六边形及圆形 SmF₃ 微米盘的水热合成与表征

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摘要: 以 Sm(NO₃)₃·6H₂O 和不同的氟化物(NaBF₄,NH₄F)在 120 ℃的低温水热条件下反应得到了六边形及圆形的 SmF₃ 微米盘。通过 X 射线衍射(XRD)、场发射扫描电子显微镜(FE-SEM)和透射电子显微镜(TEM)对产物的晶相和形貌进行了表征。XRD 结果显示所得的产物是结晶良好的六方晶系。SEM 和 TEM 测试表明得到大量均匀的厚度约为 200 nm 的盘状结构。研究发现氟化物种类以及反应时间对形成不同形貌的盘有重要影响。讨论了可能的形成机理。进一步研究了 SmF₃:Tb³⁺和 SmF₃:Eu³⁺掺杂后的产物的荧光性质。

关键词: 微米盘;稀土氟化物;水热法;荧光
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Hydrothermal Synthesis and Characterization of Hexagonal and Round SmF₃ Microplates

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Abstract: Hexagonal and round SmF₃ microplates have been prepared by low-temperature hydrothermal treatment of Sm(NO₃)₃·6H₂O and different fluoride sources (NaBF₄ or NH₄F) at 120 ℃. The structure and morphology of as-prepared products are characterized by X-ray power diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). XRD patterns show that all the as-prepared SmF₃ products have hexagonal structure and high crystallinity. FE-SEM and TEM results show that large-scale and uniform microplates with thickness about 200 nm can be easily synthesized. It is found that the fluoride source and reaction time have great effect on the formation of different morphological plates. The possible formation mechanism is discussed. Furthermore, the room temperature photoluminescent properties of SmF₃:Tb³⁺ and SmF₃:Eu³⁺ crystals have been investigated.

Key words: microplate; rare earth fluoride; hydrothermal route; photoluminescence

0　Introduction

It is known that the properties of inorganic nano-materials can be greatly changed by tailoring their morphology, size, and crystallinity. Thus, further explorations of novel nano-morphology, with controlled size and shape by convenient synthesis methods, is of great importance for the development of new functional devices. Crystal structure has been proven as being one of the most important factors that will influence the growth behavior of nanocrystals. Li have reported that binary rare earth fluorides LnF₃ (Ln=La~Eu) main be indexed to hexagonal phase[1]. Recently, some papers have indicated these hexagonal phased LnF₃ (Ln=La~

Eu) nanoparticles have a 2D disk or plate-like structures, such as CeF_3 nanodisks[2], EuF_3 nanodisks[3], LaF_3 nanoplates[4,5] and NdF_3 nanoplates[6].

As a very important binary rare earth fluoride, SmF_3 can be used as host crystal for lanthanide-doped phosphors. Some relatively mild procedures, such as hydrothermal[7], precipitation[8,9], and solid state reaction[10] have been developed to prepare SmF_3 microstructures with different sizes and morphologies. As much as we concerned, the most often used synthetic approaches employed HF, NaF, NH_4F as fluoride source under a variety of reaction conditions. Recently tetrafluroborate complexes have been used to prepare binary rare earth fluorides[3,11~14]. Our previous studies show that YF_3 hollow peanuts[11], orthorhombic phased EuF_3 nanospindles and hexagonal phased EuF_3 nanodisks[3] have been successfully prepared from $NaBF_4$, NH_4BF or KBF_4 under hydrothermal conditions or room temperature. Herein, we report the synthesis of hexagonal and round SmF_3 microplates via a simple hydrothermal route without any surfactant or polymer in the reaction mixture. It is found that fluoride source ($NaBF_4$, NH_4F) and reaction time play crucial roles in the formation of different morphologies of products. Furthermore, the photoluminescent properties of Tb^{3+} or Eu^{3+} doped SmF_3 crystals have been investigated.

