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Influence of temperature and excitation procedure on the athermal behavior of Nd$^{3+}$-doped phosphate glass: Thermal lens, interferometric, and calorimetric measurements

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In this work, thermal and optical properties of the commercial Q-98 neodymium-doped phosphate glass have been measured at low temperature, from 50 to 300 K. The time-resolved thermal lens spectrometry together with the optical interferometry and the thermal relaxation calorimetry methods were used to investigate the glass athermal characteristics described by the temperature coefficient of the optical path length change, ds/dT. The thermal diffusivity was also determined, and the temperature coefficients of electronic polarizability, linear thermal expansion, and refractive index were calculated and used to explain ds/dT behavior. ds/dT measured via thermal lens method was found to be zero at 225 K. The results provided a complete characterization of the thermo-optical properties of the Q-98 glass, which may be useful for those using this material for diode-pumped solid-state lasers. © 2009 American Institute of Physics. [doi:10.1063/1.3234396]

I. INTRODUCTION

Since the advent of lasers in the 1960s, glass materials have been extensively used in the development of resonant cavities.1–10 Either as highly transparent optical windows or mostly as host for luminescent ions. Optical glasses have also been used for high power lasers. The key point in designing an efficient conventional solid-state laser system is to minimize the beam distortion caused by thermal effects caused by the nonradiative decay processes that take place in the host. As a result, a transverse temperature field is established inducing a refractive index gradient behaving like an optical lens—the thermal lens (TL) effect. Moreover, it can also induce surface deformation/displacement, depolarization losses, and material fractures.5,11,12 In other words, it is often considered as the ultimate limitation for power scaling.13 On the other hand, as demonstrated in recent studies performed in doped dielectric microchip lasers, the TL plays a vital role in stabilizing the plane-plate cold cavity and hence enabling high quality laser output.13,14 This reinforces the importance of quantitative evaluation of the TL effect in laser materials.

The average power in solid-state lasers is limited primarily by thermo-optic effects in the solid-state gain medium. These effects include stress fracture, stress-induced birefringence, and thermo-optic distortion of the gain element. Desired properties of the gain medium include high thermal conductivity (k), low temperature coefficient of the optical path length change (ds/dT), and high luminescence quantum efficiency (\(\eta\)). For instance, ds/dT is related to the optical beam distortion. It has different definitions depending on the excitation source profile and the optical system design. When a uniformly distributed temperature rise occurs as in the case of most high power flashlamp/arclamp pumped solid-state lasers, ds/dT depends on the temperature coefficients of refractive index and thermal expansion. When the hosts are nonuniformly excited, as occurs for laser pumped sources, this parameter includes the sample surface bulging as a consequence of the localized induced temperature rise in the active medium.13,14 Then, it is necessary to combine different techniques to provide the absolute values of this parameter according to the used excitation characteristics.

Phosphate glasses have been widely used as matrices for laser applications. When doped with Nd$^{3+}$, it presents high luminescence quantum efficiency (\(\eta\)). In fact, they are the most common laser glass produced nowadays,15 operating in the power regime up to terawatt.10 In such high power domain, it is crucial to control the active medium temperature, which is directly related to the material thermo-optical properties.

The quantitative determination of the thermal and optical properties of these glasses as a function of temperature is fundamental for both their structural characterization and optical system optimization. TL spectrometry (TLS) has been applied to characterize several kinds of materials in a wide temperature range, from 4 to 800 K.16–21 Besides the thermal diffusivity (D) values, combining the data measured with this method with those by optical interferometry (OI) (Ref. 22) and thermal relaxation calorimetry (TRC),23 a general picture about the material thermo-optical properties can be obtained, such as the values of ds/dT, k, and \(\eta\).

