International Journal of
Scientific Research in Science and Technology (IJSRST)
Print ISSN : 2395-6011, Online ISSN : 2395-602X
International Conference on Advanced Materials
Held on 14, 15 December 2017, Organized by Department of Physics,
St. Joseph's College, Trichy, Tamilnadu, India

Photoluminescence Studies of $(Nd_{0.93}Sm_{0.07})_2O_3$ Nanoparticles

Morris Marieli Antoinette, S. Israel
P.G and Research Department of Physics, The American College, Madurai-625 002, India.
Corresponding Author: [2]israel.samuel@gmail.com

Abstract

$(Nd_{0.93}Sm_{0.07})_2O_3$ nanocrystalline powders were prepared using modified Pechini method. Powder X-ray diffraction was used to study the structural characterization of the synthesized sample and the results confirmed that Sm^{3+} doped Nd_2O_3 nanoparticles having a nanocrystalline structure with a hexagonal phase and $P\bar{3}m1$ space group were formed with lattice parameters a=b=3.8348Å, c=6.0031Å. These parameters were refined using CELREF software and the cell parameters were refined to give minimum R factor. The surface morphology and the size of the particles were examined using SEM and TEM. The surface micrographs showed small amount of agglomeration. TEM results also confirmed that the synthesized particles are in nanosize. The EDX spectroscopy confirmed the purity of the synthesized sample. The optical properties of the sample were studied using U-V data analysis and photoluminescence studies. The results of the optical studies proved that these materials can be highly efficient in solid state lightings.

Keywords: Modified Pechini method, Photoluminescence

1. Introduction

In recent years, nanotechnology has attracted major scientific interest because nanomaterials show distinctive or improved properties due to its nanoscale dimensions. [1] Synthesis of new materials in the nanoscale often shows unique optical, magnetic, electronic and structural properties, which are different from their respective bulk. [2-5] Rare earth elements possess unique properties and wide uses owing to their special electronic configurations. Due to the special electronic, optic, magnetic, catalytic and chemical properties, arising from the confinement of their 4f electrons, rare earth oxides with one dimensional structure such as La_2O_3, Sm_2O_3, Gd_2O_3 and Nd_2O_3 have been widely used in many functional devices. [6,7] The change in the electrical and optical characteristics of nanoparticles is caused by quantum effects due to their high surface to volume ratio, which increases the band gap. [8,9] The rare earth oxides have been synthesized by various methods including microwave-assisted, solvothermal, sol gel, hydrothermal, solution combustion, co-precipitation etc. [10-15]

Nd_2O_3 have attracted many researchers due to its extensive range of applications. It is a semiconductor with wide band gap. [16] Among rare-earth ions, the Nd^{3+} ion is one of the most efficient rare-earth ion for solid state lasers in various materials. Neodymium ions could also be good candidates for upconversion fluorescence and lasers. [17, 18] It is also used in ceramic capacitors, colour TV tubes, coloring glass, and catalyst for automotive industry. [19]

In this paper, we have synthesized Sm^{3+} doped Nd_2O_3 nanoparticles using the modified Pechini method. This method allows a molecular mixing of constituents, leading to an excellent chemical homogeneity, an increase in the reaction rate and a decrease of the temperature of crystallization. [20]

2. Experimental

2.1. Synthesis of Sm^{3+} doped Nd_2O_3 nanoparticles

Sm^{3+} doped Nd_2O_3 nanoparticles were prepared using the modified Pechini method. At first, 2 gms of Nd_2O_3 were dissolved in concentrate nitric acid under stirring to generate $Nd(NO_3)_3$. This was mixed with $Sm(NO_3)_3.6H_2O$ and dissolved in distilled water. Then EDTA was added to this solution with a molar ratio [EDTA]/[Metal] = 1, where [Metal] is the concentration of Neodymium and Samarium in the solution. In this way, a solution of metal-EDTA

International Journal of
Scientific Research in Science and Technology (IJSRST)
Print ISSN : 2395-6011, Online ISSN : 2395-602X
International Conference on Advanced Materials
Held on 14, 15 December 2017, Organized by Department of Physics,
St. Joseph's College, Trichy, Tamilnadu, India

complexes was obtained. Then ethylene glycol [EG] was added with a molar ratio [EDTA]/[EG] = 2, while stirring and heating the solution until a gel was formed. Two reactions are involved in this process: the formation of a complex between an organic acid, EDTA, with the precursor metals, and an esterification reaction with ethylene glycol (EG). The aim of the polymeric organic net produced by esterification is to reduce any segregation of the cations. It was then heated at 200 K to obtain the precursor powders. Finally, the precursor powders were calcined at 750 K for 3 hours to obtain Sm^{3+} doped Nd_2O_3 nanopowders. [16, 20-23]

