Synthesis of Cerium Tetrafluoride and Cerium Trifluoride Nanoscale Polycrystals from Ammonium Hydrogen Difluoride

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ABSTRACT: This paper reported a dry synthesis and characterization of cerium tetrafluoride (CeF₄) and cerium trifluoride (CeF₃) nanoscale polycrystals (NPs). The CeF₄ NPs were spherical or flaky and approximately 10 ± 2 nm in diameter. The CeF₃ NPs were rod-shaped nanorods with a length of about 150 ± 5 nm and a diameter of about 20 ± 2 nm. The first step was to synthesize the intermediate product—(NH₄)₂CeF₆ by mixing CeO₂ and NH₄HF₂ at a molar ratio of 1:6 at 390 K. The structural characterization was analyzed by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). Then, (NH₄)₂CeF₆ was heated in an argon gas flow to synthesize the CeF₄ and CeF₃ NPs. The products were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS). The properties of CeF₄ and CeF₃ NPs were further evaluated by transmission electron microscopy (TEM), selected area electron diffraction pattern (SAED), and high-resolution transmission electron microscopy (HRTEM). The findings provided an alternative strategy for the synthesis of nanometer fluorides, which could be a reference for high-performance research on other nanometer fluorides.

INTRODUCTION

Due to the special up-conversion luminescence performance and superior chemical and physiological properties, rare-earth fluoride up-conversion nanomaterials with a multicolor output have been widely used in the fields of multicolor displays, photonic devices, and biomedicine.¹⁻⁵ As a typical representative of rare-earth fluoride, cerium fluoride is a new type of up-conversion luminescent material, which has shown broad application prospects in many aspects such as displays, optical storage, biological analysis imaging, photodynamic therapy, etc.¹⁻⁹ Also, cerium fluoride has been abundantly applied in catalysis owing to the unique 4f electron, which is very sensitive for electron transfer and is easily involved in the hydrogen absorption/desorption of MgH₂.¹⁰ Few of the properties and reactions of CeF₃ have been described. It belongs to an isostructural group that includes the tetrafluorides of zirconium, thorium, uranium, and plutonium.¹¹ Cerium fluoride (CeF₃) has attracted increasing attention in virtue of its technological importance as an inorganic scintillating crystal. CeF₃ is considered as one of the most promising scintillators for the next-generation experiments in high-energy physics because of its high density, fast response, and high-radiation resistance. At the same time, it is also an important fluorescent matrix material due to its low vibration energy, the quenching of the excited state of rare-earth ions is minimized.¹² Also, as we all know, even a small number of radioactive materials require lots of engineering and management controls. Therefore, non-radioactive elements with similar properties to radioactive counterparts, which are called substitutes, are more efficient at the beginning of work. Cerium can be used as an alternative element to uranium for radiation-free experimental exploration.¹¹

The different application properties of nanocrystals are closely related to their morphology, structure, and size. The morphology, structure, and size of nanocrystals obtained by different preparation methods are also different. The routes for synthesizing rare-earth fluorides mainly include the wet process and dry process.¹³ Many researchers have explored the synthesis of rare-earth fluoride by the wet route.¹⁴⁻¹⁷ The wet process mainly includes the precipitation method, microemulsion method, hydrothermal method, solvothermal method, and sol–gel method. However, according to most reports so far, the uniformity and dispersion of synthesized nanomaterials are far from ideal, which will greatly limit their application in biomarkers.¹⁸ In addition, toxic organic metal precursors and hazardous coordination solvents used in the wet route have a great impact on the environment, which limits its application on the industrial scale. Therefore, the develop-
ment of effective and environmentally friendly synthetic routes for rare-earth fluorides is still a challenge. The dry process avoids most of the disadvantages of the wet process and has the advantages of a short reaction process, less impurity, low oxygen in fluoride, low reaction temperature, and safe operation. It has been considered to be one of the preferred methods for preparing high-purity fluoride, which has been used in a variety of rare-earth fluorinations.

