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Thermal and structural properties of Nd_2O_3-doped calcium boroaluminate glasses

J.D.M. Dias[1], G.H.A. Melo[1,2], T.A. Lodi[1], J.O. Carvalho[1,3], P.F. Façanha Filho[1], M.J. Barboza[1], A. Steimacher[1], F. Pedrochi[1,*]

(1. Centro de Ciências Sociais, Saúde e Tecnologia, Universidade Federal do Maranhão - Imperatriz MA; 2. Instituto Federal de Educação Ciência e Tecnologia do Maranhão, Campus Imperatriz - Imperatriz – MA; 3. Instituto Federal de Educação Ciência e Tecnologia do Tocantins, Campus Araguaína - Araguaína – TO)

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Abstract: Nd^{3+} doped CaO-Al_2O-B_2O_3-CaF_2 glasses were prepared by conventional melt-quenching technique, and their structural and thermal properties were studied. The amorphous nature of these samples was confirmed by X-ray diffraction (XRD). The measured density showed an increase with Nd_2O_3 doping, at the expense of CaO. Raman spectra presented changes with addition of Nd_2O_3, which indicated that the network structure of the glasses studied presented various borate groups, such as tetraborates, metaborates, ortho-borates and pyroborates units. The N_4 values calculated from FTIR spectra revealed that incorporation of Nd_2O_3 into glass network converted the structural units from BO_4 to BO_3. From the analysis of DTA curves, we verified that T_g increased with the addition of Nd_2O_3; it was similar to the behavior caused by modifier oxides in the structure of borate glasses. Besides that, the calculated glass stability T_x–T_g for doped samples presented a decrease if compared to the undoped glass. Specific heat and thermal conductivity did not present significant changes with Nd_2O_3 concentration, up to 2.30 mol.%. The results of density, DTA, Raman and FTIR reinforced the idea that Nd_2O_3 acted as network modifier.

Keywords: Nd^{3+}; Nd^{3+} doped glass; borate glasses; glass structure; thermal properties; rare earths

Rare earth (RE) doped glasses have become an important class of optical systems due to their applicability as solid state laser, waveguide lasers and optical amplifiers[1]. In addition, glass host matrix can be produced in volumes larger than doped crystals with adequate optical quality and good emission abilities. The Nd^{3+} ion has been one of the most studied rare earth elements and also one of the most efficient candidates for photonic devices[2,3]. Nd_2O_3 doped glasses have been applied for high power laser systems, especially because of the recent achievements in diode laser pumped solid-state lasers (DPSSL) systems[4]. Although laser action of Nd^{3+} has been demonstrated in several matrices, new solid-state hosts for this ion have been continuously sought.

The calcium boroaluminate (CaBAl) glass is an important class of optical materials due to many applications envisaged, including its use as active media for solid state lasers. CaBAl glasses are materials with a good combination of thermal, mechanical and optical properties that could be exploited in many optical applications, in particular for the use as laser host materials[5–8]. Several studies concerning the explanation of the glass formation and the structure of glasses in the CaBAl system have been published[9–12]. Most of these studies focus on explaining the structural properties in terms of non-bridging oxygen (NBO) and boron coordination number[12,13] and a few studies were concerned about understanding the role of rare-earth doping in the structure of these glasses.

The present paper reported the results of a study in CaBAl glass doped with different concentrations of Nd_2O_3, aiming at understanding how the doping changes the glass structure. Density, Raman spectra, FTIR, X-ray diffraction and thermal analysis (DTA and specific heat cp) measurements were carried out. The results of this study were discussed in terms of the thermal and structural changes with the Nd_2O_3 addition.

1 Materials and methods

1.1 Sample preparation

Glass samples were prepared by the conventional melt-quenching technique and their chemical compositions are presented in Table 1. The compounds were mixed together and melted in a platinum crucible at a temperature of 1200 ºC for 2 h to homogenize the melt, in air atmosphere, and no mass loss by volatilization was verified. The melt was then poured into a preheated steel mold and annealed at the temperature of 550 ºC for 3 h, in order to minimize internal strains.

