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Optical and structural properties of Nd_2O_3-SiO_2 nanocomposite as synthesized from sol-gel technique

ABSTRACT

Nd_2O_3-SiO_2 nanocomposite was prepared in the current work utilising the sol-gel technique. After being heated in air, the amorphous phase of silicates transformed to crystalline phase via intermediate phase as oxide. Due to its comparatively small operating temperature and ability to form nanostructures with precise size, sol-gel approach is a compelling alternative. X-ray powder diffraction (XRD), Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR), which verified the structural characteristics of neodymium silicate (Nd_2O_3-SiO_2) nanocomposites, were used to characterise the synthesised materials. The effect of duration and annealing temperature on the phase advancement of the silicates has been considered thoroughly. It was discovered that the sample was sintered for 3 hours at various temperatures, thus obtaining neodymium silicates. In addition, Optical characterization of Nd_2O_3 –SiO_2 was performed using Photoluminescence Spectroscopy (PL).

Keywords: *Nanocomposites, neodymium silicate, sol-gel, annealing*

1. INTRODUCTION

A material composed from two or more component materials that, when mixed with various metal oxides, exhibit dramatically varied properties is known as a nanocomposite. For example, colloidal crystals, core-shell nanoparticles, macro-scale spheres and mixed metal oxides, are just a few of the numerous morphologies that may be found in nanocomposite materials [1]. Due to their intriguing features and varied uses across a wide range of fields, composite materials incorporating nanostructures have recently drawn increased attention [2].

Due to their distinctive and intriguing features, in research rare earth oxides have been used on optical, ceramic, sensors, nano-electronics, semi-conductor, solar cells and catalytic applications [3]. Because of its applicability, neodymium oxide is one among the essential rare earth minerals [4]. Nd_2O_3-SiO_2 nanocomposites have received very little attention from researchers. There aren't many supports other than SiO_2 in the literature; examples are TiO_2, $NaYF_4$ for use as a sensitizer [5], $BiFe_2O_3$ to improve ferroelectric characteristics [6], and LaF_3 for optical research [7]. Neodymium oxide (Nd_2O_3) is used in coloured glass, catalysts, protective coatings and UV absorbent because of its many useful properties [8].

Due to their numerous uses, particularly in photo catalysis, doping of neodymium in silica nanocomposites constitute an essential class of nanomaterials [9]. According to the literature, nano-sized rare earth metal oxides were found to occur at low breakdown temperatures [10].

Samarium and neodymium oxide nanoparticles were produced using a two-step process, according to Liu et al. [11]. This process involved a metal precursor reaction to create nanoparticles, which was accompanied by an oxidation step to create oxides of rare earth metals. Lanthanum nanoparticles are being used efficaciously in drug administration, cell imaging, bioassays, photo degradation of dyes, and other catalytic processes. The lanthanide elements Ce, Ho, Sm, Gd, Nd, Er, and Eu are examples of lanthanide elements that can be found in nanoparticle form [12].

In the current research, we have investigated the impact of annealing time and temperature on

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the phase advancement due to the sol-gel synthesis of neodymium silicates. In a silica matrix, neodymium oxide nano-crystallites had an average size of 17 nm. Neodymium silicate data from XRD, SEM and FTIR are presented.

2. MATERIALS AND METHODS

2.1. Materials

Nd_2O_3-SiO_2 nanoparticles were prepared using the Sol-Gel methodology. For preparation the highly pure chemicals: Tetraethoxysilane (TEOS) (Merck 99%), C_2H_5OH(Merck 99%), and deionized water were used with HCl acting as a catalyst.

2.2. Method

As for the synthesis route, sol-gel technique has been used. The sample was synthesized using an initial solution ratio of 0.39:0.163:0.0924:0.032 for H_2O: C_2H_5OH: HCl: TEOS, with the addition of 4wt% of Nd_2O_3 and Nitric acid. First, the mixture of C_2H_5OH (36 mL) and TEOS (4.8 mL) was taken followed by the dropwise addition of the solution of HCl (36 mL) and H_2O (56 mL). The solution was stirred continuously at room temperature for 3 hours. The solution was placed in a quartz cuvette in the oven and heated to 80°C for drying. Gelation began after 3-4 days, and the gel was aged in the oven for four to five days, during which it continued to shrink and stiffen. However, the sample's shrinkage percentage was found to be very low after a few days. The doped sample exhibited a violet-purple tint due to the presence of neodymium oxide/silicate (figure 1).

