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室温下合成纺锤形貌六方相 $NaLnF_4$(Ln=Nd,Sm,Eu,Gd,Tb)纳米颗粒

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摘要：室温下合成长 250 nm，宽 100 nm 的纺锤形貌六方相的 $NaNdF_4$。$NaEuF_4$,$NaSmF_4$,$NaGdF_4$ 和 $NaTbF_4$ 也用同样的方法获得。产物用 XRD,TEM,HRTEM,FESEM 和 PL 进行表征。PL 光谱显示合成的 $NaEuF_4$ 的激发波长是 394 nm。$NaEuF_4$ 有 4 个特征发射谱带,分别是 591,615,650 和 681 nm。

关键词：稀土元素；氟化物；室温；EDTA；发光性能
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Synthesis of Shuttle-Like Hexagonal $NaLnF_4$(Ln=Nd, Sm, Eu, Gd, Tb) Nanocrystals at Room Temperature

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Abstract: Shuttle-like hexagonal $NaNdF_4$ nanocrystals with a diameter of 100 nm at the middle and a length of 250 nm were synthesized at room temperature. Shuttle-like $NaEuF_4$, $NaSmF_4$, $NaGdF_4$, and $NaTbF_4$ nanocrystals were also synthesized using the same method. The products were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), high resolution TEM (HRTEM), field emission scanning electron microscopy (FESEM), and photoluminescence (PL). PL spectra of the as-synthesized $NaEuF_4$ showed an excitation source wavelength of 394 nm. $NaEuF_4$ had four major emission bands at 591, 615, 650 and 681 nm.

Key words: rare earth; fluorides; room temperature; EDTA; luminescence

0 Introduction

As an important kind of rare earth fluoride materials, $NaLnF_4$ (Ln =rare earth) has received more and more attention due to its potential applications in a number of fields, such as luminescence[1-3], catalysis[4], florescence imaging[5].

Various methods have been used to synthesize $NaLnF_4$ micro- and nanocrystals. α-$NaYF_4$ spheres were obtained by a modified precipitation method in the mixed solvents of methanol and *N*-(2-hydroxyethyl)-ethylenediamine at 200 ℃[6]. Tubular and spherical $NaYF_4$ phosphors were synthesized in solvents of water, acetic acid and sodium ethoxide aided by cetyl trimethylammonium bromide (CTAB) and EDTA by a microemulsion method at 140~200 ℃[7]. Hexagonal and spherical $NaLnF_4$ (Ln =Y, Yb, Er) nanostructures was obtained via the thermolysis of metal trifluoroacetates in high-boiling solvents of oleic acid/oleylamine/1-octadecene at 250~320 ℃[8]. Recently, the β-$NaLnF_4$ microstructures have been prepared using the hydrothermal method. Tubular β-$NaHoF_4$ and β-$NaSmF_4$

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at 140 ℃[9], $NaLuF_4$ hexagonal microplates at 180 ℃[10], $NaYF_4$ hexagonal microprism crystals at 180 ℃[11] and $NaYbF_4$ microstructures at 180 ℃[12] have been hydrothermally prepared.

It is known that the luminescence of the hexagonal $NaLnF_4$ nanoparticles are larger than that of their cubic counterpart, due to the more ordered structure of hexagonal $NaLnF_4$[13].

We report here the synthesis of Shuttle-like β-$NaLnF_4$(Ln=Nd, Sm, Eu, Gd, Tb) nanocrystals at room temperature in water in the presence of ethylenediamine tetraacetic acid (EDTA). The PL results show that the Shuttle-like $NaEuF_4$ has four major emission bands at 591, 615, 650 and 681 nm.

1 Experimental

1.1 Materials

All chemical reagents used in this work were of analytical grade and used without further purification. The lanthanide oxides Ln_2O_3 (except for Tb) (purity 99.99%) and Tb_4O_7 (purity 99.99%), hydrochloric acid (HCl), sodium fluoride (NaF), ethylenediamine tetraacetic acid (EDTA) and absolute ethanol, were purchased from National Reagent Corporation (Shanghai, China). $LnCl_3$ stock solutions of 0.2 $mol\cdot L^{-1}$ were obtained from their corresponding metal oxides in hydrochloric acid at elevated temperature. Distilled water was used for the preparation of all aqueous solutions.