1 Experiment

1.1 Preparation

Rare earth oxides Ln_2O_3 (Ln=Sm, Eu, 99.99%) and Tb_4O_7(99.99%) were purchased from Shanghai Yue Long New Materials Corporation. NH_4F(A.R.) and $NaBF_4$(A.R.) were purchased from Shanghai Chemical Reagent Corporation. The rare earth nitrate $Ln(NO_3)_3 \cdot 6H_2O$ was made by dissolving rare earth oxide in nitric acid (63%~65%) and then evaporating the solvent. A typical procedure for the preparation of SmF_3 is given below. 1.0 mmol $Sm(NO_3)_3 \cdot 6H_2O$ and a certain amount of fluorides (0.75 mmol $NaBF_4$ or 3 mmol NH_4F) were dissolved in 25 mL of distilled water in a 50 mL plastic flask. After being stirred for 20 minutes at room temperature, the mixture was transferred into a 30 mL Teflon-lined stainless autoclave. The autoclave was sealed and heated at 120 ℃ for a set time and then naturally cooled to room temperature. A white solid was collected after centrifugation. It was washed with distilled water and ethanol in an ultrasonic bath for several times. The solid was collected and dried at 70 ℃ for 3 hours. At 120 ℃, Tb^{3+} or Eu^{3+} doped SmF_3 samples were prepared by the same procedure after reaction for 12h, except for additional 5% (total molar ratio) $Eu(NO_3)_3 \cdot 6H_2O$ or $Tb(NO_3)_3 \cdot 6H_2O$ into $Sm(NO_3)_3 \cdot 6H_2O$ solution at the initial stage.

1.2 Materials characterization

The crystalline phases of the products were analyzed by XRD on a Shimadzu XRD-6000 powder X-ray diffractometer (Cu $K\alpha$ radiation λ =0.154 18 nm), employing a scanning rate of 4.00° ·min^{-1}, in the 2θ range from 10° to 80°. The operation voltage and current were maintained at 40 kV and 30 mA, respectively.

The sizes and morphologies of the resulting products were studied by transmission electron microscopy (TEM, JEOL JEM-2010F) at 200 kV and by field emission scanning electron microscopy (FE-SEM, HITACHI S-4800) at 15.0 kV. The luminescent spectra of the solid samples were recorded on HITACHI F-4500 spectrophotometer at room temperature.

2 Results and discussion

2.1 Structure characterization

The X-ray diffraction patterns of the as-obtained products from different fluorides (NaBF$_4$, NH$_4$F) and different reaction stage are shown in Fig.1, respectively. All the diffraction peaks can be readily indexed to hexagonal crystalline phased SmF_3. The positions of the peaks are in good agreement with the literature values (PDF Files, No.12-0792). No impure peak is observed. Fixed the molar ratio of $NaBF_4/Sm^{3+}$ as 0.75:1, increasing the reaction time from 1 h, 9 h to 12 h, XRD analyses show that products from $NaBF_4$ are all hexagonal phased and changes of the reaction time do not vary the crystalline phase of the products (Fig.1a~c). However, the diffraction peaks obtained from 12 h are much sharper than those of the product obtained after reaction for 9 h or 1 h. It is indicated that the

product crystallinity improved and particle size increased with the prolonging of reaction time. The evolution of the products is similar to the formation of EuF_3 by using $NaBF_4$ as fluoride source[3].

