Research Article

Red Fluorescence in Doped $\text{LaF}_3\text{:Nd}^{3+}$, Sm^{3+} Nanocrystals Synthesized by Microwave Technique

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Hexagonal shaped LaF_3 nanocrystals (NC) doped by Nd^{3+} and Sm^{3+} ions are synthesized using microwave technique. The prepared LaF_3 sample was characterized by XRD to confirm the average crystalline size of the particle is close to 20 nm (JCPDS standard card (32-0483) of pure hexagonal LaF_3 crystals). The Transmission Electron Microscope (TEM) analysis which indicates the size of the primary and secondary particle is in the range between 15 nm–20 nm. Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDAX) spectrometry have been carried out. The functional groups of the synthesized nanoparticles were confirmed by Fourier transform infrared spectroscopy (FTIR). The luminescent properties of the nanoparticles have been observed by excitation and emission spectra. Energy transfer from Nd^{3+} to Sm^{3+} has been observed. The transparency of the crystals has been confirmed using UV-VIS spectra. UV-Visible absorption spectrum indicates an energy gap of 4.9 eV and shows presence of wide transparency window. Non Linear Optical (NLO) properties of the synthesized nanoparticles have been studied. It has been found that Second Harmonic Generation (SHG) efficiency of $\text{LaF}_3\text{:Nd}^{3+}$, Sm^{3+} is less than pure Potassium Dihydroxyl Phosphate (KDP) crystals.

1. Introduction

In recent years, the fields of luminescence and display materials have undergone a revival of sorts with the evolution to nanosized luminescent particles, driven primarily by an ever-increasing awareness of the unique physical and optical properties that differ from those of identical bulk materials as the size of the particle reduced to the nanometer region [1]. Studies on the luminescent properties of lanthanide-doped nanoparticles have attracted a great deal of interest since they are considered as potentially useful phosphors in lamps and display devices [2], components in optical telecommunication [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 in lubricants, additives in steel and metal alloy, electrode materials [13] chemical sensors, and biosensors [14].

LaF_3 possesses low phonon energy and adequate thermal and environmental stability [15], and hence is an excellent host matrix [16–18] for investigating luminescence properties. Nanoparticles of LaF_3 , doped with lanthanide ions, are studied in the past for their luminescence properties [19–23]. In past, several investigations have been carried to study the optical properties of $\text{LaF}_3\text{:Nd}^{3+}$ [24] for their possible applications in optoelectronics devices. In many circumstances, the use of microwave dielectric heating as a nonclassical energy source has been shown to dramatically reduce processing times, increase product yields, and enhance product purity or material properties compared to conventionally processed experiments and hence is favored here for synthesis of $\text{LaF}_3\text{:Nd}^{3+}$, Sm^{3+} nanoparticles. Microwave oven (Sharp Corporation) Sharp Carousel, made in Thailand, Model no R 210D operating voltage 230–240 V, 1.18 kW, current 5.2 A, with output power 800 W, operating at a frequency of 2.45 GHz equipped

FIGURE 1: X-ray diffraction pattern of (A) LaF₃ nanocrystals in dewater (B) LaF₃ nanocrystals in methanol (both undoped), (b) XRD pattern of LaF₃:Nd³⁺, Sm³⁺ nanocrystals.

with an external autodialer temperature monitoring system was used for this purpose.

2. Experimental

2.1. Synthesis of Nanocrystals. LaF₃:Nd³⁺ and Sm³⁺ nanocrystals were synthesized by an aqueous route using microwave oven for heating in low power range. The method is simple and cost effective. Water soluble LaCl₃ + NdCl₃ + SmCl₃ (1 unit) and NH₄F (3 units) are mixed to obtain a solution in 1:3 molar proportion [25]. We prepared a 10 mL homogenous mixture (in deionized water) in a 100 mL beaker using 0.064 mol of LaCl₃ + NdCl₃ + SmCl₃, allowed a 10 mL solution of 0.576 mol NH₄F to drip into this solution uniformly through a funnel attached with a stopper to facilitate control of dripping and placed the whole set up inside a conventional microwave set at low power range (in on-off mode set at 30 sec) for around 30 min. The low power range setting largely helped us avoiding spill off of the solution. A white ultrafine crystalline precipitate identified as doped LaF₃ nanocrystals appears almost instantly having settled down to the bottom of the beaker. We stored this white precipitate in sealed tubes after washing it several times with deionized water, absolute methanol and acetone, and then drying it in microwave oven about 15 minutes. We subjected this specimen to detailed characterization and analysis.

