

Rapid Communication

Synthesis and photoluminescence of single crystals europium ion-doped BaF₂ cubic nanorods

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Abstract

In this work, we used the hydrothermal method to synthesize Eu³⁺ ion-doped cubic BaF₂ nanorods, which is a luminescent material. The clubbed structures were well crystallized and exhibited face-centred cubic structures, as indicated by powder X-ray diffraction, scanning electron microscopy, electron diffraction, and transmission electron microscopy. The luminescent properties were studied, and local symmetry surrounding Eu³⁺ ions and electronic transition processes included. The results indicated that Eu³⁺ occupied only one C_{4v} site in nanorods.

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Over the past few years, one-dimensional nanostructures (such as nanowires, nanorods, nanobelts, and nanotubes) have attracted great interests due to their sizes, morphology-related properties, and their potential applications in functional nanodevices, such as nanowire-based nanolasers, nanobelt/ribbon-based nanosensors, field-effect transistors, and nanocantilevers [1,2].

It is well known that metal fluorides are efficient host lattices for luminescent centers because of their low phonon energy and optical transparency over a wide wavelength range. And rare-earth (RE) compounds have been extensively utilized as luminescent, magnetic, and other functional materials. A wide range of applications of fluorides doped with RE ions have been demonstrated, such as lasers [3], optical communications [4], and display devices [5]. For example, BaF₂ doped with RE ions have also been reported to display unique luminescence properties and can be used as scintillators [6]. RE-based fluorides of various nanostructures, including nanoparticles and nanowhiskers, have

been prepared by chemical routes such as chemical surface modification and hydrothermal method [7,8]. In our previous report [9], Y₂O₃:Eu nanotubes were fabricated by surfactant self-assembly and their optical properties were investigated using laser-selective spectroscopy. Bender and Burlitch [10] studies on fluoride nanoparticles showed that nanoscale fluorides exhibit enhanced luminescence and photomagnetic properties. Stouwdam and Van Veggel [11] used capping agents to incorporate Eu³⁺, Nd³⁺, and Ho³⁺ in LaF₃ nanoparticles, and the obtained nanoparticles were dispersible in organic solvents. Wang and Li [12] synthesized fullerene-like RE nanoparticles with hydrothermal method. Recently, Yan et al. [13] have reported the synthesis of LaF₃ triangular nanoplates by the thermolysis of La(CF₃COO)₃ in a hot oleic acid/octadecene solution, which has merits of one-step, mass production, and easy operation. These indicate that the synthesis and research of fluoride nanocrystals of photoluminescence properties have become hot topics of nanosized optical functional materials. However, there is no report on barium fluoride nanorods to date, to the best of our knowledge. In this letter, we reported the preparation of europium-ion-doped

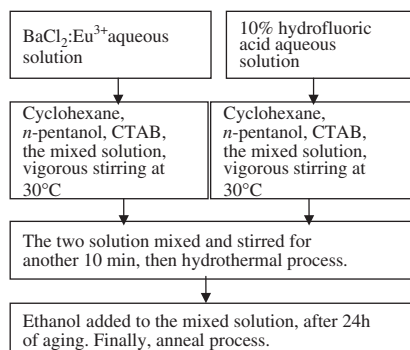
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BaF₂ nanorods and studied the photoluminescence properties.

