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Citation: *J. Appl. Phys.* **85**, 8112 (1999); doi: 10.1063/1.370649

View online: <http://dx.doi.org/10.1063/1.370649>

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Nd₂O₃ doped low silica calcium aluminosilicate glasses: Thermomechanical properties

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(Received 14 September; accepted for publication 24 November 1998)

The effects of Nd₂O₃ doping on the thermal and mechanical properties of vacuum melted, low silica, calcium aluminosilicate glasses are presented. For the doped glasses, the vitrification limit was found to correspond to a maximum load of 5 wt % Nd₂O₃. The influence of the rare earth doping on the thermal diffusivity, thermal conductivity, and Vickers hardness was such that all these physical parameters decreased by roughly the same amount, namely 8%, between the undoped and the 5 wt % doped sample. The dependence of these parameters, as a function of the Nd₂O₃ doping, strongly supports the idea that the Nd³⁺ act as network modifiers. © 1999 American Institute of Physics. [S0021-8979(99)04705-2]

INTRODUCTION

Despite the fact that the glass-forming ability of calcium aluminate has been known since 1909,¹ and that the highly refractory nature, excellent chemical durability, and high infrared transmission of these silica-free or low silica glasses were also known since the late 1950s,²⁻⁴ interest in this family of glasses has only recently gained considerable attention. Most of the papers dealing with low silica calcium aluminosilicate glasses were concerned, up to recently, with expanding the glass-forming field of these materials. It has been shown,^{5,6} for instance, that the addition of small amounts of silica^{5,6} or barium oxide³ to the base composition of calcium aluminate increases the glass-forming region in the phase diagram, without significantly affecting their infrared transmission. Furthermore, samples melted under vacuum conditions exhibit excellent transmission in the infrared spectral range up to 6 μm ,⁵⁻⁷ and phonon energies on the order of 800 cm^{-1} , which is lower than that of silicate glasses typically,^{8,9} on the order of 1000 cm^{-1} .

The combination of these properties renders this class of glass of great potential for many optical applications, in particular, as a glass laser host material.¹⁰ Although 37 years have passed since the advent of the glass laser, the search for new laser glasses continues with increasing interest. All glass lasers to date have used trivalent lanthanides as the active ions. Neodymium-doped glasses are by far the most thoroughly investigated and have the largest experimental database. As to the host glass, fluorides, phosphates, and silicates glasses have been used, with the phosphates being the most

widely used for bulk laser glasses. Despite their great potential as host glass for laser applications, only recently has interest in the investigation of low silica calcium aluminosilicate glasses doped with rare-earth elements attracted the attention of a number of researchers.^{8,11-15} In particular, it has been shown^{11,12} that vacuum melted low silica calcium aluminosilicate glasses doped with Nd₂O₃ with concentrations up to 5 wt % exhibit high quantum efficiencies.

In this paper, we report on the changes in the thermal properties, density and hardness of vacuum melted, low silica, calcium aluminosilicate glasses induced by the addition of varying concentrations of Nd₂O₃ to the base composition. As is well known, rare earth doping induces structural changes in the host glass.^{16,17} It is of utmost importance to know the dependence of the thermal and mechanical properties as a function of the doping concentration, especially for the eventual device applications.

EXPERIMENT

The glass samples were prepared from reagent grade CaCO₃, Al₂O₃, MgO, SiO₂ and Nd₂O₃ with the following compositions (in wt %): 47.4 CaO, (41.5 - x) Al₂O₃, 7.0 SiO₂, 4.1 MgO, x Nd₂O₃, where $x = 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5$, and 5.0. The batches were melted in 15 g quantities under vacuum (10^{-3} atm) in graphite crucibles for approximately 2 h at 1500 °C. After switching off the heater, the crucible was moved 60 cm upward to a cooled chamber and allowed to cool to room temperature. The samples obtained were cut in two different shapes: 3 mm thick disks 10 mm in diameter, with optical finishing, for refractive index, microhardness and thermal lens measurements, and 2 mm thick disks 6 mm in diameter for specific heat measurements.

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FIG. 1. Thermal lens experimental setup.