Therefore, in this work we measured the thermo-optical properties of the commercial Q-98 neodymium-doped phosphate glass and what was performed in the low temperature region, from 50 to 300 K. Athermal characteristics were observed for this glass around 225 K. The TLS was used, to-

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The temporal TL transient depends on the characteristic TL time constant $t_\tau$, which is related to the thermal diffusivity ($D$) by $t_\tau=\omega_p^2/4D$. The parameter $\theta$ is the probe beam phase shift induced by the TL and can be written as

$$\theta = - \frac{P_{\text{abs}}}{k\lambda_p} \left( \frac{ds}{dT} \right)_\text{TL} \phi.$$  

Here, $\lambda_p$ is the probe beam wavelength and $(ds/dT)_\text{TL}$ is the temperature coefficient of the optical path length change at the probe beam wavelength. We added the subscript TL in order to specify that it is measured with the TL data. This is the case of nonuniform excitation, which results to bulging in the sample surface as a consequence of the localized temperature rise induced by the excitation laser beam.\[12,15\]

$$(ds/dT)_\text{TL} = \left( n-1 \right) \left( 1 + \nu \right) \alpha_e + \frac{dn}{dT} + \frac{1}{4} n^2 Y \alpha_e (q_e + q_p).$$  

Here, $\nu$ is the Poisson’s ratio, $\alpha_e$ is the linear thermal expansion coefficient, $dn/dT$ is the temperature coefficient of refractive index, $Y$ is the Young’s modulus, and $q_e$ and $q_p$ are the stress-optical coefficients parallel and perpendicular to the beam direction, respectively. The first term in Eq. (3) represents the end-face curvature due to the larger expansion of the excited region hotter center as compared to the edge of the sample. As a consequence the cooler part of the sample prevents expansion of the mentioned hotter center, then thermal stress can be generated, which is what is given by the third term in Eq. (3). Generally, this term is much smaller than the two previous ones and can be omitted.\[15\] The terms $(1+\nu)$ and the stress-optical coefficients appear in Eq. (3) due to the lenslike shape of TL temperature profile.

The parameter $\phi$ is the fraction of the absorbed energy that is converted into heat. $P_{\text{abs}}$ is the absorbed pump power, which can be determined by\[11\]

$$P_{\text{abs}} = P_{\text{in}} \left[ 1 - R \right] \left[ 1 - \exp(-A_e L) \right].$$  

$P_{\text{in}}$ is the input power of the excitation laser beam, $R$ is the Fresnel reflectivity, $A_e$ is the optical absorption coefficient at the excitation wavelength, and $L$ is the sample thickness. The denominator of the $P_{\text{abs}}$ equation accounts for the multiple internal reflections of the pump beam within the sample.\[11\] 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.\[15\]

For the neodymium-doped samples, the thermal loading, i.e., the fraction of the absorbed energy converted into heat, is provided by $\phi = 1 - \eta_h / \langle \lambda_{\text{em}} \rangle$, in which $\langle \lambda_{\text{em}} \rangle$ is the average emission wavelength.

We also applied the OI technique to determine, from 120 to 430 K, the temperature dependence of $(ds/dT)_{\text{OI}}$. In this method the sample is uniformly heated and then the subscript OI specifies $ds/dT$ measured in such condition. In this technique, the reflections of a weak He–Ne laser beam (632 nm) from both sample surfaces interfere creating interference

\[1-\tan^{-1}\frac{2mv}{\left[(1+2m) + V^2 \right]2m/v + 1 + 2m + V^2}, \]

in which $m = (\omega_{p}/\omega_{0e})^2$ and $V = Z_l/Z_e$. $Z_l$ is the confocal distance of the probe beam, $Z_e$ is the distance between the probe beam waist and the sample, $\omega_{p}$ and $\omega_{0e}$ are respectively the probe and excitation beams radii at the sample position, and $I(0)=I(t)$ when the transient time $t$ or $\theta$ is zero. In this work, we used $\omega_{0e} = 37.8 \mu m$, $m = 40.1$, and $V = 2.7$ (measured as described in Ref. 18).
fringes. Using a heating device, a slow and uniform variation in the temperature can be induced in the whole sample, causing the fringes to move. Thus a temperature dependent interferogram can be obtained and used to calculate \((ds/dT)_{\text{O1}}\). Details of the experimental procedure of this method can be found in Ref. 22. It is important to reinforce that in this procedure this parameter is obtained taking in account the beam phase shift after being reflected in the two surfaces of the sample. It can be written as

\[
\frac{ds}{dT} = \frac{dn}{dT} + n\alpha_T. \tag{5}
\]

It is convenient here to differentiate this definition for \((ds/dT)_{\text{O1}}\) from that usually found in the literature to describe the \(ds/dT\) in laser hosts when a uniformly distributed temperature rise occurs, as in the case of most high power flashlamp/arclamp pumped solid-state lasers, i.e.,

\[
\frac{ds}{dT} = \frac{dn}{dT} + (n-1)\alpha_T, \tag{6}
\]

in which \(n\) is the refractive index at the respective temperature. In this case the beam phase shift is taken into account considering that it is transmitted though the sample and not via reflection in the two surfaces as the case of \((ds/dT)_{\text{O1}}\).

