

Effect of growth temperature on the structural of Nd-doped silica prepared by the chemical method

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ABSTRACT

Silica gel doped with Nd₂O₃ was prepared by solgel method, using tetra-ethoxysilane and Nd (NO₃)₃ as precursor materials and HCl as a catalyst. The prepared samples were submitted to thermal treatments in the temperature range from 600 up to 1200 °C. Structural changes were investigated by XRD, FTIR spectroscopy and SEM. The effect of thermal annealing on Nd-containing silica has been discussed in detail. At 900 °C (4 h) various structures formed, while a further increase of the temperature and annealing time resulted in the formation of cubic neodymia and neodymium disilicate crystallites. At constant sintering temperature 1200 °C for 6 h the samples show distinct formation of Nd₂O₃ nanocrystallites with average size ~16 nm.

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1. Introduction

Recently nano-rare-earth oxides containing glasses have attracted a great deal of interest due to their macroscopical properties such as high mechanical resistance, chemical stability and heat resistance, etc. Moreover, their optical and magnetic properties justify the wide use of these glasses as optical amplifiers in telecommunication fibers network, as new miniature optical devices and as components for laser technology [1–4]. One of the important applications of neodymium containing glasses is as optical amplifiers for long distance optical communications. Specially for these applications silica has been preferred as host matrix, due to its higher softening temperatures, higher thermal shock resistance, and lower index of refraction, over the other oxide glasses [5–6].

There are many methods to synthesize nanocomposites [2]. Recently methods, e.g. precipitation in high-boiling polyalcohol solutions [7], inverse microemulsion [8] and hydrothermal sol-gel auto-combustion [9], floating zone, etc.; have been used to synthesize neodymium oxides/silicates nanocrystallites in glass matrix. Besides Nd₂O₃–SiO₂ thin film samples with various

Nd₂O₃ content were prepared by impregnation of SiO₂ [3]. Many researchers [10–13] have pointed out that the formation of rare-earth oxides/silicates inside or at the surface of amorphous SiO₂ matrix mainly depends on the preparation method and calcination. In particular, using solvothermal reaction routes and neodymium nitrate and acetate as precursors, Kepinski and Wolcyrz synthesized and characterized thin film of Nd₂O₃ on glass slide and stainless steel plate [12]. Masubuchi et al. [14] investigated the oxyapatite phase (Nd_{9.33}(SiO₄)₆O₂) of the binary system by two methods: (i) means of a slow cooling floating zone method, and (ii) solid-state reaction, and pointed out that the oxyapatite phase was extremely narrow or did not occur below 1650 °C. Recently, apatite-type rare-earth silicates have gained considerable attention in the field of solid-oxide-ion conductors because of their high-ionic conductivity at relatively low temperatures (i.e., below 600 °C) [15]. It was found that ionic conductivity of the apatite was higher than that obtained with yttria stabilized zirconia.

For proper utilization of binary oxides systems, specially nanocrystalline RE₂O₃ (RE, rare-earth) containing SiO₂, in scientific and technological applications require a better understanding of the phase diagrams and inter-ionic interactions of the binary oxides. The phase evolution and interaction mechanisms are deeply involved in the fundamental physics of rare-earth ions/oxides and silica. Thus, in the present report, we have investigated effect of the temperature as well as annealing time on the binary oxide

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and found that the phase evolution of rare-earth oxides depends on thermal treatment. The binary oxide was synthesized by the solgel method. The stem of present study is in the results of our earlier report [16], in which, we reported that the influence of temperature and time on Nd_2O_3 - SiO_2 composites prepared by the solgel process plays crucial role in altering the fundamental of size controlled. In that investigation [16], it was observed that the structures of the Nd_2O_3 -doped silica powder depend on annealing temperature (900 °C) and time (12 h). Here, in the present report the solgel synthesis of Nd-doped silica nanoparticles. We have shown that calcination at high temperature with prolonged annealing time mainly supports the development of the cubic Nd_2O_3 nanocrystallites. We found average size of the neodymium oxide nanocrystallites in a silica matrix was ~ 16 nm. The X-ray diffraction (XRD), Fourier transformation infrared spectroscopy (FTIR), scanning electron microscopy (SEM) data are of the prepared samples.

2. Experimental

Powders of Nd_2O_3 (99.9%) and SiO_2 (99.9%) were used as starting materials. They were mixed in molar ratio, i.e., $\text{Nd}:\text{Si} = 1:5$. Nd_2O_3 - SiO_2 samples with 6 wt% Nd_2O_3 content were prepared by solgel of SiO_2 with an appropriate amount of $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ nitrate (Aldrich 99.9995). The pH of the resultant solutions was 3. The solutions were filled in a quartz (10 mm $\times$ 20 mm $\times$ 45 mm) and kept in a drying oven (GFL-7105) at 90 °C. It was observed that the gelation act after approximately 3 and half days. Even after the gelation the samples were still kept inside the oven for 21, 25 and 30 days for aging. The aging process allows further shrinkage and stiffening of the gel. It was found that after 21 days, the percentage of shrinkage of the samples was very low. To this end, it was noticed that the samples were transparent and colorless while the color of the doped samples was glassy violet-purple due to the presence of neodymia. The powder form of the prepared samples was obtained by pestle and mortar. The powder samples were calcined in muffle furnace (KSL 1600X, MTI) in air at different heating rates, i.e., from room temperature up to 600 °C at 1 °C h⁻¹ and after that 3 °C h⁻¹ from 600 to 1200 °C. In order to characterize the samples complementary methods were used. X-ray diffraction pattern of samples were carried out by a Philips X-ray diffractometer PW/1710; with Ni filter, using monochromatised $\text{CuK}\alpha$ radiation of wavelength 1.5418 Å at 50 kV and 40 mA. Scanning electron microscopy of the samples was done with JEOL-JSM-T330-A 35 CF microscope at an accelerating voltage of 20 kV. Infrared spectra were collected from with a PerkinElmer 1600 (spectrophotometer) in 1500–450 cm⁻¹ range.

