

Hydrothermal synthesis of NaEuF₄ spindle-like nanocrystals

ZHI-JUN WANG^{1,2*}, FENG TAO^{1,2}, WEI-LI CAI³, LIAN-ZENG YAO³ and XIAO-GUANG LI³

¹School of Mechanical and Automotive Engineering, Anhui Polytechnic University, Wuhu, Anhui 241000, P.R. China

²Anhui Provincial Laboratory of High Performance Nonferrous Metals Material, Wuhu, Anhui 241000, P.R. China

³Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, P.R. China

MS received 5 December 2008; revised 15 March 2011

Abstract. NaEuF₄ spindle-like nanocrystals have been synthesized through a simple hydrothermal method. The nanocrystals were well crystallized and exhibited fine morphology, as indicated by X-ray diffraction, transmission electron microscope and selected area electron diffractometer. The luminescence properties of these NaEuF₄ products were investigated.

Keywords. Hydrothermal synthesis; spindle-like; NaEuF₄; luminescence; nano-crystals.

1. Introduction

In recent years, the interest in using fluoride hosts doped with rare earth ions for optical applications has been widely demonstrated (Johnson and Guggenheim 1971; Macfarlane *et al* 1992; Pie and Rand 1992; Zhang *et al* 1994). Among the investigated fluorides, alkali metal rare earth tetrafluorides with general formula ARF₄ (A = Li, Na, K, R = rare earth), with large gap and low phonon energy, which result in lower multiphonon emission rates and high luminescence efficiencies, are referred to as one of the more efficient hosts for optical materials (Wegh *et al* 1999; Yi *et al* 2004; Zeng *et al* 2005). The phase, morphology and size of nanocrystals are important elements for their electrical, optical and other properties; so, controlled syntheses of well-defined crystals have become a hot research field in recent years (Klein *et al* 1997; Patzke *et al* 2002; Xia *et al* 2003; Luo *et al* 2005). However, most complex fluorides were prepared at high temperatures and pressures in traditional methods (Demianets 1990; Thoma *et al* 1966). Hence, synthesis of fluoride crystals with uniform size and morphology under milder reaction conditions is a desirable goal. Recently, some relative mild approaches have been developed to prepare alkali metal rare earth tetrafluorides. Lu *et al* (2002) reported mechano-chemical synthesis of nano-sized complex fluorides ARF₄ from the reaction of AF and RF₃ powders. The co-deposition method and the hydrothermal method have been used to synthesize

NaRF₄ nano- and micro-crystals (Xun *et al* 1997; Martin *et al* 1999; Liang *et al* 2004; Huang and Meng 2005; Wang *et al* 2005, 2006; Zeng *et al* 2006). Mai *et al* (2006) reported a general synthesis of NaRF₄ nanocrystals via the co-thermolysis of Na(CF₃COO) and RE(CF₃COO)₃. To increase the luminescence intensity for better and wider applications, the synthesis of complex fluoride nanocrystal phosphors with controlled phase, morphology and size remains a challenge. In this paper, ethylenediaminetetra-acetic acid (EDTA)-mediated hydrothermal process was developed to synthesize nanosized spindle-like NaEuF₄ structures with high yield. The luminescence properties of NaEuF₄ nanocrystals were investigated in detail.

2. Experimental

In a typical procedure, 1 mmol of Eu₂O₃ was dissolved in a dilute HNO₃ solution, after the solution was dried distilled water was added, and then 2 mmol of EDTA was added to the solution. Subsequently, 1 mmol of NaF was added into the mixture under vigorous stirring to obtain a fluoride precursor. The suspension was transferred into a 30 ml Teflon-lined stainless steel autoclave. Distilled water was added into the vessel until about 80% of its volume, and the pH was adjusted to a specific value using a dilute NaOH or HNO₃ solution. After the autoclave was tightly sealed, it was heated at 180°C for 5 h, and then cooled down to room temperature naturally. The products were collected and washed several times with distilled water and absolute ethanol in turn, and finally dried in air at about 70°C for 12 h.

*Author for correspondence (zhijunwang@ahpu.edu.cn)

The phase purity of NaEuF₄ nanocrystals was analyzed by X-ray diffraction (XRD) on an X-ray diffractometer (D/MAX- γ A) with CuK α radiation ($\lambda = 0.15418$ nm). The morphologies of NaEuF₄ nanocrystals were examined on a transmission electron microscope (TEM, H800) and a high-resolution transmission electron microscopy (HRTEM, JEOL-2010), and selected area electron diffractometer (SAED) attached to it. The photoluminescence spectra were measured with a FLUOROLOG-3-TAU steady-state/lifetime fluorescence spectrometer at room temperature. Thermogravimetric analysis (TGA) was conducted by using a TGS-2 thermogravimetric system.