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* **Corresponding author:** F. Pedrochi (**E-mail:** fpedrochi@gmail.com; **Tel.:** +55(99)3529-6061)

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Table 1 Nominal composition (wt.% and mol.%), density, T_g, T_x, T_x–T_g, specific heat and thermal conductivity of the glass samples

S. Code	CaO		Al_2O_3		B_2O_3		CaF_2		Nd_2O_3		Density/ (g/cm^3) (±0.01)	T_g/ºC (±1.0)	T_x/ºC (±1.0)	T_x–T_g/ºC (±2.0)	C_p/(J/gK) (±0.02)	K/ (W/mK) (±0.04)
	wt.%	mol.%	wt.%	mol.%	wt.%	mol.%	wt.%	mol.%	wt.%	mol.%						
CaBAl	25	30.97	15	10.22	50	49.91	10	8.90			2.68	605	795	190	0.87	0.94
CaBAl (0.2)	24	30.05	15	10.33	50	50.43	10	8.99	1	0.2	2.69	612	783	171	0.89	0.97
CaBAl (0.6)	22	28.13	15	10.55	50	51.5	10	9.18	3	0.64	2.70	617	789	172	0.86	0.93
CaBAl (1)	20	26.13	15	10.78	50	52.62	10	9.38	5	1.09	2.73	620	802	182	0.87	0.95
CaBAl (2)	15	20.73	15	11.40	50	55.65	10	9.92	10	2.30	2.76	624	–	–	0.86	0.95
*SiO_2												1120	1215	95		
**$60GeO_2$-40PbO (mol.%)												422	570	148		
***$90TeO_2$-$5WO_3$-$5Li_2O$ (mol.%)												302	352	50		
****YalB (20)																1.03
****YAlB (Nd01)																1.03
****YAlB (Nd075)																1.03

*Ref. [15]; **Ref. [36]; ***Ref. [38]; ****Ref. [16]

1.2 Characterization

A RIGAKU Miniflex II X-ray Diffractometer (Cu Kα, λ=0.154434 nm), at the rate of 0.02 (°)/s and the variation of 2θ from 10° to 80°, was employed to confirm the amorphous/crystalline nature of the sample. The densities (ρ) of the glasses were measured by the Archimedes′ method, using distilled water as the immersion fluid, at room temperature.

Raman spectra were realized with a Trivista 557 triple spectrometer, of Princeton Instruments, operating in the subtractive configuration and equipped with a thermoelectric cooled charge couple device (CCD) detector system. The slits were set for a spectral resolution of 2 cm^{-1}. A 632.8 nm helium-neon ion laser, operating at 75 mW, was used as exciting source.

The glass transition temperatures (T_g) and crystallization temperature (T_x) were determined by differential thermal analysis, in a simultaneous DTA-TG model DTG-60 SHIMADZU. The heat process was performed from 26 to 900 ºC, in an atmosphere of nitrogen, at a rate of 10 ºC/min. Samples with mass of about 28 mg were used for all the measurements.

The FTIR spectra were recorded by an infrared spectrophotometer Bruker model Vertex 70V (Beam Spliter KBr). The samples were ground in a mortar into fine powder, mixed with KBr and pressed to form transparent pellets. The pellets were used to obtain the infrared spectra of the glasses, at room temperature, in a wavenumber range of 4000–400 cm^{-1}, with a resolution of 4 cm^{-1}.

The specific heat measurements, at room temperature, were carried out in a thermal relaxation calorimeter, with a laser beam as heat source. The theory and the experimental setup for this method were previously described by Medina et al.[14].

2 Results

The composition of the samples studied are presented in Table 1. The samples were prepared starting from CaBAl matrix composition and presented total vitrification, as confirmed by visual inspection and by XRD pattern. The glasses obtained are highly transparent, without visible crystallites and the color of the samples varies from light blue to violet with Nd_2O_3 concentration.

XRD patterns of the glass, with different concentrations of Nd_2O_3, are shown in Fig. 1. The spectra obtained for all the samples show no continuous or discrete sharp peaks, a fact that reflects the amorphous glass structure characteristic.

The behavior of the density as a function of Nd_2O_3 concentration (mol.%) can be seen in Fig. 2. The result shows a linear increase with Nd_2O_3 addition, which indicates a structural modification in the network due to incorporation of the rare earth ions.

Fig. 3(a) and (b), shows the Raman spectra of the undoped and Nd_2O_3 doped CaBAl glasses, which present the following bands: ~534, ~662, ~761, ~896, ~969, ~1250, ~1362, ~1507 cm^{-1}. The band positions (centers)

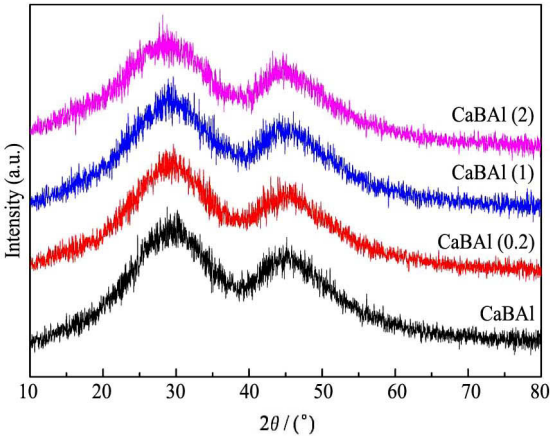

Fig. 1 XRD spectra of CaBAl glasses