Thermal and structural analysis of germanate glass and thin films co-doped with silver nanoparticles and rare earth ions with insights from visible and Raman spectroscopy

E.A. Carvalho[a], A.M. Freitas[b], G.H. Silva[b], M.J.V. Bell[b], L.R.P. Kassab[c], V. Anjos[b],*

[a] Instituto Federal de Educação, Ciência e Tecnologia do Sudeste de Minas Gerais, Campus São João Del Rei, São João Del Rei, MG, Brazil
[b] Laboratório de Espectroscopia de Materiais, Dep. de Física, Universidade Federal de Juiz de Fora, Juiz de Fora, MG, Brazil
[c] Laboratório de Tecnologia em Materiais Fotônicos e Optoeletrônicos, Faculdade de Tecnologia de São Paulo, CEETEPS/UNESP, 01124-060 São Paulo, SP, Brazil

A B S T R A C T

This paper reports on the thermal and optical properties of germanate glasses GeO_2–PbO co-doped with silver nanoparticles and rare earth ions (Tm^{3+}, Er^{3+} and Yb^{3+}) with a focus on the thermal diffusivity (D). The presence of rare earth ions and nanoparticles is evidenced by absorption spectra and TEM images, respectively. Additionally, a structural comparison between thin films and bulk glass with the same nominal composition is given. It is found that D increases up to 20% in samples where nanoparticles are present, although their quantity corresponds only to a volume fraction of 1.7%. Therefore, such enhancement could be associated with the nanoparticles. Nevertheless, a Raman analysis revealed a structural change after the thermal treatment used for the nucleation of the nanoparticles. A decrease in the intensity of the band at $534\,cm^{-1}$ in the Raman spectra is interpreted as the disruption of the 3-membered rings of the GeO_4 tetrahedra. The Raman analysis also revealed the formation of small crystals of α-GeO_2 type quartz and the adsorption of carbon dioxide on the surface of the silver nanoparticles inserted in the germanate thin film.

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1. Introduction

Germanate glass is a suitable material for doping with Rare Earth (RE) ions due to their large transmittance window (from visible to the infrared region) and a low phonon energy ($800\,cm^{-1}$) when compared with silicate glasses ($1150\,cm^{-1}$) [1,2]. Vitreous systems with low phonon energy are desirable in order to minimize non-radiative processes, which imply, in another perspective, an increase in the probability of radiative decays. Other properties of the germanate glass matrix are its high refractive index (≈ 2) and a large chemical stability. Recently, the growth of metallic nanoparticles (NP) inside germanate glasses has been achieved by thermal treatment of the samples. It has been verified that the presence of silver and gold NPs contribute to enhanced luminescence efficiency and nonlinear optical improvements [3–8].

The use of new systems in optical devices also depends on the knowledge of their thermal properties that are often crucial for a better performance. For example, materials with high thermal diffusivity are required to dissipate heat efficiently in computer processors and lasers. In contrast, materials with low thermal diffusivity are required for thermo-electric devices and thermal barriers, in order to enhance their figures of merit [9]. Moreover, it is also expected that thermal properties should be modified due to the NPs presence. In fact, the thermal diffusivity of materials depends on the size and concentration of the NPs. In the former case, surface effects become prominent when the thermal wavelength is comparable to the size of the NPs. Considering the latter, percolative thermal transport may occur after a critical density. In general, the theory of heat transport of nanoparticles is basically phenomenological which implies that this subject is still a matter of many discussions in the literature [10].

In the present work, GeO_2–PbO glasses co-doped with RE ions (Thulium, Erbium and Ytterbium) and silver NPs are investigated via their absorption spectra, transmission electron microscopy (TEM), thermal lens technique and Raman scattering aiming to understand the influence of the silver NPs in the thermal diffusivity. Finally, Raman spectra of a thin germanate film and of the bulk glass with the same composition are compared, searching for structural changes.

* Corresponding author.
E-mail addresses: virgilio@fisica.ufjf.br, virgilio.anjos@gmail.com (V. Anjos).

2. Experimental procedure

2.1. Samples production

The glass samples were prepared by the melting-quenching technique using the following composition: $58.7GeO_2$–$41.3PbO$ (mol%). The doping species were ErO_3 (0.5 mass fraction%), Tm_2O_3 (0.25 mass fraction%), Yb_2O_3 (3.0 mass fraction%) and $AgNO_3$ (3.0 mass fraction%), according to Table 1. A sample without $AgNO_3$ was prepared as reference. The reagents were melted at 1200 °C in an alumina crucible for 1 h, quenched in a pre-heated brass mold, annealed at 420 °C for 1 h and cooled to room temperature inside a furnace to avoid internal stress. After cooling the samples were polished and those with $AgNO_3$ were heat-treated at 420 °C during 2 and 48 h, to nucleate and grow silver nanoparticles.

A lead-germanate film was deposited on a silicon substrate by RF co-sputtering (13.56 MHz), which uses two targets simultaneously inside a vacuum chamber. For the preparation of one target, labeled by GP, the oxide powders ($58.7GeO_2$–$41.3PbO$) were mixed and then submitted to 8 t of uniaxial pressure, followed by synthesis at 750 °C for 10 h. The second target used was metallic silver, with a purity of 99.99%. Silica substrates were placed at 15 cm from the target. Before the film deposition, the base pressure was $\sim 1.3 \times 10^{-3}$ Pa to minimize the presence of contaminants. During the process, Ar plasma was used at 0.7 Pa and 50 W was used as applied rf power maximum. The film containing silver was submitted to a thermal treatment at 420 °C during 10 h to induce the growth of metallic nanoparticles.