X-ray diffraction and optical microscopy showed that this sample preparation procedure resulted in amorphous, homogeneous, bubble-free transparent glasses with no evidence of devitrification. For the current base composition, the vitrification limit was found to correspond to a maximum Nd_2O_3 doping concentration of 5 wt %. The doping concentrations in our samples were checked by measuring the optical absorption coefficient at the peak absorption band centered at 590 nm. We have also carried out infrared transmission measurements to determine whether the OH absorption has been eliminated by the vacuum melting procedure. As additional complementary information on the eventual changes induced by the neodymium oxide doping, we have measured the refractive index of all samples investigated using an Abbe refractometer at the sodium D line, as well as the glass transition temperature T_g , using 150 mg samples in a simultaneous thermal analyzer (Netzsch, STA 409-EP).

The density was measured at room temperature using the buoyancy method based on Archimede's principle with CCl_4 as the immersion liquid, whereas the Vickers hardness was measured using a Leitz Wetzlar microhardness tester. In order to minimize the experimental errors, the hardness measurements were carried out using loads of 25, 50, 100, 200, and 300 g. The thermal properties were measured using a

conventional calorimeter for the specific heat measurements, and the thermal lens technique^{18,19} for the thermal diffusivity measurements. This technique, whose setup is schematically shown in Fig. 1, has been proven to be a reliable technique for the thermal diffusivity measurements, especially for optically transparent samples. The thermal lens technique is a noncontact technique, which uses an excitation laser to heat the sample and a probe laser beam to sense the changes of the optical path as it crosses the heated region of the sample. We used an argon ion laser (Coherent Innova 90 Plus) at 514.5 nm as the excitation laser and a 20 mW He-Ne laser (Uniphase) as the probe beam. The sample was placed at the waist of the excitation beam at a confocal position of the probe beam. The thermal lens effect is induced as a result of the temperature rise within the sample due to nonradiative de-excitation processes, following the absorption of the excitation laser beam energy. As a result of this temperature rise within the excitation beam waist region, the optical path in this region will vary proportionally to this temperature shift due to the changes of the refractive index with temperature. The resulting change in the optical path produces a lenslike optical element within the sample, which is monitored by measuring the changes of the probe laser beam intensity as it crosses this heated region. We refer to Refs. 18 and 19 for a more detailed discussion on this technique. It has been well established that by measuring the buildup of the thermal lens within the sample, the sample thermal diffusivity can be accurately determined.

RESULTS AND DISCUSSION

The results of our measurements for the mass density, hardness, thermal diffusivity, and specific heat are summarized in Table I. The change of the density as a function of the Nd_2O_3 content is shown in Fig. 2. The solid curve in Fig. 2 corresponds to the data fitting to a rising logistic curve, namely,

$$\rho = \rho_0 + \Delta\rho e^{(x-x_0)/\Delta x} / (1 + e^{(x-x_0)/\Delta x}), \quad (1)$$

where ρ_0 denotes the undoped glass density, $\Delta\rho$ is the excursion of the glass density in going to its saturation value, x_0 denotes the Nd_2O_3 concentration at which the density

TABLE I. Measured values of the physical parameters of our calcium aluminosilicate glass samples, as a function of the Nd_2O_3 doping concentration.

Nd_2O_3 doping concentration (wt %)	ρ (g/cm ³)	H (kg/mm ²)	α (10 ⁻³ cm ² /s)	c (J/gK)	κ (mW/cmK)
0.0	2.928±0.002	865±25	5.69±0.05	0.929±0.007	15.48±0.31
0.5	2.936±0.002	862±25	5.63±0.05	0.923±0.007	15.25±0.30
1.0	2.959±0.002	851±19	5.67±0.11	0.929±0.007	15.59±0.43
1.5	2.973±0.002	847±16	5.65±0.09	0.920±0.007	15.45±0.38
2.0	2.979±0.002	832±20	5.55±0.04	0.928±0.007	15.34±0.31
2.5	2.998±0.002	824±21	5.44±0.04	0.916±0.007	14.94±0.30
3.0	2.999±0.002	819±22	5.55±0.04	0.926±0.007	15.41±0.31
3.5	3.017±0.002	815±22	5.44±0.03	0.911±0.007	14.95±0.30
4.0	3.024±0.002	804±20	5.39±0.03	0.914±0.007	14.90±0.30
4.5	3.012±0.002	800±16	5.36±0.03	0.915±0.007	14.77±0.29
5.0	3.008±0.002	798±22	5.22±0.03	0.913±0.007	14.33±0.29

FIG. 2. Mass density as a function of the Nd_2O_3 content.

