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Large-Scale Synthesis of Isotropic Single-Crystalline ScF_3 Cubes by Hydrothermal Method

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Scandium fluoride (ScF_3) belongs to one of the rare compounds which exhibit isotropic negative thermal expansion. Here, a facile and environmentally friendly hydrothermal synthesis method has been presented. High-quality single-crystalline ScF_3 cubes, with an average size of 200 nm, can be easily fabricated in a large scale. $Sc(NO_3)_3$ and NH_4HF_2 were used as precursors. The as-prepared ScF_3 demonstrates cubic symmetry (*Pm*-3 *m*), which was confirmed by X-ray diffraction and selected-area electron diffraction. Its uniform morphology and size were characterized by high-resolution transmission electron microscopy. Furthermore, thermal analysis was also performed in argon gas atmosphere to investigate its thermal stability.

I. Introduction

GENERALLY, majority of materials expand on heating and contract on cooling. However, an opposite phenomenon that some of materials tend to expand on cooling and thus feature negative thermal expansion (NTE) behavior has sparked considerable interest in the past decades.[1,2] Actually, the NTE effect of most materials is minute and anisotropic, and occurs only over a limited temperature range.[3,4] However, potentially technical applications require materials revealing isotropic NTE over a large temperature zone.[5] To date, isotropic NTE materials have been documented just in a small amount of compounds, such as ZrW_2O_8,[6,7] ZrV_2O_7,[8] and $ZrMo_2O_8$.[9,10] Very recently, it was reported that ScF_3 with a cubic ReO_3-type structure demonstrates a pronounced isotropic NTE over a large temperature range from about 10 to 1100 K (60–110 K, $\alpha_l \approx -14$ ppm/K).[11,12] Furthermore, its NTE mechanism was investigated with the assistance of inelastic neutron diffraction.[13] In addition, its open framework structure provides an opportunity to tune thermal expansion by substitution Sc^{3+} with other ions, such as rare-earth ions.[14] However, there are very few reports on the fabrication of high-quality ScF_3 in a large scale.[15] Traditionally, there are two methods to prepare ScF_3. One is the solid-state reaction in which Sc_2O_3 and NH_4HF_2 are treated as precursors. However, the problem is related to the synthesis of ScF_3 with the moderately high $ScF_{2.76}$ impurity.[16,17] The other method is wet chemical reaction in which $ScCl_3$ or Sc_2O_3 are dissolved by hydrofluoric acid followed by dehydration and calcination in an inert atmosphere. However, the toxic precursor, similar to HF, makes this method unsafe and environmentally unfriendly.

Recently, the synthesis of rare-earth fluorides on precisely controlling size and morphology has attracted intense research attention. By means of a $La(CF_3COO)_3$ pyrolysis route, single-crystalline LaF_3 triangular nanoplates has been produced.[18] Similarly, fullerene-like nanoparticles and Ln^{3+}-doped bundle like YF_3 phosphors have been successfully prepared by a hydrothermal approach.[19–22] In addition, CeF_3 nanocrystals in various forms of disks, rods, and dots have been obtained in a mild ultrasound-assisted route.[23] And a microemulsion fabrication of hexagonal and triangular YF_3 nanocrystals has been presented.[24] With the assistance of organics such as surfactants or co-surfactants, these unique methods could facilitate precisely tailoring of size and morphology. However, the introduction of all kinds of organics not only gives rise to environmental pollution but also increase costs when it comes to practical application in huge-scale production. So it is known that there is still a big challenge to explore a simple, environmentally friendly, and low-cost synthesis method without templates or surfactants. Herein, we report a simple and efficient hydrothermal approach to prepare ScF_3 cubes with single-crystalline nature. The crystal structure and morphology are characterized by X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM), respectively. The thermal stability of the as-prepared ScF_3 is also investigated.

II. Experimental Section

(1) Hydrothermal Synthesis

Scandium nitrate [$Sc(NO_3)_3$] and ammonium bifluoride (NH_4HF_2) were of analytical grade, supplied by Beijing Chemical Reagent Company. All these reagents were used to fabricate the target product without further purification. Deionized water was prepared to dissolve these reagents.