The dried samples were then pulverized using a pestle and mortar. The binary system powder was subjected to heating in an air-tight muffle furnace at various temperatures: starting from 25ºC to 780°C for 3 hours, 980°C for 3 hours, and 1180°C for 6 hours.

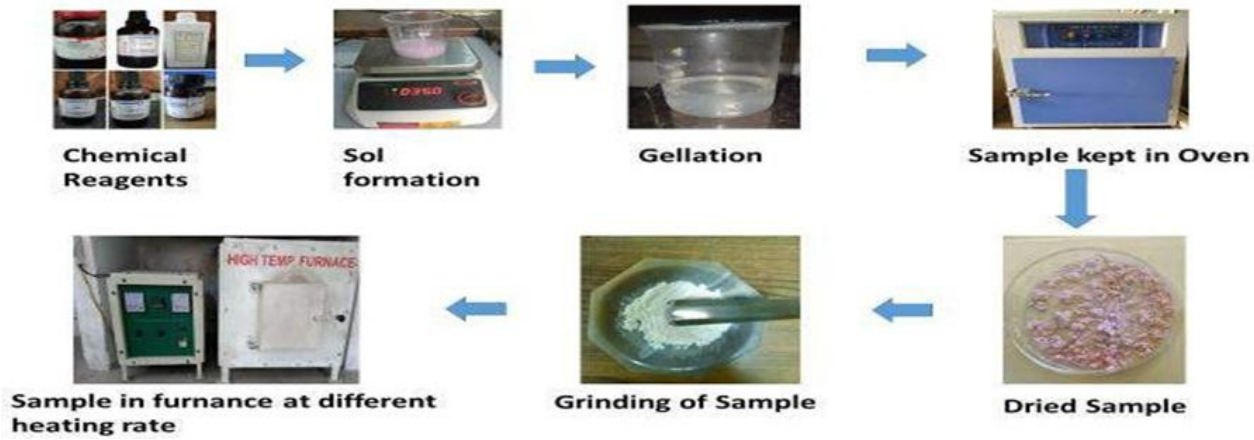

Figure 1. Experimental view of preparation of samples via sol-gel route

Slika 1. Eksperimentalni prikaz pripreme uzoraka sol-gel putem

3. RESULTS AND DISCUSSION

3.1. XRD Analysis

Figure 2 demonstrates the XRD plot of Nd_2O_3-SiO_2 samples annealed in air with variety of temperatures for different amount of time. The sample annealed at 780ºC (3h), 980ºC (3h) and 1180ºC (6h). Aiming crystallinity as the target, the temperature raised to 980 ºC the sample was annealed for 3h show a structural change in the binary oxide and further increase to 1180ºC (6h) [13]. Broad reflections with their centres around 2θ≈ 21.9º, 27.5º, 32.7º, 38.06º, 40.5º and 45.3º can be used to depict the former structure of the evolved phase. The highly intense peak at 2θ ~ 21.9º can be for (101) of crystallite structure [JCPDS file no. 39- 1425]. The crystallite phase suggests the tenacity of H_2O present in the sample. The reflection around 2θ ≈ 27.5º can be designated to (010) representing monoclinic phase Nd_2O_3, respectively (JCPDS File No. 28-0671) [14]. The most intense peak is around 38.06º. The strongest reflection around 38.06º was taken to get the idea of the mean crystalline size which was found to be D≈17.04nm (a=8.17Å and d=2.36Å).

The plots of Figure 2 shows that, by raising the heat treatment temperature to a very high values, the amorphous phase of silica changes to crystalline phase [15].