The method of fabricating BaF₂:Eu³⁺ microrods is as follows. In typical synthesis, two identical solutions were prepared by dissolving cetyltrimethylammonium bromide (CTAB; Aldrich) (0.4 g) in 6 mL of cyclohexane and 0.5 mL of *n*-pentanol. The mixing solution was stirred for 30 min until it became transparent. Quantities of 0.38 mmol BaCl₂ (Aldrich) and 0.02 mmol EuCl₃·6H₂O (Aldrich) were dissolved in 2 mL deionized water to form a clear solution, and 1 mL of 40% HF (Aldrich) aqueous solution was added in the solution; after stirring vigorously at 30 °C, the two optically transparent microemulsion solutions were mixed and stirred for another 10 min. Then, the resulting microemulsion solution was then transferred into a 25 mL stainless Teflon-lined autoclave and heated at 130 °C for 12 h. The resulting suspension was immediately cooled to room temperature, and ethanol was added in. The resulting compounds were stored at a constant temperature of 35 °C. After aging for 24 h, samples were collected and washed several times with absolute ethanol and distilled water. Following the BaF₂, powder was obtained after the samples were centrifuged and dried in vacuum at room temperature. The powder was calcined at 500 °C for 30 min in an inert atmosphere. The synthesis route was shown in Scheme 1.

Phase identification was performed via X-ray diffraction (XRD) (model Rigaku RU-200b), using nickel-filtered CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). The size and morphology were characterized by scanning electron microscopy (SEM) and JEM-2010 transmission electron microscopy (TEM) (JEOL Company, Japan). The specimens for TEM observations were supported by copper substrate. The samples were mounted in the helium exchange gas chamber of a closed cycle refrigeration system and their temperature maintained at 10 K. A rhodamine 6 G dye laser pumped by the second harmonic of an Nd:YAG pulsed laser was used as the excitation source. The pulse duration was 10 ns, and the repetition frequency was 10 Hz. The fluorescence spectra were obtained with a Spex 1403 spectrometer. Photoluminescence signals were detected by a photomultiplier, which was averaged with a boxcar integrator and processed by a computer. Room temperature emission



Scheme 1. Synthesis route of BaF₂:Eu³⁺ nanorods.

spectra were recorded with a Hatachi F-4500 fluorescence spectrometer with an Xe lamp as the excitation source.

Fig. 1 shows the XRD pattern of the as-prepared samples calcined at 500 °C. All of the diffraction peaks can be readily indexed to that of the hexagonal phase BaF₂ (space group *Fm* $\bar{3}$ *m* (225)) with lattice constants $a = 6.200 \text{ \AA}$, which is in good agreement with the standard values for the bulk cubic BaF₂ (JCPDS 85-1342). No impurity can be identified from the XRD pattern, which suggests that our synthesis is a promising method to prepare pure and single-phased barium fluoride. In addition, it was found peak (111) is the only peak gaining substantial increases in relative intensity, which indicates that the rods growth may occur along the (111) direction.

Fig. 2a is a wide-field SEM image of the as-prepared BaF₂ nanorods, which clearly indicates that the product is entirely comprised of a relatively uniform, rod-like morphology. More details about the structure of rods were investigated by the selected area electron diffraction

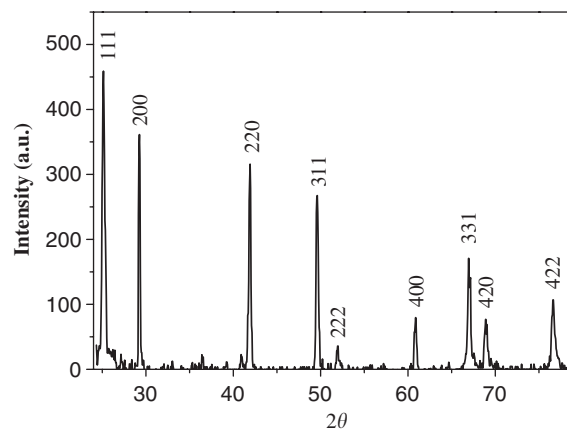


Fig. 1. XRD pattern of BaF₂:Eu³⁺ nanorods.