1.2 Synthesis

In a typical procedure for the preparation of hexagonal $NaNdF_4$ microcrystals, 10 mL of $NdCl_3$(0.2 $mol\cdot L^{-1}$) was added to 10 mL of aqueous solution containing 2 mmol of EDTA. After vigorous stirring for 10 min, 0.024 mol of NaF was introduced. Then, the as-obtained mixing solution was stirred at room temperature for 24 h. The resulting hexagonal $NaNdF_4$ precipitate was then centrifuged, washed with deionized water and absolute ethanol several times, and finally dried under vacuum at 60 ℃ for 12 h(Sample 1).

Similarly, $NaEuF_4$, $NaSmF_4$, $NaGdF_4$, and $NaTbF_4$ were also synthesized. 10 mL of $LnCl_3$(Ln=Sm, Eu, Gd, Tb) was added to 10 mL of aqueous solution containing 2 mmol of EDTA. After vigorous stirring for 10 min, 0.024 mol of NaF was introduced. Then, the as-obtained mixing solution was stirred at room temperature for 24 h. The resulting hexagonal $NaLnF_4$ (Ln=Sm, Eu, Gd, Tb) precipitate was then centrifuged, washed with deionized water and absolute ethanol several times, and finally dried under vacuum at 60 ℃ for 12 h.

1.3 Characterization

XRD analysis was performed using a Japanese Rigaku D/max-rA rotating anode X-ray diffractometer equipped with a monochromatic high-intensity Cu $K\alpha$ radiation (λ=0.154 18 nm), scanning from 10°~60° (2θ) in speed of $0.05°\cdot s^{-1}$. The transmission electron microscopy (TEM) images were taken with a Hitachi model H-800 transmission electron microscope. The scanning electron microscopy (SEM) images were taken by using a JEOL-JSM-6700F field-emitting scanning electron microscope (FESEM). High-resolution (HR) TEM images were taken with a JEOL-2010 transmission electron microscope with an accelerating voltage of 200 kV. The fluorescence of the products was determined by a Hitachi 850-luminescence spectrophotometer with a Xe lamp at room temperature.

2 Results and discussion

The corresponding chemical reaction for the synthesis is as follows:

$$LnCl_3 + NaF \rightarrow NaLnF_4(Ln=Nd, Sm, Eu, Gd, Tb)$$

The synthetic conditions and characteristics of samples prepared are listed in Table 1.

Fig.1A(b) shows the XRD patterns of Sample 1. All of the diffraction peaks can be readily indexed to a hexagonal phase $NaNdF_4$ with calculated lattice constants of a=0.610 7 nm, c=0.371 2 nm, which is in good agreement with lattice constants of a=0.610 0 nm, c=0.371 1 nm (PDF: 72-1532). Fig.2(A) indicates that the Sample 1 is composed of uniform shuttle-like nanocrystals with a size of ~250 nm×100 nm (side length×thickness). Fig.3 (A) shows TEM image of a single shuttle-like $NaNdF_4$ nanocrystal in Sample 1. The HRTEM image of Fig.3(B) clearly demonstrates the high crystallinity of the particles. Lattice fringes corresponding to the (100) lattice plane of the β-$NaNdF_4$

Table 1 Synthesis conditions and characteristics of the samples prepared

No.	$n_{NaF}:n_{EDTA}:n_{Nd}$	EDTA / mol	Water / mL	Time / h	Product	Reference	XRD
S1	12:1:1	0.002	20	24	β-$NaNdF_4$	Fig.2A	Fig.1A(b)
S2	12:0:1	0	20	24	NdF_3 and α-$NaNdF_4$	Fig.2B	Fig.1D
S3	12:0:1	0	200	24	β-NdF_3	Fig.2C	Fig.1B(a)
S4	4:1:1	0.002	20	24	α and β-$NaNdF_4$	Fig.2D	Fig.1C(a)
S5	8:1:1	0.002	20	24	β-$NaNdF_4$	Fig.2E	Fig.1A(a)
S6	12:1:1	0.002	100	24	α and β-$NaNdF_4$	Fig.2F	Fig.1C(b)
S7	12:1:1	0.002	200	24	β-NdF_3	Fig.2G	Fig.1B(b)