(a) NaBF₄ (12 h), (b) NaBF₄ (9 h),
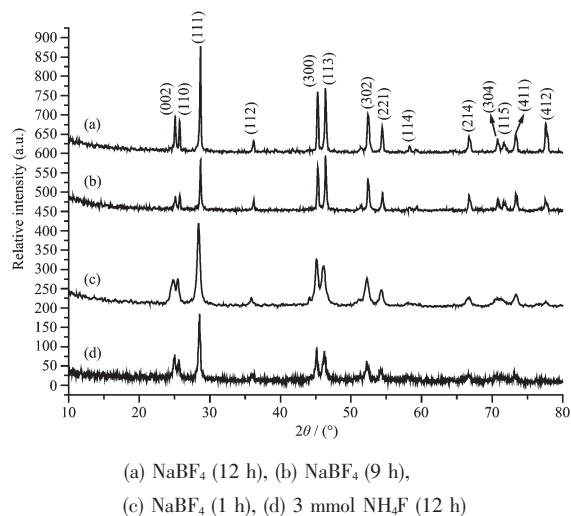(c) NaBF₄ (1 h), (d) 3 mmol NH₄F (12 h)

Fig.1　XRD patterns of SmF₃ from different fluorides

2.2　Morphology characterization

Since the morphology, size, and crystallinity of the products are greatly affected by reaction time, a series of detailed time-dependent experiments are carried out. SmF_3 solids are obtained from the reaction of $Sm(NO_3)_3 \cdot 6H_2O$ with $NaBF_4$ ($NaBF_4/Sm^{3+}=0.75:1$), their TEM and SEM images are shown in Fig.2a~f. When the reaction time is 1 h, the SmF_3 have hexagonal plates shape with the edge length of 300~500 nm and thickness about 100~200 nm. Particularly, some hexagonal microplates assembled face-to-face together into plate-columns (Fig. 2b~c), these unique shapes are similar to those earlier reported results in the formation of EuF_3 or LaF_3 by oriental aggregation mechanism[3,5]. The ED pattern from a single plate indicates it is single crystal(inset in Fig. 2c). After 6 h, some of the hexagonal plates have grown into polygonal plates(Fig.2d). Complete polygonal plates are formed in a period of 9 h (Fig.2e). Finally, the products have turned into complete round microplates after 12 h (Fig.2f). In addition, reaction temperature has no great effect on the phase and the morphologies of the products, etc 140 ℃, 160 ℃.

As mentioned above, when $NaBF_4$ are used as fluoride source, it is found that the reaction time have a significant effect on the morphologies and size of the as-obtained SmF_3 microcrystal. The intermediate steps in the formation from hexagonal plates to round plates SmF_3 micro-structures are schematically illustrated in Fig.3. At the beginning, adding $NaBF_4$ into the solution, hexagonal plates are immediately obtained (1 h, Fig.3a). With the increasing of the reaction time, the angels of some hexagonal plate is truncated, as a result,
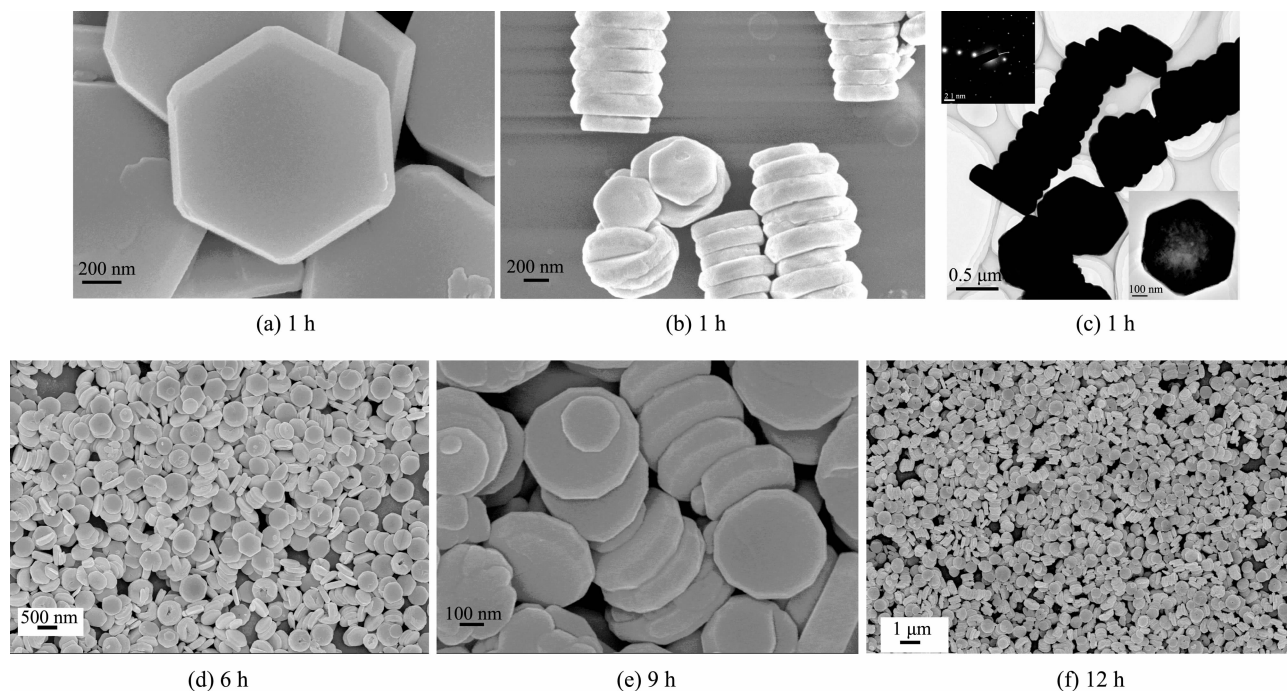