LaF₃:Nd³⁺ and Sm³⁺ nanocrystals were also prepared by using methanol in place of deionized water with the method given above.

3. Characterizations

Powder X-ray diffraction (XRD) measurements have been performed using a PANALYTICAL X'PERT PROMPD diffractometer model using Cu K_α radiation $\lambda = 1.5405 \text{ \AA}$ with scanning rate of 2° per min in the 2θ range from 0°

to 80°. Transmission electron microscope (TEM) analysis has been carried out for different magnification by PHILIPS (CM 200), 0.24 nm resolution at an operating voltage of 200 kV. SEM images have been obtained using ZEISS ULTRA FESEM, with accelerating voltage from 0.1 kV to 30 kV at beam current up to 100 nA, resolution 0.8 nm at 30 kV, magnification 10x to 1000x, and image structure down to 10 nm size. Energy dispersive X-ray (EDAX) spectrometry has been done using a Quanta 200 FEG scanning electron microanalysis instrument. The UV-visible spectrum of the samples was recorded in the spectral range of 200–800 nm using a double beam (Perkin Elmer Corp.) spectrophotometer. The fluorescence spectrum was measured on LS 45 luminescence spectrometer (Perkin Elmer Corp.) using a high energy pulsed Xenon source for excitation and FL Win Lab software. NLO studies for the measurements of SHG efficiency, are obtained through the crystalline powder sample by using Kurtz and Perry technique.

4. Result and Discussion

The XRD results are shown in Figure 1(b) which indicates that LaF₃:Nd³⁺, Sm³⁺ nanoparticles are well crystallized, and the patterns are in good agreement with hexagonal structure (space group: P_3cl (165), cell = $0.7187 \times 0.7187 \times 0.735 \text{ nm}^3$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$) known for bulk LaF₃ (JCPDS card no. 32-0483) [26]. The standard formula has been used for the determination of a , b , and c parameters for hexagonal structure

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}, \quad (1)$$

where h , k , and l are the Miller indices for the XRD peaks.

The calculated cell parameters $a = b = 0.7126 \text{ nm}$ and $c = 0.7255 \text{ nm}$ for the LaF₃:Nd³⁺ Sm³⁺ nanoparticles are smaller than those of LaF₃ nanoparticles ($a = b = 0.7187 \text{ nm}$ and $c = 0.735 \text{ nm}$). The decrease in the lattice parameters

FIGURE 2: TEM image of Nd^{3+} , Sm^{3+} doped LaF_3 nanocrystals (Inset: SAED spectra).

FIGURE 3: SEM image of Nd^{3+} , Sm^{3+} doped LaF_3 nanocrystals.

of $\text{LaF}_3:\text{Nd}^{3+}$, Sm^{3+} nanoparticles can be attributed to the smaller radius of Nd^{3+} ion (0.99 nm) and Sm^{3+} ion (0.96 nm) as compared with that of La^{3+} ion (0.106 nm) [27–29]. This indicates that Nd^{3+} ions and Sm^{3+} ions are doped into the LaF_3 lattice and occupied the site of La^{3+} ions, with the formation of a $\text{LaF}_3:\text{Nd}^{3+}$, Sm^{3+} solid solution. The broadening of diffraction peaks for $\text{LaF}_3:\text{Nd}^{3+}$, Sm^{3+} nanoparticles is also shown by Figure 1, which reveals the nanocrystalline nature of the samples. According to Scherrer equation, $D = 0.90\lambda/\beta\cos\theta$, where D is the average crystallite 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 $2\theta = 27.9^\circ$ helps to calculate the average crystalline size of $\text{LaF}_3:\text{Nd}^{3+}$, Sm^{3+} nanoparticles as 15–20 nm.

The transmission electron microscopy (TEM) image in Figure 2 shows that the particles are well separated from each other. The nanocrystals have a hexagonal shape and a particle size of 6–20 nm. When these nanocrystals are incorporated in the polymer matrix, these particles are so small that the Rayleigh scattering can be nearly neglected. The selected area electron diffraction (SAED) pattern in Figure 2 inset shows 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

FIGURE 4: EDAX image of doped Nd^{3+} , Sm^{3+} LaF_3 nanocrystals.

