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Synthesis and Characterization of Nd_2O_3 Nanoparticles Using Urea as Precipitation Agent

Bahram Khoshnevisan[1*], Maryam Mohammadi[1], Mohsen Moradian[2]

[1]*Department of Physics, University of Kashan, Kashan, Iran*

[2]*Department of Chemistry, University of Kashan, Kashan, Iran*

ABSTRACT

Nano Particles (NPs) of Neodymium oxide were prepared by homogeneous co-precipitation method using Neodymium nitrate and urea as precursors. X-Ray Diffraction (XRD) patterns have been refined by the Rietveld method and the Fourier Transform-Infrared Spectroscopy (FT-IR) showed that the sample had a band gap about 4.59 eV. On the other hand, the Photoluminescence (PL) spectrum indicated that the sample had a low concentration of singly ionized oxygen vacancies. The paramagnetic property of the NPs has been also tested by Vibrating Sample Magnetometer (VSM) measurements.

Keywords: Rare earth elements; Homogeneous precipitation; Urea; Nd_2O_3 NPs; optical properties; Rietveld refinement

INTRODUCTION

Rare earth elements are strategic resource with widespread use in industry, agriculture, military industry, environmental protection and medicine. Their compounds are widely used in high performance luminescence devices, magnets, catalysts, display devices, solid state lasers and other basic materials due to the electronic, optical and chemical properties of their 4f-shell ions [1-3]. Among them, neodymium based materials have found their place in various applications and products including magnetic suspensions, photoluminescence, photo materials, magnetic molecules, soft glass and soft magnets (hexagonal or garnet crystal structure for hard magnets and crystalline structure for soft magnets) [4-7]. For instance Nd_2O_3 is widely used in the fields of photonics, super capacitor applications, luminescence and thermo-luminescent materials, protective coatings, thin films, sensors (e.g. CO and hydrogen gas, etc.) [8-13].

In addition, Nd_2O_3 Nano Particles (NPs) are widely used for making glass, capacitor and magnets, so have received special attention due to their optical properties. Since the size and morphology of the particles have influence on their properties and applications, such as ceramic catalyst applications therefore; scientists are seeking to improve their sensitizing methods (hydrothermal, combustion solution, sol-gel, micro emulsion, etc.) [14-20]. Nd_2O_3 NPs have also luminescence applications because their band gap is in the range of 5.25-5.70 eV and the possibility of obtaining UV, blue, green and red luminescence (emission range of 200-800 nm) for specific purposes is the most important in the fields of optics and luminescence materials. The synthesis of nanocrystalline Nd_2O_3 through an inductively coupled

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Corresponding author Bahram Khoshnevisan, Department of Physics, University of Kashan, Kashan, Iran; E-mail: b.khosh@kashanu.ac.ir

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radiofrequency thermal plasma route could be led to a stable hexagonal crystal structure and the synthesized nanoparticles are highly uniform with an average size around 20 nm. Production of fine NPs from starting nitrate water soluble salts by homogeneous precipitation using urea is introduced as a successful and efficient method to synthesize metal oxide powders. Metal (hydrous) oxides with uniform particle size in an aqueous medium were prepared and nowadays the method is a promising issue used this method to synthesize amorphous and crystalline metal (hydrous) oxide and according to their study, the decomposition of urea in the aqueous medium causes the formation of ammonia and carbon dioxide slowly in the solution. The smooth pH increase resulting from this degradation at the same time, along with the releasing of OH^- and CO_2 ions usually leads to the precipitation of metal oxide particles with controlled morphology. In this study, Nd_2O_3 NPs have been prepared by homogeneous co precipitation using urea and their structure and the nanoparticles were characterized in terms of XRD Rietveld refinement, morphology, size distribution and nature of their chemical bonds. The XRD and scanning electron microscopy are used for structural and morphological studies. Fourier transform infrared spectroscopy is used to investigate the nature of existing bonds. The optical response of the nanoparticles is investigated through the electronic transition of Nd^{3+} ions in its crystalline structure *via* DRS technique. PL was used for studying presence of defect states and corresponding activation energies in the samples and to investigate the samples magnetic properties VSM technique was employed, respectively.