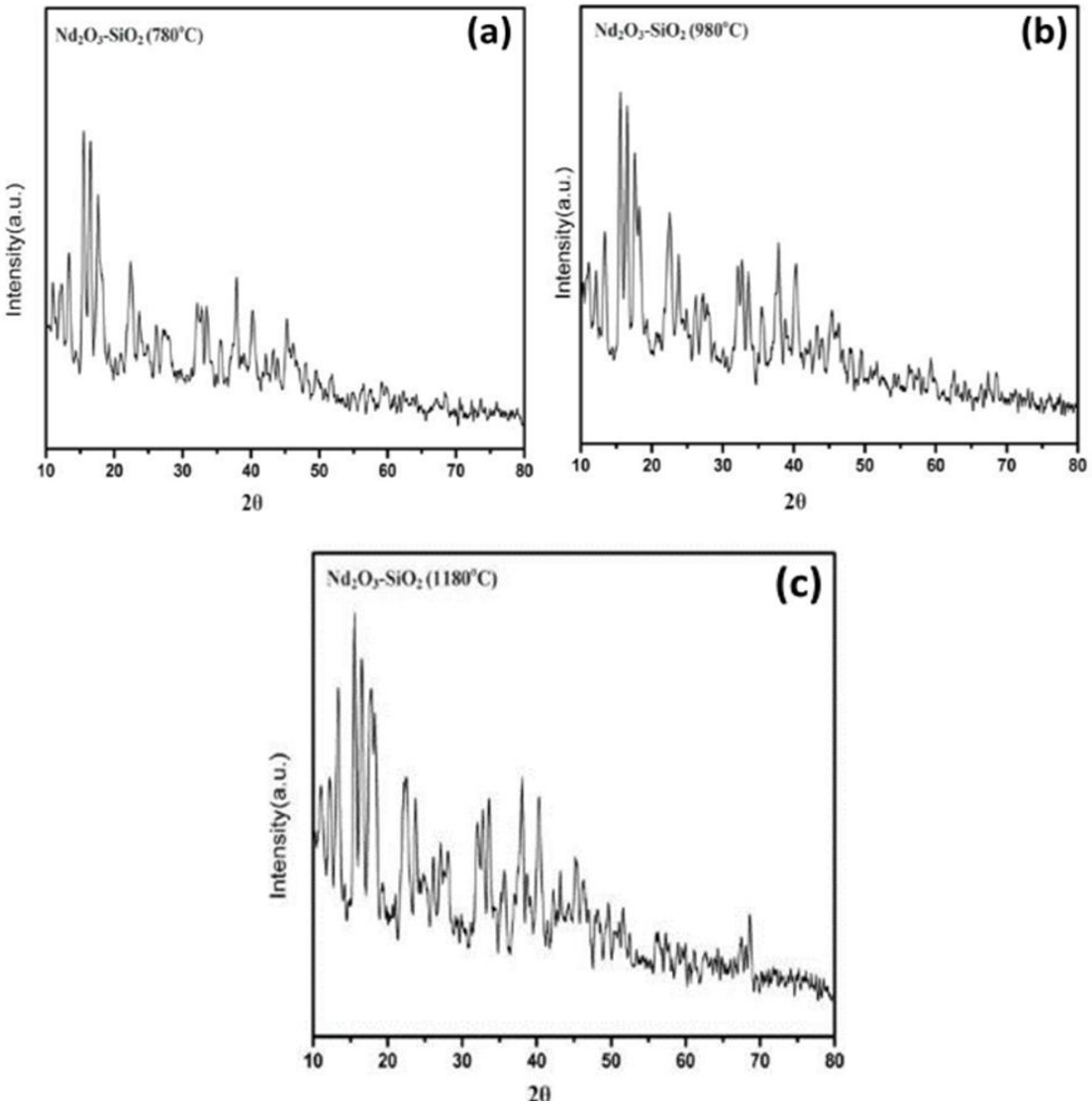

Figure 2. XRD Plot of Nd_2O_3-SiO_2 sample (a) annealed at 780ºC (3h) (b) annealed at 980ºC (3h) (c) annealed at 1180ºC (6h)

Slika 2. XRD dijagram uzorka Nd_2O_3-SiO_2 (a) žarenog na 780ºC (3h) (b) žarenog na 980ºC (3h) (c) žarenog na 1180ºC (6h)

3.2. FTIR Analysis

Some significant information regarding the structural changes can be found in the infrared absorbed peaks of the Nd_2O_3-SiO_2 samples. The heat-treated doped materials' FTIR spectra (4,000–500 cm^{-1}) are displayed in Figure 3. Many distinct bands formed between 560 and 1,040 cm^{-1} at temperatures between 700 and 1,200ºC. A very wide and powerful band with a centre of 3,409.2 cm^{-1} was seen at 780ºC (3 hours). 3,452 and 3,409 cm^{-1} often denotes to the transmission percentage peaks of the H_2O band and the Si-OH band respectively, in FTIR spectra. The overlapping of H–O–H band with the surface hydroxyl group vibration results in the widening of the band is showed in the present study [16]. The bending modes of H–O–H corresponds to the band at around 1,604 cm^{-1}. A broad band around 1,042 cm^{-1} can be ascribed to Nd_2O_3. A strong peak appeared at around 900 cm^{-1} of the FTIR spectra and this peak may be described as absorption caused by Si–O–Nd bonds. Nd – OH bond was assigned to the band about 655 cm^{-1}. The absorption of the bands 655 cm^{-1} and 1,042 cm^{-1} reduced marginally whereas the absorption of the widened band (3,410–3,510 cm^{-1}) reduced extensively as the sample was annealed at 980ºC for 3h. The heat treatment at 980ºC (3 h) moulded Nd – OH bond into cubic Nd_2O_3 which decreased

