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Nd^{3+} doped CAS glasses: A thermo-optical and spectroscopic investigation

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ABSTRACT

Previous works have showed that calcium aluminosilicate (CAS) glasses, when prepared under vacuum conditions, are good candidates for solid state laser medium hosts and optical devices due to their appropriated thermal, optical and mechanical properties. These promising results led us to investigate the thermo-optical properties and emission spectra as a function of temperature in Nd^{3+} doped CAS glasses. Temperature changes in optical systems can cause structural modifications to the host, as well as other effects, such as emission quenching, or self-focalization. In this work, two series of CAS glasses, doped up to 5 wt.% Nd_2O_3, were prepared and characterized. Measurements of thermal coefficient of optical path length (dS/dT) and emission were performed on both series of Nd^{3+} doped CAS. In addition, measurements of optical absorption coefficient and emission lifetime were carried out. The results are discussed in terms of temperature dependence of these properties and Nd_2O_3 content. Comparisons with other glasses, such as LSCAS (low-silica calcium aluminosilicate) are also presented.

1. Introduction

Interest in calcium aluminosilicate (CAS) glasses has risen due to their appropriated 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. In a previous work [1], mechanical and thermo-optical properties of several compositions of CAS glasses were studied indicating that these glasses are promising materials for laser system optics. The compositions which have presented the best combination of mechanical and thermo-optical properties were chosen to be doped with rare-earth in this research. Rare earth doped glasses have been studied and applied for several years in a variety of photonic applications. For instance, doped glasses have been used as optical amplifiers and solid state lasers [2,3]. Indeed, Nd^{3+} is one of the most studied rare earth and also one the most efficient candidate for photonic devices [2,4–8]. Here, we prepare and characterize two series of Nd^{3+} doped calcium aluminosilicate glasses melted under vacuum atmosphere [9]. The first series was prepared using ordinary reagent material (98–99% purity), and the second using pure reagent materials (>99.9% purity), in order to study how the purity of raw materials influences luminescent properties of glasses. Both series were doped with high purity of Nd_2O_3 (99.999%). The dopant solubility is investigated up to 5 wt.% on both series. The samples obtained presented blue color and no visible crystallites. We perform measurements of optical coefficient absorption, temperature coefficient of the optical path length change, thermal expansion coefficient, emission spectra and emission lifetime. The knowledge of these properties is very important to laser systems application, because they are submitted to temperature variations when in operation mode. As far as we know, this is the first report on the thermo-optical and spectroscopy properties of Nd^{3+}:CAS compositions, melted under vacuum conditions.

2. Experimental procedure

2.1. Sample preparation

The glass samples studied in this work were prepared under vacuum conditions in order to eliminate OH^- absorption bands in the mid infrared, which is predicted to occur between 2.8 and

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Table 1
Sample compositions and concentration of Nd_2O_3.

Series	Reagent powder purity %	Composition (wt.%)	Nd_2O_3 content
1-CAS(X)	98 a 99.8	34 CaO, $(27.9-X/2)Al_2O_3$, $(34-X/2)$ SiO_2, 4.1 MgO, XNd_2O_3	$X = 0, 0.5, 1, 2, 3, 5$
2-CAS(X)	>99.99	35.9 CaO, $(30-X)Al_2O_3$, 30 SiO_2, 4.1 MgO, XNd_2O_3	$X = 0, 0.5, 1, 2, 3, 5$

Table 2
Sample name and Nd_2O_3 content, optical absorption coefficient (A_e), refractive index (n), temperature coefficient of the optical path length (dS/dT) obtained at room temperature.

Sample	Nd_2O_3 content (wt.%)	A_e (cm^{-1}) (±0.05)	n[a] (±0.006)	dS/dT (10^{-6} K^{-1}) (±0.5)
1-CAS	0	0.10	1.615	16.2
1-CAS(0.5)	0.5	0.23	1.622	–
1-CAS(1)	1	0.46	1.624	–
1-CAS(2)	2	0.82	1.634	–
1-CAS(3)	3	1.49	1.635	16.4
1-CAS(5)	5	2.35	1.659	16.4
2-CAS	0	0.05	1.609	16.4
2-CAS(0.5)	0.5	0.23	1.621	–
2-CAS(1)	1	0.46	1.616	–
2-CAS(2)	2	0.87	1.638	–
2-CAS(3)	3	1.35	1.651	16.5
2-CAS(5)	5	2.30	1.665	16.4
LSCA[a]	0	–	1.66	19.5
SiO2[a]	0	–	1.47	11.7
Phosphate[b]	–	–	1.55	15

[a] Ref. [9].
[b] Q-88 Kigre – Ref. [18].