A Quantum design Physical Property Measurement System (PPMS) and a homemade thermal relaxation\(^{23}\) calorimeters were used to measure the specific heat from 2 to 150 K and from 150 to 470 K, respectively.

### III. RESULTS AND DISCUSSION

Figure 2 shows two examples of normalized TL transient for the Q-98 sample at 100 and 300 K, with \(P_{\text{in}}=350\) mW and \(P_{\text{in}}=200\) mW, respectively. At 300 K, the optical element created in the sample converges the probe beam leading the signal at the detector to increase. This behavior is expected for materials with \((ds/dT)_{\text{TL}}>0\). On the other hand, in the low temperature region the transient displays the divergent nature of the TL optical element, characteristic of \((ds/dT)_{\text{TL}}<0\).

The continuous lines in Fig. 2 correspond to the least square curve fitting using Eq. (1), which provided the values of the TL characteristic time response \(t_c\) as \((1.54 \pm 0.03)\) ms at 300 K and \((0.76 \pm 0.03)\) ms at 100 K, and the probe beam phase shift normalized by \(P_{\text{in}}\), \(\theta/P_{\text{in}}\) as \(-(0.122 \pm 0.003)\) W\(^{-1}\) at 300 K and \((0.245 \pm 0.009)\) W\(^{-1}\) at 100 K.

The temperature dependence of \(t_c\) and \(\theta/P_{\text{in}}\) was obtained by performing the acquisition of the TL transients ranging from 50 to 300 K. The thermal diffusivity can be directly calculated using \(D=\varepsilon\omega_c^2/4\pi\). Figure 3(a) presents \(D(T)\) values, which decrease with increasing temperature, varying from \((6.9 \pm 0.3)\times10^{-3}\) cm\(^2\)/s at 50 K to \((2.3 \pm 0.1)\times10^{-3}\) cm\(^2\)/s at 300 K. It also shows two regimes, varying with \(T^{-0.56 \pm 0.02}\) below 130 K and with \(T^{-0.77 \pm 0.02}\) afterward, as shown in log-log plot in the inset of Fig. 3(a). Figure 3(b) shows the normalized TL phase shift, \(\theta/P_{\text{abs}}(T)\). Since the refractive index variation in this temperature range is very small,\(^{15}\) we considered \(A_s\) and \(R\) constant and equal to their respective values at room temperature. Then, \(P_{\text{abs}}(T)\) was calculated. It is interesting to note that \(\theta/P_{\text{abs}}(T)\) presents positive values below 225 K, it means \((ds/dT)_{\text{TL}}<0\), and negative ones above 225 K, i.e., \((ds/dT)_{\text{TL}}>0\).

As observed for other glasses,\(^{11,17}\) \(D(T)\) values eventually reach a constant value as the temperature is increased. The thermal diffusivity depends on the average sound velocity \(v_s\) and the phonon mean free path \(\ell\) as \(D=\langle1/3\rangle v_s\ell\). 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.\(^{11,24,25}\) Therefore, the results presented here indicate that the mean free path is not the unique quantity driving \(D\) in the low temperature range. \(D(T)\), therefore, reflects the variation in both the mean free path and the sound velocity. This happens due to the fact that at high temperature range is very small,\(^{15}\) we considered \(A_s\) and \(R\) constant and equal to their respective values at room temperature. Then, \(P_{\text{abs}}(T)\) was calculated. It is interesting to note that \(\theta/P_{\text{abs}}(T)\) presents positive values below 225 K, it means \((ds/dT)_{\text{TL}}<0\), and negative ones above 225 K, i.e., \((ds/dT)_{\text{TL}}>0\).