FIGURE 5: FTIR spectrum of the from Nd^{3+} , Sm^{3+} doped LaF_3 nanocrystals.

structure of LaF_3 is retained even after the modification. The results are that particle size from TEM measurements is in agreement with those obtained from XRD studies.

Figure 3 shows the particle morphology of the prepared nanocrystals by using SEM image of $\text{LaF}_3:\text{Nd}^{3+}$ and Sm^{3+} nanocrystals under low magnification. The hexagonal nano-sized $\text{LaF}_3:\text{Nd}^{3+}$ and Sm^{3+} particles are seen as aggregates of microdimensions. These aggregates of nanocrystals of large dimensions and of assorted sizes have been observed.

Figure 4 shows energy dispersive (EDAX) spectra of the synthesized $\text{LaF}_3:\text{Nd}^{3+}$, Sm^{3+} nanoparticles. The peaks for the element, namely, lanthanide, neodymium, and samarium are clearly visible along with other trace (impurity) elements.

Figure 5 has shown FTIR spectrum of the $\text{LaF}_3:\text{Nd}^{3+}$, Sm^{3+} nanocrystals. The characteristic absorption peaks have been observed in the range from 4000 cm^{-1} to 500 cm^{-1} . The broad absorption band at about 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} can be attributed to ν_{as} (C–H)

FIGURE 6: Excitation ($\lambda_{em} = 654$ nm) and emission ($\lambda_{ex} = 357$ nm) spectra of LaF_3 nanocrystals doped Nd^{3+} , Sm^{3+} .

group of the long alkyl chain [31]. The characteristic IR peaks located at 1632 cm^{-1} could be assigned to δ (H_2O) bending vibrations from the residual absorbed water and 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 are obtained due to use of methanol and acetone while preparing the sample.

The excitation (monitored at 654 nm) and emission (excited at 357 nm) spectra of $\text{LaF}_3:\text{Nd}^{3+}$, Sm^{3+} nanocrystals are shown in Figure 6. The excited peak centered at around 327 nm corresponds to the transition $4I_{9/2} \rightarrow 4D_{7/2}$ for Nd^{3+} ion and a transition of samarium ions from $6H_{5/2}$ to $5I_{5/2}$. The emission spectrum shows a typical band between 600 and 700 nm corresponding to the $4I_{9/2} \rightarrow 4F_{9/2}$ transition of Nd^{3+} ions, with peak at 654 nm, corresponding to red coloured emission from the nanocrystals [32].

The energy level scheme of synthesized nanocrystals is shown in Figure 7. Here, Nd^{3+} energy levels arise from the $4f^3$ electronic configurations. The emission from the $4f^25d$ higher lying states is in the UV range. Some transitions among $4f^3$ levels of Nd^{3+} ion are spin-allowed, such as $4I_{9/2}$, $4F_{3/2}$, $4F_{5/2}$, $4F_{7/2}$, $4F_{9/2}$, $4G_{7/2}$ or $4F_{3/2}$, $4G_{7/2}$, $4D_{3/2}$ but this is not valid for the remaining ones. Neodymium has been recognized as one of the most efficient rare-earth luminescence centers in minerals, while its emission has been found only in the IR part of the spectrum. Nevertheless, it is well known that Nd^{3+} may also generate UV-visible luminescence in certain matrixes, for example, in laser (YAG-Nd). The Nd^{3+} UV and visible luminescence spectra consists of many narrow lines whose half-widths reach only several cm^{-1} . It has been found that the Nd^{3+} UV and visible luminescence depend on the excitation wavelength [33].

The observed Nd^{3+} UV and visible luminescence spectra are interpreted in the following way: the most intense lines originates from level $2F_{5/2}$ to $4F_{5/2}$ of Nd^{3+} resulting in UV emission, $2H_{9/2}$ (lines around 400 nm) to $4F_{9/2}$ (lines around 435 nm) and $2H_{11/2}$ (lines in the range 450–464 nm),

FIGURE 7: Energy level scheme of $\text{LaF}_3:\text{Nd}^{3+}$, Sm^{3+} nanocrystals.