value reaches half way to its excursion to saturation, and Δx corresponds to the range of doping concentration within which the jump to saturation occurs. In carrying on the data fitting we have left ρ_0 , $\Delta\rho$, x_0 , and Δx as fitting parameters. The logistic curve is a type of an S-shaped curve describing processes in which a given quantity, say f , evolves from an initial state into a final saturation state f_s such that its rate of change $\partial f/\partial x$ is proportional to the product of its actual value times the space left to reach its saturation value, namely $\partial f/\partial x \propto f(f_s - f)$. Our density data as a function of the doping concentration exhibit the two basic aspects of a logistic type of behavior. First, it closely follows an S-shape curve and second, there is an upper bound on the doping concentration which can be added to the base composition without devitrification, namely, 5 wt %. The increase in the density of the glasses with neodymium content can be explained by simply considering the relative masses of the rare-earth ions in comparison with those of the other ions in the glasses, assuming that no significant increase in specific volume takes place.

Figure 3 shows the dependence of Vickers hardness on the neodymium oxide content. The solid curve in this figure corresponds to the data fitting to a decreasing logistic curve of the following type:

$$H = H_s + \Delta H / (1 + e^{(x-x_0)/\Delta x}), \quad (2)$$

where, similarly to the case of the density data fitting, x denotes the neodymium oxide concentration, H_s is the saturation hardness value at the high doping limit, and ΔH represents the excursion of the glass hardness in going from the undoped to the highly doped region. The overall decrease in the glass hardness was on the order of 8%. This behavior of the hardness of our calcium aluminosilicate glasses as a function of the rare-earth doping may be explained as follows. As discussed in previous works^{6,16,17,20-22} on the ternary system $\text{Al}_2\text{O}_3\text{--CaO--SiO}_2$ and in the case $\text{Al}_2\text{O}_3\text{--CaO--MgO--SiO}_2$, the short-range structure of these glasses consists of a network based on a tetrahedral coordination in which there are Al–O–Si bonds and $(\text{AlO}_4)^-$ tet-

FIG. 3. Vickers hardness as a function of the Nd_2O_3 content.

rahedra associated with Ca^{2+} ions. The decrease of hardness as the rare-earth content increases may be explained by assuming that the rare-earth ions disrupt the tetrahedral network, thereby decreasing the network connectivity. Network modifiers inducing nonbridging oxygen are associated with the decrease of the network connectivity.⁶ This presence of nonbridging oxygen and the resulting decrease of the network connectivity has two implications, namely, a decrease in T_g and an increase in the refractive index as the concentration of nonbridging oxygen increases. As discussed in Ref 23, by increasing the concentration of nonbridging oxygen in the glass structure, the polarizability of the oxygen ions increases, causing an increase in the refractive index. The overall increase of the refractive index we have found, between the undoped and the 5 wt % doped sample, was on the order of 0.004. Even though the changes in the refractive

FIG. 4. Correlation between the sample hardness and density for the Nd_2O_3 doped calcium aluminosilicate glass. The data linear regression is represented by the solid line.

FIG. 5. Correlation between (a) the glass transition temperature and the sample specific volume, and between (b) the glass transition temperature and the sample hardness, for the Nd_2O_3 doped calcium aluminosilicate glass. The data linear regressions are represented by the solid lines.

index we have found are smaller than those reported⁶ for the ternary system Al_2O_3 – CaO – SiO_2 when varying the SiO_2 content, it nevertheless indicates the tendency of n_D to increase on increasing the neodymium oxide concentration. In contrast, the behavior of T_g was such that it decreased roughly 41 K on increasing the Nd^{3+} concentration suggesting, accordingly, that the role of the Nd^{3+} ions seems to be that of disrupting the tetrahedral network characteristic of the low silica, calcium aluminosilicate glasses. Here we note that in the case of silica-free calcium aluminate a 12 K decrease in T_g has been observed⁶ as the ratio $\text{CaO}/\text{Al}_2\text{O}_3$ increases from 1.34 to 1.8. This network modifier role of the Nd^{3+} ions also reflects on the molar volume of the glass. The replacement of Al_2O_3 by Nd_2O_3 is expected to increase the molar volume due to both the decrease of the glass connectivity as well as to the larger size of the rare-earth ions. We should, accordingly, expect that the changes in both hardness and density as a function of the doping concentration will be correlated. This is, indeed, what we have found for the

FIG. 6. Time evolution of the thermal lens signal for the 4 wt % Nd_2O_3 doped sample. The solid curve represents the data best fitting to Eq. (3).

present system as shown in Fig. 4, in which we plot the hardness against the glass density. The solid curve in Fig. 4 represents the data linear regression. This result indicates that the changes in the glass network induced by the Nd^{3+} doping affect the sample's hardness and density in a similar manner. A closer comparison between the T_g data with those of H and ρ shows us that the correlation among these physical properties is of a more general character. This aspect is quite evident in Figs. 5(a) and 5(b) in which we plot the correlation between T_g and the specific volume, and between T_g and the sample hardness, respectively.