3. Results and discussion

XRD patterns of the obtained NaEuF₄ nanocrystals are shown in figure 1. All the diffraction peaks agree well with those of hexagonal phase NaEuF₄ (JCPDS No. 49, 1987), although the diffraction peaks are broadened owing to the small particle size. No peaks of other impurities were detected in the experimental error range, which implies pure phase NaEuF₄ has been synthesized.

The shapes and structures of the as-obtained hexagonal NaEuF₄ nanocrystals were further investigated by SEM and TEM. The shape and the crystallinity of the products were found to be correlative with the molar ratio of F⁻/Eu³⁺, pH value of the mother liquors and the reaction time. Table 1 lists the preparation conditions for NaEuF₄. As shown in figure 2, it is very clear that when the molar ratio of F⁻/Eu³⁺ is 4, the other reaction conditions being fixed, the obtained samples are well-defined spindle-like nanocrystals with length *a* of about 500 nm and by width *b* of around 150 nm as shown in figure 2a. The width of the samples increases from the ends to the centre. The spindle-like nanocrystals could be useful for studying the facet-specified photochemical and chemical processes, which

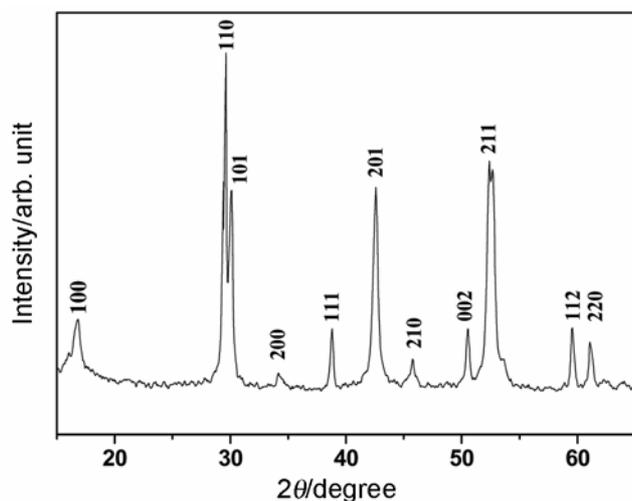


Figure 1. XRD pattern of NaEuF₄ spindle-like nanocrystals.

occurred at the interface between a nanocrystal and its surroundings (Aldana *et al* 2001), because these spindle-shaped nanocrystals exclude any facets perpendicular to the *c*-axis. Figure 2b gives the HRTEM image recorded on a part of a spindle-like nanocrystal and its corresponding electron diffraction (ED) pattern. The diffraction spots in ED pattern indicate that the samples are of the single crystallinity in nature, which was further supported by the HRTEM image. Lattice fringes corresponding to the lattice spacing of (001) planes and (110) planes of hexagonal NaEuF₄ can be observed on the individual particles. The calculated angle between [001] and [110] is about 90°, which is consistent with the measured values. Thus, it can be presumed that the growth direction is along the [001] (the *c*-axis).

Interestingly, when increasing the molar ratio F⁻/Eu³⁺ to 6, the spindle shape gradually change to a relatively round rod shape (figure 3a), and when the molar ratio of F⁻ to Eu³⁺ is 7.5, the obtained samples are nanoprisms with a size of ~150 nm × 600 nm (length × thickness) (figure 3b), which shows that the aspect ratio of nanocrystals increased as the molar ratio of F⁻ to Eu³⁺ is increased. When fixing the other reaction conditions, the pH value was found to be as an important factor to determine the crystalline of the resulting nanocrystals. When the pH value increases, the crystallinity of the as-obtained NaEuF₄ nanocrystals is relatively low and the uniformity is not perfect (figure 3c).