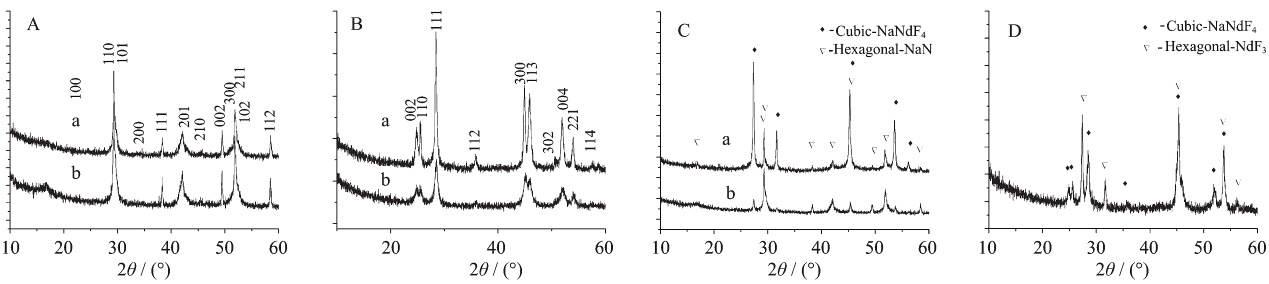

Fig.1 XRD patterns of the as-prepared samples A (a) S5, A (b) S1, B(a) S3, B(b) S7, C(a) S4, C(b) S6, D S2

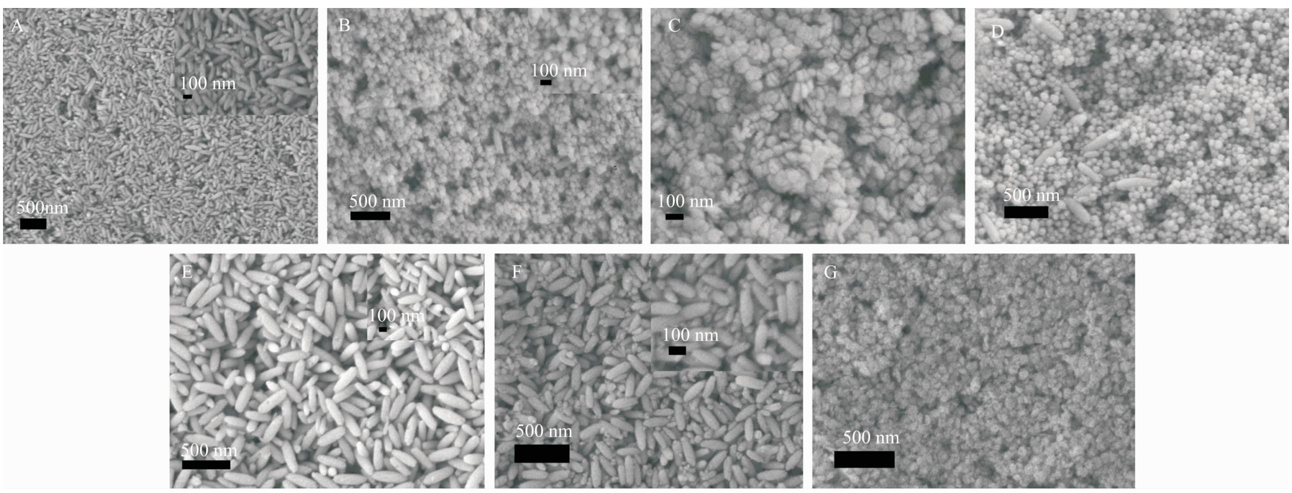

Fig.2 SEM images of (A) S1, (B) S2, (C) S3, (D) S4, (E) S5, (F) S6, (G) S7

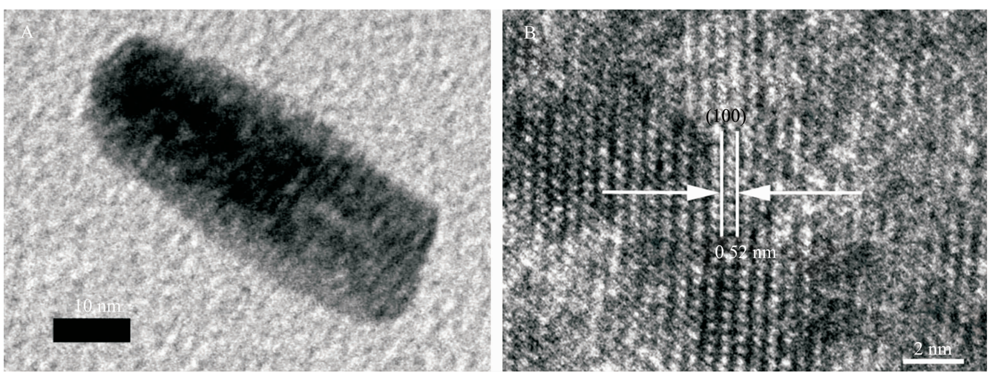

Fig.3 (A) TEM and (B) HRTEM images of shuttle-like β-$NaNdF_4$ nanocrystals (Table 1, Sample 1) lying flat on the face

structure can be observed on the individual particles. All of the particles observed in the HRTEM images are composed of single crystallites.