In Fig. 6 we show a typical thermal lens signal from which the thermal diffusivity was obtained. The data in this figure correspond to the intensity of the probe beam sensed by the photodetector, for the 4.0 wt % Nd_2O_3 doped sample. The solid curve in Fig. 6 corresponds to the data fitting to the theoretical expression for the thermal lens signal,^{18,19} as given by the probe beam intensity $I(t)$, namely,

FIG. 7. Thermal diffusivity as a function of the Nd_2O_3 content.

FIG. 8. Specific heat as a function of the Nd_2O_3 content.

$$I(t) = I(0) \{1 - \theta/2 \tan^{-1}[2mv/(1 + 2m + v^2 + \gamma t_c/2t)]\}^2, \quad (3)$$

where

$$m = (\omega_p/\omega_e)^2; \quad v = Z_1/Z_c; \quad t_c = \omega_e^2/4\alpha;$$

$$\gamma = [(1 + 2m)^2 + v^2]$$

and

$$\theta = -[(P_e A_e l_0)/\kappa \lambda_p] \partial s / \partial T.$$

Here, ω_p/ω_e is the ratio of the probe beam and excitation beam spot sizes in the sample position, Z_1 is the distance between the probe beam waist and the sample, Z_c is the confocal distance of the beam probe, P_e is the excitation laser power, A_e is the sample optical absorption coefficient at the excitation wavelength, l_0 is the sample thickness, κ is the

FIG. 9. Correlation between the sample hardness and thermal diffusivity for the Nd_2O_3 doped calcium aluminosilicate glass. The solid line represents the data linear regression. FIG. 10. Thermal conductivity, as obtained from the measured values of the thermal diffusivity, specific heat, and mass density, as a function of the Nd_2O_3 content. The solid curve represents the theoretical curve obtained from the fitted expressions for α , ρ , and c .

sample thermal conductivity, λ_p is the probe beam wavelength, ω_e is the excitation beam radius, $\alpha = \kappa/\rho c$ is the sample thermal diffusivity and c is its specific heat. The term $\partial s/\partial T$ in the expression for θ denotes the rate of change of the optical path within the sample with the temperature. The thermal diffusivity α is obtained from the thermal lens signal buildup by fitting the experimental data to Eq. (3). From the value of $t_c = \omega_e^2/4\alpha$, one readily gets α . For the case of the 4.0 wt % Nd_2O_3 doped sample shown in Fig. 6, the thermal diffusivity was found to be $\alpha = 5.69 \times 10^{-3} \text{ cm}^2/\text{s}$. In Fig. 7, we plot the thermal diffusivity data as a function of the Nd_2O_3 content. Figure 7 shows that the thermal diffusivity decreases as Nd_2O_3 replaces Al_2O_3 , changing from $5.69 \times 10^{-3} \text{ cm}^2/\text{s}$ for the undoped sample to $5.22 \times 10^{-3} \text{ cm}^2/\text{s}$ for the 5.0 wt % Nd_2O_3 doped one. Next, we show in Fig. 8 the variation of the specific heat with the Nd_2O_3 content. We note from Figs. 7 and 8 that both the thermal diffusivity and the specific heat decrease with increasing Nd_2O_3 content, similarly to the behavior of the sample hardness presented in Fig. 3. Accordingly, we have fitted the data shown in Figs. 7 and 8 to a decreasing logistic function [c.f., Eq. (2)] as in the case of the hardness measurements. The result of these data fittings is represented in Figs. 7 and 8 by the corresponding solid curves. In particular, we note that the observed decrease of the thermal diffusivity in Fig. 7 was also on the order of 8%, similar to the decrease observed in the hardness measurements. This apparent correlation between the changes of α and H is more evident in Fig. 9, in which we plot the values of hardness versus the samples' thermal diffusivity. The solid line in Fig. 9 represents the result of data linear regression.