3. Results and discussion

3.1. XRD

XRD data of the annealed Nd oxides/silicates-containing silica (binary system) is shown in Fig. 1. The dried Nd-containing

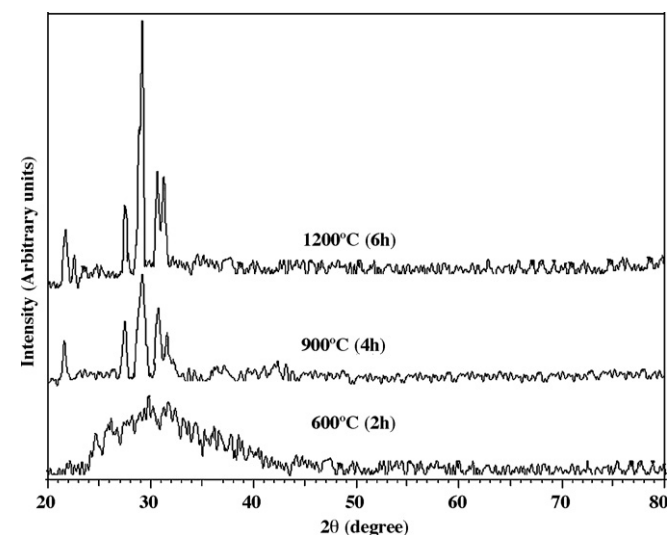


Fig. 1. XRD pattern of the Nd-containing silica powder samples annealed in air. Sample “a”: 600 °C (2 h), sample “b”: 900 °C (4 h) and sample “c”: 1200 °C (6 h).

gel was heated in air at $T = 600$ °C for 2 h (say sample “a”), 900 °C for 4 h (“b”) and 1200 °C for 6 h (“c”). Sample “a” shows no particular reflection peak in the XRD pattern which indicates that nature of Nd-containing was amorphous for $T \leq 600$ °C. When the binary system was heated at 900 °C for 4 h (sample “b”) a significant change in the reflections pattern of the XRD was observed because of formation of various structures. The initial structure of the formed oxide/silicates may be described by broad reflections centered about $2\theta \sim 21.8^\circ$, 27.5° , 29.2° and 30.8° . These reflections may be assigned to cristobalite [JCPDS File No. 39-1425], monoclinic Nd_2O_3 [JCPDS File No. 28-0671], cubic Nd_2O_3 [JCPDS File No. 45-0087] and tetragonal $\text{Nd}_2\text{Si}_2\text{O}_7$ [JCPDS File No. 22-1177], respectively. It is worth pointing out that the persistence of molecular H_2O in the prepared sample heated up to 900 °C (4 h) may also explain why the crystallization of SiO_2 into cristobalite instead into quartz. From the above discussions, it is worth recalling that the formation of rare-earth oxide/silicates inside or at the surface of amorphous SiO_2 matrix mainly depends on the preparation method and calcination [10–13]. Results of XRD of the sample “b” infer that the calcination of moderately Nd-doped silica at low temperature (nearly 0.45 times of the melting temperature) with prolonged annealing time can develop crystalline phase of silica Nd_2O_3 and $\text{Nd}_2\text{Si}_2\text{O}_7$.

In order to study the effect of high temperature and prolonged annealing time on Nd-containing-silica the temperature was increased up to 1200 °C and the sample was heated for 6 h (sample “c”). The XRD pattern of this sample shows strengthening and sharpening of the reflections around $2\theta \sim 27.5^\circ$ and 29.2° and also indicates growth of the crystallites. However, the reflection of tetragonal $\text{Nd}_2\text{Si}_2\text{O}_7$ phase exhibits only strengthening. This typical heat treatment also resulted in the weakened of the cristobalite phase while development of the quartz phase. Such structural changes indicate the elimination of H_2O from the sample. The most interesting result of this heat treatment is the slight shifting of the reflection pattern towards small 2θ angle. In particular, the strongest peak shifts from $2\theta \sim 29.2^\circ$ to 28.8° . This result suggests that with increasing the annealing temperature and the plateau-annealing-time, the interplaner distances increases. We found that at $T = 1200$ °C (6 h), the interplaner distance of Nd_2O_3 was increased from 3.052 to 3.092 Å in the binary system. The increase in the interplaner distance may be due to fact that the radius of Nd^{3+} is a little bigger than Si^{4+} and on calcination at 1200 °C for 6 h, the cell parameters of cubic Nd_2O_3 increases and interplaner increases too. These results suggest that the heat treatment of rare-earth containing silica at high temperature for prolonged time period supports coalescence of individual nanoparticles. In case of the Nd-doped silica such heat treatment mainly supports formation of the cubic phase of Nd_2O_3 nanocrystallites over the other phases. The strongest reflection centered about 28.8° was employed to estimate the mean crystallite size of Nd_2O_3 from Scherrer formula and was found ~ 16 nm ($a = 1.24$ Å [17] and $d = 3.0973$ nm). We know that around the high sintering temperature (nearly 0.8 times of the melting temperature) dislocations (micro-grains) become the main lattice defect, which decreases with further increase in temperature [18]. By the knowledge of the average size of crystallites [19], one may also estimate minimum dislocation density of that structure. The dislocation density of nano-neodymium oxide was found to be 7×10^{11} cm⁻². This value is well in agreement with the available literature [20]. From the above results, we may conclude that the heat treatment around the high sintering temperature with elongated plateau-annealing-time increases the crystallinity and also the size of the neodymium oxide, while reduces its dislocation density.

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