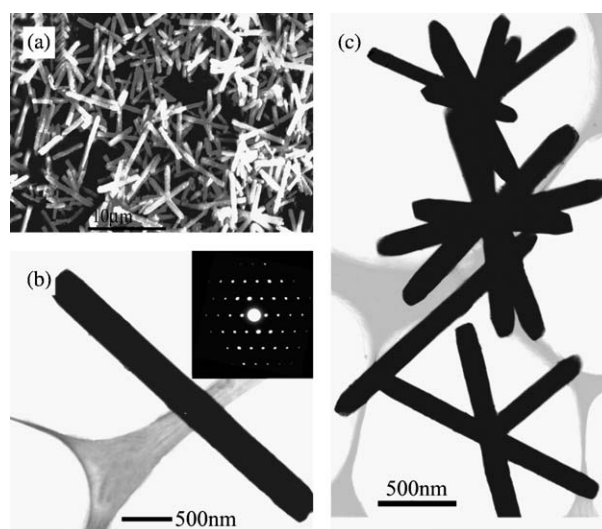


Fig. 2. (a) SEM image of the BaF₂:Eu³⁺ nanorods. (b) TEM image of an individual BaF₂:Eu³⁺ nanorod. Inset: Electron diffraction patterns of the nanorods. (c) TEM image of BaF₂:Eu³⁺ nanopropellers.

(SAED) pattern and TEM analysis. The inset in Fig. 2b shows the electron diffraction pattern recorded perpendicularly to the nanorod [310] zone axis, which reveals that the nanorods were single-phased crystals and also stable enough to withstand the irradiation of convergent high-energy electron beam. The SAED image taken from the rods indicated in Fig. 2c can be indexed as a cubic BaF_2 single-phased crystal, which is in good agreement with the XRD results presented above. Moreover, the SAED images taken from different positions along the rod are found to be almost identical. This indicates that the entire rod is a single-phased crystal. TEM observations reveal the column of nanopropeller [14] (Fig. 2c). Fig. 2c shows the surfaces of BaF_2 nanorods are clean and smooth. SAED images have been measured and no movement has been observed. In our opinion, the rods were grown from one point but not the easy stack. The nanorods are rather straight and have a uniform diameter along the entire

length. According to the SEM and TEM images, the rods are 1.5–3.0 μm in length, and 200–250 nm in diameter, which accounts for their aspect ratios as high as 10.

Fig. 3a shows the excitation wavelength was 393 nm of $\text{BaF}_2:\text{Eu}$ nanorods. The wide band extending from 215 to 276.7 nm was associated with the charge transfer transition from the $2p$ orbital of F^- ions to the $4f$ orbital of Eu^{3+} ions, and the sharp lines were associated with the direct excitation of the $f-f$ shell transitions of Eu^{3+} .

Fig. 3b present the room temperature emission spectra of $\text{BaF}_2:\text{Eu}$ nanorods under 393 nm excitation. The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ transitions ($J = 1, 2, 3, 4$) were observed, as labelled in Fig. 3b. Among them, the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transitions were the strongest one. In Fig. 3b, the intensity ratio of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ in nanorods is 0.14. As is well known, the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ lines originate from magnetic dipole transition, while the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ lines originate from electric dipole transition. In terms of the Judd–Ofelt theory [15–17], the magnetic dipole transition is permitted. The electric dipole transition is allowed only on the condition that the europium ion occupies a site without an inversion centre and is sensitive to local symmetry. Subsequently, when Eu^{3+} ions occupy inversion centre sites, the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition should be relatively strong, while the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$