(a) 1 h　　　　　　　　　　　　(b) 1 h　　　　　　　　　　　　(c) 1 h

(d) 6 h　　　　　　　　　　　　(e) 9 h　　　　　　　　　　　　(f) 12 h

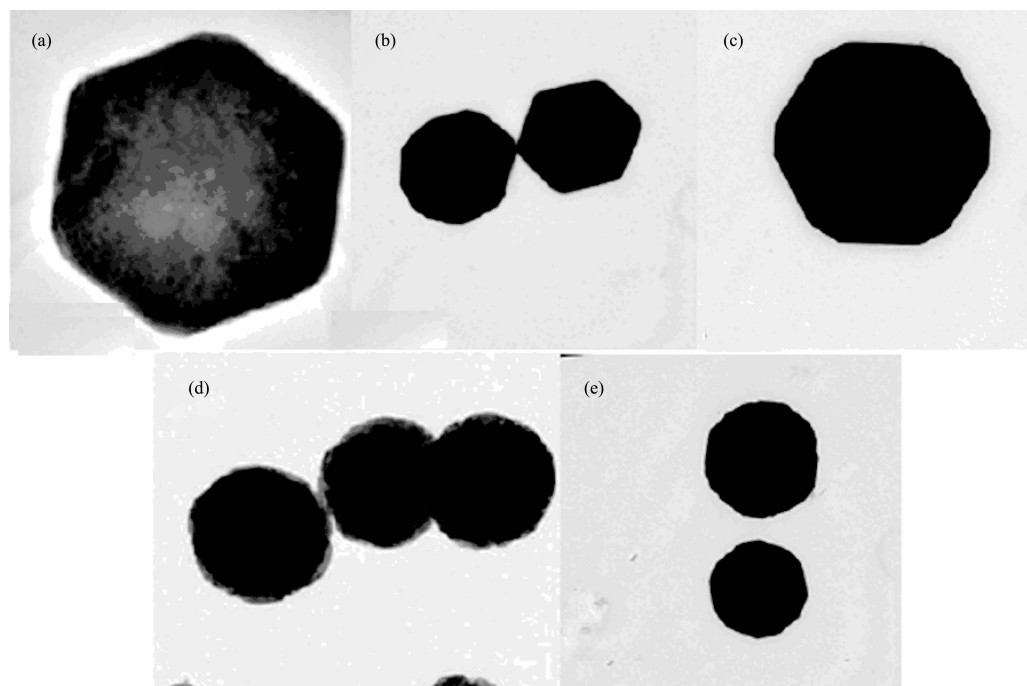Fig.2　TEM and SEM images of the SmF₃ prepared from NaBF₄ at different reaction time

