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**A B S T R A C T**

This work reports on the thermal diffusivity of the SiO$_2$–Na$_2$CO$_3$–B$_2$O$_3$–Al$_2$O$_3$ (SNAB) glass system doped with semiconductor nanocrystals of CdS and Nd$^{3+}$ ions. Thermal diffusivity ($D$) was obtained by the Thermal Lens technique. It is shown that $D$ decreases up to 30% when SNAB is doped with CdS nanocrystals. The effect is discussed in terms of heat transport by phonons as well as interface and surface scattering.

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1. Introduction

Glass doped with semiconductor nanocrystals and Rare Earth ions have attracted much attention due to their optical and electronic properties and potential use in technological applications, such as displays, lasers and fluorescent markers [1]. Most studied nanocrystalline semiconductors belong to the II–VI group and special attention has been paid to CdS and CdSe. Among Rare Earth ions, Nd$^{3+}$ has been widely investigated due to its sharp intra-4f transitions, which are strongly shielded by the outer lying closed external shell. Consequently, their transition energies are practically host and temperature independent. Moreover, Nd$^{3+}$ ions may be excited by different mechanisms such as direct excitation, energy migration or upconversion [2–6] and present radiative transitions ranging from UV to near infrared.

SNAB glass is used due to its feasibility of doping with Pb$_{0.8}$Mn$_{0.2}$S [7–8] Cd$_{1-x}$Mn$_x$S [9], and Pb$_{1-x}$Mn$_x$Se [10] nanocrystals and its transparent range from ultraviolet to near infrared. In particular, SNAB glasses doped with Nd$^{3+}$ and CdS have shown a strong energy transfer from CdS to Nd$^{3+}$, improving the optical performance of the system [11].

Even though an extensive number of works report on the optical and magnetic properties nanocrystals doped glass [7–10], there are few studies on their thermal characteristics [12–15], such as the thermal diffusivity ($D$) and thermal conductivity ($K$). When considering the performance of optical devices, thermal issues have to be evaluated, especially heat dissipation. In this work, probably for the first time, the thermo-optical properties of SNAB glass doped with CdS nanocrystals and Nd$^{3+}$ ions are investigated.

The thermal conductivity is a property that determines how much heat will flow in a material, while thermal diffusivity ($D$) determines how rapidly heat will flow within it. To efficiently dissipate heat, high $K$ is desired, while low $K$ materials are required for thermo-electric devices.

Usual failures and deterioration of optoelectronic devices, such as lasers originate from thermal induced stresses produced by thermal accumulation. It is also well known that depolarization losses, beam distortion, thermal lensing, and even fracture in high power laser systems can be assigned to the heating of the active medium [16,17]. Moreover, the rate of heat diffusion determines the thermal shock resistance.

In order to overcome such problems, new materials have been proposed. In this sense, nanocomposites have deserved special attention since they exhibit different thermal characteristics compared to the intrinsic bulk specimen [18]. Such materials can be tailored according to the desired thermal, optical and mechanic properties. It is expected that Rare Earth doped systems may be optically and thermally optimized by appropriate doping with nanoparticles.

Some techniques, mainly photoacoustic [19] and laser flash [20], have been used to obtain $D$ and $K$ in solids. More recently, the so called Thermal Lens (TL) technique has proved to be very useful in obtaining $D$ in solids. It is advantageous compared to the conventional techniques because it is remote, nondestructive and fast (usually in the millisecond scale). Although TL has been used in a wide range of materials such as glass, polymers and liquid crystals, it was only used to determine $D$ in colloidal solutions doped with semiconductor nanocrystals [12–15,20]. To our knowledge this is the first time the TL technique has been used to determine the contribution of semiconductor nanocrystals and Nd$^{3+}$ ions to the thermal diffusivity of a glass matrix host. This result is important when considering tailoring of optoelectronic devices, where cooling is one of the most important technical challenges to overcome.
2. Thermal Lens technique

The Thermal Lens experiment was performed according to the two-beam mode mismatched experimental setup [21,22], shown in Figure 1. The excitation and probe laser beams are superimposed into the sample, making a small angle $\alpha$ of about 10°. The excitation laser beam impinges into the sample and a fraction of absorbed energy is converted into heat. As a consequence, the pump beam generates a temperature gradient, which in turn produces a refractive index gradient. The latter gives rise to the Thermal Lens effect, which means that the sample behaves like a convergent or divergent lens. The TL lens effect is tested by a probe beam, and measured by the photodetector PD (Figure 1).

By means of a theoretical model, the transient thermal lens signal (that means the intensity of the probe beam as a function of time) is fitted. Since the probe beam intensity is detected by the photodetector PD, the sample should be semi-transparent.