2.1 Effect of EDTA on products

When EDTA is used, the NaF/Nd ratio is taken as 12, and the volume of water is 20 mL, the as-obtained product is β-$NaNdF_4$ (Table 1, Sample 1). However, the products contain NdF_3 and α-$NaNdF_4$ (Table 1, Sample 2) when prepared without EDTA while keeping other experimental conditions identical. Fig.1D shows the XRD pattern of as-prepared products of Sample 2. As seen from The SEM image of Fig.2(B) for Sample 2, the products are composed of nanocrystals with an average size of 80 nm. The EDTA as an organic additive plays a critical role in the crystal growth, due to its ability to complex with rare-eath ions.

2.2 Effect of NaF/Nd ratio

To investigate the effect of the NaF/Nd ratio on the products, the NaF/Nd ratio was taken as 4, 8, and 12, respectively. The XRD patterns of the nanocrystals are given in Fig.1C(a), Fig.1A(a) and Fig.1A(b). It can be seen that the as-prepared nanocrystals are α and β-$NaNdF_4$ (Fig.1C (a)) when the NaF/Nd ratio is 4 (Table 1 Sample 4). Fig.2 (D) shows the corresponding SEM images of Sample 4, which can be seen that the products are composed of shuttles and irregular nanoparticles. When the ratio reaches 8 (Table 1, Sample 5), shuttle-like $NaNdF_4$ nanocrystals are formed with a size of ~300 nm×120 nm (side length×thickness, Fig.2E). When the ratio increases further to 12 (Table 1, Sample 1), however, the products are still shuttle-like $NaNdF_4$ nanocrystals with a size of ~250 nm×100 nm (side length×thickness, Fig.2(A)). The amount of F^- ions affects significantly the crystallization of the product. In order to investigate the influence of other parameters, the NaF/Ln ratio is kept at 12 unless otherwise specified.

2.3 Effect of water amount

Increasing the amount of water from 20 mL to 200 mL leads to completely different products. As EDTA is used, the NaF/Nd ratio is taken as 12 and the amount of water is 20 mL, the products (table 1, Sample 1) are β-$NaNdF_4$. However, the products are α and β-$NaNdF_4$ nanocrystals (Fig.1C(b)) when the experimental conditions are the same except the water amount (100 mL) (Table 1, Sample 6). It is found that the Sample 6 is composed of shuttles and irregular nanoparticles (Fig. 2F). Compared to Sample 4, the shuttle-like nanoparticles are much more in Sample 6. When other experimental conditions are identical and the amount of water is increased to 200 mL, it can get β-NdF_3 (Table 1, Sample 7). Fig.1B (b) shows the XRD pattern of Sample 7. All of the diffraction peaks can be readily indexed to a hexagonal phase NdF_3 of a=0.680 0 nm, c=0.718 1 nm, in good agreement with lattice constants of a=0.703 0 nm, c=0.719 9 nm (PDF: 09-0416). Fig.2G shows the SEM of Sample 7. It is found that the sample is composed of thin flakes with an average length of 100 nm. When EDTA is not used, the NaF/Nd ratio is taken as 12 and the amount of water is 20 mL, the products (Table 1, Sample 2) are NdF_3 and α-$NaNdF_4$ nanocrystals (Fig.1D). When other experimental conditions are identical and the amount of water is increased to 200 mL, the products are β-NdF_3 (Table 1, Sample 3). Fig.1B (a) shows the XRD pattern of Sample 3. The SEM image of Sample 3, shown in Fig.2 (C), indicates a mean size of 100 nm very similar to the Sample 7.

It turns out that the phases of products and shapes of the nanocrystals are influenced by the presence of EDTA, the NaF/Nd molar ratio and the amount of water. The optimal synthetic parameters for uniform shuttle-like $NaNdF_4$ nanoparticles are a molar ratio of NaF/EDTA/Nd of approximately 12:1:1, 20 mL water and 24 h at room temperature.

