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Preparation and spectral properties of Nd_2O_3-doped silica-based glasses prepared by the sol–gel process

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Abstract

The characteristics of gels and the spectral-luminescence of Nd_2O_3-doped SiO_2 and Al_2O_3-SiO_2 gel-glasses have been studied. By dipping the gel into CCl_4 solution followed by heat treatment, the hydroxyl levels in the glass could be reduced to below 10 ppm. The fluorescence spectra for sol–gel-derived Nd_2O_3-doped SiO_2 and Al_2O_3-SiO_2 glasses show that the peak position shifts from 1.082 μm (in the Nd_2O_3-doped SiO_2 glass) to 1.061 μm (in the Nd_2O_3-doped Al_2O_3-SiO_2 glass).

Keywords: A. Sol–gel processes; D. Glass; Rare-earth; Spectra; Luminescence

1. Introduction

Rare-earth-doped glasses [1–7] and planar waveguides [8–14] have begun to arouse considerable interest owing to their potential applications in lasers and amplifiers. Increasing the rare-earth concentration permits the fabrication of short and compact optical amplifiers. However, high doping levels of rare-earths quench the fluorescent emission and reduce the performance. The sol-gel process is a good method for producing rare-earth-doped glasses and planar waveguides for integrated optical components [1–6, 11–14]. The interest in the use of sol–gel methods is due to several advantages: processing temperatures lower than those used in traditional melt glass techniques, good homogeneity, ease of composition control, and low equipment cost.

Silica glass has many favorable properties for uses in high-power glass lasers, such as: (1) a broad transmission range from ultraviolet to infrared, (2) a low nonlinear index of refraction, and (3) a low coefficient of thermal expansion. With the sol–gel process, the shortcomings of the silica host, such as the rather high processing temperature and low solubility of neodymium oxide can be overcome. The processing temperature is higher than 1600 °C in the traditional melt glass techniques [15,16].

Nd_2O_3-doped fused silica prepared by conventional melting demonstrates lasing action but only at neodymium levels of less than 0.1 mol% [17]. At higher levels, nce is quenched as a result of clustering of the Nd_2O_3 in the silica matrix. It was found that the addition of a third component, such as Al_2O_3, served to disperse the Nd_2O_3 and lasing action was observed at 1 mol% Nd_2O_3 [14].

It is well known that the presence of OH groups can quench neodymium luminescence [7] and the high residual OH concentration in a glass must be the cause of the low quantum yields [7]. In the sol–gel process, the removal method for the OH groups in the gel is very important in order to obtain high quantum yields. The present work aims to describe the preparation methods, especially for removal the OH groups from the gel, and the transmission and fluorescence spectra of Nd_2O_3-doped SiO_2 and Al_2O_3-SiO_2 glass prepared by the sol–gel process.

2. Experimental procedure

Tetraethyl orthosilicate $Si(OC_2H_5)_4$ (TEOS purity $\geqslant$ 99%, Shanghai Chemical Reagent Co.) and aluminum iso-propoxide $Al(C_3H_7O)_3$ (purity $\geqslant$ 98%, Shanghai

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Chemical Reagent Co.) was mixed with ethanol, deionized water, and several drops of HNO_3 to bring the pH to 2. (TEOS + $Al(C_3H_7O)_3$):ethanol:deionized water: HNO_3 = 1:4:4:0.05 in molar ratio). The solution was refluxed at 70 °C for 60 min in a 3-neck flask. In a separate 100 ml beaker, neodymium nitrate ($Nd(NO_3)_3$ $5H_2O$, purity ⩾ 99.5%, Shanghai Chemical Reagent Co.) was dissolved in deionized water ($Nd(NO_3)_3$ $5H_2O$: H_2O = 1:10 in molar ratio), after which the two solutions were mixed in a 250 ml beaker and stirred using a magnetic stirrer for 30 min. This sol was cast into 60 mm petri dishes, where it was allowed to gel and age at room temperature over a period of ~60 h. The wet gel was dried at 120 °C in a controlled-temperature oven for 100 h and then a transparent gel monolith was obtained. Samples containing silica with Nd_2O_3 levels of 1.0 mol%, 2.0 mol%, and 3.0 mol% were prepared. All the sol-gel samples were transparent, reddish purple, and monolithic after processing except those heated to 1100 °C and above, which became white and opaque with the onset of foaming.