MATERIALS AND METHODS

Sample Preparation

To make the neodymium oxide NPs, according to the literature with some modification, first 0.05 gr of Nd $(NO_3)_3.6H_2O$ and 0.5 gr of urea was dissolved in 40 ml of deionized water, and then the solution was solicited for 30 minutes. The mixtures were heated to 90°C and maintained for 3 to 4 hours for sedimentation. This sediment was calculated for 3 hours in the furnace at 800°C to obtain neodymium oxide NPs. The chemical process would be along the following relation:

$$2Nd(NO_3)_3+5CH_4N_2O \rightarrow Nd_2O_3+5CO_2+8N_2+10H_2O$$

Characterization

XRD has been employed for structural studies of the synthesized NPs (XRD, philips expert pro, with Cu kα radiation with λ=1.5405 Å), and the result was analyzed by Rietveld refinement technique *via* GSAS (General Structure Analyze System) software. The magnetic properties were studied by VSM with the maximum field up to 10 kOe at room temperature. The morphology and microstructure of the sample were observed with a Field Emission Scanning Electron Microscope (FESEM) (TESCAN BRNO-Mira3 LMU), and Energy Dispersive X-ray (EDX) analysis was used for testing elemental composition (with accelerating voltage of 25.0 kV). IR spectrum was recorded with a KBr pellet on a Perkin Elmer 781 Spectrophotometer. The Photoluminescence (PL) studies have been carried out using a Perkin Elmer LS-55 luminescence spectrophotometer equipped with Xe lamp and also The UV-Vis spectra of the Nd_2O_3 sample was obtained by a Diffuse Reflection Spectroscopy (DRS) method (Shimadzu, UV-1800, Japan).

RESULTS AND DISCUSSION

The phase and crystal structure of the prepared Nd_2O_3 NPs by the homogenous urea co precipitation method was examined by rietveld refinements of the XRD pattern which is a unique and comprehensive method for the determination of crystal structures, which it makes a modeled (calculated) diffraction pattern *via* the crystallographic features of the sample and proceed for an interactive curve fitting with the observed diffraction pattern. The refined profile is shown in **Figure 1**, and some of the refined structural parameters like atomic site occupancy and the relative position of the atoms in the unit cell (x,y,z) are listed in **Table 1**.

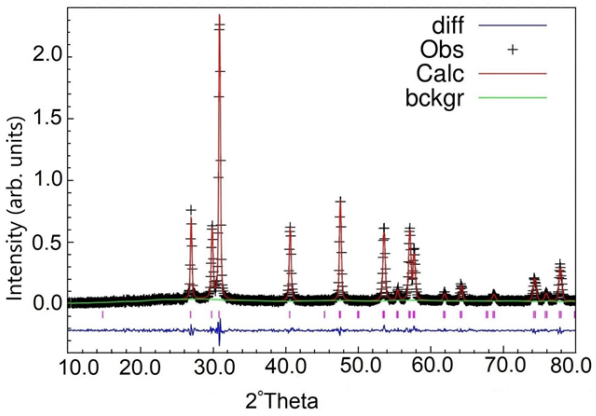

Figure 1: Rietveld refinement of the Nd_2O_3 NPs. Comparison between the diffraction data (Obs) and the modeled data (Calc) is shown by the difference cure (diff) which is almost negligible and horizontal. The little tags in beneath of each peak show the exact angle for the peaks.

According to the reference (JCPDS Card No.074-2139) the structure was hexagonal and the difference curve indicated a significant confirmation between the calculated and the collected XRD pattern. The lattice parameter values were obtained a=b=3.83Å; c=6.00Å and the cell volume was calculated 77.68A3. The NPs were well crystallized with very high purity. By using Scherrer's equation:

$$D=k\lambda/\beta\cos\Theta$$

(Where k=0.89 is a constant, Θ is Bragg's angle and β is full width at half maximum (FWHM) of the peaks), and with consideration of refinement results in several directions, the average size of the NPs was ~ 30 nm.

