NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2013, 4 (2), P. 241–246

SYNTHESIS OF HEXAGONAL LAF_3: ND^{3+}, SM^{3+} NANO CRYSTALS AND STUDIES OF NLO PROPERTIES

S. G. Gaurkhede[1], M. M. Khandpekar[2], S. P. Pati[3], A. T. Singh[4]

[1] Department of Physics, Bhavans College of ASC, Andheri (W) Mumbai-400058.India
[2] Material Research Lab, Department of Physics, Birla College, Kalyan – 421304.India
[3] National Institute of Science and Technology,Palur Hills,Behrampur-761008, Odisha.India
[4] Department of Physics, K. M. Agarwal College of ASC, Kalyan-421301.India
[1]s.gaurkhede@gmail.com

Hexagonal shaped LaF_3 nanocrystals (NC) doped by Nd^{3+} and Sm^{3+} ions were synthesized using a domestic microwave oven. The powder XRD study confirmed that the crystalline size of the particle was approximately 20 nm (JCPDS standard card (32–0483) of pure hexagonal LaF_3 crystals).The Transmission Electron Microscope (TEM) analysis indicated the size of the primary and secondary particles were between 15–20 nm. The presence of fundamental groups was verified by FTIR spectra. The synthesized nanocrystals were also studied for Non-Linear Optical (NLO) properties. The Second Harmonic Generation (SHG) efficiencies of LaF_3: Nd^{3+}, Sm^{3+} containing rare earth elements were found to be less than that of pure Potassium Dihydroxyl Phosphate (KDP) crystals.

Keywords: microwave radiation, hexagonal shape, luminescent properties, x-ray diffraction.

1. Introduction

In recent years, the fields of luminescence and display materials have undergone a revival of sorts with the evolution of nano-sized luminescent particles, driven primarily by an ever-increasing awareness of the unique physical and optical properties that nanometer-scale particles have when compared to their identical bulk material analogs [1]. Studies on the luminescent properties of lanthanide-doped nanoparticles have attracted a great deal of interest, since they have utility in the following applications: phosphors in lamps and display devices [2], components in optical telecommunication equipment [3], active materials in lasers [4], new optoelectronics devices [5], up converters [6–8], magnetic resonance imaging (MRI) [9], and biological fluorescent labels [10–12]. LaF_3 nanocrystals are widely used as: lubricants, additives in steel and metal alloys, electrode materials [13] and chemical- and biosensors [14]. LaF_3 possesses low phonon energy, adequate thermal and environmental stability [15], and hence, is an excellent host matrix [16–18] for investigating luminescence . Nanoparticles of LaF_3 doped with other lanthanide ions, have been studied for their luminescent properties [19–23]. In Several investigations were performed to investigate the optical properties of LaF_3:Nd^{3+} [24] for their possible use in optoelectronics devices. This paper presents a study of LaF_3:Nd^{3+}, Sm^{3+} nanoparticles synthesized in laboratory with a simple method utilizing microwave irradiation. The nanoparticles synthesized in this manner have hexagonal shape and exhibit luminescence.

2. Experimental

LaF_3: Nd^{3+} and Sm^{3+} nanocrystals were synthesized in an aqueous medium using microwave irradiation for low power heating. The method was characterized by its simplicity and cost-effectiveness. Water soluble $LaCl_3$+$NdCl_3$+ $SmCl_3$ (1 unit) and NH_4F (3 units) were mixed to obtain a solution in 1:3 molar ratio [25]. A 10 ml solution was prepared with de-ionized water in a 100 ml beaker using 0.064 mol $LaCl_3$+$NdCl_3$+$SmCl_3$. To this, a 10 ml solution of 0.576 mol NH_4F was added in a dropwise manner via a funnel fitted with a stopper to control the addition rate. The whole set up can be placed in a conventional microwave oven during reaction. The microwave oven was operated using the low power setting (in on-off mode set at 30 sec) for 30 minutes. The low power range helps to avoid overheating and bumping, thus improving the yield . A white ultrafine crystalline precipitate identified as doped LaF_3 nanocrystals appeared almost instantly at the bottom of the beaker. The precipitate was washed several times with de-ionized water, absolute methanol and acetone, and then dried it in the microwave oven for approximately 15 minutes. The dried sample was then stored in sealed tubes for further characterization.

