by the field strength  $Z/a^2$ , with  $a$  as the interionic distance in the dipoles and  $Z$  its total charge. The author observed that a decrease in the ratio  $Z/a^2$  produces an increase in the  $\Phi$  values, indicating that  $\Phi$  is mainly determined by the elongation of the interionic distance  $a$ . Therefore, the influence of temperature in  $\Phi$  value may be understood as follows: The distance  $a$  is expected to increase as the temperature increases, resulting in a decrease of the field strength. As a consequence,  $\Phi$  goes to higher values as the temperature increases, similar to  $\alpha(T)$ . Taking  $\Phi$  values at room temperature reported for typical glass components such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$  as  $1.7 \times 10^{-5} \text{ K}^{-1}$ ,  $2.2 \times 10^{-5} \text{ K}^{-1}$ , and  $4.2 \times 10^{-5} \text{ K}^{-1}$ , respectively, we observe that they are about one order of magnitude greater than those reported for  $\alpha$ . From the mentioned values it may be concluded that the main contribution for the strong increase of  $ds/dT$  values as a function of temperature for both LSCAS and soda lime glasses, shown in Fig. 6, is a consequence of the increase in the electronic polarizability coefficient with temperature. Finally it is important to mention that the thermo-optical properties of LSCAS glass at low temperature are not available in the literature. Therefore, the data pre-

sented in this work may be useful for future application using this material.

#### IV. CONCLUSIONS

In summary, in the present work we used the time resolved TL method for low temperature measurements of the thermo-optical properties of low silica calcium aluminosilicate and soda lime glasses. Our results showed a marked decrease of the thermal diffusivity with the temperature rise, with a  $T^{-1}$  dependence between 20 and 70 K and  $T^{-0.3}$  between 70 and 300 K. The strong variation of  $ds/dT$  with temperature was attributed to the behavior of the temperature coefficient of the electronic polarizability. The results also showed that the  $T_{\max}$  in  $c_p/T^3$ , which is correlated to the

boson peak, occurred at about 17 K for LSCAS glass, higher than that of soda lime known to occur at about 12 K. We also observed that the relation between the maximum in  $c_p/T^3$  and the Debye temperature is around 26 for LSCAS, which is well below what is observed for others glasses. Finally, the results of this work indicate that time resolved TL can be advantageously used to determine the thermo-optical properties of glasses at low temperatures bringing possibilities for experiments in a wide range of optical materials.

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