LaF₃ 薄片的液相合成和表征

张悠悠∗，胡启秀，管航敏，胡 标，方智勇，成 涛，张祖德∗
（中国科学技术大学化学系，合肥 230026）

摘要：在氨水或无水乙二胺体系中通过液相反应制备了单晶六方相LaF₃薄片。用X射线衍射、透射电子显微镜、选区电子成像、X射线条射电子能谱等对产物进行了表征，研究了反应时间对产物形
貌的影响。结果表明，随着反应时间的延长，薄片尺寸变大。讨论了薄片生长的可能机理，当溶剂有配位作用时，如氨水或无水乙二胺，最终形成的LaF₃沉淀溶解、重结晶，最终形成无规则的薄片；当溶剂无配位作用时，如四氯化
碳或无水乙醇，最终产物为球形颗粒。

关键词：氟化镧；薄片；制备；表征；液相法
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Synthesis and Characterization of LaF₃

Flakes Through a Solution-phase Approach

Zhang Youjin∗，Hu Qixiu，Guan Hangmin，Hu Biao，Fang Zhiyong，Cheng Tao，Zhang Zude∗
（Department of Chemistry，University of Science and Technology of China，Hefei 230026）

Abstract Single-crystalline LaF₃ flakes was synthesized through a facile solution-phase approach in aqueous
ammonia and ethylenediamine. Applying the thermal treatment at 100 °C for 20 h, the LaF₃ recrystallized, grew
epitaxially and precipitated into flakes in aqueous ammonia or ethylenediamine. The formation of flakes could be
attributed to the coordination effect of the solvent.

Key words Lanthanum fluoride，Flake，Synthesis，Characterization，Solution-phase approach

1 Introduction

Lanthanum fluoride has been studied extensively because of its intrinsic properties and potential
applications. Lanthanum fluoride can serve as high-temperature solid lubricant[1]. Additionally it is
extremely effective in increasing the load-carrying capacity of lubricating grease[2]. It has been reported
that the surface-modified LaF₃ nanoparticles and nanoclusters demonstrate good load-carrying capacity,
lubricating and antiwear properties[3]. Furthermore, lanthanum fluoride has potential applications in sensing
fluorine, oxygen and carbon monoxide because of its high chemical stability and ionic conductivity[4-8]. In
the determination of Th-232, Th-230 and Th-228 in environmental samples, thorium isotopes are co-
precipitated with lanthanum fluoride before counting in alpha spectrometers[9]. Furthermore, LaF₃ can be used
as photonic host material due to its lack of adsorption. Finally LaF₃ doped with rare earth can act as X-ray
storage phosphor[10].

So far several methods have been used to
synthesize lanthanum fluoride. Wang synthesized fullerence-like rare-earth fluoride nanoparticles through a hydrothermal route\(^{11}\). Fujihara obtained LaF\(_3\) nanoparticles in sol-gel silica\(^{12}\). LaF\(_3\) films have been fabricated by using various PVD processes such as vacuum evaporation\(^{13-16}\), molecular beam epitaxy\(^{17}\), ion assisted deposition\(^{18,19}\), and ion beam sputtering\(^{20}\). However, the reports of the preparation of LaF\(_3\) flakes through a solution route are still quite limited. In this work, we decide how hexagonal LaF\(_3\) flakes were synthesized though a solution-phase approach under very mild conditions and the possible formation mechanism of LaF\(_3\) flakes is discussed.

2 Experiment

All reagents, La\(_2\)O\(_3\), NaF and solvents, were of analytic purity, obtained from Shanghai Chemical Reagent Company of China, without further purification.

In a typical procedure, 0.325 g La\(_2\)O\(_3\) was dissolved with 3 mL 3 mol/L HCl in a beaker, while 0.260 g NaF (a little excess) was dissolved with 4 mL distilled water first in another beaker and then some solvent, such as aqueous ammonia, was added. The solutions were mixed together while stirring and some white precipitate appeared immediately. The mixture was transferred into a Teflon liner. More solvent was added until the Teflon liner (60 mL) was filled to 80% of its capacity. The Teflon liner was put into a stainless autoclave and heated to 100 °C for 20 h after sealing, and then was cooled to room temperature naturally. The precipitate was centrifuged and washed with 0.5 mol/L HCl, distilled water and pure ethanol, respectively. Then, the sample was dried in vacuum at 80 °C for 6 h. This produced a white powder.

The crystalline phases and structure parameters of as-prepared products were identified by X-ray diffraction (XRD) (MXP18AHF X-ray diffractometer, MAC Science Co., Ltd.), equipped with a graphite monochromatized CuK\(_\alpha\) radiation (\(\lambda = 0.15418\) nm), by a scanning rate of 0.05°/s in the 2\(\theta\) range from 10° to 70°. Transmission electron microscopy (TEM) analysis was carried out on a Hitachi Model H-800 transmission electron microscope performing at 200 kV. The crystallinity and selected area electron diffraction (SAED) of the as-prepared product was identified on a JEOL 2010 high-resolution transmission electron microscope (HRTEM) running at 200 kV. In order to identify the valence states of La and F, the X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB MK II X-ray photoelectron spectrometer, using Mg K\(_\alpha\) radiation as the exciting source. The XPS spectra were corrected using C1s.

3 Results and discussion

Figure 1a shows the X-ray powder diffraction patterns of LaF\(_3\) flakes obtained in aqueous ammonia at 100 °C for 20 h. It can be observed that all the diffraction peaks can be indexed as the hexagonal phase LaF\(_3\). The lattice constants of as-prepared LaF\(_3\) (\(a = 0.715\) nm, \(c = 0.732\) nm) can be obtained from Fig. 1a, which are consistent with the literature data (JCPDS. Card 72-1435, \(a = 0.7163\) nm, \(c = 0.7329\) nm)\(^{21}\).