Fig.3   Schematic illustration of the formation of the SmF₃ plates from hexagonal to round.

hexagonal plates have evolved into polygonal plates (6 h, Fig.3b). Gradually, more and more polygonal plate angels are truncated (Fig.3c~d). Finally, the truncated parts of the polygonal plates have grown completely into round plates with clear borders (12 h, Fig.3e). From the morphological evolution, it can be deduced that the whole process may be driven by surface effect.

In order to investigate the roles of fluoride source, NH₄F is also used as fluoride source to synthesize SmF₃ by an identical procedure. The XRD pattern of the SmF₃ obtained with 12 h is shown in Fig.1d. All the diffraction peaks can be indexed to hexagonal phased SmF₃ (PDF Files, No.12-0792), which is identical with that from NaBF₄. Fig.4a~d show the SEM images of the SmF₃ prepared from NH₄F during different reaction time (1 h, 6 h, 9 h and 12 h), respectively. It reveals a highly mono-dispersed distribution round plates with diameter of 400~600 nm and thickness of 200~300 nm. Furthermore, the time-dependent experiments indicate that the reaction time has no significant influence on the crystalline phase and the shape of the as-prepared SmF₃. At the early stage of the reactions, it is quite possible that NH_4^+ are absorbed on the surface of the initially formed SmF₃ particles during the nucleation process, due to the strong interactions between the cations and the fluoride anions on the particle surface. Consequently, during the later growing process, it would inhibit the morphological evolution and control the final shape of the products.
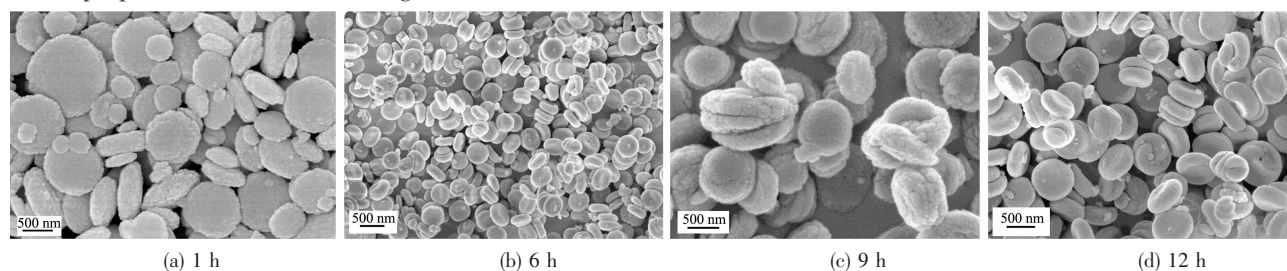

(a) 1 h   (b) 6 h   (c) 9 h   (d) 12 h

Fig.4   SEM images of the SmF₃ prepared from NH₄F in different periods

2.3   Formation mechanism of SmF₃

$$BF_4^- + 3H_2O \rightarrow H_3BO_3 + 3HF + F^- \tag{1}$$

$$Sm^{3+} + 3F^- \rightarrow SmF_3 \tag{2}$$

$$Sm^{3+} + 3NH_4F \rightarrow SmF_3 + 3NH_4^+ \tag{3}$$

The Eqs(**1**) have been reported earlier. It is known that $NaBF_4$ yields F^- and borate anions by hydrolysis of BF_4^-, and then F^- ions react with Sm^{3+} to form SmF_3 (Eqs.**1~2**). Our previous research have revealed that the cations of the simple binary fluoride sources XF (X=K, H, NH_4, Na, Rb, or Cs) play an important role in the formation of EuF_3 nanocrystals with different morphologies[15]. EuF_3 rings formed in the case of KBF_4 while EuF_3 ovals formed with KPF_6 and K_2SiF_6, respectively[16]. In the current study, it is obvious that the morphology of SmF_3 can be controllably synthesized by varying the fluoride sources. Therefore, it is possible that the positive ion and the negative central ion in the fluoride sources are responsible for the different morphologies of the as-prepared SmF_3. As a result, a morphological evolution from hexagonal plates to round plates occurred when $NaBF_4$ used as fluoride source, meanwhile, only round plates were obtained from NH_4F. However, the detailed reaction mechanism is still not clear.