In this paper, we demonstrated a dry synthesis route on CeF₄ and CeF₃ NPs that could be developed into a commercial fabrication process for cerium fluoride. CeO₂ and NH₄HF₂ were mixed at a molar ratio of 1:6, ground, and then reacted at 390 K in vacuum for 4 h to obtain (NH₄)₄CeF₈. After that, these ammonium cerium fluoride species were decomposed by heating to 570 and 1070 K for 10 h to get CeF₄ and CeF₃ nanoscale polycrystals. The effect of the temperature and ratio of raw materials on the fluorination rate was investigated with cerium oxide and ammonium fluoride as raw materials. Furthermore, the optimal experimental conditions for the preparation of CeF₄ and CeF₃ nanoscale polycrystals by dry fluorination were determined.

# METHOD

## Materials and Characterization

Cerium dioxide (99.9%, Aladdin) and ammonium bifluoride (98%, Aladdin) were used as received. Ar was dried with CaCl₂ (96%, Aladdin) to remove water.

For the sample for SEM observation, powders (1 mg) were pasted on a conductive adhesive, and after vacuum pumping to remove the excess powders, the powders were sprayed with gold and were then scanned.

For the sample for TEM observation, the specimen was prepared by the following steps: (i) the powder was dispersed in cyclohexane by ultrasonic agitation; (ii) then, the suspension was filtered to remove the excess powders, the powders were sprayed with gold and were then scanned.

The X-ray powder diffraction pattern of the samples was recorded at ambient temperature using a Bruker D8 Phaser powder X-ray diffractometer with Cu Kα radiation.

Scanning electron microscopy—energy-dispersive X-ray spectroscopy (SEM—EDS, ZEISS EVO MA) with an acceleration voltage of 15 kV was used for sample morphological characterization.

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed on an FEI Tecnai F20 S-TWIN transmission electron microscope with a field emission gun operating at 200 kV.

## Reaction of CeO₂ and NH₄HF₂

The synthesis of (NH₄)₄CeF₈ was explored by molar ratios of CeO₂ and NH₄HF₂ of 1:4, 1:6, and 1:8 at temperatures ranging from room temperature to 430 K. All operations were carried out under anaerobic conditions. NH₄HF₂ used in the reaction easily absorbed water from the air. Before the experiment, NH₄HF₂ was dried in an oven at 350 K for 60 min. The precursor powders were placed in a vessel made from polytetrafluoroethylene tubes (100 mm high with 50 mm in diameter and 5 mm thick), and the vessel was placed in a vacuum oven. First, the powders were treated in an inert glove box at room temperature for 2 months.

After that, we chose a molar ratio of 1:6 to study the influence of temperature on the synthesis process of ammonium cerium fluoride. According to the properties of NH₄HF₂, synthesis experiments were conducted at 380, 390, 400, 410, and 420 K. The composition and structure of the products were characterized by XRD, and the morphology was observed by SEM.

### Synthesis of CF₄ NPs

CeO₂ and NH₄HF₂ were synthesized by heating (NH₄)₄CeF₈ from the reaction of CeO₂ and NH₄HF₂. The powder of (NH₄)₄CeF₈ was placed in an agate mortar, ground for 10 min, and then transferred to a platinum crucible, which was in a quartz tube closed at one end. At the beginning of the experiment, the argon gas was fed at a speed of 10 mL/min for 30 min to clean up the furnace tube. Then, the furnace was heated to 570 K at 5 k/min and kept for 10 h, during which the argon continued flowing into the furnace tube at a rate of 8 mL/min until the reaction was completed and the temperature was cooled down to room temperature. The morphology and structure of CeF₄ NPs were determined by SEM, TEM, and HRTEM.

### Synthesis of CF₃ NPs

The powders of (NH₄)₄CeF₈ synthesized in step 2.1 were put into a platinum crucible, which was in a quartz tube sealed at one end. After being cleaned with argon gas for 30 min, the furnace was heated to 1070 K by 5 k/min and kept for 10 h, during which the flow rate of argon was maintained at 8 mL/min until it was reduced to room temperature. The product was characterized by XRD, SEM, TEM, and HRTEM.

