Research Letter

Synthesis and Characterization of Neodymium Oxide in Silica Matrix by Solgel Protocol Method

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Formation of nanocrystalline rare earth was prepared by solgel route, using tetra-ethoxysilane and Nd (NO 3) 3 as precursor materials and HCl as a catalyst. The prepared samples were submitted to thermal treatments at temperature 500 °C (5 hours) and 800 °C (10 hours). Structural changes were investigated by XRD, FTIR spectroscopy, and SEM. At 800 °C (10 hours) resulted in the formation of cubic Nd 2O 3 nanocrystallites with average size ∼ 20 nm.

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1. INTRODUCTION

There is growing interest in nanostructured inorganic materials in large part because they often exhibit properties distinct from those of the bulk, that can prove usefulness in various applications. Recently, nanolanthanide oxides containing silica have attracted a great deal of interest due to their macroscopical properties such as high mechanical resistance, chemical stability, and heat resistance [1–5]. 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 [6–12].

There are many methods to synthesize nanocomposites. Recently, methods, for example, precipitation in high-boiling polyalcohol solutions, inverse microemulsion, and hydrothermal solgel auto combustion, and so forth have been used to synthesize neodymium oxides nanocrystallites in glass matrix. Many researchers [10–12] have pointed out that the formation of rare-earth oxides inside or at the surface of amorphous SiO 2 matrix mainly depends on the preparation method and calcination. In particular, Kepinski et al. [4] synthesized and characterized thin film of Nd 2O 3 on the glass slide and the stainless steel plate. For proper utilization of binary oxides systems, specially nanocrystalline Ln 2O 3 (Ln, lanthanide) containing SiO 2, in scientific and technological applications, requires a better understanding of the phase diagrams and interionic 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 and found that the phase evolution of rare-earth oxides depends on thermal treatment. The binary oxide was synthesized by the solgel protocol method. The stem of present study is in the results of our earlier report [13], in which we reported that the thermal annealing history plays crucial role in altering the fundamental of size on Nd 2O 3 -doped silica powder prepared by the solgel protocol method. In that investigation [13], it was observed that the nanostructures of the Nd 2O 3 -doped silica powder can be obtained annealing at temperature (1200 °C) for (6 hours). However, in the present paper we have shown that calcination at low temperature (800 °C) with prolonged annealing time (10 hours) mainly supports the development of the cubic Nd 2O 3 nanocrystallites in case of neodymium-containing silica. We found average size of the neodymium oxide nanocrystallites in a silica matrix was ∼20 nm. The X-ray diffraction (XRD), Fourier transformation infrared spectroscopy (FTIR), scanning electron microscopy (SEM) data are obtained of heat treated samples.
2. EXPERIMENTAL

Using solgel technique, Nd-containing silica gel was prepared by refluxing high purity reagents. Tetraethoxy silane (Aldrich 99.999%), ethanol (Aldrich 99.9995%), and deionized water were mixed in the presence of hydrochloric acid as catalyst (Aldrich 99.995%). 8wt% neodymium oxide was introduced in the prehydrolyzed solution in the form of nitrate under heating. The hygroscopic nature of the Nd (NO)₃ salt does not allow its exact weighing, thus the salt was dissolved in deionized water and metal content was determined by standard titration. The pH of the resultant solutions was 5. The solutions were filled in a quartz (10 × 20 × 45 mm) and kept in a drying oven (GFL-7105) at 100°C. It was observed that the gelation act after approximately four days. Even after the gelation, the samples were still kept inside the oven for 20 and 35 days for aging. The aging process allows further shrinkage and stiffening of the gel. It was found that after 20 days, the percentage of shrinkage of the samples was very low. To this end, it was observed that the undoped samples were transparent and colorless, while the color of the doped samples was glassy violet-purple due to the presence of neodymia. 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 monochromatized CuKa radiation of wavelength 1.5418 Å at 50 KV and 40 mA. Scanning electron microscopy (SEM) 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 Perkin Elmer 1600 (spectrophotometer) in 2000–500 cm⁻¹ range.