Table 1: Rietveld refinement results for Nd_2O_3.

a	Oxidation state	x	y	Z	occupancy
Nd_1	+3	0.333301	0.666700	0.240802	1
Nd_2	+3	0.666600	0.333299	0.747891	1
O_1	-2	0.000000	0.000000	0.034332	1
O_2	-2	0.333301	0.666700	0.633250	1
O_3	-2	0.666600	0.333299	0.346650	1

Figure 2 Shows the IR spectrum of the fabricated Nd_2O_3 NPs, and the absorption peak at 409.58 cm^{-1} indicated Nd-O bond vibrations.

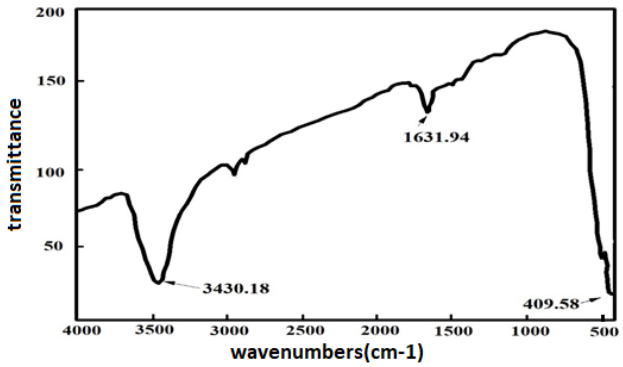

Figure 2: FTIR spectra of Nd_2O_3 NPs.

As the NPs are prepared in an aqueous medium and since the organic material used in this study is urea, based on the literature, urea reacts with water above 70°C and forms ammonium, hydroxide, and carbonate ions (carbon dioxide), which causes the pH rise up to 9 during the aging period about 1 to 2 hours at 85°C, hence the absorption band at 1631 cm^{-1} and 3430 cm^{-1} are related to the stretching vibration of C=O and the bending vibrations of OH, respectively. Also the weak bands over the range 2500 to 3000 cm^{-1} suggest intermolecular H-bonds of water with carbonate ions. Since urea is water soluble and is slowly hydrolyzed only by heating above 70°C, result in a uniform release of OH^- ions and ammonia in the reaction system according to the equation below:

$$(H_2N_2)_2CO+3H_2O \rightarrow CO_2+2NH_4^++2OH^-$$

Therefore Nd $(OH)_3$ is precipitated by Nd $(NO_3)_3$ in the presence of ammonia, which upon further heat treatment transformed into neodymium oxide.

Figure 3 shows the morphology (ellipsoidal) of the Nd_2O_3 NPs as formed after heat treated at 800°C for 3 hours and its fractional NPs size range is also shown inset. The NPs average size is about 60 to 80 nm and according to the FESEM of nanoparticles in two different scales of 1 µm (for general view of the agglomerated sample) and 200 nm (to see the shape of the individual NPs clearly). They were mostly ellipsoidal, agglomerated and consisting of several interconnected crystallites.

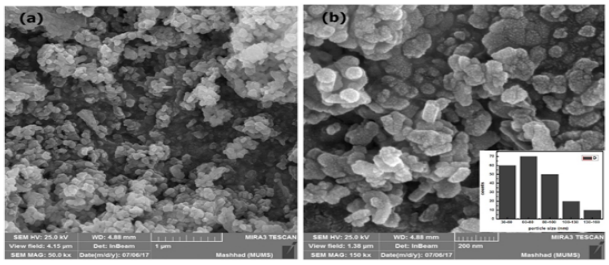

Figure 3: FESEM of the prepared Nd_2O_3 calcinated at 800°C (a) 1 µm; (b) 200 nm and the inset shows size distribution of the NPs.