# RESULTS AND DISCUSSION

## Synthesis of Ammonium Cerium Fluoride

The synthesis of ammonium cerium fluoride by the solid–solid reaction between CeO₂ and NH₄HF₂ was explored in this paper. The reaction was based on the following stoichiometric equations

\[
\text{CeO}_2 + 4\text{NH}_4\text{HF}_2 \rightarrow (\text{NH}_4)_4\text{CeF}_8 + 2\text{H}_2\text{O}
\]  

(1)

The product ammonium cerium fluoride was determined by XRD.

## Reaction at Room Temperature

The mixtures of CeO₂ and NH₄HF₂ at molar ratios of 1:4, 1:6, and 1:8 were milled for 10 min under anaerobic conditions and then reacted at room temperature for 2 months. The products were analyzed by XRD, as shown in Figure 1.

Peaks of (NH₄)₄CeF₈ were detected in the samples. The diffraction peaks of (NH₄)₄CeF₈ were detected at angles of 15.3, 15.8, 19.0, and 24.0. At a stoichiometry molar ratio of 1:4, CeO₂ (at angles of 28.5, 33.0, 47.4, and 56.3) remained in the product after 2 months, which was difficult to remove in the subsequent reaction. At a molar ratio of 1:6, there was a small amount of residual NH₄HF₂, and no CeO₂ remained after 2 months. At a molar ratio of 1:8, CeO₂ could not be detected in the product, but there was a large amount of remaining NH₄HF₂. Also, the intermediate product (NH₄)₄CeF₆ appeared (at angles of 14.6, 28.1, 46.4) in the XRD images of molar ratios of 1:4 and 1:8.

In this reaction, one of the substances was NH₄HF₂, which melted at 401 K and dissociated into HF, H₂, and N₂ above 514.5 K.

\[
\text{NH}_4\text{HF}_2(s) \xrightarrow{\Delta} 2\text{HF}(g) + 1.5\text{H}_2(g) + 0.5\text{N}_2(g)
\]  

(2)

Therefore, to ensure the reaction, CeO₂ should be converted to ammonium cerium fluoride completely. So, NH₄HF₂ should be above stoichiometry in the reaction. However, excessive NH₄HF₂ contained a large number of non-decomposed
impurities, which affected the purity of the product. In summary, the product was relatively pure \((\text{NH}_4)_4\text{CeF}_8\) with remaining \(\text{NH}_4\text{HF}_2\) at a molar ratio of \(\text{CeO}_2\) and \(\text{NH}_4\text{HF}_2\) of 1:6.

So, the following explorations were carried out with a molar ratio of 1:6. For the mixtures with a molar ratio of 1:6, the SEM images of the starting powders and products mixed at room temperature for 10 days, 30 days, and 2 months are shown in Figure 2.

Figure 2 shows the morphologies of the starting powders and the products based on eq 1. (a) Starting powders; (b) mixed for 10 days; (c) mixed for 30 days; (d) mixed for 2 months.

Reaction at Different Temperatures. According to the thermal properties of raw material \(\text{NH}_4\text{HF}_2\), the reaction temperature of the mixture was studied, which is shown in Figure 3.