The following method was used to remove the OH groups. The gels were dipped into CCl_4 solution (purity ⩾ 99%, Shanghai Chemical Reagent Co.) for 2 h. Heat treatment (1 °C /min) at 900 °C was carried out in a tube furnace under flowing (~12 cm^3/min) instrument-grade oxygen, followed by cooling to room temperature at 10 °C/min. The CCl_4 solution was able to penetrate into the pores and produced the following reaction:

$$CCl_4 + 2H_2O \rightarrow 4HCl\uparrow + CO_2\uparrow$$

The bulk density of the samples was obtained by the hydrostatic weighing method using ethanol as the bouyant fluid. The bulk density was taken as the average of at least three measurements. The shrinkage of the samples was determined by measuring the diameter of the sample before and after heat treatment at each of the selected temperatures. The specific surface area and total pore volume of the sol–gel monoliths were measured using an ASAP 2010 Nitrogen System from Maiker Corporation; alumina was used as the reference. The results were analyzed according to the BET theory. In order to observe the existence of neodymium oxide aggregation in the silica matrix, transmission electron microscopy (TEM) was carried out on a sample using a JEM-200CX from the Hitachi Corporation. The samples were prepared as follows. A Pt meshwork was dipped into the solution two times, followed by processing of the gel and heat treatment as for the monolithic samples. The phase structure of the gel heat treated at 900 °C was observed with a Rigaku K/max 2400 type diffractometer with CuKα radiation, operated at 60 kV and 100 mA. The scans covered the range 10–70° 2θ, with a step size of 0.02° and a scanning speed of 5°/min. The optical transmission spectra measurements of the sol–gel samples were carried out using a Shimadzu Co. UV-VIS-IR-365 spectrophotometer at normal incidence with a fused-quartz glass substrate inserted into the reference beam path of the spectrophotometer.

3. Results and discussion

3.1. Gel characteristics

Fig. 1 shows the bulk density of the samples and the diametral shrinkage versus heat treatment temperature. The characteristics of gels versus heat-treatment temperature are shown in Table 1. As the gels were heated, the specific surface area and total pore volume decreased while the bulk density and the shrinkage of the samples increased. This change occurred slowly until the temperature reached 800 °C, at which point it changed much more quickly as the pore volume and specific surface area decreased. During the heat treatment, the gels appeared to be resistant to cracking and/or crazing. The structure of all of the gels heat treated at 900 °C for 2 h was amorphous to X-ray diffraction.

TEM of a sample on the edge of the Pt meshwork revealed the existence of neodymium oxide aggregation in the silica matrix. This clustering alteration was observed in the Nd_2O_3-doped Al_2O_3-SiO_2 glass. Thus, the addition of Al_2O_3 did not eliminate Nd_2O_3 clusters.

3.2. OH content of Nd_2O_3-doped silica glass

The OH content of the Nd_2O_3-doped silica glass samples was calculated from infrared transmission spectra using the "baseline absorbance method" as described previously in [15], i.e.

$$[OH](ppm) = (1000/t)\log(T_a/T_b)$$

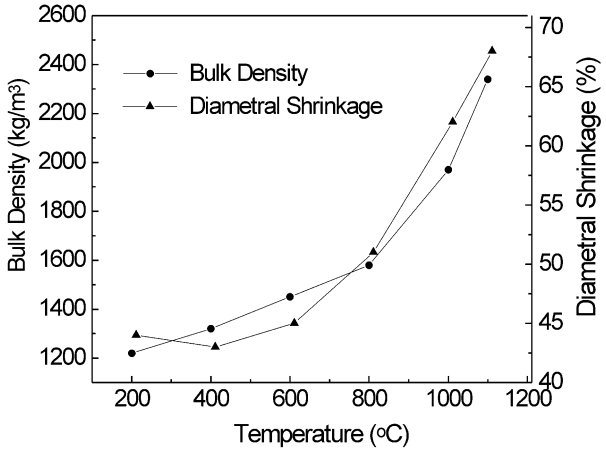

Fig. 1. Sample bulk density and average diametral shrinkage vs. heat treatment temperature.

where t = sample thickness (mm); T_a = transmission at 2.60 μm; and T_b = transmission at 2.73 μm.

Based on the transmittance intensity of the infrared spectra at 2.60 and 2.73 μm (as shown in Fig. 2), the OH content in the glasses was calculated.