The elemental composition is shown by the EDX analysis and there is somehow discrepancy between the reported atomic ratio and its chemical anticipation but it must be recalled that the EDX measurements for light elements like Oxygen would not be very exact, at all (**Figure 4**).

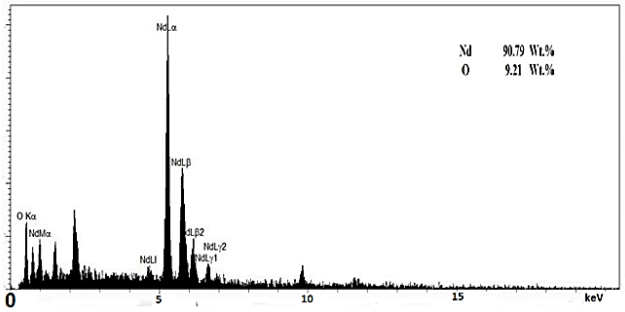

Figure 4: EDX result of Nd_2O_3 nanoparticles for elemental composition of materials

DRS technique was employed to investigate the optical property of the Nd_2O_3 NPs.The optical energy band gaps Eg of the nano-and microcrystalline materials are calculated by using the Tauc relation.

$$(\alpha h\nu)^2=A(h\nu-E_g)$$

Where α is the optical absorption coefficient near the fundamental absorption edge and the band gap is obtained from the intersection of the tangential slope of the high energy range of the DRS spectrum and the horizontal axis (**Figure 5**).

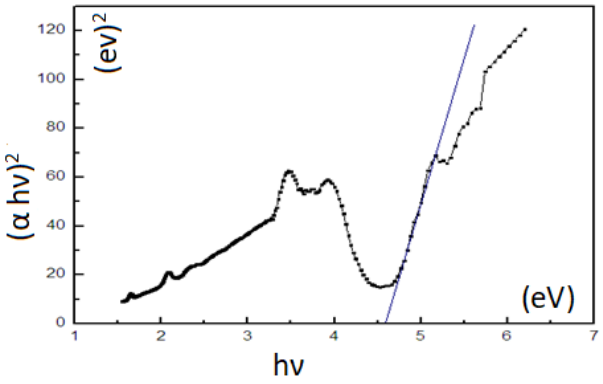

Figure 5: Finding the band gap of the Nd_2O_3 NPs.

The energy band gap of these nanoparticles is about 4.59 eV and indicated that the Nd_2O_3 sample might be employed as a photo catalyst under ultraviolet light. The complementary study of the emission property of nanoparticles has been done by PL spectroscopy and the spectrum was scanned in the wide wavelength range of 200 nm ~ 800 nm. The excitation wavelengths were 300, 340, 380 nm. The weak peaks were observed at ~ 368-398 nm (UV) shown in **Figure 6** related to the excitation wavelengths of 300 nm which these emissions in UV region was attributed to singly ionized oxygen vacancies in the Nd_2O_3 NPs (by the radioactive recombination of photo generated holes and electron occupying the oxygen vacancies. It is worth noting that the relatively low intensity of the PL spectrum in this range(compared to the literature) means that the sample had a low concentration of singly ionized oxygen vacancies *via* this fabrication method, moreover, the emission spectra also exhibit a series of emission peaks with maxima at 418–481 nm (blue). The PL peak 340 nm excitation shows series of emission peaks with maxima at 440-484 nm (blue) and 519 nm (green), and also the 380 nm excitation wavelength shows a maximum peak at 540 nm (green) (**Figure 7**). In general, The UV, blue and green emissions exhibited the presence of surface defects and recombination of electrons by shallow defect levels exciting holes in the valence band. The blue and green emissions are presumably due to surface defects such as Scotty and Frankel in the lattice. In addition, they indicated that the fabricated Nd_2O_3 NPs are a promising candidate for optical and biomedical applications because the blue and the green emission bands were result from ($^4I_{9/2}\rightarrow{}^2P_{3/2}$, $^2K_{15/2}$) and ($^4I_{9/2}\rightarrow{}^4G_{5/2}$, $^4G_{7/2}$) transitions, respectively.