2.2. Experimental set-up

Optical absorption spectra were recorded by a Shimadzu UV1800 spectrometer operating in the wavelength range of 190–1100 nm, with a spectral resolution of 1 nm. A 200 kV TEM from Zeiss was used to determine the size distribution of the nanoparticles. Glass samples were ground down to powder, mixed with distilled water, and partially decanted. The floating part was taken using a metallic screen as sample holder and analyzed by TEM.

Raman spectra were recorded at room temperature with a T64000 Horiba – Jobin Yvon spectrometer coupled to liquid nitrogen cooled CCD. The spectra were collected with the backscattering geometry, with a spectral resolution of 1 cm^{-1} and were recorded in a polarization (HH) configuration. This means that if one is staring in front of the microscope, the electric field of the incident laser light is oscillating along the left-right direction. The same type of polarization was chosen for the scattered light. The excitation sources were a He – Ne laser emitting at 632.8 nm with 35 mW or an Ar laser tuned at 488 nm with 130 mW, which corresponds to 1 or 5 mW on the surface of the samples after passing through the microscope, respectively.

A thermal lens (TL) experiment was performed in the dual beam mode-mismatched configuration. Experimental setup and TL theory can be found in previous papers [5,11]. Basically, the TL

occurs when a high power and Gaussian profile laser, known as excitation laser beam, produces a local heating in the sample that alters the refractive index. As a consequence it causes a variation of the optical path of light in the material. This variation can be detected by a second laser, called probe laser, which has its beam converged or diverged depending on the material.

The temporal evolution of the thermal lens signal I(t) is given by:

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

where $m = (\omega_p/\omega_e)^2$, $V = Z_1/Z_c$ with $Z_c \ll Z_2$. ω_p and ω_e are the radius of the waist of the probe and the excitation laser beam in the sample, respectively. $Z_c = (\pi\omega_{op}^2)/\lambda_p$ 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 detector, ω_{po}^2 is the minimum probe laser beam radius and $I(t) = I(0)$ when the transient time t or θ is zero.

In our experimental arrangement, an Argon laser at 514.5 nm was used as excitation beam and a He – Ne laser at 632.8 nm as a probe beam. The used parameters for the TL configuration were V = 1.73 and m = 21.69. The excitation and probe beam diameters at the sample were measured with a perfilometer which furnished values of $\omega_e = 41.7$ μm and $\omega_p = 192.5$ μm, respectively.

The amplitude of the thermal lens signal θ which is a measure of the phase difference between the probe beam at r = 0 and $r = 2\omega_e$ is given by:

$$\theta = \frac{P_{abs}}{K\lambda_p} \varphi \frac{ds}{dT}, \quad (2)$$

where λ_p is the probe beam wavelength, K represents the thermal conductivity, φ is the fraction of energy converted into heat and P_{abs} is the absorbed power, obtained from the relation $P_{abs} = P_{in} (1-R) [1 - \exp(-A_eL)][1 - R \exp(-A_eL)]^{-1}$. P_{in} is the input power of the excitation beam, R corresponds to the Fresnel reflectivity, A_e is the optical absorption coefficient at the excitation wavelength, L is the sample thickness and ds/dT is the temperature coefficient of the optical path length change of the sample at the probe beam wavelength. In the materials studied, we have considered $\varphi = 1$ since no luminescence was observed for the used excitation wavelength. The characteristic time constant, t_c, is related to the thermal diffusivity, D, through the following equation:

$$t_c = \frac{\omega_e^2}{4D}. \quad (3)$$

Finally, a fit of Eq. (1) is performed being t_c and θ adjustable parameters. From Eq. (3) the thermal diffusivity is calculated.

3. Results and discussion

3.1. Absorption spectra and microscope images

The incorporation of RE ions in the glass matrix can be verified by the absorption spectra as shown in Fig. 1. The emission bands centered at 380, 407, 490, 522, 545, 654 and 800 nm are attributed to the $^4I_{15/2} \rightarrow ^4G_{11/2}$, $^4I_{15/2} \rightarrow ^2H_{9/2}$, $^4I_{15/2} \rightarrow ^4F_{7/2}$, $^4I_{15/2} \rightarrow ^4H_{11/2}$, $^4I_{15/2} \rightarrow ^4S_{3/2}$, $^4I_{15/2} \rightarrow ^4F_{9/2}$ and $^4I_{15/2} \rightarrow ^4I_{9/2}$ transition of Er^{3+}, respectively. The weak absorption band at ≈ 450 nm is due to the $^4I_{15/2} \rightarrow ^4F_{3/2} + ^4F_{5/2}$ transition. An intense absorption band at ≈ 980 nm, is mainly due to the $^2F_{7/2} \rightarrow ^2F_{5/2}$ transition of Yb^{3+} ions that overlaps with the weaker $^4I_{15/2} \rightarrow ^4I_{11/2}$ transition of the Er^{3+} ions [12]. The incorporation of Tm^{3+} ions in the glass matrix can be confirmed by the band at 780 nm, corresponding to the $^3H_6 \rightarrow ^2F_2 + ^3F_3$.

Table 1
Details of the doping of the GP glasses.

Glass	Doping Species (mass fraction%)				Thermal Treatment
	Er_2O_3	Tm_2O_3	Yb_2O_3	$AgNO_3$	
GPsAg	0.5	0.25	3.0	–	420 °C/1 h
GPAg2H	0.5	0.25	3.0	3.0	420 °C/2 h
GPAg48H	0.5	0.25	3.0	3.0	420 °C/48 h