2.2. Instruments used

The powder X-ray diffraction studies have been carried out by using Bruker AXS D 8 Advance X-ray diffractometer equipped with monochromatic CuK_α radiation in the 2θ range of 10-120° (λ=1.5406Å). The morphologies and composition of the prepared samples were inspected on a scanning electron microscope (SEM,VEGA 3 TESCAN, USA) equipped with an energy- dispersive X-ray spectrum (EDS, Bruker Nano, German). The transmission electron microscope (TEM, JEOL JEM-2100) studies were performed (accelerating voltage upto 200kV). The UV-VIS absorption of the sample was recorded on Varian Cary 5000 UV-VIS Spectrophotometer. Room temperature photoluminescence measurements were performed on Jobin Yvon FloroMax-3 spectroflourometer as the excitation source at 230 nm.

3. Results and Discussion

Figure 1 shows the powder X-ray diffraction pattern of the synthesized Sm^{3+} doped Nd_2O_3. Using the software Powder X the diffractogram is imported. The data is smoothened using the adaptive smooth technique. After separating the background and subtracting from the total profile, Cu-$K\alpha_2$ profile has been stripped out of the recorded profile. Sample peaks have been identified and indexing was done. On comparing these peaks with JCPDS data, it was confirmed that these belong to hexagonal system with lattice parameters a=b=3.8348Å, c=6.0031Å. These parameters were refined using CELREF software and the cell parameters were refined to give minimum R factor (R (%) =0.031). The crystallite size was calculated using the Scherrer equation,

$$\tau = \frac{0.9\lambda}{\beta \cos\theta}$$

where τ is the average grain size of the crystallites, λ is the incident wave length, β is the line broadening at half the maximum intensity (FWHM), θ is the diffraction angle.[24] The crystallite size was found to be 27 nm.

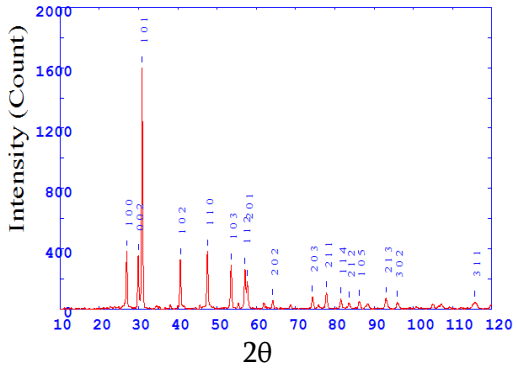

Figure 1. Indexed XRD of $(Nd_{0.93}\ Sm_{0.07})_2O_3$ nanoparticles

The morphologies of the grown nanostructures were examined using a scanning electron microscope (SEM). The morphologies of the nanostructures are demonstrated by SEM images as shown in Figure 2.

The surface morphology observed in SEM micrograph of Sm^{3+} doped Nd_2O_3 showed small amount of agglomeration which may be due to the strong interactions among the nanoparticles owing to their high surface energy during calcination. These appeared to be sponge-like structures. To get better informations, it further needs to be characterized by Transmission electron microscopy (TEM) to obtain exact morphology and size of the particles.

International Journal of
Scientific Research in Science and Technology (IJSRST)
Print ISSN : 2395-6011, Online ISSN : 2395-602X
International Conference on Advanced Materials
Held on 14, 15 December 2017, Organized by Department of Physics,
St. Joseph's College, Trichy, Tamilnadu, India

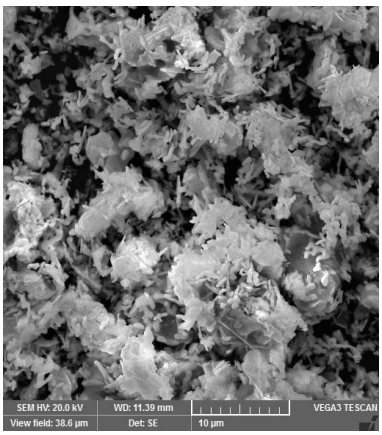

Figure 2. SEM image of $(Nd_{0.93}\ Sm_{0.07})_2O_3$ nanoparticles

The EDX spectroscopy was performed to know the percentage of the elements present in the samples and to examine the purity of the sample. The obtained percentage of the elements is shown in Table 1. The EDX spectrum observed is shown in Figure 3. It was observed that the spectrum consisted of neodymium, samarium and oxygen and there was no presence of other elements from the organic compounds which were initially used in the synthesis.