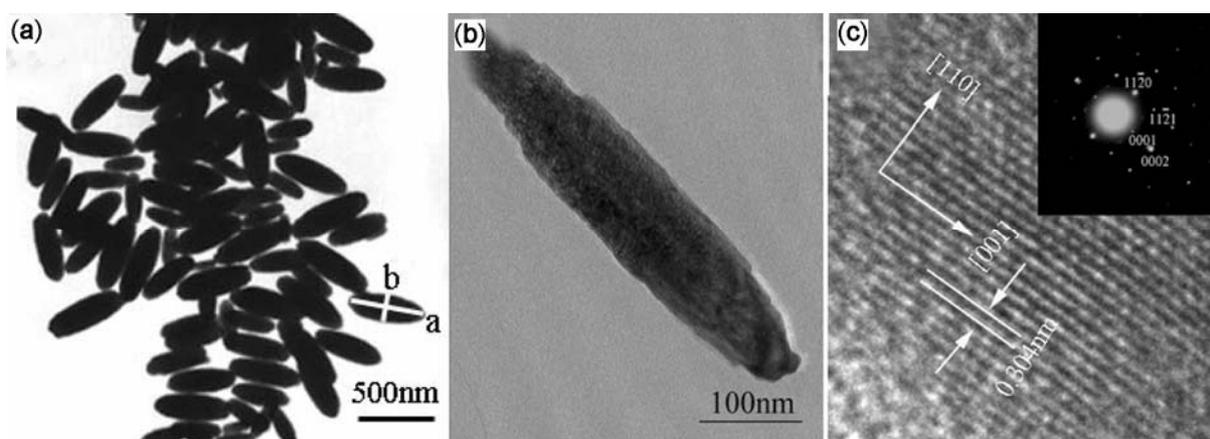
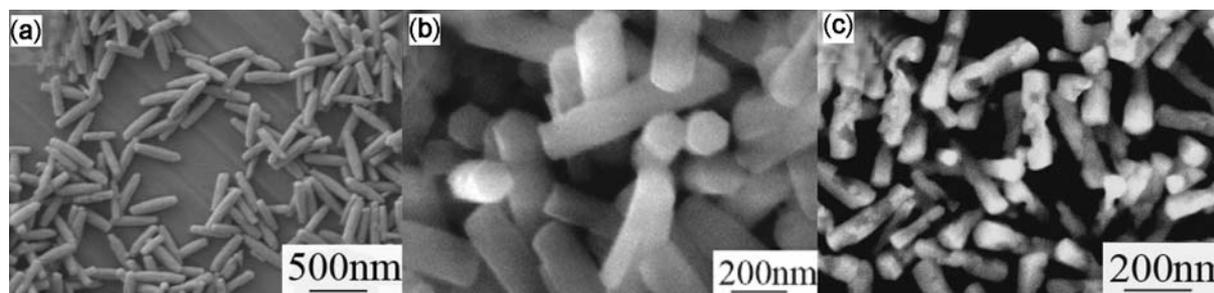
Some experiments were carried out in order to study the effects of the mediated reagent EDTA. It is found that without the addition of EDTA, a mixture of NaEuF₄ and EuF₃ is obtained. And other ligands such as cetyltrimethyl ammonium bromide (CTAB) and sodium dodecyl benzene sulfonate (SDBS), lacking of chelation capability, are also used to mediate the growth in this hydrothermal reaction when fixing other conditions. However, the obtained samples are not pure NaEuF₄. It is believed that the use of EDTA is critical for the successful synthesis of the pure phase NaEuF₄ at the same reaction condition.

The thermal stability of the as-prepared NaEuF₄ was studied by TG analyses in air. As shown in figure 4, no phase transition or mass loss was observed from 14°C up to 600°C. These observations indicated that the NaEuF₄ are stable in dry air, which, is consistent with the results reported previously (Xun *et al* 1997).

Room temperature emission spectra of the as-obtained NaEuF₄ spindle-like nanocrystals are presented in figure 5. When excited at about 394 nm, the emission spectrum consists of lines mainly located in the orange to red spectral area (from 580 nm to 720 nm). These lines correspond to transitions from the excited ⁵D₀ levels to ⁷F_J (*J* = 1, 2, 3, 4) levels of 4*f*⁶ configuration in Eu³⁺. The most intense peaks are centered at 615 and 591 nm in the red spectrum region. The peak at 580 nm is the fine splitting of the ⁵D₀–⁷F₁. The 4*f* energy levels of Eu³⁺ are hardly affected

Table 1. Hydrothermal synthesis conditions of samples prepared.