The solid phase reaction at room temperature was so slow that the reaction between \(\text{CeO}_2\) and \(\text{NH}_4\text{HF}_2\) took about 2 months. Theoretically, some reactions are favored by raising the temperature in a specific range. At 380 K, the reaction between \(\text{CeO}_2\) and \(\text{NH}_4\text{HF}_2\) was a solid–solid reaction. The reaction was relatively slow, but due to sufficient reaction time, the products were mainly \((\text{NH}_4)_2\text{CeF}_6\). The diffraction peaks of \((\text{NH}_4)_2\text{CeF}_6\) were detected in the sample. Further analysis of the product at 390 K showed the disappearance of \((\text{NH}_4)_2\text{CeF}_6\). In addition to that, the XRD analysis indicated that \((\text{NH}_4)_2\text{CeF}_6\) diffraction peaks were stronger. For the reaction between 400 and 514.5 K, the \(\text{NH}_4\text{HF}_2\) became liquid for solid–liquid reaction and solid–gas reaction. So, there would be partial loss of \(\text{NH}_4\text{HF}_2\). In addition, the heating rate played an important role in the loss of \(\text{NH}_4\text{HF}_2\); a quick temperature rise may lead to the rapid volatilization of \(\text{NH}_4\text{HF}_2\). The analysis has verified the formation of \((\text{NH}_4)_2\text{CeF}_6\) of the product of 400–420 K where the peaks of \((\text{NH}_4)_2\text{CeF}_6\) are reobserved and those of \((\text{NH}_4)_4\text{CeF}_8\) are diminished. Intermediates such as \((\text{NH}_4)_2\text{CeF}_6\) were produced due to the volatilization loss of \(\text{NH}_4\text{HF}_2\) within this temperature range. When the temperature reached 514.5 K, \(\text{NH}_4\text{HF}_2\) would be decomposed into HF, H2, and N2, just as shown in eq 2. The decomposed gas flowed out of the vessel with Ar quickly, causing the reactants to fail to react adequately. At this point, the peaks of \((\text{NH}_4)_4\text{CeF}_8\) became weak, almost disappearing, while the peaks of \((\text{NH}_4)_2\text{CeF}_6\) became stronger and even became the main products. At the
higher temperature, amounts of intermediates might be generated in the product due to the rapid decomposition and escape of NH$_4$HF$_2$. Similar reactions were reported before.\textsuperscript{24−26}

Rietveld refinements of the as-synthesized nanomaterials at 390 K were performed by using the general structure analysis system (TOPAS academic) program and are diagrammatically plotted in Figure 4. It can be seen from the figure that the product was a pure (NH$_4$)$_4$CeF$_8$ phase at 390 K. The Rietveld refinement results manifest that the measured and calculated diffraction peaks are well matched. The reliable parameters fit well with a space group of C$\overline{2}$/c. The refined lattice parameters were $a = 13.05131$ Å, $b = 6.67305$ Å, and $c = 13.63411$ Å.

Based on the theoretical and experimental results, the temperature was set at about 390 K, the molar ratio of CeO$_2$ and NH$_4$HF$_2$ was 1:6, and the reaction time was 4 h in the synthesis of ammonium cerium fluoride.

**Formation of CeF$_4$ NPs.** When the reaction temperature was between 470 and 620 K, the fluorine compound would be decomposed into tetrafluoride. The reaction for the formation of CeF$_4$ is given in eq 3.

$$\text{(NH}_4\text{)}_4\text{CeF}_8 \xrightarrow{\Delta} \text{CeF}_4 + 6\text{H}_2 + 2\text{N}_2 + 4\text{HF}$$ (3)

The ingredient characterization of the samples was performed with SEM, EDS, and SAED, which are shown in Figure 5.

The SEM micrographs of CeF$_4$ are shown in Figure 5a, which shows the almost uniform distribution of CeF$_4$ NPs (marked by white arrows). The sizes of CeF$_4$ NPs were about 10 ± 2 nm. The cobalt fluoride (CoF$_2$) nanoparticles (NPs) were 20−70 nm and prepared by the reverse microemulsion method for the first time by Khan et al.\textsuperscript{27} The EDS analysis shown in Figure 5b reveals the presence of Ce and F at atomic percentages of 80 and 20%, respectively. Figure 5c shows the TEM and HRTEM images of CeF$_4$. It could be seen that CeF$_4$ NPs were composed of flat-elongated nanoparticles with a much larger particle size. The obvious lattice fringes indicated...
that NPs were highly crystalline. The bright circular rings and spots in the SAED pattern (Figure 5d) showed the presence of CeF₄ NPs (ICSD #089621). However, CeF₄ could not be detected after prolonged heating to 20 h when the temperature was lower than 470 K. As if the temperature was higher than 720 K, CeF₃ was produced in the product. Moreover, the conditions under which CeF₄ converted to CeF₃ in different reaction vessels were not completely the same.¹² The decomposition proceeds with the elimination of molecular fluorine, according to the following equation (eq 4):²⁹

\[
\text{CeF}_4 \rightarrow \text{CeF}_3 + \frac{1}{2} \text{F}_2
\]  

(4)