The above correlation between α and H is not as surprising as it may look at a first glance. The thermal diffusivity measures essentially the thermalization time within the sample and, like the optical absorption coefficient, it is unique for each material. This can be appreciated from the tabulated values of α presented by Touloukian *et al.*²⁴ for a

TABLE II. Comparison of the physical parameters of our base composition calcium aluminosilicate (CA) glass, as reported in the present work, with those of some common optical quality glasses. The values of the physical parameters for the common optical glasses quoted above were taken from Ref. 27.

Glass	ρ (g/cm ³)	c (J/gK)	κ (mW/cm K)	α (cm ² /s)	T_g (K)	H (kg/mm ²)	n_D
CA	2.93	0.929	15.48	0.0057	1114	865 ^a	1.6555
BK-7	2.51	0.858	11.14	0.0052	836	520 ^b	1.5168
Pyrex	2.23	1.05	11.3	0.0048	560	481 ^b	1.474
Fused silica	2.20	0.746	13.8	0.0084	1273	635 ^b	1.4586

^aVickers hardness value.

^bKnoop hardness value.

wide range of materials. Furthermore, the thermal diffusivity is extremely dependent upon the effects of compositional and microstructural variables²⁵ as well as processing conditions. In a previous work²⁶ on silicate glasses doped with Fe₂O₃, we have shown that there are two distinct situations in which the doping controls the behavior of the thermal diffusivity. When the Fe³⁺ ions behave as a network former, the sample thermal diffusivity becomes greater than that of the undoped sample, while when they behave as a network modifier the thermal diffusivity decreases with increasing doping concentration. Thus, the decrease of the thermal diffusivity with increasing Nd₂O₃ concentration shown in Fig. 7 may be explained as resulting from the network modifier character of the Nd³⁺ ions in our calcium aluminate glasses. The decrease in the network connectivity due to the presence of rare-earth ions induces additional thermal barriers in the glass structure, thereby decreasing the heat diffusion through the sample. This explanation is also consistent with the behavior of the sample hardness, and is reflected in the apparently good correlation we have found between α and H shown in Fig. 9. Finally, in Fig. 10, we show the behavior of the thermal conductivity κ as a function of the Nd₂O₃ content. The thermal conductivity data shown in Fig. 10 were calculated from the measured values of α , ρ , and c , namely, $\kappa = \alpha \rho c$. The dependence of κ on the Nd₂O₃ content follows closely those we have found for α and H . In fact, all three parameters exhibited a decrease of roughly the same order, namely 8%, between the undoped and the 5% doped sample. The solid line in Fig. 10 represents the theoretical curve for κ obtained using the fitted expressions for α , ρ , and c . This result suggests that the logistic behavior we have used for the description of the different data dependence on the doping concentration is, indeed, a reasonable assumption. The reason for this is that this curve describes processes involving the transition from an initial state into a final saturation state in a smooth continuous manner.

To conclude, we present in Table II a comparison between the thermal properties of our base composition calcium aluminosilicate (CA) glass with those of some common optical quality glasses. For instance, as compared with fused silica, our calcium aluminosilicate exhibits a 33% larger density, 36% larger hardness, and a 12% larger thermal conduc-

CONCLUSION

In this paper we have investigated the effects of the replacement of Al₂O₃ by Nd₂O₃ on the thermomechanical properties of low silica calcium aluminosilicate glasses. The maximum Nd₂O₃ that our base composition would accept without devitrification was found to be 5 wt %. The influence of the rare-earth doping on the thermal diffusivity, thermal conductivity, and hardness, all pointed in the same direction, namely, a decrease of roughly 8% as we move from the undoped to the 5 wt % doped sample. This result strongly supports the idea that the Nd³⁺ ions act as network modifiers, similar to the cases reported for other oxide glasses. This explanation for the role played by the rare-earth ions seems to be further supported by complementary thermal analysis measurements on our samples in which a decrease of T_g was observed with increasing doping concentration. We have also found that the observed change of the sample hardness, as a function of the Nd₂O₃ content, is linearly correlated with the changes of the thermal diffusivity, the glass transition temperature, and the sample mass density.

ACKNOWLEDGMENTS

The authors are grateful to Brazilian Agencies CNPq, CAPES and FAPESP for partial financial support of this work.

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