Mediated reagent	$n(F^-) : n(Eu^{3+})$	pH value	React time	Crystallinity	Product
EDTA	4	3	5	Good	H-NaEuF ₄ , spindle
EDTA	6	3	5	Good	H-NaEuF ₄ , rod
EDTA	7.5	3	5	Good	H-NaEuF ₄ , rod
EDTA	7.5	7	5	Bad	H-NaEuF ₄ , rod
EDTA	7.5	3	10	Good	H-NaEuF ₄ , rod
No added	4	3	5	Bad	H-NaEuF ₄ and O-EuF ₃
No added	7.5	3	5	Bad	H-NaEuF ₄ , irregular particle
CTAB	4	3	5	Bad	O-EuF ₃ , irregular
SDBS	4	3	5	Bad	O-EuF ₃ , irregular

**Figure 2.** (a) TEM image of NaEuF₄ spindle-like nanocrystals; (b) magnified TEM image of single NaEuF₄ spindle-like nanocrystal and (c) the corresponding HRTEM image and SAED pattern.**Figure 3.** SEM image obtained at different conditions: (a) molar ratio F⁻/Eu³⁺ = 6; (b) molar ratio F⁻/Eu³⁺ = 7.5 and (c) pH = 7.

by the crystal field, due to the shielding of the $5s^25p^6$ electrons, and therefore there is no prominent shift in the positions of the emission peaks compared with other Eu³⁺ doped materials. The intensity ratio of $I(^5D_{0-7}F_2)/I(^5D_{0-7}F_1)$ is larger than that reported previously (Mai *et al* 2006; Shi *et al* 2010).

Compared to the bulk NaEuF₄, the ratio of I_{615}/I_{591} is >1 , while the ratio of I_{615}/I_{591} for bulk NaEuF₄ is <1 . This is because the surface effect of nano-materials is conducive to electric dipole transitions (Zakaria *et al* 1997; Tian *et al* 2009). In addition, the ratio of I_{615}/I_{591} also relate to the symmetry of the coordination environ-

ment for Eu³⁺ ions. The symmetry of the crystal sites in which Eu³⁺ ions are located is determined by the ratio of $^5D_{0-7}F_1$ and $^5D_{0-7}F_2$ transitions. In a site with inversion symmetry the $^5D_{0-7}F_1$ magnetic-dipole transition is dominant, while in a site without inversion symmetry the $^5D_{0-7}F_2$ electric-dipole transition is dominant. As shown in figure 5, peaks correspond to $^5D_{0-7}F_2$ transition are stronger than the peaks correspond to $^5D_{0-7}F_1$ transition, revealing that the Eu³⁺ ions occupy the lattice sites without inversion centre-symmetry. That is to say, the crystal structure of hexagonal phase NaEuF₄ belongs to a non-centre-symmetric space group.

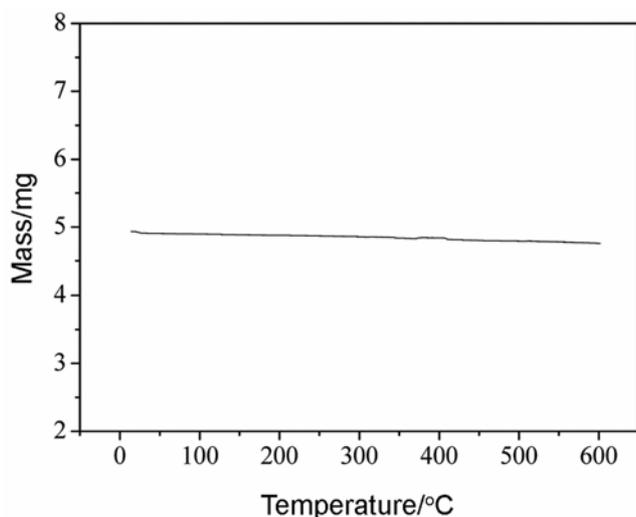


Figure 4. TGA curve of NaEuF₄ nanocrystal.

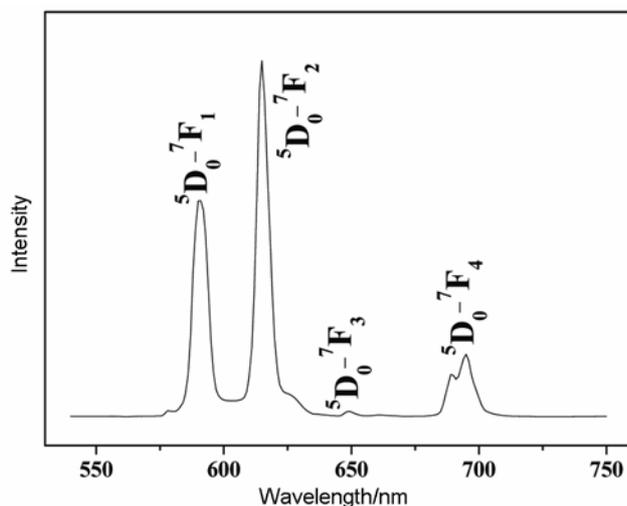


Figure 5. Room temperature emission spectra of NaEuF₄ spindle-like nanocrystals when excited at 394 nm.