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temperatures the mean free path in amorphous materials coincides with the interatomic separation, whereas the bonding forces between two neighboring atoms drive the sound velocity.11

Figure 4(a) shows the specific heat of the Q-98 sample in $c_p/T^3$ scale. It presents a bump at the temperature called $T_M$. $T_M=11.2\, \text{K}$, This is the anomalous behavior that is well known to occur in the specific heat of glasses at low temperature.25–30 It is not expected to happen in materials that obey the Debye law-crystalline solids. It is driven by the presence of additional phonon states in the glassy system. It has also been reported as a bump in the phonon spectrum, commonly referred as the “boson peak,” which is obtained from the plot of the number of phonon against their respective frequency.29

The values of $k(T)$ were calculated using the relation $k=Dpc_p$ using $D(T)$ and $c_p(T)$ data. The thermal expansion coefficient of this glass is approximately $1 \times 10^{-5}\, \text{K}^{-1}$ (Ref. 15) at room temperature, and even lower at low temperature, which causes the sample total volume to change less than 1% during the considered temperature interval. Thus, the mass density $\rho=3.1\, \text{g/cm}^3$ (Ref. 15) is assumed to have a negligible variation with the increasing temperature. Figure 4(b) shows the $k(T)$ from 50 to 300 K. $k(T)$ values increase from $(2.6 \pm 0.1) \times 10^{-3}\, \text{W/cm K}$ at 50 K to $(5.0 \pm 0.1) \times 10^{-3}\, \text{W/cm K}$ at 300 K.

Once for this glass $\phi$ can be calculated from the luminescence quantum efficiency $\eta$ of the $^4F_{3/2}$ Nd$^{3+}$ level previously determined at room temperature,15 as $\eta =0.91 \pm 0.05$. $(ds/dT)_{\text{TL}}$ can be obtained using Eq. (2). Although $\eta$ values are expected to be higher as the temperature is decreased, as shown in Ref. 17 for the Nd$^{3+}$ doped aluminosilicate glasses, this high value for this glass at room temperature indicates that the mentioned variation may not be significant. Then, we assumed $\eta(T)$ constant in the temperature range of the experiments, resulting in $\phi=0.57 \pm 0.04$. This introduces additional uncertainty in $\phi$, but allows to calculate $(ds/dT)_{\text{TL}}$. Thus, using $k(T)$ and $\theta/P_{\text{abs}}(T)$, $(ds/dT)_{\text{TL}}(T)$ was calculated, as shown in Fig. 5(a). For comparison, Fig. 5(b) shows $(ds/dT)_{\text{OI}}(T)$ measured via the OI method. In addition, Fig. 5(a) shows $(ds/dT)_{\text{TL}}$ calculated with the expression

$$(ds/dT)_{\text{TL}}(T)=dn/dT(T)+[n(T)-1]\alpha_T(T)$$

Then, $\alpha_T(T)$ can be calculated. The results are shown in Fig. 6(a) (open circles). In this calculations we used $n=1.555$ and $\nu=0.24$.15

The thermal expansion coefficient originates from vibrational anharmonicity in the potential energy and it is usually measured by the Grüneisen parameter.11,31 As the temperature decreases, 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. The value for the $\alpha_T$ at 300 K was $(11.0 \pm 0.8) \times 10^{-6}\, \text{K}^{-1}$, which is in good agreement with the literature value for this glass.15

The results presented above can also be used to determine the temperature dependence of the temperature coeffi-
IV. CONCLUSIONS

In conclusion, this work describes low temperature measurements of the thermal and optical properties of Q-98 phosphate glass. The TL method was used together with the OI and specific heat measurement methods. Our results showed a decrease in the thermal diffusivity with the temperature rise, with a $T^{-0.56}$ dependence between 50 and 130 K and $T^{-0.77}$ between 130 and 300 K. We observed that $(ds/dT)_{TL}(T)$ measured via TL technique presented negative values for temperatures below 225 K and positive ones above that. In addition, it is zero at 225 K, temperature in which the glass presents athermal behavior. Finally, the results of this work showed once again that the time resolved TL can be used to determine the thermo-optical properties of glasses at low temperature, providing a differentiation between the changes in the optical path according to the nature of the excited excitation.

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