3. RESULTS AND DISCUSSION

3.1. XRD

Figure 1 shows the XRD pattern of neodymium oxide doped silica powder calcined in air at different temperatures (500–800°C) for different hours. The powdered sample calcined at 500°C (5 hours) shows no particular reflection peak, which infers that the powder is still amorphous. Thus, we may say that the annealing at much below the melting temperature of the binary oxides even for five hours did not play any effective role in altering the amorphous phase of the Nd₂O₃–SiO₂. When the calcination temperature was increased up to 800°C and clamped for the 10 hours, a significant change in the pattern of reflections can be clearly seen. The two major reflections appeared at angle 2θ ∼ 21.9° and 27.8°. The broad peak centered about 2θ ∼ 21.9 may be assigned (101) reflection of cristobalite structure [JCPDS file no. 39-1425]. The cristobalite phase indicates persistence of water molecules in the sample. However, the sharp peak may be attributed to Miller indices (222) reflection of cubic Nd₂O₃ phase [JCPDS file no. 21-0579]. It is expected that the heat treatment of the sample at 800°C temperature for 10 hours reduces the number of pores and their connectivity and thus significantly alter the amorphous phase. Here, it is worth pointing that in the previous investigation [4] such major reflections were not observed in annealed (1000°C) high Nd₂O₃ loaded sample. However, when the sample was annealed in vacuum at 850°C, a weak reflection was appeared [4]. The narrow diffraction pattern around 27.8° was employed to estimate the mean crystallite size from Scherrer formula and found ∼20 nm. These results suggest that crystallite size increases during sintering for longer annealing time because of the coalescence of nanoparticles. Above results suggests that the heat treatment at low temperature (500–800°C) with prolonged annealing time increases the crystallinity as well as size of nanocomposites.
3.2. FTIR

Figure 2 shows FTIR transmittance spectra (range of 2000–500 cm\(^{-1}\)) of the heat treated doped samples. At temperature 800\(^\circ\)C, many discrete bands appeared 650, 800, 970, and 1040 cm\(^{-1}\) which may be assigned to Si–O–Si symmetric bond stretching vibration or vibration mode of ring structure of SiO\(_2\) tetrahedra, stretching mode Si–OH typical of the gel structure, TO mode of the Si–O–Si asymmetric bond stretching vibration and bending modes of water adsorbed at the silica surface, respectively. In low frequency region of the FTIR spectra, the strong band centered about 650 cm\(^{-1}\) may be assigned to Nd–OH bond. The heat treatment of the sample at high temperature prolonged sintering transforms Nd–OH into cubic Nd\(_2\)O\(_3\) phase [14].

Interestingly, the TO mode the Si–O–Si slightly shifted toward a higher wave number as the calcinations temperature of the sample was increased up to 800\(^\circ\)C calcined for 10 hours. Calcinations at high temperature with prolonged plateau-sintering, the band centered at 1640 cm\(^{-1}\) disappeared. The disappearance of this band allowed the binary oxide to act almost transparent material in spatial frequency ranges from 2000 to 1500 cm\(^{-1}\). Results of FTIR complement and support the XRD data.

3.3. SEM

Figure 3 shows different types of morphologies of neodymium oxide as viewed under scanning electron microscope. Micrograph “a” (calcined at 500\(^\circ\)C (5 hours)) shows the morphology of the amorphous Nd-containing silica. As expected, micrograph “b” (calcined 800\(^\circ\)C (10 hours)) clearly shows that prolonged sintering significantly alter the shape and crystallinity of the neodymium oxide doped silica. The shape of crystallites appears to be nearly spherical. SEM data support the XRD data of that condition.

4. CONCLUSIONS

Upon heat treatment of xerogel, nanostructure cubic neodymium oxide in SiO\(_2\) matrix was successfully prepared. The phase evolution, absorption spectra, and morphology of the Nd-containing silica have been studied with the objective to better understand the effect of thermal annealing. Calcinations of the Nd-containing silica at 800\(^\circ\)C for 10 hours mainly support the formation of cubic neodymium oxidenanocrystallites in silica matrix because of coalescences of individual nanoparticles.

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