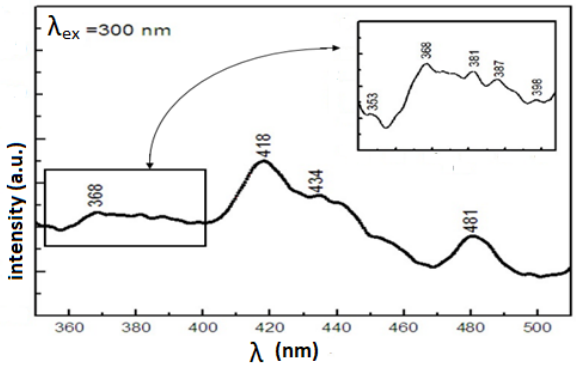

Figure 6: PL spectra of the Nd_2O_3 NPs in the range of 340 ~ 520 nm.

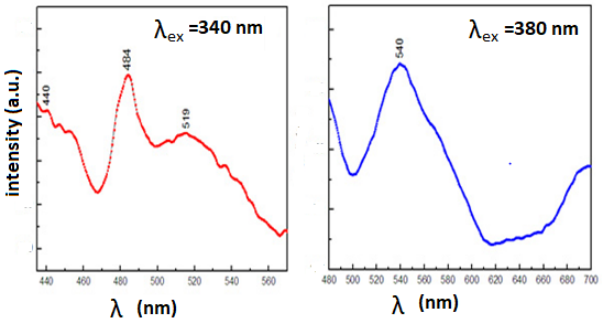

Figure 7: PL spectra of the Nd_2O_3 NPs in the range of 430~ 580 nm and 480-700 nm.

For the investigation of the magnetic properties of the sample, we have employed VSM measurement (**Figure 8**). The coercively magnitude of these NPs was about 23.29 Oe. In addition, the magnetization is linear with the applied field and does not saturate even at a maximum applied field of 10 kOe which reflected the paramagnetic nature of these NPs. This paramagnetic property can be attributed to the relatively unbalanced spins of the 3d electrons of the Nd^{3+} ion magnetic moments.

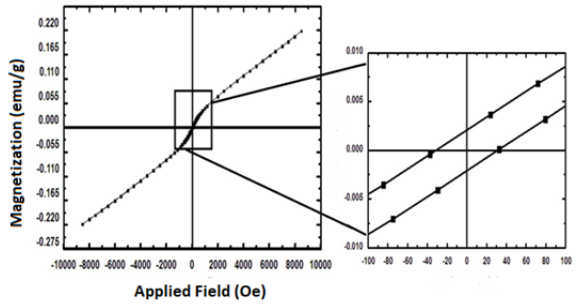

Figure 8: VSM of Nd_2O_3 NPs at room temperature.

CONCLUSION

In this study, the synthesis of Nd_2O_3 NPs by using the urea co precipitation method was investigated, which was confirmed by Rietveld refinement of the XRD pattern with the lattice parameters of a=b=3.83 Å; c=6.00 and volume cell 77.68 Å3

and space group of p3 m1. SEM image shows that the NPs were agglomerated and the average size of nanoparticles was in the range of 60 nm-80 nm. The energy gap of the NPs was obtained using the DRS analysis (~ 4.59eV). The PL spectrum of these NP investigated with excitation wavelengths of 300, 340 and 380 nm. At the excitation of 300 nm, the NPs showed the weak emission peaks at ~ 368 nm-398 nm in the UV region which means this sample has a low concentration of singly ionized oxygen vacancies. The 340 nm excitation wavelength showed series of emission peaks with the maximum at 440 nm-484 nm (blue) and 519 nm (green), and also at the 380 nm excitation wavelength showed a peak at 540 nm (green). By the VSM, it was found that the sample is paramagnetic that arising from the unpaired spins of the 3d electrons of the neodymium ions.

CONFLICTS OF INTERESTS

The authors indicate that there is no potential competing interest.

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