The infrared transmission spectra for a 1.0 mol% Nd_2O_3-99.0 mol% SiO_2 glass are presented in Fig. 2. Curve a shows the transmission spectrum for a gel that was dipped into CCl_4 solution for 2 h and then heat treated at 900 °C for 2 h in O_2. Curve b shows the spectrum for a sample of similar thickness (~2.4 mm) heat treated identically but without dipping in CCl_4. According to the equation, curves a and b give OH contents of ~10 and 150 ppm, respectively. Thus, it can be concluded that treatment with CCl_4 is effective in reducing the OH level.

3.3. Transmission spectroscopy

Figs. 3 and 4 show the transmission spectra of 1.0 and 2.0 mol% Nd_2O_3-doped silica, respectively. The gel was oxidized of organic residues and dehydration of the gel occurred with increasing heat treatment temperature, but the neodymium nitrate was decomposed and the neodymium oxide formed clusters or aggregates due to the solubility limit. Pope and Mackenzie [18] indicated that, for a 5% weight neodymia-silica gel composition, the peak position representing the $^4I_{9/2}$ to $^4F_{5/2}$ transition shifted from 794 to 806 nm as treatment temperature increased. This peak position was 794 nm for the dried porous gel; for the dense glass, this peak position shifted to the higher wavelength of 806 nm. In the present work, the transmission peak was 807nm for the gel heat treated at 900 °C for 2 h in O_2. The 806 nm peak corresponds to the $^4I_{9/2}$ to $^4F_{5/2}$ transition [18]. It is assured that the peak at 794 nm shifted to the higher wavelength upon densification.

Table 1
Characteristics of Nd_2O_3-doped SiO_2 glass vs. heat treatment temperature

Heat treatment temperature (°C)	Specific surface area (m^3/g)	Total pore volume (cm^3/g)
200	841	0.632
400	784	0.526
700	668	0.426
900	437	0.287

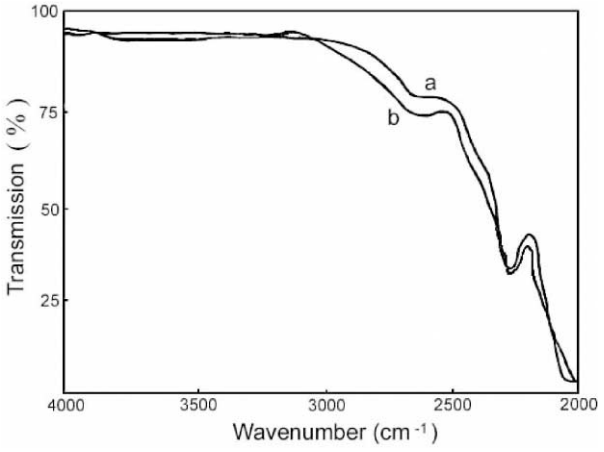

Fig. 2. Infrared transmission spectra for samples processed (a) with dipping into CCl_4 solution; (b) Without dipping into CCl_4 solution.

3.4. Fluorescence spectroscopy

The fluorescence spectra of the 2.0 mol% Nd_2O_3-doped silica glass and Nd_2O_3-doped Al_2O_3-SiO_2 glass

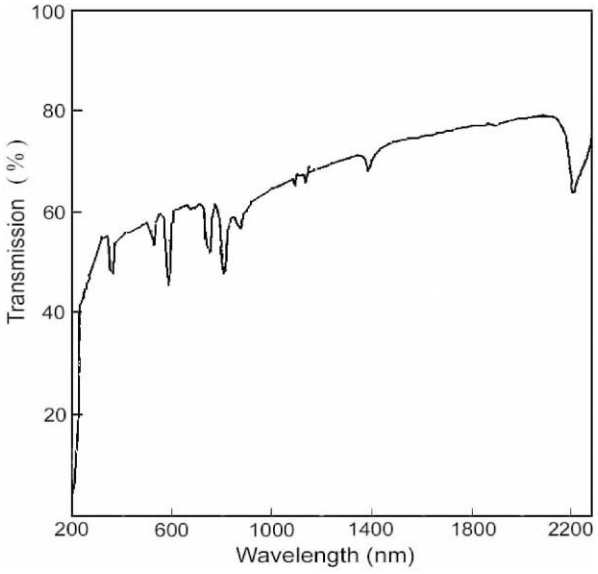

Fig. 3. Transmission spectrum of 1.0 mol% Nd_2O_3–99.0 mol% SiO_2 glass.