the absorption at 650 cm^{-1} [17]. As opposed to the above observations, the Nd-silicates structures turn out to be more strengthened due to the Si–O–Nd bond. In conclusion, heat treatment at 1180ºC (6 h), deduced H_2O molecules, Si–OH and volatiles makes the system almost transparent for spatial frequency and authorizes densification of the binary system. Here, Bouajaj et al. results of FTIR is in full agreement with the XRD data which is worth in pointing out [15].

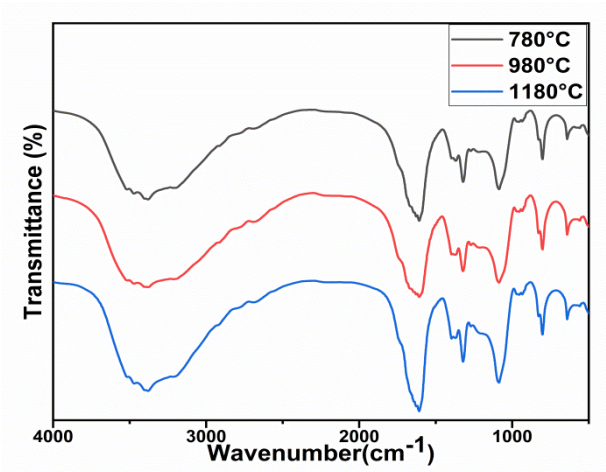

Figure 3. FTIR Plots of Nd_2O_3-SiO_2 at various temperature: 780ºC (3h), 980ºC (3h) and 1180ºC (6h)

Slika 3. FTIR dijagrami Nd_2O_3-SiO_2 na različitim temperaturama: 780ºC (3h), 980ºC (3h) i 1180ºC (6h

3.3. FE-SEM

In order to comprehend the situation more fully, incorporation of Nd_2O_3 Nanoparticles, the surface and elemental constitutions were analyzed using FESEM and EDX.

The micrographs (Figure 4) obtained at magnifications (200 nm) demonstrated the observed surface features, such as roughness, cracks, pores, or particle distribution for the sample annealed at different temperatures. Nd_2O_3-SiO_2 samples annealed in presence of air at variety of temperature range variations i.e. sample annealed at 780 ºC (3h), 980 ºC (3h) and 1180 ºC (6h). By raising the temperature to 1180 ºC, the microstructure transforms from coarse scale to excellent ones [18]. Due to their tiny size and high surface energy, it appears that primary particles can aggregate into secondary particles [19].

The FESEM observation supported the benefits of the sol-gel technique for producing amorphous materials at less temperatures & the finding that higher temperatures produced dense, more homogeneous materials [20]. The FESEM process also determines the diameters of the metal oxide particles. Nd_2O_3 nanoclusters are observed to be widely dispersed, with average sizes between 15 and 30 nm. This agrees with the XRD data.

The high-resolution images highlighted specific details, such as nanoscale structures, grain boundaries, or surface defects.