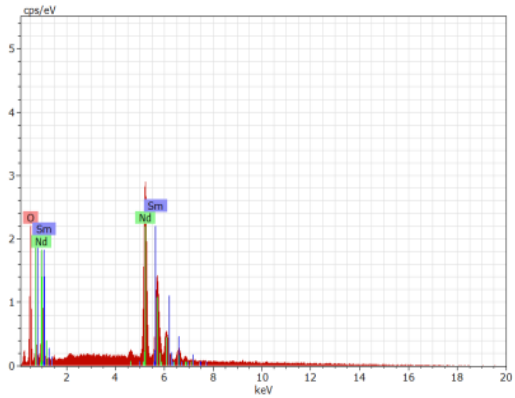

Figure 3. EDX spectra for $(Nd_{0.93}\ Sm_{0.07})_2O_3$ nanoparticles

Table 1. Percentage of elements present in the sample

Element	Wgt.%	At.%
Nd	78.53	36.22
Sm	6.86	3.03
O	14.61	60.75

TEM results confirmed that the particles are in nanosize. The TEM image obtained are shown in the Figure 4. The morphology obtained in TEM analysis was similar to SEM analysis. The particle size obtained from TEM was found to be around 35 nm, approximately equal to that of Scherrer's equation.

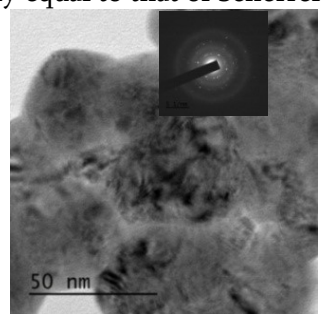

Figure 4. TEM image of $(Nd_{0.93}\ Sm_{0.07})_2O_3$ Nanoparticles

Figure 5 represents UV-VIS absorption spectrum of Sm^{3+} doped Nd_2O_3 nanoparticles. It is found that the absorption peak of nanomaterials, unlike that of bulk (~264 nm) occurs at 239 nm clearly indicating a widening of band gap. The calculated band gap value of Nd_2O_3 nanoparticles was 5.2 eV which are higher than the value of bulk Nd_2O_3, 4.7 eV. This can be attributed to the quantum confinement effect of the nanoparticles. [25]

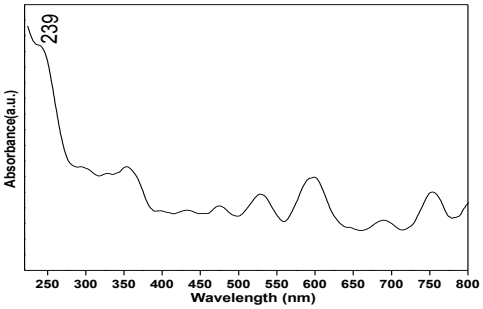

Figure 5. Absorption spectrum of $(Nd_{0.93}\ Sm_{0.07})_2O_3$ nanoparticles

International Journal of
Scientific Research in Science and Technology (IJSRST)
Print ISSN : 2395-6011, Online ISSN : 2395-602X
International Conference on Advanced Materials
Held on 14, 15 December 2017, Organized by Department of Physics,
St. Joseph's College, Trichy, Tamilnadu, India

The photoluminescence spectrum of the synthesized Sm^{3+} doped Nd_2O_3 excited under 230 nm wavelength is shown in Figure 6. The PL spectra shows a broad series of emission bands at ~ 320 - 367 nm (UV) which can be attributed to the singly ionized oxygen vacancies in Nd_2O_3. [19] It is reported that the broad UV emission can also arise due to radiative recombination of photo-generated hole with an electron occupying the oxygen vacancy. [26] The peaks at 381 and 390 nm are mainly due to the presence of surface defects that exists in the lattice. The peak at 460 nm is formed due to the second order diffraction from the source.