The temporal evolution of the on-axis probe beam intensity is measured in the far field region. The transient thermal lens signal is given by [21]:

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

where $t_c = \frac{x^2}{2D}$ is the characteristic decay time, $m = \left( \frac{\omega_p}{\omega_e} \right)^2$ and $V = \frac{Z_c}{Z_1}$. $Z_0$ is the confocal distance of the probe beam, $Z_1$ is the distance between the probe beam waist and the sample, $\omega_p$ 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 $t$ is zero. $\theta$ is the phase difference induced by the lens effect, measured between the probe beam phase at the beam center $r = 0$ and $r = \sqrt{2} \omega_r$, where $r$ is the radial distance from the beam center in the sample. According to theory [21] $\theta$ is given by:

$$\theta = -\frac{PA_e L}{K dT} ds$$

where $K$ is the thermal conductivity, $dS/dT$ is the temperature coefficient of the optical path length and $\phi$, the fraction of absorbed energy converted into heat. $P$ is the transmitted laser power, $\omega_p$ is the probe beam wavelength, $A_e$ is the optical absorption coefficient and $L$ is the sample thickness. Additional measurements are the laser beam waist measured by means of a CCD perfilometer at the sample position.

3. Experimental setup

The SNAB glass matrix (40SiO$_2$-30Na$_2$CO$_3$-1Al$_2$O$_3$-29B$_2$O$_3$ (mol%)) was synthesized by the fusion method both un-doped and doped with Nd$^{3+}$ ions and CdS nanocrystal precursors (bulk CdS) resulting in the following glass samples: SNAB + XNd$_2$O$_3$ (wt.%), with $X = 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, \text{and} 5.0$, SNAB + 2CdS-bulk (wt.%); SNAB + 2[Nd$_2$O$_3$ + CdS-bulk] (wt.%). These glass samples were synthesized at 1300 °C for 15 min in a carbon rich atmosphere using porcelain crucibles. The melt was rapidly cooled by pressing it between two brass plates at approximately 0 °C which...
yielded glass sheets. Next, the glass transition temperature of the SNAB glass matrix was determined (T_g = 484 °C) by Differential Scanning Calorimetry (DSC). The SNAB + 2CdS-bulk (wt.%) and SNAB + 2[Nd_2O_3 + CdS-bulk] (wt.%) glass samples were subjected to 560 °C for 0, 2, 4, 6, 8 and 10 h, to induce CdS nanocrystal nucleation and growth in the SNAB glass matrix by diffusion of Cd^{2+} and S^{2-} resulting in CdS-bulk fusion. Samples were cut with the following dimensions: 1 cm × 1 cm × 2 mm.

The optical absorption spectra (AO) were obtained in a range from 200 to 3300 nm using a VARIAN 500 SCAN spectrophotometer. TL transient measurements were performed using the mode-mismatched dual beam configuration. A He–Ne laser at 632.8 nm was used as the probe beam and an Ar+ laser at 488 nm as pump beam (10–100 mW). The excitation and probe beam diameters at the sample were measured with a profilometer as \( \omega_p = 31.6 \mu m \) and \( \omega_e = 192.5 \mu m \), respectively. The degree of mode mismatching of the probe and excitation beams in the sample and the geometric position of the probe beam were measured as \( m = 37 \) and \( V = 1.73 \), respectively. The transient curve \( I(t) \) is provided by the probe beam and is detected by a photodiode connected to a Tektronix TDS2020 digital oscilloscope.

The atomic force microscopy (AFM) images were obtained with a Multimode Nanoscope IIIa (Digital Instruments–Veeco). All AFM images were obtained at room temperature under ambient conditions.

4. Results

Figure 2 shows atomic force microscopy images, for the SNAB + 2[Nd_2O_3 + CdS-bulk] (wt.%) glass samples treated at 560 °C for 2 and 10 h (Figure 2a and b, respectively). The mean size of the nanoparticles was observed to increase as the time of thermal treatment increased. For the sample with 2 h of heat treatment, the average size was about 4.18 nm (the insert in Figure 1a) while for 10 h of thermal treatment, the mean size was 4678 nm. Figure 2b also indicates particles with average size of about 6 and 8 nm. Additionally, it can also be seen that some big nanoparticles were formed with dimensions in the range from 50 to 100 nm.