In this work, the platinum crucible reactor was used and the temperature should be controlled below 1114 K. Formation of CeF₃ NPs. The composition of the product was characterized by XRD. The XRD diffraction peaks for the synthesized CeF₃ NPs are shown in Figure 6. The decomposition product of ammonium cerium fluoride at 1070 K was flaky and porous CeF₃ NPs. Figure 6 shows the XRD pattern of CeF₃ NPs by heating (NH₄)₄CeF₈ at 1070 K. All the peaks at 2θ values of 24.40, 24.95, 27.83, 43.96, 45.13, 50.91, 52.83, 64.83, 68.76, 69.65, 71.09, and 81.69 could be indexed to the cubic cell of the CeF₃ phase (002), (110), (111), (300), (113), (302), (221), (214), (304), (115), (411), and (404), respectively, which were in good agreement with the reported value for pure CeF₃. Also, the XRD measurement results were in agreement with a previous report.³⁰ The SEM, TEM, SAED, and HRTEM characterizations of the product are shown in Figure 7. The CeF₃ NPs were rod-shaped nanoparticles with a length of about 150 ± 20 nm and a diameter of about 20 ± 2 nm, which are shown in Figure 7a. It could be observed from Figure 7a that the particles seem to be porous. Particles mostly contained voids of different sizes due to the evolution of large amounts of gases during the combustion. The particles with agglomeration are observed in Figure 7b. From the SAED pattern shown in Figure 7c, the bright circular rings and spots were entirely consistent with CeF₃ NPs. The polycrystalline nature of the sample was further confirmed by SAED patterns. The HRTEM image as shown in Figure 7d further confirms the synthesis of CeF₃ NPs. Tashi et al.³¹ reported a facile hydrothermal synthesis and characterization of hexagonal Eu³⁺ doped and Eu³⁺/Ce³⁺ co-doped NaGdF₄ nanophosphors and the influence of different radii of rare-earth ions on crystal morphology. Furthermore, on the basis of this study, they also demonstrated a Ser-CS (serine-functionalized NaYF₄:Ce³⁺/Gd³⁺/Eu³⁺@NaGdF₄:Tb³⁺ core shell) nanophosphor for the effective detection of nitroaromatic derivatives.³² Also, the heating rate and the maximum reaction temperature needed to be controlled. When the heating rate reached above 8 K/s, CeOF would appear in the product, which was difficult to remove. Similarly, when the reaction temperature reached 1170 K, a certain amount of CeOF would also appear in the product.

**CONCLUSIONS**

In summary, a dry process by mixing CeO₂ and NH₄HF₂ and the decomposition of the intermediate were devised for the formation of CeF₄ and CeF₃ NPs. The reaction conditions were evaluated by adjusting the molar ratio, reaction temperature, and reaction time. After various characterization methods, the rod-shaped CeF₃ NPs about 150 ± 5 nm long and 20 ± 2 nm in diameter and the spherical or flaky CeF₄ with 10 ± 2 nm were obtained. The exploration process of the route provided a certain reference for the following study of fluoride.

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Author Contributions
Y.S. and H.M. conceived the idea and designed the experiments. Y.S. and X.Y. performed the spectroscopic and morphological measurements and analyses. The manuscript was written by Y.S. with input from all authors. All authors read and approved the final manuscript.

Notes
The authors declare no competing financial interest. All data generated or analyzed during this study are included in this published article and its supplementary information files and are available from the corresponding author on reasonable request.

■ ACKNOWLEDGMENTS
This work was supported by the Key Research Program of the Chinese Academy of Sciences (Grant no. ZDRW-KT-2019-1-0202).

■ ABBREVIATIONS
CeF₄: cerium tetrafluoride; CeF₃: cerium trifluoride; NH₄HF₂: ammonium hydrogen difluoride; NPs: nanoscale polycrystals; CeO₂: cerium dioxide; XRD: X-ray powder diffraction; SEM: scanning electron microscopy; EDS: energy-dispersive X-ray spectroscopy; TEM: transmission electron microscopy; SAED: selected area electron diffraction pattern; HRTEM: high-resolution transmission electron microscopy.

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