FIGURE 8: UV-Vis absorption spectrum of $\text{LaF}_3:\text{Nd}^{3+}$, Sm^{3+} nanocrystals.

to $4G_{5/2}$ (lines around 480 nm) and to $2G_{7/2}$ (lines around 488 nm). In minerals, such luminescence is mixed with other rare earth elements (REE) lines and hence is not detected by steady-state spectroscopy. Trivalent samarium (Sm^{3+}) activated minerals usually display an intense luminescence spectrum with a distinct line structure in the red-orange part of the spectrum. The radiating term $4G_{5/2}$ is separated from the nearest lower level $6F_{11/2}$ by an energy interval of $\sim 7,500\text{ cm}^{-1}$. This distance is too large compared to the energy of phonons capable to accomplish an effective non-radiative relaxation of excited levels and these processes do not significantly affect the nature of the spectra in minerals. Thus, all detected lines of the Sm^{3+} luminescence take place from one excited level and are usually characterized by a long decay time [34]. UV-visible range investigated from the absorption spectra shows that the cut-off wavelength λ_{max} lies at 250 nm with a corresponding energy gap of 4.9 eV suggesting its use in optoelectronics devices as shown in Figure 8.

It is observed that the measured relative SHG efficiency of LaF_3 doped Nd^{3+} , Sm^{3+} in deionized water with KDP crystal is 0.281 and that of LaF_3 doped Nd^{3+} , Sm^{3+} in methanol with KDP crystal is 0.513 by using Kurtz and Perry technique [35].

5. Conclusions

Nanocrystals of $\text{LaF}_3:\text{Nd}^{3+}$, Sm^{3+} have been rapidly synthesized by chemical route using domestic microwave oven at low power range. Nanocrystals of hexagonal geometry with particle size varying from 15 nm to 20 nm have been located by TEM analysis which is in agreement with the average crystalline size obtained from XRD studies. SEM pattern shows dispersed particles with traces of aggregates; EDAX spectra confirm the elemental components in the nanocrystals. The FTIR spectrum has been used for identification of fundamental groups present in the material. The absorption edge in UV spectra is found at 250 nm (corresponding to 4.9 eV) and a wide window between 250 nm to 800 nm has been observed. Emission of red color (654 nm) has been observed for $\text{LaF}_3:\text{Nd}^{3+}$, Sm^{3+} nanocrystals at an excitation wavelength of 357 nm. It has been found that relative SHG efficiency of $\text{LaF}_3 = \text{Ln}^{3+}$ ($\text{Ln}^{3+} = \text{Nd}^{3+}$, Sm^{3+}) containing rare earth elements are less than pure KDP crystals.