The method described above can also be extended to the synthesis of some other rare earth fluorides. For example, β-$NaSmF_4$, β-$NaEuF_4$, β-$NaGdF_4$, and β-$NaTbF_4$ have been prepared using corresponding $LnCl_3$ (Ln=Sm, Eu, Gd, Tb), NaF_4 and EDTA as reactants by similar procedures. Fig.4 shows the XRD patterns of (a) β-$NaSmF_4$ (PDF: 27-0779), (b) β-$NaEuF_4$ (PDF: 49-1897), (c) β-$NaGdF_4$ (PDF: 27-0699), and (d) β-$NaTbF_4$ (PDF: 27-0809) prepared with $LnCl_3$ (Ln=Sm, Eu, Gd, Tb) 2 mmol, NaF 24 mmol, EDTA 2 mmol, and 20 mL

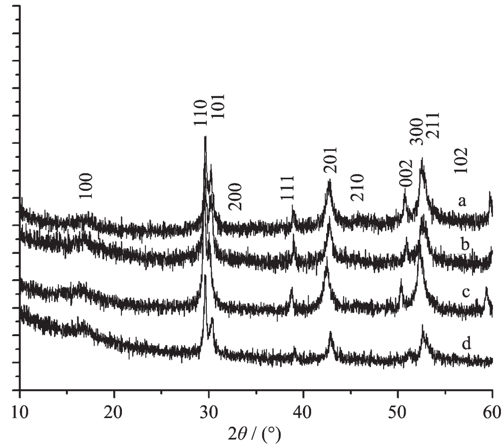

Fig.4 XRD patterns of the as-prepared samples of (a) $NaSmF_4$, (b) $NaEuF_4$, (c) $NaGdF_4$, (d) $NaTbF_4$

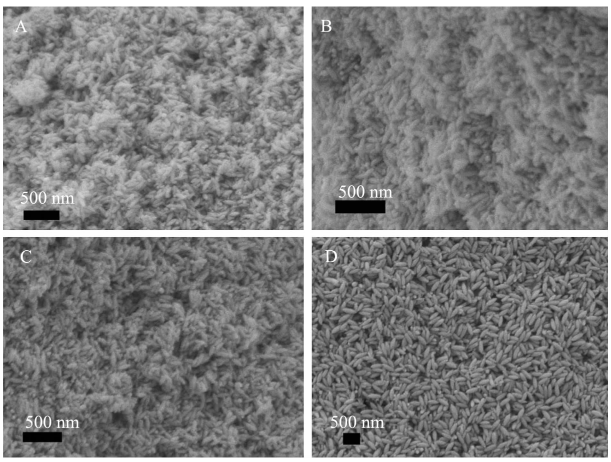

Fig.5 SEM images of the particles of some other rare earth fluorides (A) $NaSmF_4$, (B) $NaEuF_4$, (C) $NaGdF_4$ and (D) $NaTbF_4$

water. Fig.5 shows the corresponding SEM images of (A) $NaSmF_4$, (B) $NaEuF_4$, (C) $NaGdF_4$, and (D) $NaTbF_4$.

2.4 Photoluminescent Properties

PL spectra of the as-synthesized β-$NaEuF_4$ were measured with an excitation source wavelength of 394 nm. As shown in Fig.6, there are four emission bands at 591, 615, 650 and 681 nm in each PL spectrum; these are assigned to $^5D_0 \rightarrow {}^7F_J$ (J=1, 2, 3, 4)[14], respectively.

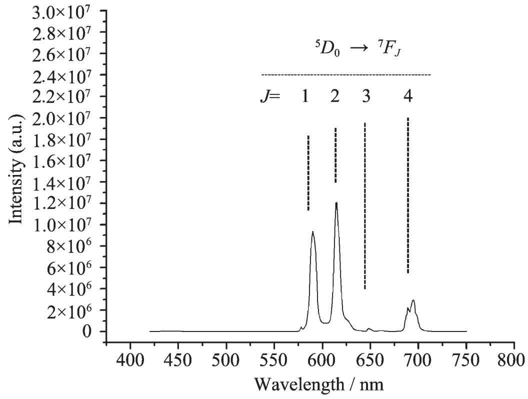

Fig.6 PL spectra of $NaEuF_4$

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