2.4　Luminescent properties

The as-prepared SmF_3 microplates doped with either Eu^{3+} or Tb^{3+} ions displays either red or green luminescence, respectively. Fig.5a ~b show the room-temperature emission spectra of SmF_3 microplates with a doping concentration of 5mol% Eu^{3+} ions and Tb^{3+} ions, respectively. When excited at 395 nm, the corresponding emission peaks centered at 592, 615, 651 and 692 nm are observed, originating from the transitions from the $^5D_0$ excited-state to the ^7F_J (J=1, 2, 3, 4) ground states of Eu^{3+} ion[17]. The emission spectrum exhibits four well-resolved peaks centered at 489, 544, 583, and 620 nm, which have been observed for SmF_3:Tb^{3+}, corresponding to Tb^{3+} transitions of $^5D_4{\rightarrow}^7F_J$ (where J=6, 5, 4, 3)[18]. Among them, the bright-green emission at 544 nm which corresponds to $^5D_4{\rightarrow}^7F_5$ is the strongest.
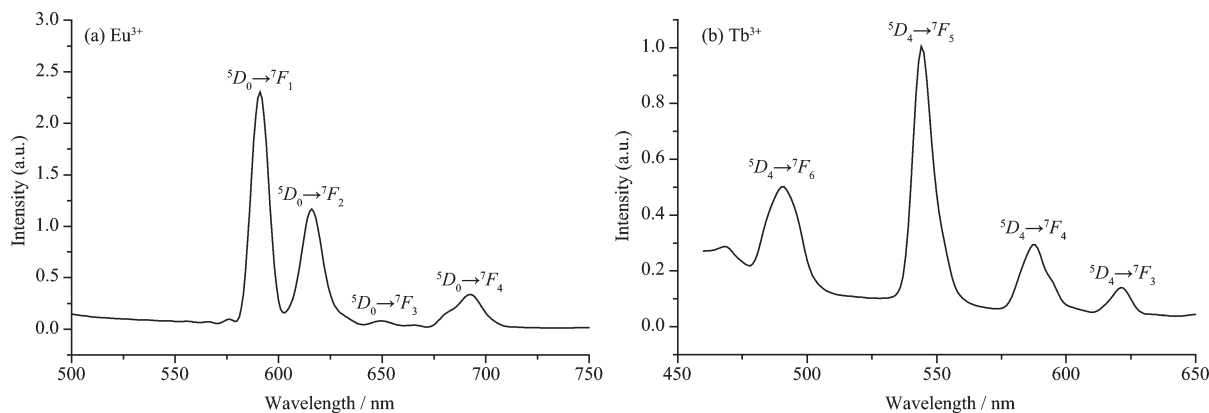

Fig.5　Emission spectra of as-prepared SmF_3 doped with (5mol%)

3　Conclusion

Hexagonal crystalline phased SmF_3 structures with different shape (hexagonal and round microplates) have been prepared by a hydrothermal route using different fluoride sources ($NaBF_4$ or NH_4F). The time-dependent studies of SmF_3 obtained from $NaBF_4$ reveal a gradually morphological evolution from hexagonal to round plate. However, no identical evolution occurred by using NH_4F, but only round SmF_3 submicroplates obtained. It is expected that the novel and simple hydrothermal reaction using complex fluoride can be employed to synthesize other rare earth fluoride.

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