LaF_3: Nd^{3+} and Sm^{3+} nanocrystals were also prepared using methanol in place of deionized water with the method described above.

3. Characterization

Powder x-ray diffraction (XRD) measurements were performed using a PANALYTICAL X'PERT PROMPD diffractometer model. Transmission electron microscope (TEM) analysis was performed t for different magnifications using a PHILIPS (CM 200). Fundamental groups were verified by FTIR spectra using a Spectrum one: FT-IR Spectrometer. The fluorescence spectrum was measured with a LS 45 luminescence spectrometer (Perkin Elmer Corp). NLO studies, as measured by SHG efficiency, was obtained from the crystalline powder sample by using the method of Kurtz and Perry.

4. Result and Discussion

The XRD results are shown in Fig.1 which indicated that LaF_3: $Nd^{3+}Sm^{3+}$ nanoparticles were well crystallized, and the patterns are in good agreement with hexagonal structure (Space group: P_3cl (165), Cell=0.7187×0.7187×0.735 nm^3, $\alpha = \beta = 90$ °, $\gamma = 120$ °) known for bulk LaF_3 (JCPDS card No. 32-0483) [26]. The calculated cell parameters $a = b = 0.7126$ nm and $c = 0.7255$ nm for the LaF_3: $Nd^{3+}Sm^{3+}$ nanoparticles, are smaller than those of undoped LaF_3 nanoparticles ($a = b = 0.7187$ nm and $c = 0.735$ nm.

The decrease in the lattice parameters of LaF_3: Nd^{3+} , Sm^{3+} nanoparticles can be attributed to the smaller radius of Nd^{3+} ion (0.99 nm) and Sm^{3+} ion (0.96 nm) in comparison to the La^{3+} ion (0.106 nm) [27–29]. This indicated that Nd^{3+} ions and Sm^{3+} ions were doped into the LaF_3 lattice and occupied the site of La^{3+} ions, with the formation of a LaF_3: Nd^{3+}, Sm^{3+} solid solution. The broadening of diffraction peaks for LaF_3: Nd^{3+}, Sm^{3+} nanoparticles is also shown by Fig. 1, which revealed the nanocrystalline nature of the samples. According to the Scherrer equation, $D = 0.90\lambda/\beta\cos\theta$, where D is the average crystal size, λ is the x-ray wavelength (0.15405 nm); θ and β being the diffraction angle and full width at half maximum of an observed peak, respectively. After subtraction of the equipment broadening, the full width at half maximum (FWHM) of the strongest peak (111) at $2\theta = 27.9$ ° helped to calculate the average crystalline size of LaF_3: Nd^{3+}, Sm^{3+} nanoparticles as 15–20 nm.

The transmission electron microscopy (TEM) image in Fig. 2 showed that the particles were well separated from each other. The nanocrystals had a hexagonal shape and a particle size of 6–20 nm. When these nanocrystals were incorporated into the polymer matrix, these particles were so small that the Rayleigh scattering was negligible. The selected area electron diffraction (SAED) pattern in (Fig. 2 inset) showed three strong diffraction rings corresponding to the (002), (111) and (300) reflections, which is in agreement with the hexagonal LaF_3 structure [30], suggesting that the original structure of LaF_3 was retained even after the modification. The particle sizes derived using TEM were in agreement with the values obtained from XRD studies.

