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Influence of Temperature and Time on Nd_2O_3–SiO_2 Composite Prepared by the Solgel Process

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Using solgel method $Nd_2O_3-SiO_2$ binary oxide systems were prepared. The binary oxide transformed from the amorphous phase to nanocrystalline phase upon heat treatment in air. Characterization of the Nd_2O_3–SiO_2 was carried out by using X-ray diffraction, Fourier transform infrared spectroscopy, and scanning electron microscopy. The effect of the sintering temperature and time on the evolution of the binary oxide system was discussed. It is found that sintering time plays a pivotal role to obtain Nd_2O_3–SiO_2 nanocomposite. At temperature of 900°C, the sample was sintered for 12 h and monoclinic Nd_2O_3 nanocrystallites, with average crystallite size $\approx$ 12 nm, were obtained.

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1. Introduction

Nanocrystalline materials with tailored structure and properties are expected to have a great technological importance. Over the past few years, there has been considerable interest in the study of binary oxide systems containing nanocrystalline Ln_2O_3 (Ln, lanthanide) and silica due to their importance in many fields of technology, to name a few, photonics, microelectronics, sensors and catalysts, etc. [1, 2]. Applications of the nanomaterials are very interesting specially in the field of photonics and catalysis because of a quantum size phenomenon. This

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phenomenon significantly affects characteristics and performance of the photonics and catalysts, e.g. enhancement of emission lifetime, luminescence, quantum efficiency, optical nonlinearity and chemical activity (dehydrogenation/hydrogenation and esterfication etc.) [3–6].

Recently, a large variety of techniques have been turned out for preparing of composites at the nanometer scale. Among lanthanides, Nd_2O_3 has been widely used in photonic applications [7], luminescence [8], catalyst or catalyst promoters [9–12] and protective coatings etc. [13, 14]. For the most of these applications the ultrafine (in nanometer scale) neodymium oxides with well defined particle morphology are the most essential materials. Therefore, preparation and characterization of Nd_2O_3 nanoparticles have attracted much attention in recent years. Recently, Nd_2O_3 nanocrystalline has been synthesized by the inverse micro-emulsion technique, direct precipitation from high boiling polyalcohol solutions, solvothermal and hydrothermal reaction routes [8, 15, 16]. In the present article, solgel technique is being used for the preparation of Nd_2O_3 nanocrystallites in a silica matrix. Silica has been used as a host matrix due to its high softening temperatures, high thermal shock resistance, and low index of refraction [17–19].

The solgel processes combine the advantage of lower temperature and possibility of making of finely dispersed powders, films, fibers and coating [20]. Rare-earth oxides, due to their special properties, have also been used in many fields such as ceramic industry and sensors. As we know, the smaller the particles size, the larger the specific surface area, and the higher the activity. Thus synthesis of different structure/phases of Ln oxides nanocrystallites, is in great demand to fulfill the requirements of technology and industry. The development of new binary (rare-earth oxides and silica) systems and their characterization are important not only for technological reasons but also for obtaining a better understanding. Literature survey [12, 21, 22] reveals that formation of rare-earth oxides/silicates inside or at the surface of amorphous SiO_2 matrix depends on the synthesis method, rare-earth oxide and silica molar ratio and thermal/pressure treatment.

In the present report, the effect of sintering temperature and time on the evolution of the Nd_2O_3–SiO_2 has been investigated and found that the thermal treatment at temperature of 900°C with prolonged sintering (12 h) develops the monoclinic Nd_2O_3 phase with well defined particle morphology. The Nd_2O_3–SiO_2 binary oxide system is characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). The average size of neodymium oxide nanocrystallites in a fused silica matrix was found to be ≈ 12 nm.

2. Experimental

2.1, Sample preparation

Neodymia–silica (binary oxide) composites were prepared by the solgel method. The 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). 6 wt% neodymium oxide was introduced in the pre-hydrolyzed 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 3.5. The solutions were filled in quartz ($10 \times 20 \times 45$ mm^3) and kept in a drying oven (GFL-7105) at 120°C. It was observed that the gelation acts after approximately 3 days. Even after the gelation, the samples were still kept inside the oven for few days for aging. The aging process allows further shrinkage and stiffening of the gel. The color of the doped samples was glassy violet-purple due to the presence of neodymia. The powder form of the doped samples was obtained by pestle and mortar. The powder samples were sintered in muffle furnace (KSL 1600X, MTI) in air.

