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Preparation of Nd_2O_3-doped calcium aluminosilicate glasses and thermo-optical and mechanical characterization

A. Steimacher [a,*], M.J. Barboza [a], A.M. Farias [a], O.A. Sakai [a], J.H. Rohling [a], A.C. Bento [a], M.L. Baesso [a], A.N. Medina [a,*], C.M. Lepienski [b]

[a] Departamento de Física, Universidade Estadual de Maringá – CEP 87020-900 Maringá, PR, Brazil
[b] Departamento de Física, Universidade Federal do Paraná, Centro Politécnico, CEP 81531-900 Curitiba, PR, Brazil

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ABSTRACT

The calcium aluminosilicate glass (CAS) is an important class of optical materials due to the many applications envisaged, including its use as active media for glass lasers. In order to study how Nd_2O_3 doping affects the mechanical and the thermo-optical properties of CAS glass, two series of CAS glass, doped with Nd_2O_3 up to 5 wt%, were prepared in a vacuum atmosphere. The rare earth changes the physical properties, and this influence of doping ion content is discussed for both the series of samples in terms of mechanical, thermal, and thermo-optical properties. The study analyzed hardness and elastic moduli, glass transition temperature, crystallization temperature, thermal diffusivity, specific heat, density, thermal conductivity, refractive index, and thermo-optical properties, like temperature coefficient of the optical path length (dS/dT). The results presented provide information about the sample's structure, and show that for Nd_2O_3 concentration up to 5 wt% there were no significant changes in the glass host material.
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1. Introduction

Since the first solid state laser glass was flashed by Snitzer in 1961 [1], novel glass compositions have been studied in order to improve their physical properties as active media. Interest in calcium aluminosilicate (CAS) glasses has risen due to their physical properties: high thermal conductivity, high glass transition temperature, high mechanical strength, good chemical durability, and transparency in the infrared spectrum up to 5 μm, when prepared in a vacuum atmosphere [2–6]. In a previous work, the mechanical and thermo-optical properties of several compositions of CAS glass were studied [4]. The compositions which presented the best combination of mechanical and thermo-optical properties were chosen for the first rare-earth doping. Rare earth-doped glasses have been studied and applied for several years in a variety of photonic applications, for example, as optical amplifiers and solid state lasers. Among the possible rare earth ions, Nd^{3+} was one of the most studied rare earth ions and was also one of the most efficient candidates for photonic devices [7,8]. We recently prepared and characterized two series of Nd^{3+}-doped calcium aluminosilicate glasses, prepared in a vacuum atmosphere. The first was prepared using ordinary reagent material (98–99% purity), and the second was prepared using pure reagent material (>99.9% purity). Both series were doped with high purity Nd_2O_3 (99.999%). The dopant solubility up to 5 wt%, was investigated for both the series, and the obtained samples presented blue color and no visible crystallites. This study measured density, refractive index, optical coefficient absorption, specific heat, thermal diffusivity, hardness, Young's modulus and temperature coefficient of the optical path length change. The knowledge of these properties is very important to laser systems application, because they are submitted to great temperature variations when in operation. As far as we know, this is the first report on the mechanical and thermo-optical properties of these Nd^{3+}: CAS compositions, melted under vacuum conditions.

* Corresponding authors.
E-mail addresses: steimacher@hotmail.com (A. Steimacher), medina@pq.cnpq.br (A.N. Medina).

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2. Experimental procedure

2.1. Sample preparation

The glass samples studied in this work were prepared under vacuum conditions, because it eliminates the OH absorption bands in the mid infrared range, predicted to occur between 2.8 and 4 μm, as shown in the previous work [4]. The samples were prepared from the following raw material: $CaCO_3$, Al_2O_3, MgO, SiO_2 and Nd_2O_3, in order to obtain 6 g of glasses. Two series of Nd_2O_3-doped calcium aluminosilicates were prepared using reagent grade powder with different degrees of purity. The first (1-CAS) was prepared with a common reagent powder (98–99% purity), and the second (2-CAS) was prepared with pure reagents (>99.99% purity). The calcium aluminosilicate glass batch compositions were (in wt%): 34 CaO, $(27.9 - X/2)Al_2O_3$, $(34 - X/2)$ SiO_2, 4.1 MgO, and XNd_2O_3, for samples named 1-CAS, and 35.9 CaO, $(30 - X)Al_2O_3$, 30 SiO_2, 4.1 MgO, XNd_2O_3, for samples named 2-CAS. X = 0, 0.5, 1, 2, 3, 5 for both the compositions. The compositions were melted in a vacuum atmosphere (10^{-3} atm) in graphite crucibles for 2 h at about 1500 °C. The batch was cooled down to room temperature by moving the crucible to a chamber connected to the furnace, which is also maintained at a vacuum atmosphere. In order to release the thermal stress, the samples were annealed at around 800 °C and cooled naturally, maintaining the vacuum condition. This process took about 5 h. Finally, the samples were cut and polished for optical measurements.