4 μm, as shown in a previous work [9]. 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 samples with 6 g. Two series of Nd_2O_3 doped calcium aluminosilicate were prepared using reagent grade powder with different degrees of purity. The first one (1-CAS) was prepared with common reagent powder (98–99% purity), and the second one (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, XNd_2O_3, to samples named 1-CAS, and 35.9 CaO, $(30-X)Al_2O_3$, 30 SiO_2, 4.1 MgO, XNd_2O_3, to samples named 2-CAS, which $X = 0$, 0.5, 1, 2, 3, 5 to both compositions. The slightly differences between the compositions were necessary to keep the optical quality of glasses. The chosen compositions were melted under 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 vacuum atmosphere. In order to release thermal stress, the samples were annealed at around 800 °C and cooled naturally, maintaining the vacuum condition. This process takes about five hours to minimize the mechanical stress due to thermal shock. Finally, the samples were cut and polished for optical measurements.

2.2. Characterization

The refractive index was measured at room temperature by using a Michelson interferometer at 632.8 nm with an accuracy of ±0.01, following the method described in Ref. [10].

The optical transmittance spectra in the ultraviolet–visible were obtained using a UV–VIS Hitachi (U-2000) spectrophotometer. The optical absorption coefficient (A_e) was measured for each sample concentration, using an argon ion laser ($\lambda = 514.5$ nm). The A_e was obtained from the linear regression of $\ln(I/I_0)$ versus L, where I and I_0 are the transmitted and incident light intensity, respectively. Samples with different thicknesses were used (0.7, 1.5, and 2.5 mm).

To determine the thermal coefficient of the optical path length change ($dS/dT = 1/L(dS/dT)$), an optical interferometric technique was used. The experimental setup and the theory for this method is described in details in Ref. [11]. 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.

The thermal expansion coefficients (α) were obtained from interferometric technique, similar to the procedure described in Ref. [11].

The luminescence signals were measured using a monochromator (Oriel 77250, 1/8 m) coupled to a Si sensor coupled to a lock-in amplifier. The obtained curves were normalized by response curve of the Si sensor. The fluorescence decay curves were recorded with the same monochromator, a HP 54615B 500 MHz digital oscilloscope and a chopper. The samples were excited using an argon ion laser at 514.5 nm. The instrumental error of the spectrometric measurements was estimated to be 1%, although for extremely weak transitions the error may reach 5%.

For the measurements carried out as a function of the temperature, the samples were placed in a resistive furnace, whose temperature was changed using a temperature controller Lakeshore 340.

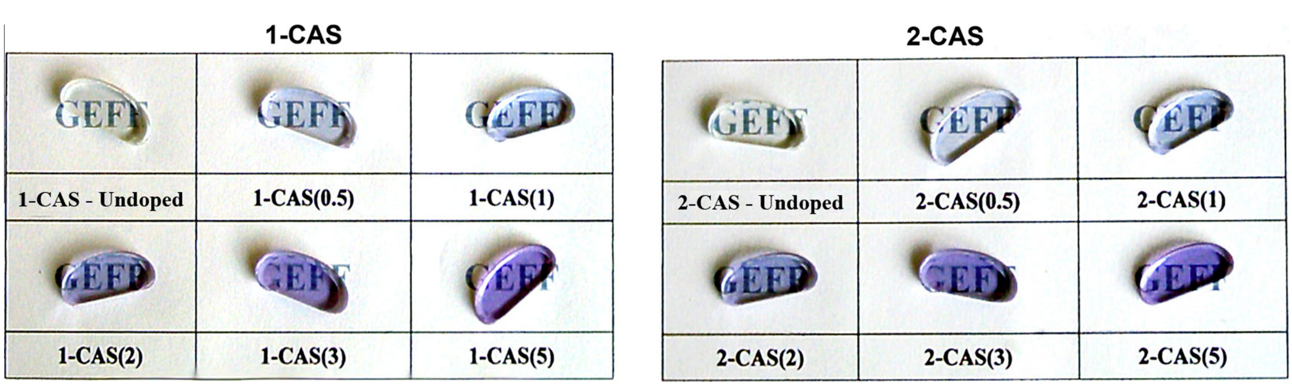

Fig. 1. Two series of Nd_2O_3 doped calcium aluminosilicate prepared using reagent grade powder with different degrees of purity.