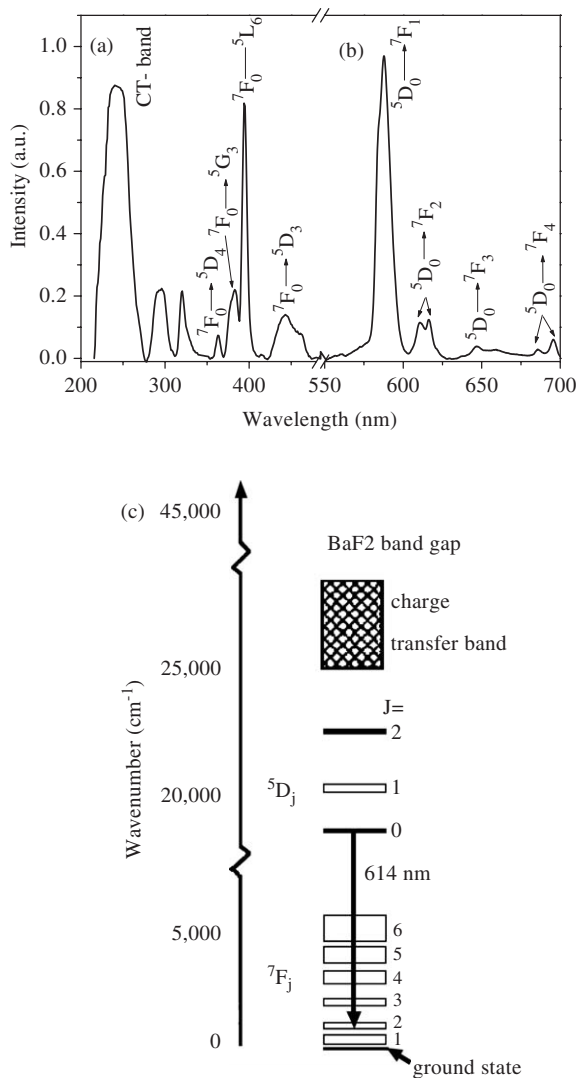


Fig. 3. (a) Excitation spectra of $\text{BaF}_2:\text{Eu}^{3+}$ nanorods, monitored at 614.5 nm emission position at room temperature. (b) Emission spectra of $\text{BaF}_2:\text{Eu}^{3+}$ nanorods under 393 nm excitation at room temperature. (c) Partial energy level diagram for Eu^{3+} in BaF_2 .

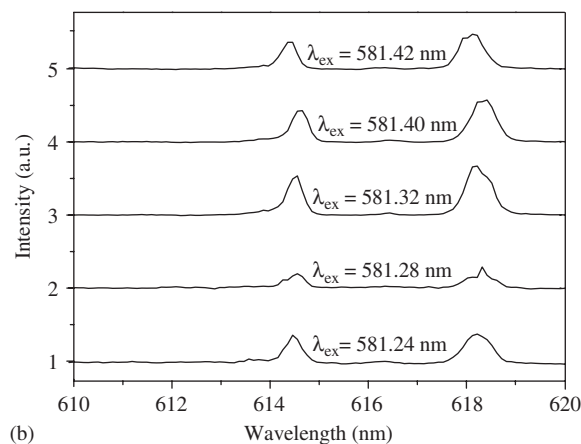
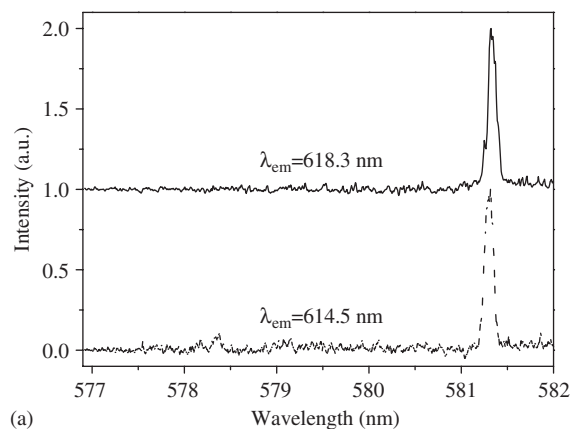


Fig. 4. (a) ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$ excitation spectra monitoring different sites and (b) site-selective emission spectra of $\text{BaF}_2:\text{Eu}^{3+}$ nanorods at 10 K (delay time is 50 μs).

transition should be relatively weak. Fig. 3c shows energy level diagrams of Eu^{3+} -doped BaF_2 .