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References

- [1] B. M. Tissue, "Synthesis and luminescence of lanthanide ions in nanoscale insulating hosts," *Chemistry of Materials*, vol. 10, no. 10, pp. 2837–2845, 1998.
- [2] H. Song, B. Chen, B. Sun, J. Zhang, and S. Lu, "Ultraviolet light-induced spectral change in cubic nanocrystalline $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$," *Chemical Physics Letters*, vol. 372, no. 3-4, pp. 368–372, 2003.
- [3] M. Nishi, S. Tanabe, M. Inoue, M. Takahashi, K. Fujita, and K. Hirao, "Optical-telecommunication-band fluorescence properties of Er^{3+} -doped YAG nanocrystals synthesized by glycothermal method," *Optical Materials*, vol. 27, no. 4, pp. 655–662, 2005.
- [4] M. M. Lezhnina, H. Kaetker, and U. H. Kynast, "Synthesis and optical characterization of rare earth nanofluorides," *Optical Materials*, vol. 30, no. 2, pp. 264–272, 2007.
- [5] Y. X. Pan, Q. Su, H. Xu et al., "Synthesis and red luminescence of Pr^{3+} -doped CaTiO_3 nanophosphor from polymer precursor," *Journal of Solid State Chemistry*, vol. 174, no. 1, pp. 69–73, 2003.
- [6] P. Y. Jia, J. Lin, and M. Yu, "Sol-gel deposition and luminescence properties of $\text{LiYF}_4:\text{Tb}^{3+}$ thin films," *Journal of Luminescence*, vol. 122-123, no. 1-2, pp. 134–136, 2007.
- [7] S. Sivakumar, F. C. J. M. van Veggel, and P. S. May, "Near-infrared (NIR) to red and green up-conversion emission from silica sol-gel thin films made with $\text{La}_{0.45}\text{Yb}_{0.50}\text{Er}_{0.05}\text{F}_3$ nanoparticles, hetero-looping-enhanced energy-transfer (Hetero-LEET): a new up-conversion process," *Journal of the American Chemical Society*, vol. 129, no. 3, pp. 620–625, 2007.
- [8] J. S. Zhang, W. P. Qin, D. Zhao et al., "Spectral variations and energy transfer processes on both Er^{3+} ion concentration and excitation densities in Yb^{3+} - Er^{3+} codoped LaF_3 materials," *Journal of Luminescence*, vol. 122-123, no. 1-2, pp. 506–508, 2007.
- [9] F. Evanics, P. R. Diamante, F. C. J. M. van Veggel, G. J. Stanis, and R. S. Prosser, "Water-soluble GdF_3 and $\text{GdF}_3/\text{LaF}_3$ nanoparticles-physical characterization and NMR relaxation properties," *Chemistry of Materials*, vol. 18, no. 10, pp. 2499–2505, 2006.
- [10] F. Wang, Y. Zhang, X. Fan, and M. Wang, "One-pot synthesis of chitosan/ $\text{LaF}_3:\text{Eu}^{3+}$ nanocrystals for bio-applications," *Nanotechnology*, vol. 17, no. 5, pp. 1527–1532, 2006.
- [11] P. R. Diamante and 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*, vol. 15, no. 4, pp. 543–551, 2005.
- [12] D. Y. Kong, Z. L. Wang, C. K. Lin, and Z. W. Quan, "Biofunctionalization of $\text{CeF}_3:\text{Tb}^{3+}$ nanoparticles," *Nanotechnology*, vol. 18, no. 7, Article ID 075601, 2007.
- [13] M. Bralic, N. Radic, S. Brinic, and E. Generalic, "Fluoride electrode with LaF_3 -membrane and simple disjoining solid-state internal contact," *Talanta*, vol. 55, no. 3, pp. 581–586, 2001.
- [14] N. Miura, J. Hisamoto, N. Yamazoe, S. Kuwata, and J. Salardenne, "Solid-state oxygen sensor using sputtered LaF_3 film," *Sensors and Actuators*, vol. 16, no. 4, pp. 301–310, 1989.
- [15] O. V. Kudryavtseva, L. S. Garashina, K. K. Rivkina, and B. P. Sobolev, "Solubility of LnF_3 in lanthanum fluoride," *Soviet Physics-Crystallography*, vol. 18, p. 531, 1974.
- [16] H. R. Zheng, X.-J. Wang, M. J. Dejneka, W. M. Yen, and R. S. Meltzer, "Up-converted emission in Pr^{3+} -doped fluoride nanocrystals-based oxyfluoride glass ceramics," *Journal of Luminescence*, vol. 108, no. 1–4, pp. 395–399, 2004.
- [17] X. J. Wang, S. H. Huang, R. Reeves et al., "Studies of the spectroscopic properties of Pr^{3+} doped LaF_3 nanocrystals/glass," *Journal of Luminescence*, vol. 94-95, pp. 229–233, 2001.
- [18] S. Tanabe, H. Hayashi, T. Hanada, and N. Onodera, "Fluorescence properties of Er^{3+} ions in glass ceramics containing LaF_3 nanocrystals," *Optical Materials*, vol. 19, no. 3, pp. 343–349, 2002.
- [19] M. J. Dejneka, "The luminescence and structure of novel transparent oxyfluoride glass-ceramics," *Journal of Non-Crystalline Solids*, vol. 239, no. 1–3, pp. 149–155, 1998.
- [20] S. Fujihara, C. Mochizuki, and T. Kimura, "Formation of LaF_3 microcrystals in sol-gel silica," *Journal of Non-Crystalline Solids*, vol. 244, no. 2, pp. 267–274, 1999.
- [21] B. S. Zhuchkov, V. P. Tolstoy, and I. V. Murin, "Synthesis of ScF_3 , LaF_3 nanolayers and $n\text{LaF}_3$ - $m\text{ScF}_3$ multilayers at the surface of silicon by successive ionic layer deposition method," *Solid State Ionics*, vol. 101-103, no. 1, pp. 165–170, 1997.
- [22] J. F. Zhou, Z. S. Wu, Z. J. Zhang, W. M. Liu, and H. X. Dang, "Study on an antiwear and extreme pressure additive of surface coated LaF_3 nanoparticles in liquid paraffin," *Wear*, vol. 249, no. 5-6, pp. 333–337, 2001.