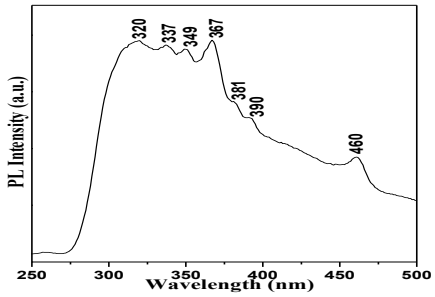

Figure 6. PL spectra of $(Nd_{0.93}\ Sm_{0.07})_2O_3$ nanoparticles

4. Conclusion

$(Nd_{0.93}Sm_{0.07})_2O_3$ nanoparticles were synthesized using modified Pechini method and were calcined at 750^{0}C. $(Nd_{0.93}\ Sm_{0.07})_2O_3$ nanoparticles were found to be highly crystalline and hexagonal in structure. Scherrer formula was used to calculate the size of the particles and the average crystallite size of the synthesized sample was 27 nm. SEM was used for surface morphology studies. SEM micrograph of the prepared samples showed small amount of agglomeration. The percentage of composition of the elements present in the sample was found from the EDAX analysis. TEM results also confirmed that the particles are in nanosize. The surface morphology obtained in TEM analysis was similar to SEM analysis. The optical band gap of Nd_2O_3 was calculated as Sm^{3+} doped 5.2 eV which are higher than the required value of bulk Nd_2O_3, 4.7 eV. This can be attributed to the quantum confinement effect of the nanoparticles. Upon 230 nm excitation, Sm^{3+} doped Nd_2O_3 nanoparticles showed a series of emission bands in the range 319 - 367 nm (UV) which reveals that the synthesized material is a promising candidate in applications for solid state lightings.

Acknowledgements

The characterization facilities provided by STIC, CUSAT, Cochin and GRI-SEM are gratefully acknowledged.

References

[1] Mortazavi-Derazkola, S., Zinatloo-Ajabshir, S., and Salavati-Niasari, M., "Preparation and characterization of Nd_2O_3 nanostructures via a new facile solvent-less route", J Mater Sci: Mater Electron, 26, 2015, pp. 5658-5667.

[2] Neto, M.C., Silva, G.H., Carmo, A.P., Pinheiro, A.S., Dantas, N.O., Bell, M.J.V., and Anjos, V., "Optical properties of oxide glasses with semiconductor nanoparticles co-doped with rare earth ions", Chem. Phy. Lett., 588, 2013, pp. 188-192.

[3] Tsuchiya, T., Watanabe, A. , Nakajima, T., and Kumagai, T., "Preparation of Y_2O_3:Eu thin films by excimer-laser-assisted metal organic deposition", Appl. Phys. A, 101, 2010, pp. 681-684.

[4] Jun, H., Qi, P., Xia, L. and Jie, L.C., "Luminescence properties of YAG: Nd^{3+} nano-sized ceramic powders via co-microemulsion and microwave heating", Bull. Mater. Sci., 36, 2013, pp. 1191–1194.

[5] Wang, G., Peng, Q., and Li, Y., "Lanthanide-doped nanocrystals: Synthesis, optical-magnetic properties and applications", Acc. Chem. Res., 44, 2011, pp. 322–332.

[6] Zhang, N., Yi, R., Zhou, L., Gao, G., Shi, R., Qui, G., and Liu, X., "Lanthanide hydroxide nanorods and their thermal decomposition to lanthanide oxide nanorods", Mater. Chem. Phys., 114, 2009, pp. 160-167.

[7] Panda, A.B., Glaspell G., and El-Shall, M. S., "Microwave synthesis and optical properties of uniform nanorods and nanoplates of rare earth oxides", J. Phys. Chem. C, 111, 2007, pp.1861-1864.

[8] Umesh, B., Eraiah, B., Nagabhushana, H., Sharma, S.C., Sunitha, D.V., Nagabhushana, B.M., Shivakumara, C., Rao, J.L., and Chakradhar, R.P.S., "Thermoluminescence and EPR studies of nanocrystalline Nd_2O_3:Ni^{2+} phosphor", Spectrochim. Acta, Part A 93, 2012, pp. 228-234.

[9] Liu, T., Zhang, Y., Shao, H. and Li, X., "Synthesis and Characteristics of Sm_2O_3 and Nd_2O_3 Nanoparticles", Langmuir, 19, 2003, pp. 7569-7572.

[10] Zawadzki, M., "Microwave-assisted synthesis and characterization of ultrafine neodymium oxide particles", J. Alloys Compd., 451, 2008, pp. 297–300.

[11] Zawadzki, M., and Kepinski, L., "Synthesis and characterization of neodymium oxide nanoparticles", J. Alloys and Compd., 380, 2004, pp. 255–259.

[12] Liu, L., Jiang, H., Chen, Y., Zhang, X., Zhang, Z. and Wang, Y., "Power dependence of upconversion luminescence of Er^{3+} doped Yttria nanocrystals and their bulk counterpart.", J. Lumin., 143, 2013, pp. 423–431.