Figure 3 has shown FTIR spectrum of the LaF_3: Nd^{3+}, Sm^{3+} nanocrystals. The characteristic absorption peaks were observed in the 4000–500 cm^{-1} range. The broad absorption band

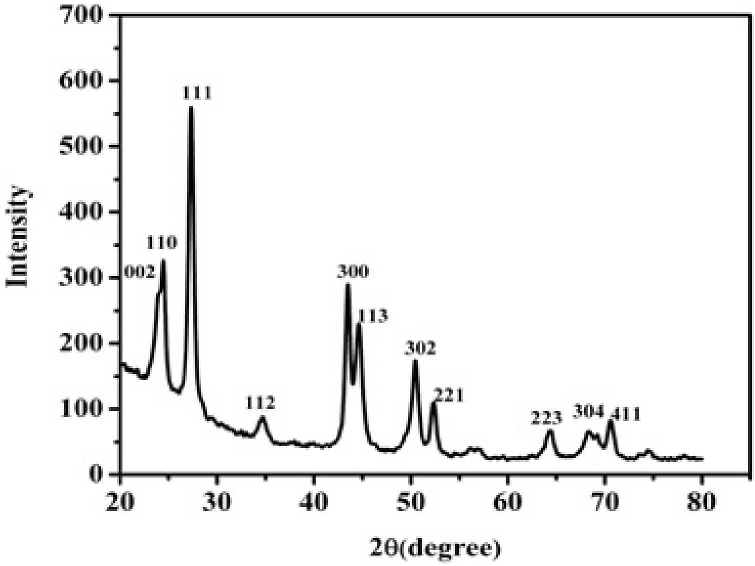

FIG. 1. XRD pattern of LaF_3: Nd^{3+}, Sm^{3+} nanocrystals

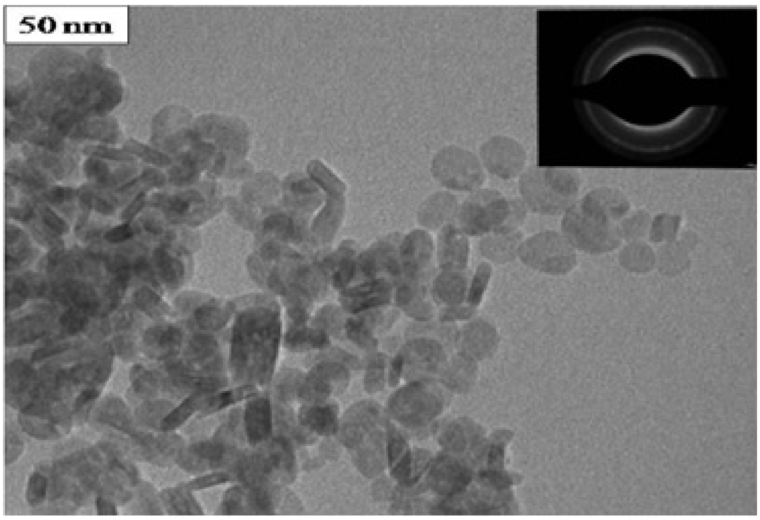

FIG. 2. TEM image of Nd^{3+}, Sm^{3+} doped LaF_3 nanocrystals

at 3434 cm^{-1} can be attributed to ν_{as} (O–H) stretching and bending vibrations. The peaks at 2925 cm^{-1} and 2853 cm^{-1} correspond to the ν_{as} (C–H) group of the long alkyl chain [31–34]. The peak at 1632 cm^{-1} could be assigned to δ (H_2O) bending vibrations from the residual water, while the one at 1439 cm^{-1} can be assigned to the asymmetric (ν_{as}) and symmetric (ν_{as}) bending vibrations of δ (O–H) group from methanol. Other absorptions can be assigned to methanol and acetone as a result of their use in the preparation of the sample.