2.2. Characterization

Complementary methods were used to characterize the structure of the doped samples. X-ray diffraction pattern of samples were carried out by a Philips X-ray diffractometer PW/1710; with Ni filter, using monochromatic Cu K_α radiation of wavelength 1.5418 Å at 50 kV and 40 mA. 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 with a Perkin Elmer 1600 (spectrophotometer) in 1250–500 cm^{-1} range.

3. Results and discussion

3.1. XRD

X-ray diffraction patterns of sintered binary oxides (Nd_2O_3–SiO_2) are shown in Fig. 1. The powdered sample sintered at 600°C (6 h) shows no strong and sharp diffraction peak, which infers that the powder is still amorphous. This result suggests that heating of binary oxides at low temperature for six hours is not effective for achieving initial crystallization phase of the Nd_2O_3–SiO_2. In order to achieve crystallinity, the sintering temperature was increased up to 900°C and the sample was sintered for 12 h. In this condition a significant change in the diffraction patterns was observed. The two major strong diffraction peaks appeared around $2\theta \approx 27.5°$ and 29.2°. These peaks may be assigned to (010) and ($\bar{4}02$) of monoclinic Nd_2O_3 phase, respectively (JCPDS File No. 28-0671). Here, it is worth pointing out that in the previous investigation [22] such major diffraction peaks were not observed even in a high Nd_2O_3 loaded sample (36 wt%). Moreover, high loaded sample was annealed in air at comparatively high temperature (1000°C). It is expected that the absence of the strong diffraction peaks in the above study [22] is probably due to short sintering time. However, in our case, prolonged sintering at temperature of 900°C produces sharp diffraction peaks. We expect that during prolonged sintering, individual nanostructures merge together (process of particle fusion) and the activation energy becomes much larger and therefore

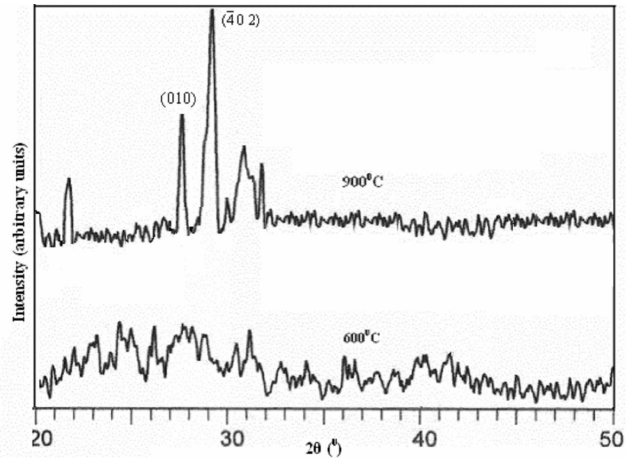

Fig. 1. XRD pattern of the Nd_2O_3-doped silica powder sample annealed at 600°C (6 h), and 900°C (12 h).

cross grain-boundary diffusion dominates over surface and volume diffusion process and eventually crystallinity increases. The sharp and strongest diffraction peak around $2\theta \approx 29.2°$ was employed to estimate the mean crystallite size of Nd_2O_3 from the Scherrer formula and found to be ≈ 12 nm. The above results suggest that the thermal treatment of Nd_2O_3–SiO_2 composite system, synthesized by the solgel technique, at temperature of 900°C with prolonged sintering time (12 h) produces Nd_2O_3–SiO_2 nanocomposite system with distinct grain boundaries.

3.2. FTIR

FTIR transmittance spectra (range 1250–500 cm^{-1}) of the heat-treated doped powdered samples are shown in Fig. 2. These spectra provide valuable information about the phase composition as well as bonding in the sintered composites. In FTIR spectrum of the sample sintered at 600°C for 6 h, 800, 970 and 1090 cm^{-1} are the characteristics bands of amorphous SiO_2. The band at ≈ 800 cm^{-1} may be assigned to vibration modes of ring structure of SiO_4 tetrahedra [23]. The involvement of the polycondensation process is supported by the behavior of IR band at ≈ 960 cm^{-1} associated with the stretching mode Si–OH of typical gel structure. The broad band ≈ 1090 cm^{-1} is associated with the transversal optical (TO) mode of the Si–O–Si asymmetric stretching bond vibration. However, when the sample was sintered at 900°C for 12 h, many discrete bands appeared between 640 and 970 cm^{-1}. In low frequency region of FTIR spectrum, the peak centered about 650 cm^{-1} may be assigned to Nd–OH bond [16], while the weak peak at 700 cm^{-1} is the metal–oxygen peak [24]. The characteristics band of neodymium silicates appeared around 905 cm^{-1} and this band may be explained by the absorption due to asymmetric stretching mode vibration of Si–O–Nd bond. However, Ono and Katsumata [25] reported that asymmetric