[13] Kepinski, L., Zawadzki, M. and Mista, W., "Hydrothermal synthesis of precursors of neodymium oxide nanoparticles", Solid State Sciences, 6, 2004, pp. 1327-1336.

[14] Jayasimhadri, M., Ratnam, B.V., Jang, K., Lee, H. S., Yi, S-S., and Jeong, J-H, "Conversion of green emission into white light in Gd_2O_3 nanophosphors", Thin Solid Films, 518, 2010, pp. 6210–6213.

[15] Chandrasekhar, M., Nagabhushana, H., Sudheerkumar, K.H., Dhananjaya, N., Sharma, S.C., Kavyashree, D., Shivakumara, C., and Nagabhushana, B.M., "Comparison of structural and luminescence properties of Dy_2O_3 nanopowders synthesized by co-precipitation and green combustion routes.", Mater. Res. Bull., 55, 2014, pp. 237–245.

[16] Mendez, M., Carvajal, J.J., Cesteros, Y., Aguilo, M., Diaz, F., Giguere, A., Drouin, D., Martinez-Ferrero, E., Salagre, P., Formentin, P., Pallares, J. and Marsal, L.F., "Sol–gel Pechini synthesis and optical spectroscopy of nanocrystalline La_2O_3 doped with Eu^{3+} ", Opt. Mater., 32, 2010, pp. 1686-1692.

[17] Que, W., Kam, C. H., Zhou, Y., Lam, Y.L., and Chan, Y.C., "Yellow-to-violet upconversion in neodymium oxide nanocrystal / titania / ormosil composite sol–gel thin films derived at low temperature", J. Appl. Phys., 90, 2001, pp. 4865-4867.

[18] Lupei, V., Lupei, A. and Ikesue, A., "Transparent Nd and (Nd, Yb)-doped Sc_2O_3 ceramics as potential laser materials", Appl. Phy. Lett., 86, 2005, pp. 111118.

[19] Jian-Hua, R., Tong-Gang, Z., Jian-Hua, L., Juan, K., Jia-Xin, H., and Lin, G., "Synthesis and photoluminescence properties of Nd_2O_3 nanoparticles modified by sodium bis(2- ethylhexyl) sulfosuccinate", Chinese Phy. B, 17, 2008, pp. 4669-4672.

[20] Galceran, M., Pujol, M.C., Aguilo, M., and Diaz, F., "Sol-gel modified Pechini method for obtaining nanocrystalline $KRE(WO_4)_2$ (RE=Gd and Yb)", J. Sol–Gel Sci. Technol., 42, 2007, pp. 79-88.

[21] William, E.B., Pujol, M.C., Cascales, C., Carvajal, J.J., Mateos, X., Aguilo, M. and Diaz, F., "Synthesis and structural characterization of Tm:Lu_2O_3 nanocrystals. An approach towards new laser Ceramics", Opt. Mater., 33, 2011, pp. 722-727.

[22] Galceran, M., Pujol, M.C., Carvajal, J.J., Mateos, X., Zaldo, C., Aguilo, M., and Diaz, F., "Structural characterization and ytterbium spectroscopy in Sc_2O_3 nanocrystals.", J. Lumin., 130, 2010, pp. 1437-1443.

[23] Galceran, M., Pujol, M.C., Aguilo, M., and Diaz, F., "Synthesis and characterization of nanocrystalline Yb:Lu_2O_3 by modified Pechini method", Mater. Sci. Eng. B, 146, 2008, pp. 7-15.

[24] Kulkarni, S.K., "Analysis Techniques" in Nanotechnology: Principles and Practices, Springer, New Delhi, 2015, pp.169.

[25] Umesh, B., Eraiah, B., Nagabhushana, H., Sharma, S.C., Nagabhushana, B.M., Shivakumara, C., Rao, J.L., and Chakradhar, R.P.S., "Structural, EPR, optical and Raman studies of $Nd_2O_3:Cu^{2+}$ Nanophosphors", Spectrochim. Acta, Part A, 94, 2012, pp. 365– 371.

[26] Umesh, B., Eraiah, B., Nagabhushana, H., Nagabhushana, B.M., Nagaraja, G., Shivakumara, C., and Chakradhar, R.P.S., "Synthesis and characterization of spherical and rod like nanocrystalline Nd_2O_3 phosphors", J. Alloys and Compd., 509, 2011, pp.1146–1151.