4. Conclusions

In summary, we have successfully synthesized NaEuF₄ nanocrystals with spindle-like structures by controlling the solution reaction conditions. SAED and HRTEM studies indicate that as-prepared NaEuF₄ nanocrystals have the [001] growth direction. Strong orange and red light emission is observed from room temperature emission spectrum of as-prepared NaEuF₄ spindle-like nanocrystals.

Acknowledgements

The authors would like to thank Science and Technological Fund of Anhui Province for Outstanding Youth

(08040106824) and Scientific Research Foundation of Anhui Polytechnic University (2007YQ004, 2007YQ003) for financial support.

References

- Aldana J, Wang Y and Peng X 2001 *J. Am. Chem. Soc.* **123** 8844
- Demianets L N 1990 *Prog. Cryst. Growth Charact.* **21** 299
- Huang M W and Meng F Y 2005 *Lumin.* **20** 276
- Johnson L F and Guggenheim G J 1971 *Appl. Phys. Mater.* **19** 44
- Klein D I, Roth R, Lim A K L, Alivisatos A P and McEuen P L 1997 *Nature* **389** 699
- Liang L F, Xu H X, Su Q, Konishi H, Jiang Y B, Wu M M, Wang Y F and Xia D Y 2004 *Inorg. Chem.* **43** 1594
- Lu J F, Zhang Q W and Saito F 2002 *Chem. Lett.* **30** 1176
- Luo F, Jia C J, Song W, You L P and Yan C H 2005 *Cryst. Growth Des.* **5** 137
- Macfarlane R M, Wittaker E A and Lenth W 1992 *Electron. Lett.* **28** 2136
- Mai H X, Zhang Y W, Si R, Yan Z G, Sun L D, You L P and Yan C H 2006 *J. Am. Chem. Soc.* **128** 6426
- Martin N, Boutinaud P, Mahiou R, Cousseins J C and Bouderbala M 1999 *J. Mater. Chem.* **9** 125
- Patzke G R, Krumeich F and Nesper R 2002 *Angew. Chem. Int. Ed.* **41** 2446
- Pie P and Rand S C 1992 *Opt. Lett.* **17** 1198
- Shi S J, Zhu Y C, Bi H Y and Qian Y T 2010 *Chinese J. Inorg. Chem.* **26** 1590
- Thoma R E, Insley H and Hebert G M 1966 *Inorg. Chem.* **5** 1222
- Tian Q W, Yang S P and Li F Y 2009 *J. Shanghai. Norm. Univ. Nat* **38** 63
- Wang M, Huang Q L, Hong J M, Wu W H, Yu Z, Chen X T and Xue Z L 2005 *Solid State Commun.* **136** 210
- Wang X, Zhang J, Peng Q and Li Y D 2006 *Inorg. Chem.* **45** 6661
- Wegh R T, Donker H, Oskam K D and Meijerink A 1999 *Science* **283** 663
- Xia Y N, Yang P D, Sun Y G, Wu Y Y, Mayers B, Gates B, Yin Y D, Kim F and Yan H Q 2003 *Adv. Mater.* **15** 353
- Xun X M, Feng S H, Wang J Z and Xu R R 1997 *Chem. Mater.* **9** 2966
- Yi G S, Lu H C, Zhao S Y, Ge Y, Yang W J, Chen D P and Guo L H 2004 *Nano Lett.* **4** 2191
- Zakaria D, Mahiou R, Avignat D and Zahir M 1997 *J. Alloys Compd.* **257** 65
- Zeng J H, Li Z H, Su J, Wang L Y, Yan R X and Li Y D 2006 *Nanotechnology* **17** 3549
- Zeng J H, Su J, Li Z H, Yan R X and Li Y D 2005 *Adv. Mater.* **17** 2119
- Zhang X X, Hong P, Bass M and Chai B H T 1994 *Phys. Rev.* **B51** 9298