The typical TEM, SAED and HRTEM images of the sample obtained in ammonia are illustrated in Fig. 2. Figure 2a displays the TEM image of the sample. The selected area electron diffraction (SAED) pattern of LaF\(_3\) flakes is shown in Fig. 2b. This pattern indicates that the flakes have single-crystal nature.
These diffraction dots can be indexed as (110), (300) of the hexagonal phase LaF₃, respectively. They are consistent with the result of the XRD. Furthermore, the HRTEM image (Fig. 2c) demonstrates that the sample is of high crystallinity and the fringe spacing is about 0.202 nm, which corresponds to the (113) crystal plane spacing of hexagonal phase LaF₃.

Figure 3a indicates that there is no other elements except for La, F, C and O. Figure 3b shows that the binding energy of La 3d₃/₂ and La 3d₅/₂ is 836.65 and 863.5 eV, respectively. The binding energy of F1s is 684.50 eV (shown in Fig. 3c). The spectra indicate that elemental lanthanum exists solely in the form of La³⁺ and elemental fluorine exists exclusively in the form of F⁻[22]. O1s peaks originate from a combination of several kinds of oxygen, such as O₂, H₂O, O²⁻, and OH⁻ (Fig. 3d). The oxygen spectrum for the surface of the flakes demonstrates a single oxygen peak at 531.4 eV, corresponding to the absorbed molecular oxygen[16]. At the same time, the spectrum exhibits a peak from H₂O due to the absorbed H₂O on the surface of the sample[24]. The powder surface exposed to the air may be oxidized and hydroxidized because of chemical reactions with water and molecular oxygen adsorbed[24]. The presence of O²⁻ will lead to the formation of LaOF. The existence of LaOF in lanthanum fluoride powders has been reported[15,16,25,26]. The amount of LaOF is too small to appear in the XRD patterns. Due to the similarity in size for oxide ions and fluoride ions, oxide ions can be substituted or incorporated for fluoride ions or vacant

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**Fig. 2** TEM (a), SAED (b) and HRTEM (c) images of hexagonal LaF₃ flakes obtained in aqueous ammonia

**Fig. 3** XPS analysis of LaF₃ flakes obtained in aqueous ammonia
a. Survey spectrum, b. La 3d region, c. F1s region, d. O1s region.
sites in the lanthanum fluoride. This is represented in Kroger-Vink equation as:

\[ \text{O}^{2-} + 2F_	ext{r}^- = O_	ext{r}^- + 2F^- \]
\[ \text{OH}^- + F_	ext{r}^- = \text{OH}_r^- + F^- \]

In an aqueous ammonia system, a study of the crystallization as a function of aging time was carried out for this paper. It was found that the average size of flakes increased when the aging time was prolonged. TEM images of the products formed in 10 and 50 h are shown in Fig. 4 a and b respectively. Fig. 5 shows the TEM image of the products obtained in ethylenediamine. It can be observed that the products are flakes.

![Fig. 5](image)

In the heating process, the \( \text{LaF}_3 \) and \( \text{La} (\text{OH})_3 \) dissolve slowly resulting in \( \text{La} (\text{NH}_3)_m^{3+} \) ( or \( \text{La} (\text{en})_n^{3+} \) and \( F^- \). Once the concentrations of \( \text{La} (\text{NH}_3)_m^{3+} \) ( or \( \text{La} (\text{en})_n^{3+} \) ) and \( F^- \) reach saturation, \( \text{LaF}_3 \) recrystallize and grow epitaxially due to the coordination of \( \text{NH}_3 \) ( or \text{en} ), forming flakes-shaped single crystals in aqueous ammonia or ethylenediamine. Though the coordination of \( \text{NH}_3 \) ( or \text{en} ) to \( \text{La}^{3+} \) is weak, especially the \( \text{NH}_3 \), it is still believed that \( \text{NH}_3 \) or \text{en} can affect the structure of products during the solvothermal process. It has been reported that aqueous ammonia and ethylenediamine can affect the structure of products and flakes can be formed due to their coordination effect \(^{[27,28]} \). When non-ligand effect, such as carbon tetrachloride and pure ethanol, were taken as solvents, the products were nanoparticles ( shown in Fig. 6 a and b ). Its reason may be that carbon tetrachloride and pure

![Fig. 6](image)
ethanol don’t have any coordination with La$^{3+}$, LaF$_3$ grows along all the directions to form nanoparticles. The SAED and HRTEM images of the nanoparticles formed in pure ethanol are shown in Fig. 6 c and d. In order to prove this assumption, another experiment was carried out. When aqueous ammonia was used as the solvent and the pH value was adjusted to 3, the products were nanoparticles. Its reason may be that when the solution is acidic, ammonia mainly exists in the form of NH$_4^+$, which does not have any coordination to La$^{3+}$, the products are nanoparticles. But when the solution is alkaline, ammonia mainly exists in the form of NH$_3$, which has weak coordination to La$^{3+}$, the products are flakes.

4 Conclusion

The preparation of single-crystalline LaF$_3$ flakes through a solution-phase approach in aqueous ammonia and ethylenediamine was reported in this paper. The products were characterized by XRD, TEM, SAED, HRTEM and XPS. The possible formation mechanism of LaF$_3$ flakes was discussed.

References

[21] JCPDFS Files No. 72-1435 for hexagonal LaF3.