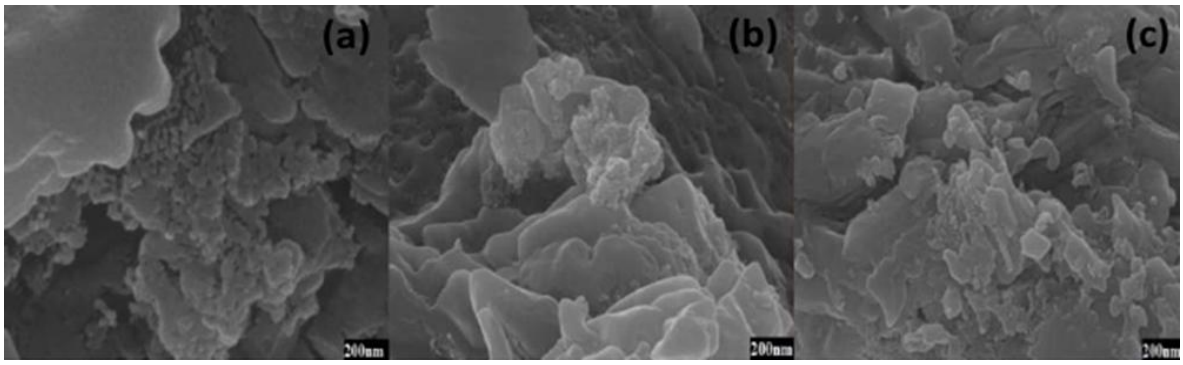

Figure 4. FE-SEM photographs of Nd_2O_3–SiO_2 Powder sample (a) Annealed at 780ºC (3h) (b) Annealed at 980ºC(3h) (c) Annealed at 1180ºC(6h)

Slika 4. FE-SEM fotografije uzorka praha Nd_2O_3–SiO_2 (a) žarenog na 780ºC (3h) (b) žarenog na 980ºC(3h) (c) žarenog na 1180ºC(6h)

3.4. Elemental Mapping (EDAX)

FE-SEM often allows for elemental mapping using EDAX. EDAX enables identification and mapping of elements present in the sample analyse the elemental maps to understand the spatial distribution of different elements and their correlation with the observed feature [21]. The elemental composition of the sample was analysed using the EDAX detector. The presence of Nd, Si, Cl etc. was confirmed, indicating relevant findings, such as the presence of impurities, chemical composition, or elemental distribution as shown in Figure 5.

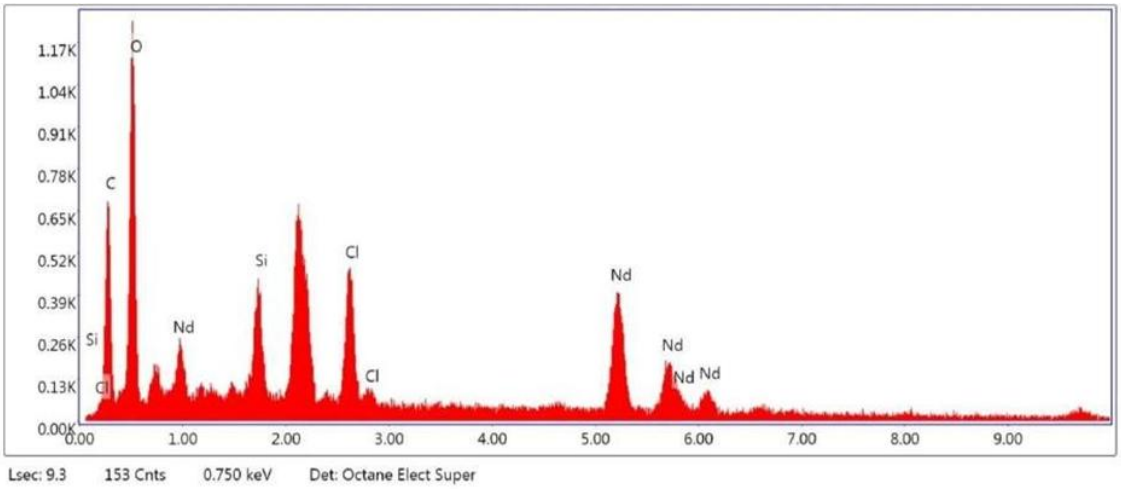

Figure 5. EDAX spectra of Nd_2O_3–SiO_2 powder sample

Slika 5. EDAX spektri uzorka praha Nd_2O_3–SiO_2

3.5. Optical Property Analysis (PL)

Figure 6 displays the PL spectra of distinctive powdered Nd_2O_3-SiO_2 samples which were annealed in air at variety of temperatures and times to describe their optical properties. The sample annealed at 780ºC (3h), 980ºC (3h) and 1180ºC (6h). All of the spectra are clearly wide continuous spectrums, as can be observed. Around 1,080 nm, a significant luminescence peak is visible, which correlates with the 4F3/2-4 I11/2 transition [7].