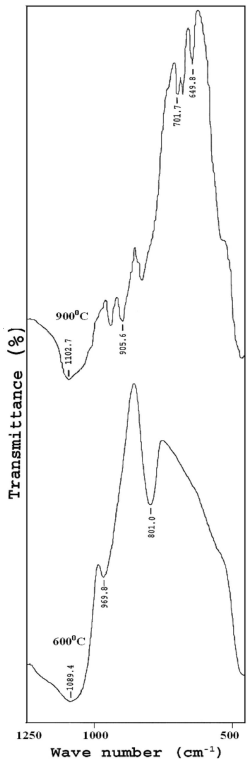

Fig. 2. FTIR spectra of Nd_2O_3-doped silica at different temperatures: 600°C (6 h), and 900°C (12 h).

stretching mode vibration of Si–O–Pr appears at 900 cm^{-1}. In the present study the shift of the Si–O–Nd peak towards higher spatial frequency is a consequence of higher ionic radius of Nd than Pr. In addition, it was also observed that TO mode of the Si–O–Si slightly shifts towards a higher wave number with increasing sintering temperature and time. Similar behaviors of Si–O–Si band in annealed SiO_x (x — contents) sample were noticed by many workers [26–28]. They pointed out that the peak position of the asymmetric stretching broad band of the SiO_x sample depends on the oxygen contents. Nakamura et al. [26] and Milutinovic et al. [27] found that the oxygen contents decreases with increasing annealing temperature and time and as a result the peak position shifts towards higher wave number and eventually the density of SiO_x increases.

3.3. SEM

Figure 3 shows morphologies of the sintered composites systems (Nd_2O_3–SiO_2) as viewed under SEM. The SEM image (a) and (b) shows the morphology of agglomerated particles and quasi-spherical particles, respectively. Calcination of the sample at 600°C for 6 h may be contributed to agglomeration of the Nd_2O_3 (in irregular shape) in silica matrix. It is expected that screening of uniform dis-

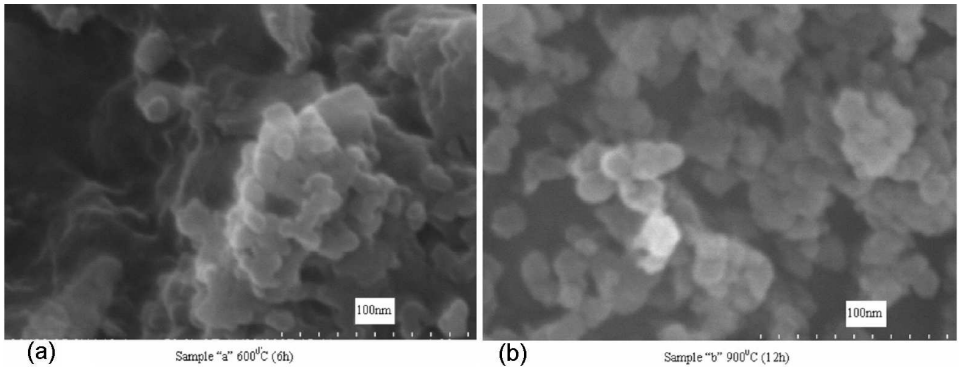

Fig. 3. SEM photograph of Nd_2O_3–SiO_2 at (a) 600°C and (b) 900°C, respectively.

persion/distribution of Nd_2O_3 in SiO_2 matrix is due to concentration quenching. In order to overcome this problem, introduction and effect of the glass modifiers such as aluminum or phosphorous or suitable surfactants in Nd_2O_3–SiO_2 binary system should be the subject of further investigation. Thermal treatment of the sample at comparatively high temperature (900°C) with prolonged sintering provides much-improved dispersion of Nd_2O_3 in a fused silica matrix. Moreover, in this condition the shape of the particles is quasi-spherical with well defined grain boundaries. Here, it is worth pointing out that prolonged sintering favors the formation of a neodymium oxide with a fine substructure. This result also supports the observation made in X-ray diffraction. The above results infer that the microstructure of the Nd_2O_3–SiO_2 composites obtained by solgel method can be controlled by selecting correctly both the heat treatment time and temperature.

4. Conclusions

Using solgel method Nd_2O_3–SiO_2 binary oxides (composites) with different structures were successfully obtained upon thermal treatment in air. During typical thermal treatment (900°C/12 h) the aggregation of powders is due to solid--state bonds formed between nanoparticles and fused silica matrix. The results suggest that sintering time and temperature plays pivotal role in the formation of monoclinic Nd_2O_3 nanocrystallites as well as their distribution in fused silica matrix.

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