Nonlinear optics (NLO) is the branch of optics which studies the nonlinear interactions of electromagnetic radiation and the medium through which it is propagated. The nonlinear interactions arise when the medium responds in a nonlinear manner to the incident radiation fields, this being characterized as a change in the wavelength frequency of the incident electromagnetic waves. Typically, these nonlinear interactions are observed only with very high intensity (electric field) light. Second-harmonic generation (SHG) is a second-order nonlinear phenomenon, whereby a fundamental wave is partially converted into a second-harmonic (SH)

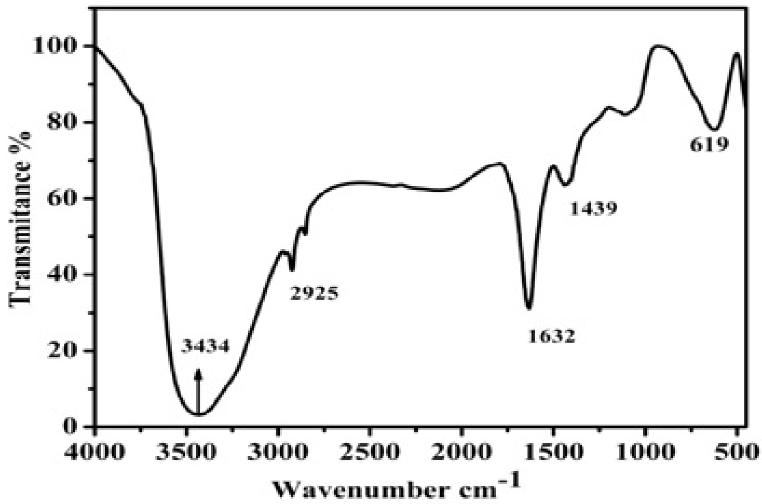

FIG. 3. FTIR spectrum of the of Nd^{3+}, Sm^{3+} doped LaF_3 nanocrystals

wave with twice the initial frequency. The experimental setup for SHG studies used a mirror and a 50/50 beam splitter. A Q – switched Nd: YAG laser (1064 nm) was used with input pulse energy of 6 mJ/pulse and pulse width of 8 ns which is incident on the LaF_3 powder. The particles were grained into fine powder and packed in the micro capillary tube after sieving. The generation of the second harmonic (SHG) was confirmed by the emission of green radiation (532 nm).

SHG is a key technology as frequency doublers of laser light. The second harmonic generation (SHG) efficiency of the LaF_3 doped Nd^{3+}, Sm^{3+} nanocrystals was studied by using modified version of the Kurtz and Perry [35] methodology with Potassium dihydrogen phosphate (KDP) as the reference material. In comparison to the harmonic signal of 22 mV produced from KDP, an SHG efficiency of 0.281 (6.2 mV) was recorded in de-ionized water and 0.513 (11.3 mV) for LaF_3 doped Nd^{3+}, Sm^{3+} in methanol. Less work has been done on SHG efficiency.

5. Conclusions

Nanocrystals of LaF_3: Nd^{3+}, Sm^{3+} have been rapidly synthesized by chemical route in an aqueous medium using domestic microwave oven at low power range. These hexagonal lanthanide-doped nanocrystals had particle sizes varying from 15–20 nm, as confirmed by both TEM and XRD studies. FTIR analysis was used for the identification of fundamental groups present in the materials. The SHG efficiency of LaF_3:Ln^{3+} (Ln^{3+}: Nd^{3+}, Sm^{3+}) containing rare earth elements was determined to be less than the value obtained for pure KDP crystals.

References

[1] B.M. Tissue. Synthesis and luminescence of lanthanide ions in nanoscale insulating hosts. *Chemistry of Materials*, **10** (10), P. 2837–2845 (1998).

[2] H. Song, B. Chen, et al. Ultraviolet light-induced spectral change in cubic nano-crystalline Y_2O_3: Eu^{3+}. *Chemical Physics Letters*, **372** (3), P. 368–372 (2003).

[3] M. Nishi, S. Tanabe, et al. Optical telecommunication- band fluorescence properties of Er^{3+}-doped YAG nanocrystals synthesized by glycothermal method. *Optical Materials*, **27** (4), P. 655–662 (2005).