As mentioned already, BaF_2 belongs to the face-centred cubic type. In BaF_2 systems, Ba^{2+} ions occupy C_{4v} point group. In Eu^{3+} -doped BaF_2 , Eu^{3+} ions substitute for some of Ba^{2+} ions. Figs. 4a and b shows, respectively, the ${}^7F_0 \rightarrow {}^5D_0$ excitation spectra monitoring different ${}^5D_0 \rightarrow {}^7F_2$ sites, and ${}^5D_0 \rightarrow {}^7F_0$ emission spectra selectively exciting ${}^7F_0 \rightarrow {}^5D_0$ transitions in the nanorods. In Fig. 4a, only excitation line was observed. The peak location of the line had only a little shift, and the spectral configuration almost did not change as it monitored different ${}^5D_0 \rightarrow {}^7F_2$ sites. In Fig. 4b, from the spectral configuration, five lines were distinguished. These results indicate that in nanorods, the ${}^5D_0 \rightarrow {}^7F_2$ transitions originated from one symmetry site [9,18].

In conclusion, $\text{BaF}_2:\text{Eu}$ rod like were synthesized by a simple hydrothermal method. XRD analysis showed that the products were single cubic phase. SEM and TEM images confirmed the formation of the three-dimensional rods structures. The results of low temperature (10 K) laser-selective excitation indicated that there is only one emission centre (C_{4v}).

Acknowledgments

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References

- [1] M.H. Huang, S. Mao, H. Feick, H.Q. Yan, Y.Y. Wu, H. Kind, E. Weber, R. Russo, P.D. Yang, *Science* 292 (2001) 1897.
- [2] J. Hu, M. Ouyang, C.M. Lieber, *Nature* 399 (1999) 48.
- [3] R. Reisfeld, C.K. Jorgensen, *Lasers and Excited States of Rare Earths*, Springer, Berlin, 1997.
- [4] P.C. Becker, N.A. Olsson, J.R. Simpson, *Erbium Doped Amplifiers: Fundamentals and Technology*, Academic Press, San Diego, CA, 1999.
- [5] G. Blasse, B.C. Grabmaier, *Luminescent Materials*, Springer, Berlin, 1994.
- [6] A. Wojtowicz, *J. Nucl. Instrum. Methods A* 486 (2002) 201.
- [7] M.H. Cao, C.W. Hu, E.B. Wang, *J. Am. Chem. Soc.* 125 (2003) 11196.
- [8] J. Zhou, Z. Wu, W. Liu, H. Dang, *Wear* 249 (2001) 333.
- [9] C. Wu, W. Ping, G. Qin, D. Zhao, J. Zhang, S. Huang, S. Lu, H. Liu, H. Yan, *Appl. Phys. Lett.* 82 (2003) 520.
- [10] C.M. Bender, J.M. Burlitch, *Chem. Mater.* 12 (2000) 1969.
- [11] J.W. Stouwdam, F.C.J.M. Van Veggel, *Nanoletters* 2 (2002) 733.
- [12] X. Wang, Y.D. Li, *Angew. Chem. Int. Ed.* 42 (2003) 3497.
- [13] Y.W. Zhang, X. Sun, R. Si, L.P. You, C.H. Yan, *Am. Chem. Soc.* 127 (2005) 3260.
- [14] P.X. Gao, Z.L. Wang, *Appl. Phys. Lett.* 84 (2004) 2883.
- [15] I.V. Kityk, *J. Phys. Condens. Matter* 17 (2005) 5235.
- [16] B.R. Judd, *Phys. Rev.* 127 (1962) 750.
- [17] G.S. Ofelt, *J. Chem. Phys.* 37 (1962) 511.
- [18] L.X. Yu, H.W. Song, S.Z. Lu, Z.X. Liu, L.M. Yang, X.G. Kong, *J. Phys. Chem. B* 108 (2004) 16697.