- [23] D. B. Pi, F. Wang, X. P. Fan, M. Wang, and Y. Zhang, "Luminescence behavior of Eu^{3+} doped LaF_3 nanoparticles," *Spectrochimica Acta A*, vol. 61, no. 11-12, pp. 2455–2459, 2005.
- [24] J. W. Stouwdam, G. A. Hebbink, J. Huskens, and F. C. J. M. Van Veggel, "Lanthanide-doped nanoparticles with excellent luminescent properties in organic media," *Chemistry of Materials*, vol. 15, no. 24, pp. 4604–4616, 2003.
- [25] J. X. Meng, M. F. Zhang, and Y. L. Liu, "Hydrothermal preparation and luminescence of $\text{LaF}_3:\text{Eu}^{3+}$ nanoparticles," *Spectrochimica Acta A*, vol. 66, no. 1, pp. 81–85, 2007.
- [26] W. T. Carnall, G. L. Goodman, K. Rajnak, and R. S. Rana, "A systematic analysis of the spectra of the lanthanides doped into single crystal LaF_3 ," *The Journal of Chemical Physics*, vol. 90, no. 7, pp. 3443–3457, 1989.
- [27] Y. F. Liu, W. Chen, S. Wang, A. G. Joly, S. Westcott, and B. K. Woo, "X-ray luminescence of $\text{LaF}_3:\text{Tb}^{3+}$ and $\text{LaF}_3:\text{Ce}^{3+}, \text{Tb}^{3+}$ water-soluble nanoparticles," *Journal of Applied Physics*, vol. 103, no. 6, Article ID 063105, 2008.
- [28] F. Wang, Y. Zhang, X. Fan, and M. Wang, "Facile synthesis of water-soluble $\text{LaF}_3:\text{Ln}^{3+}$ nanocrystals," *Journal of Materials Chemistry*, vol. 16, no. 11, pp. 1031–1034, 2006.
- [29] J. Wang, J. Hu, D. Tang, X. Liu, and Z. Zhen, "Oleic acid (OA)-modified $\text{LaF}_3:\text{Er}, \text{Yb}$ nanocrystals and their polymer hybrid materials for potential optical-amplification applications," *Journal of Materials Chemistry*, vol. 17, no. 16, pp. 1597–1601, 2007.
- [30] X. Wang, J. Zhuang, Q. Peng, and Y. Li, "Hydrothermal synthesis of rare-earth fluoride nanocrystals," *Inorganic Chemistry*, vol. 45, no. 17, pp. 6661–6665, 2006.
- [31] H. Guo, T. Zhang, Y. Qiao, L. Zhao, and Z. Li, "Ionic liquid-based approach to monodisperse luminescent $\text{LaF}_3:\text{Ce}, \text{Tb}$ nanodiskettes: synthesis, structural and photoluminescent properties," *Journal of Nanoscience and Nanotechnology*, vol. 10, no. 3, pp. 1913–1919, 2010.
- [32] C. Kai, G. Chao, P. Bo, and W. Wei, "The influence of SiO_2 shell on fluorescent properties of $\text{LaF}_3:\text{Nd}^{3+}/\text{SiO}_2$ core/shell nanoparticles," *Journal of Nanomaterials*, vol. 2010, Article ID 238792, 5 pages, 2010.
- [33] K. Binnemans and C. Görller-Walrand, "On the color of the trivalent lanthanide ions," *Chemical Physics Letters*, vol. 235, pp. 163–174, 1995.
- [34] L. Van Pieterson, R. T. Wegh, A. Meijerink, and M. F. Reid, "Emission spectra and trends for $4f^n-1\ 5d \leftrightarrow 4f^n$ transitions of lanthanide ions: experiment and theory," *Journal of Chemical Physics*, vol. 115, no. 20, pp. 9382–9392, 2001.
- [35] S. K. Kurtz and T. T. Perry, "A powder technique for the evaluation of nonlinear optical materials," *Journal of Applied Physics*, vol. 39, no. 8, pp. 3798–3813, 1968.