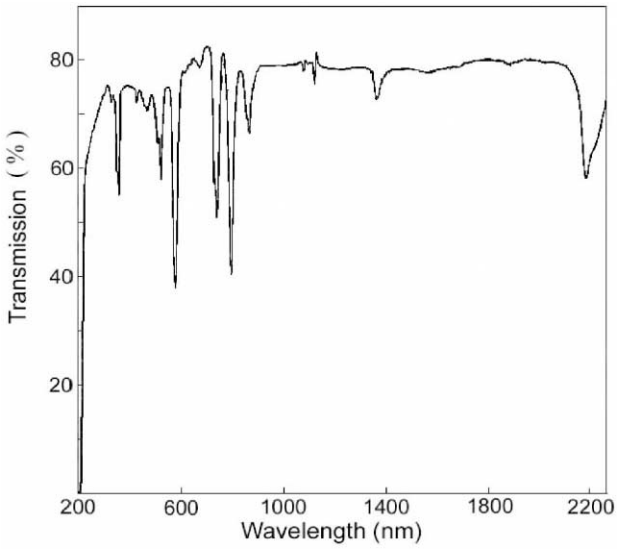

Fig. 4. Transmission spectrum of 2.0 mol% Nd_2O_3–98.0 mol% SiO_2 glass.

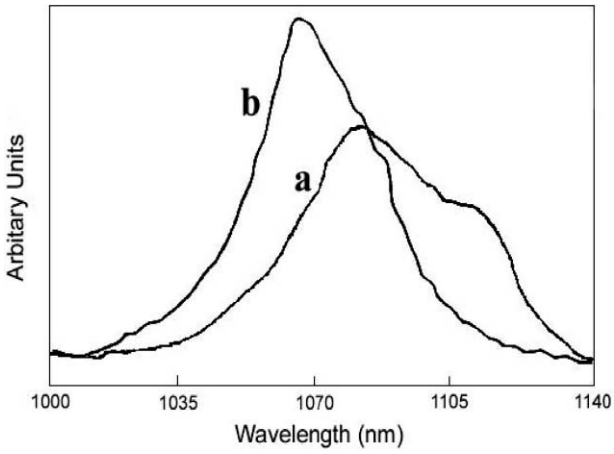

Fig. 5. Fluorescence spectra of (a) 2.0 mol% Nd_2O_3–98.0 mol% SiO_2 glass and (b) 2.0 mol% Nd_2O_3–2.0 mol% Al_2O_3–96.0 mol% SiO_2 glass.

are shown in Fig. 5. The fluorescence peak position was 1.082 μm for the Nd-doped silica glass (curve a), while it was 1.061 μm for the Nd_2O_3-Al_2O_3-SiO_2 glass (curve b). The spectra show maximal emission near 1.07 μm due to the $^4F_{3/2}$-$^4I_{11/2}$ lasing transition. This observation is in agreement with the fluorescence peak positions measured for Nd_2O_3-doped silica glass prepared by conventional processing methods containing lower doping levels of neodymium [19].

The fluorescence peak position is affected by the local environment surrounding the neodymium ion in a glass or crystalline host. The local environment of the neodymium ion in pure silica is unique and different from that in the Al_2O_3-SiO_2 glass host. It is evident that the variation in sol–gel composition does not eliminate the problem of clustering of Nd_2O_3. The shift in the fluorescence spectrum of Nd_2O_3-doped silica glass to a lower wavelength with respect to Nd_2O_3-doped Al_2O_3-SiO_2 glass suggests that the initial structure of the double metal alkoxide was retained until the glassy state was obtained [6]. This explanation requires rigorous experimental verification.

4. Conclusions

The Nd_2O_3-doped silica glass and Nd_2O_3-doped Al_2O_3-SiO_2 glass were prepared by a sol–gel process; these glasses exhibit fluorescence properties. Through careful processing, the OH levels in the gel glass can be brought below 10 ppm. The fluorescence peak position shifts from 1.082 to 1.061 μm upon addition of Al_2O_3 to the Nd_2O_3-doped SiO_2 glass.

Acknowledgements

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