For a typical hydrothermal synthesis method, 0.001 mol $Sc(NO_3)_3$ and 0.0015 mol NH_4HF_2 were dissolved in 30 mL deionized water in a stainless-steel autoclave lined with Teflon. Then, the autoclave was placed in a furnace at 180°C for 10 h after which it was allowed to cool down to room temperature. Subsequently, precipitates in the autoclave were washed with excess ethanol and water. After separation by centrifugation, the sample was dried under a vacuum oven at 80°C for 10 h and collected for the next step characterization.

(2) Characterization

The structure of ScF_3 was characterized by XRD operating at 40 kV and 30 mA, where λ = 0.15418 nm (Rigaku D/Max 2200PC diffractometer; Rigaku Corp.,Tokyo, Japan). Its lattice parameters were calculated by *PowderX* (Institute of Physics, Chinese Academy of Sciences, Beijing, China) and *TREOR* software (Department of Structural Chemistry, University of Stockholm, Stockholm, Sweden). The size and

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morphology of the sample were determined by transmission electron microscope (TEM, TecnaiG2 20; FEI, Hillsboro, OR) operating at 20 kV. The microstructure of the as-prepared sample was studied by selected-area electron diffraction (SAED) and HRTEM with an accelerating voltage of 200 kV. The thermal stability was also investigated in the argon atmosphere with a ramping rate of 10°C per min by thermogravimetric analysis and differential scanning calorimetry (DSC/TG, Labsys™ Evo, Setaram Corp., Lyon, France).

III. Results and Discussion

The typical diffraction peaks of the sample have been clearly showed in the powder X-ray diffraction pattern (Fig. 1). The sharp diffraction peaks indicate a perfect crystalline structure. And all peaks of the sample are in good agreement with the previously reported cubic structure for crystalline ScF_3 (space group: Pm-$3m$, JCPDS card 46-1243). The lattice parameters of the as-prepared ScF_3 sample were calculated to be $a = b = c = 4.020$ Å, and unit cell volume is 64.73 Å^3.

The morphology and particle size of as-prepared ScF_3 were investigated by typical TEM image. As-prepared ScF_3 particles demonstrate almost uniform distribution of shape and size. And the average size of these particles is about 200 nm [Fig. 2(a)]. The SAED pattern was also performed on a typical individual cube of the sample [inset in Fig. 2(a)]. The sharp diffraction spots show its single-crystalline structure with a crystallographic orientation [001]. The cube of the ScF_3 sample grows along the {100} crystal planes. Its microstructure information was further characterized by HRTEM. The distinct lattice fringes on the surface of these cubes [Fig. 2(b)] display its good crystallization. Furthermore, the fast Fourier transform pattern [FFT, inset in Fig. 2(b)] also confirms its single-crystalline nature. The interplanar spacing of 0.401 Å corresponds to {100} planes of cubic ScF_3.

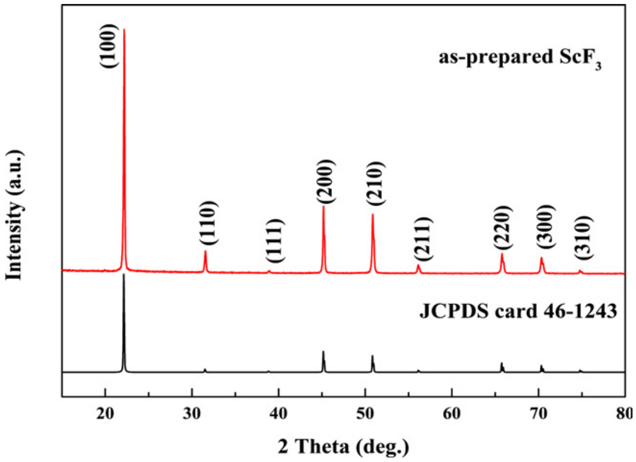

Fig. 1. XRD patterns of pure phase of ScF_3 (red line) and bulk ScF_3 (black line, JCPDS card 46-1243).