[4] M.M. Lezhnina, H. Kaetker, U.H. Kynast. Synthesis and optical characterization of rare earth nanofluorides. *Optical Materials*, **30** (2), P. 264–272 (2007).

[5] Y.X. Pan , Q. Su, et al. Synthesis and red luminescence of Pr^{3+} doped $CaTiO_3$ nanophosphor from polymer precursor. *J. Solid State Chem*, **174** (1), P. 69–73 (2003).
[6] P.Y. Jia, J. Lin, M. Yu. Sol-gel deposition and luminescence properties of $LiYF_4$: Tb^{3+} thin films. *Journal of Luminescence*, **122** (1), P. 134–136 (2007).
[7] S. Sivakumar, F.C.J.M. Van Veggel, P.S. May. Near-infrared (NIR) to red and green up-conversion emission from silica sol-gel thin films made with $La_{0.45}Yb_{0.50}Er_{0.05}F_3$ nanoparticles, hetero-looping-enhanced energy-transfer (Hetero LEET): a new up-conversion process. *Journal of the American Chemical Society*, **129** (3), P. 620–625 (2007).
[8] J.S. Zhang, W.P. Qin, D. Zhao. Spectral variations and energy transfer processes on both Er^{3+} ion concentration and excitation densities in Yb^{3+}-Er^{3+} co-doped LaF_3 materials. *Journal of Luminescence*, **122** (2), P. 506–508 (2007).
[9] F. Evanics, P.R. Diamente, et al. Water-soluble GdF_3 and GdF_3/LaF_3 nanoparticles-physical characterization and NMR relaxation properties. *Chemistry of Materials*, **18** (10), P. 2499–2505 (2006).
[10] F. Wang, Y. Zhang, X. Fan, M. Wang. One-pot synthesis of chitosan / LaF_3:Eu^{3+} nanocrystals for bio-applications. *Nanotechnology*, **17** (5), P. 1527–1532 (2006).
[11] P.R. Diamente, F.C.J.M. Van Veggel. Water-soluble Ln^{3+}-doped LaF_3 nanoparticles: retention of strong luminescence and potential as biolabels. *Journal of Fluorescence*, **15** (4), P. 543–551 (2005).
[12] D.Y. Kong, Z.L. Wang, C.K. Lin, Z.W. Quan. Bio-functionalization of CeF_3:Tb^{3+} nanoparticles. *Nanotechnology*, **18** (7), Article ID 075601 (2007).
[13] M. Bralic, N. Radic, S. Brinic, E. Generalic. Fluoride electrode with LaF_3-membrane and simple disjoining solid state internal contact. *Talanta*, **55** (3), P. 581–586 (2001).
[14] N. Miura, J. Hisamoto, et al. Solid-state oxygen sensor using sputtered LaF_3 film. *Sensors and Actuators*, **16** (4), P. 301–310 (2001).
[15] O.V. Kudryavtseva, L.S. Garashina, K.K. Rivkina, B.P. Sobolev. Solubility of LnF_3 in lanthanum fluoride. *Soviet Physics-Crystallography*, **18** (2), P. 531–536 (1974).
[16] H.R. Zheng, X.J. Wang, et al. Up-converted emission in Pr^{3+} doped fluoride nanocrystals-based oxyfluoride glass ceramics. *Journal of Luminescence*, **108** (14), P. 395–399 (2004).
[17] X.J. Wang, S.H. Huang, R. Reeves. Studies of the spectroscopic properties of Pr^{3+} doped LaF_3 nanocrystals/glass. *Journal of Luminescence*, **94**, P. 229–233 (2001).
[18] S. Tanabe, H. Hayashi, T. Hanada, N. Onodera. Fluorescence properties of Er^{3+} ions in glass ceramics containing LaF_3 nanocrystals. *Optical Materials*, **19** (3), P. 343–349 (2002).
[19] M.J. Dejneka. The luminescence and structure of novel transparent oxyfluoride glass-ceramics. *Journal of Non- Crystalline Solids*, **239** (1), P. 149–155 (1998).