Figure 3 displays the optical absorption spectra of the SNAB glass matrix of the SNAB + 2[Nd_2O_3 + CdS-bulk] (wt.%) glass sample 560 °C for 0, 2, 4, 6, 8 and 10 h. The absorption bands are originated from Nd^{3+} intra-4f electronic transitions and CdS crystals. The former are observed in the spectral range from 500 nm to 1000 nm. The latter can be separated in two different contributions: one from the band centered at 480 nm (2.58 eV), independent of thermal annealing, and the other around 400 nm, that shifts to higher energies as thermal annealing time increases. According to the model proposed by Brus, based on effective mass approximation [23], CdS crystals with quantum confinement effects present absorption bands shifted to higher energies. In this case, the energy of the lowest exciton state in NCs of radius \( R \) smaller than the exciton Bohr radius \( a_B \) can be estimated by

\[
E_{\text{conf}}(R) = E_g + \frac{\hbar^2 \pi^2}{2R^2} - \frac{1.8 e^2}{\varepsilon R}
\]

where \( E_g \) is the material (bulk) energy gap, \( \mu \) is the reduced effective mass, \( e \) is the elementary charge, \( \varepsilon \) is the dielectric constant. In order to estimate the energy of CdS nanocrystals, the following parameters were used: \( E_g = 2.58 \text{ eV} \), \( \mu = 0.153 \text{m}_e \) (where \( m_e \) is the mass of a free electron) and \( e = 5.7 \) [23,24]. According to Eq. (3), particles with higher sizes present absorption bands tending to the bulk CdS absorption at 2.58 eV (480 nm). The limit size is about 10 nm, which means that higher particles present a bulk like absorption behavior. The inset of Figure 3 shows the estimated mean radius of CdS nanocrystals as a function of thermal treatment time, based on the absorption band around 400 nm that shifts to higher energies as thermal annealing time increases.

Such a result is in accordance with the AFM images that indicate the formation of particles with size from 4.18 nm to 4678 nm with heat treatment and bulk behavior, with sizes higher than 10 nm.

Figure 4 shows typical transient Thermal Lens signal for samples of SNAB, SNAB + 2CdS (wt.%) and SNAB + 2[Nd_2O_3 + CdS-bulk] (wt.%) subjected to 560 °C for 2 h. According to Eq. (2), it can be seen that all samples present a convergent signal, since \( \frac{dI}{dT} > 0 \), indicating that \( ds/dT \) is positive for all samples. The inset shows the behavior of \( D \) as a function of the heat treatment time of the SNAB, SNAB + 2CdS (wt.%) and SNAB + 2[Nd_2O_3 + CdS-bulk] (wt.%) samples. A non-doped SNAB glass is also shown for comparison purposes. It can be seen that there is a very small dependence of \( D \) on the thermal annealing time for all samples. Additionally, the SNAB glass host presents higher thermal diffusivities, independent of the thermal annealing time. On the other hand, the thermal
diffusivity is about 30% lower for SNAB + 2CdS (wt.%) and SNAB + 2[Nd2O3 + CdS-bulk] (wt.%) than for the non-doped SNAB glass matrix.

5. Discussion

It is known that the thermal conductivity of a bulk material is given by $K=Cv_s^2/3$, where $v_s$ is the average phonon velocity, $\lambda$ is the phonon mean free path and $C$ is the thermal capacity. $\lambda$ is limited by anharmonic interactions with other phonons or scattering with imperfections, electrons or impurities. As $D$ is related to $K$ by $D=pC\rho$ where $\rho$ is the density, then $D=\lambda v_s^2/3p$ [25–28].

On the other hand, the behavior of thermal conductivity and thermal diffusivity of nanocomposite materials is still a matter of debate in the literature [25,26]. Some of the most investigated systems are the so called nanofluids (metallic or semiconductor nanocrystals in liquid solvents, like water, ethanol and others), where nanocrystals, especially oxygen, which is known to efficiently scatter elements variations of local density due to different atoms and vacancies, and Nd3+ concentrations increase may be attributed to additional heat transport mechanism, due to interface and surface scattering.

Figure 5 shows thermal diffusivity as a function of the concentration ($X$) of SNAB + XNd2O3 (wt.%). The decrease of $D$ as Nd3+ concentrations increase may be attributed to additional variations of local density due to different atoms and vacancies, especially oxygen, which is known to efficiently scatter elements [25,28–30]. Similar results were observed in Yb3+ doped laser crystals [25].

6. Conclusion

In conclusion, it has been shown that Thermal Lens is a sensitive technique to evaluate the thermal diffusivity of semiconductor nanocrystal and Nd3+ ion doped glass. The technique has the advantages of being remote, fast, nondestructive and do not require sample preparation. The presence of CdS and Nd3+ ions decreased the thermal diffusivity of the SNAB glass, and the effect was attributed to interface scattering. It was also shown that thermal diffusivity decreases as Nd3+ concentration increases.

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