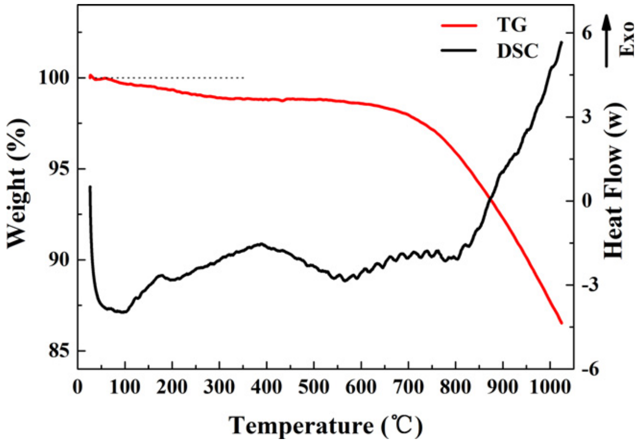

Fig. 3. TG-DSC trace of the as-prepared ScF_3 cubes.

In the simple hydrothermal reaction, the morphology of as-prepared ScF_3 is solely determined by intrinsic factors. The faces comprising the crystal habit correspond directly with the most energetically stable atomic planes in ScF_3. The planes of {100} have low Miller indices in the cubic symmetry of ScF_3 and are often relatively stable, because they contain densely packed arrays of strongly bonded atoms. So the morphology of ScF_3 here corresponds to the symmetry of the Bravais lattice, and its cubic crystal shape is a macroscopic expression of the unit cell.[25]

To study the thermal stability of the as-prepared ScF_3 cubes, thermal analysis was also performed in high pure argon gas atmosphere by TG/DSC (Fig. 3). The sample undergoes a weight loss about 2% below 200°C. It is likely that this weight loss arises from the evaporation of adsorbed water and the decomposition of crystallized water. The heat flow curve also shows a corresponding broad endothermic peak. With the temperature increasing, the weight of ScF_3 almost keeps unchanged. It demonstrates that ScF_3 would be stable among the temperature range from 200°C to 700°C. When the sample is heated to 700°C, its weight is inclined to

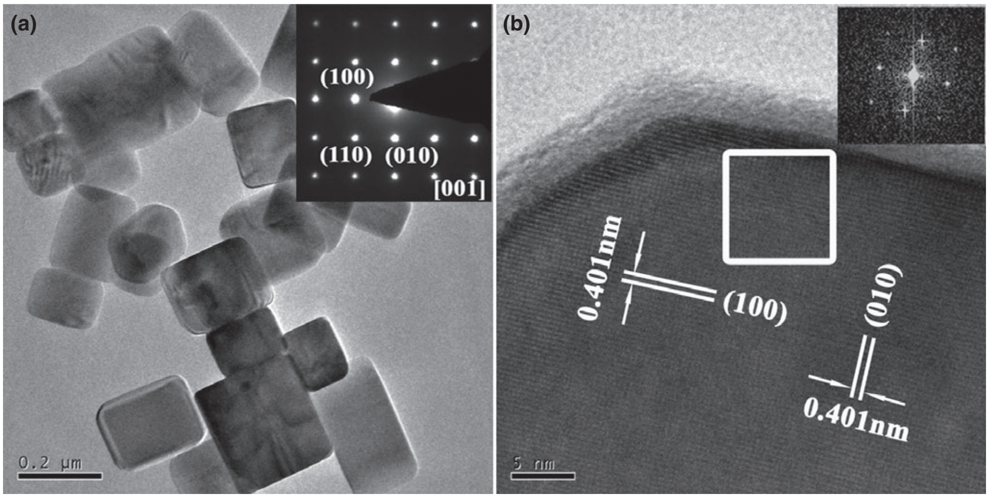

Fig. 2. (a) TEM image and SAED image (inset) (b) HRTEM image and FFT pattern of ScF_3 (inset).

decrease. And there also appears an endothermic peak in the heat flow curve. With temperature further increasing, the weight of ScF_3 continues to decrease. And it probably arises from pyrohydrolysis, in which ScF_3 reacts with residual moisture in the system.

Compared to the traditional solid-state reaction, not only could the present hydrothermal method be beneficial to tailoring the NTE effect by large substitution of other ions for Sc^{3+} or F^-, but it also facilitate precisely controlling of morphology and size.

IV. Conclusion

In summary, single-crystalline ScF_3 cubes were prepared by means of a simple, efficient and environmentally friendly hydrothermal synthesis method. ScF_3 cubes display uniform morphology and size, with an average size of ~200 nm. TG-DSC analysis demonstrates that ScF_3 can keep stable until 700°C in an inert atmosphere. As this hydrothermal method could prepare ScF_3 without the assistance of surfactants or templates, it is more likely to economically produce ScF_3 in a large scale.

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