[20] S. Fujihara, C. Mochizuki, T. Kimura. Formation of LaF_3 microcrystals in sol-gel silica. *Journal of Non-Crystalline Solids*, **244** (2), P. 267–274 (1999).
[21] B.S. Zhuchkov, V.P. Tolstoy, I.V. Murin. Synthesis of ScF_3, LaF_3 nanolayers and $nLaF_3$-$mScF_3$ multinanolayers at the surface of silicon by successive ionic layer deposition method. *Solid State Ionics*, **101** (1), P. 165–170 (1997).
[22] J.F. Zhou, Z.S. Wu, et al. Study on an antiwear and extreme pressure additive of surface coated LaF_3 nanoparticles in liquid paraffin. *Wear*, **249** (6), P. 333–337 (2001).
[23] D.B. Pi, F. Wang et al. Luminescence behavior of Eu^{3+} doped LaF_3 nanoparticles. *Spectrochimica Acta A*, **61** (11), P. 2455–2459 (2005).
[24] J.W. Stouwdam, G.A. Hebbink, et al. Lanthanide-doped nanoparticles with excellent luminescent properties in organic media. *Chemistry of Materials*, **15** (24), P. 4604–4616 (2003).
[25] J.X. Meng, M.F. Zhang, Y.L. Liu. Hydrothermal preparation and luminescence of LaF_3:Eu^{3+} nanoparticles. *Spectrochimica Acta A*, **66** (1), P. 81–85 (2007).
[26] W.T. Carnall, G.L. Goodman, K. Rajnak, R.S. Rana. A systematic analysis of the spectra of the lanthanides doped into single crystal LaF_3. *The Journal of Chemical Physics*, **90** (7), P. 3443–3457 (1989).
[27] Y.F. Liu, W. Chen, et al. X-ray luminescence of LaF_3:Tb^{3+} and LaF_3:Ce^{3+}, Tb^{3+} water-soluble nanoparticles. *Journal of Applied Physics*, **103** (6), Article ID 063105 (2008).
[28] F. Wang, Y. Zhang, X. Fan, M. Wang. Facile synthesis of water-soluble LaF_3:Ln^{3+} nanocrystals. *Journal of Materials Chemistry*, **16** (11), P. 1031–1034 (2006).
[29] J. Wang, J. Hu, et al. Oleic acid (OA)-modified LaF_3: Er,Yb nanocrystals and their polymer hybrid materials for potential optical-amplificationapplications. *Journal of Materials Chemistry*, **17** (16), P. 1597–1601 (2007).
[30] X. Wang, J. Zhuang, Q. Peng, Y. Li. Hydrothermal synthesis of rare-earth fluoride nanocrystals. *Inorganic Chemistry*, **45** (17), P. 6661–6665 (2006).

[31] H. Guo, T. Zhang, et al. Ionic liquid based approach to monodisperse luminescent LaF_3:Ce,Tb nanodiskettes: synthesis, structural and photoluminescent properties. *Journal of Nanoscience and Nanotechnology*, **10** (3), P. 1913–1919 (2010).

[32] W.Y. Feng, T.Y. Wen, et al. Synthesis of LaF_3 superfine powder by microwave heating method. *Trans. Nonferrous Met. Soc. China*, **14** (4), P.738–741 (2004).

[33] P.J. Thistlethwaite, M.S. Hook. Diffuse reflectance fourier transform infrared study of the adsorption of oleate/oleic acid onto titania. *Langmuir*, **16** (11), P.4993–4998 (2000).

[34] P.J. Thistlethwaite, M.L. Gee, D. Wilson. Diffuse reflectance infrared fourier transform spectroscopic studies of the adsorption of oleate/oleic acid onto zirconia, Langmuir, **12** (26), P. 6487–6491 (1996).

[35] S.K. Kurtz, T.T. Perry. A powder technique for the evaluation of nonlinear optical materials. *Journal of Applied Physics*, **39** (8), P. 3798–3813 (1968).