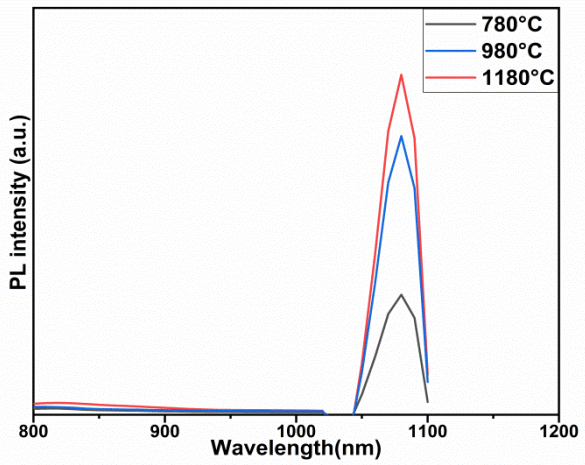

Figure 6. PL of Nd_2O_3–SiO_2 at: 780ºC (3h), 980ºC (3h) and 1180ºC (6h)

Slika 6. PL Nd_2O_3–SiO_2 na: 780ºC (3 h), 980 ºC (3 h) i 1180 ºC (6 h)

With the rise in annealing temperature, the PL Intensity rises. The PL Intensity at 1,080 nm for the sample annealed at 1180ºC is around three times greater than that for the sample annealed at 780ºC. In accordance with XRD data, increasing the annealing temperature causes the PL Intensity to increase because the crystallinity has improved i.e. by increasing the heat treatment temperature to a very high values, the amorphous phase of silica changes to crystalline phase [22].

Neodymium crystallites may have caused a considerable luminescence despite concentration quenching. Bazzi et al. have reported similar outcomes [23].

4. CONCLUSION

By using the Sol Gel technique and Tetraethoxysilane (TEOS) as the SiO_2 precursor, the Nd_2O_3–SiO_2 binary oxide system was made employing hydrochloric acid as a catalyst. During heat treatment in air, the binary oxide transitioned into the crystalline phase from the amorphous phase through the intermediate oxide phase. Using the Sol Gel method powdered Nd_2O_3–SiO_2 samples annealed at variety of temperatures and time durations in the presence of air. The sample annealed at 780ºC (3h), 980ºC (3h) and 1180ºC (6h). Powders aggregate during annealing as a result of solid-state bonds that form amongst the gel and the nanoparticles. As the annealing temperature is raised, Nd_2O_3 nanoparticle sizes grow. At 1180ºC (6h), cubic Nd_2O_3 nano-crystallites phase was discovered. By making the use of Scherrer formula, the crystallite size of Nd_2O_3 was discovered as D≈17.04nm (a=8.17Å and d=2.36Å). The heat-treated samples have shown infrared absorption spectra which showed some significant information regarding the structural changes. In order to comprehend more fully of the incorporation of Nd_2O_3 nanoparticles, the elemental constitutions and surface morphology were analysed using

FESEM and EDAX. A typical nano-neodymium oxide had a broad, continuous spectrum of light. Around 1,080 nm was where the major excitation peak was located. Due to the enhancement in crystallinity, a rise in annealing temperature results in an increased PL Intensity.

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IZVOD

OPTIČKE I STRUKTURNE OSOBINE Nd_2O_3-SiO_2 NANOKOMPOZITA SINTETIZOVANOG IZ SOL-GEL TEHNIKE

Nanokompozit Nd_2O_3-SiO_2 je pripremljen u radu primenom sol-gel tehnike. Nakon zagrevanja na vazduhu, amorfna faza silikata se transformiše u kristalnu fazu preko međufaze kao oksid. Zbog svoje relativno male radne temperature i sposobnosti formiranja nanostruktura sa preciznom veličinom, sol-gel pristup je ubedljiva alternativa. Rendgenska difrakcija praha (XRD), skenirajuća elektronska mikroskopija (SEM) i infracrvena spektroskopija Furijeove transformacije (FTIR), kojima su verifikovane strukturne karakteristike neodimijum silikata (Nd_2O_3-SiO_2) nanokompozita, korišćeni su za karakterizaciju sintetizovanih materijala.

Uticaj trajanja i temperature žarenja na napredovanje faze silikata je detaljno razmotren. Otkriveno je da kada se uzorak sinteruje 3 sata na različitim temperaturama, dobija se neodimijum silikati. Pored toga, izvršena je optička karakterizacija Nd_2O_3 –SiO_2 korišćenjem fotoluminiscencione spektroskopije (PL).

Ključne reči: *nanokompoziti, neodimijum silikat, sol-gel, žarenje*

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