2.2. Characterization

The optical absorption coefficient (A_e) was measured at three thicknesses (0.7, 1.5, and 2.5 mm) for each sample concentration, using an argon laser (λ = 514 nm). The A_e was obtained from the linear coefficient of plotting values of $\ln(I/I_0)$ as a function of thickness L, where I and I_0 are the transmitted and incident intensity of light.

The refractive index (n) was measured at room temperature, using a Michelson interferometer at λ = 632.8 nm with an accuracy of ±0.01, following the method described in Ref. [9]. The samples used were about 2 mm thickness.

The glass densities (ρ) were measured by the Archimedes method, with H_2O as the immersion liquid, at room temperature, using an analytical balance. The samples used to perform the measurements were about 2 g.

The glass transition temperature (T_g), crystallization temperature (T_x), and peak temperature (T_p) were determined from the differential scanning calorimetry (DSC). The DSC was performed using a Netzsch, STA 409 PC device, under N_2 atmosphere at a constant heating rate of 10 °C/min up to 1200 °C, in an alumina crucible and using ~40 mg of mass.

Hardness (H) and Young's modulus (E) of the 1 mm thick optically polished samples were measured with a Nanoindenter XP TM machine. The maximum load used in these measurements was 400 mN; at least nine indentations were measured in order to obtain each data point.

The specific heat (C_p) measurements were performed using a thermal relaxation calorimeter with a laser beam as the heat source, as described in Ref. [10]. The samples used in these measurements were 1 mm thick with about 30 mg, in this condition the internal relaxation time is negligible.

Thermal diffusivity (D) measurements were performed using the thermal lens technique in the mismatched experimental configuration mode described elsewhere [11,12]. The excitation laser was an argon ion laser (Coherent Innova 90 Plus) at 514.5 nm and a HeNe laser as the probe beam at 632.8 nm. The samples were placed at the waist of the excitation beam and at the confocal position of the probe beam. The experiments were performed by using the time-resolved measurement method. In this procedure, the thermal lens can be used to measure the sample thermal diffusivity [11,12]. The thermal conductivity K was calculated using the relation $K = \rho C_p D$.

To determine the temperature coefficient of the optical path length change ($dS/dT = 1/L(ds/dT)$), an optical interferometric technique was used. The samples, with thickness around 4mm, were optically polished to have parallel sides. Under these conditions, the sample acted like a Fabri–Perot interferometer, and a helium–neon laser (632.8 nm) was used as light source. A slow and uniform variation of temperature was induced in the whole sample, using a temperature-controlled heater and the shift in the interference fringes pattern was monitored by a photodiode. The obtained signal was measured by a nanovoltimeter and stored in a microcomputer for posterior analysis. The experimental setup and the theory for the used interferometric technique were previously described [13]. The dS/dT values measured with this technique is given by $(dS/dT) = n\alpha + (dn/dT)$, where n is the refractive index, α is the linear thermal expansion coefficient, and (dn/dT) is the thermal coefficient of the refractive index.

3. Results

Table 1 presents the composition names and the concentration of Nd_2O_3. The first batch of the studied samples (1-CAS) was prepared using a common material to verify the doping solubility of Nd_2O_3 up to 5 wt%. In order to verify how the quality of raw material affects their physical properties, a second series with pure material was prepared. However, when the same composition was used small crystallites were verified, and then slight differences between the composition 1-CAS and second series (2-CAS) were necessary to keep the same optical quality. The composition 2-CAS was chosen from a previous work [4], and presents similar mechanical and thermo-optical properties. Both compositions chosen presented an excellent combination of their mechanical and thermo-optical properties, when compared with other silicates and phosphate glasses [4]. They also present good optical quality, without visible crystallites. Table 1 shows a summary of the optical and thermo-optical parameters measured in this work. The T_g (glass transition temperature), T_x, and T_p (onset and maximum of crystallization peak) were determined as indicated in Ref. [4]. These results and the difference $T_x - T_g$, reported by Hruby [14] as indicative of crystallization tendency, are also shown in Table 1. Table 2 presents the hardness and Young's modulus for all samples.

Fig. 1 shows the optical absorption coefficient as a function of Nd_2O_3 concentration, which presents a linear behavior up to 5 wt%.

The glass density and the refractive index as a function of Nd_2O_3 (wt%) are presented in Figs. 2 and 3, respectively. The density showed an increase with the Nd_2O_3 concentration and the same behavior was observed for the refractive index.

Fig. 4 shows the behavior of thermal diffusivity, which decreased with the increase of the Nd_2O_3. The specific heat at room temperature is shown in Fig. 5.

4. Discussion

The doping solubility of Nd_2O_3 in these CAS glasses was verified up to 5 wt% without any effect in the glass formation field. The obtained samples presented good optical quality, without visible crystallites.

The doping concentration for all samples was verified by measuring the optical absorption coefficient at 514.5 nm, which pre-

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