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Solid-solid synthesis and structural phase transition process of SmF_3

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ABSTRACT

Mazes of contradictory conclusions have been obtained by previous researches about structural phase transition process of SmF_3. In this paper, the single crystals of SmF_3 (hexagonal and orthorhombic) were prepared by solid-solid synthesis, which have shown gradual changes in crystal growth modes with the increase temperature and holding time. Furthermore, we propose the phase transition process of in SmF_3. Hexagonal symmetry of SmF_3 (space group *Pnma*) was prepared firstly by heating Sm_2O_3 and NH_4HF_2 over 40 min at 270 °C. And then orthorhombic symmetry of SmF_3 (space group *P63mc*) was obtained by heating hexagonal symmetry over 10 h at 650 °C. The reaction of SmF_3 (hexagonal) = SmF_3 (orthorhombic) is extremely sluggish at a low temperature (less than 650 °C), which was seen as a Mixed Grown Region.

1. Introduction

In the recent years, a number of studies have been devoted to samarium trifluoride crystals, which are especially well known because of its luminescence and catalytic properties [1–3]. The properties make it very attractive for synthesizing various kinds of chemical products, but these strongly dependent on the crystal structure of SmF_3, which is important to understand if one is aiming to obtain a single phase of SmF_3 with good qualities [4–7]. In general, the SmF_3 compound is known with two polymorph modifications: hexagonal and orthorhombic phase that affords a different crystal structure, which is crucial for various applications [8–10]. Rotereau and Spedding reported that the single orthorhombic phase of SmF_3 was obtained by cooling of pure melt, and the orthorhombic SmF_3 crystal exhibits at room temperature while the hexagonal one at high temperature. The transition temperature was determined to be 495 °C [11,12]. Greis et al. investigated that SmF_3 was obtained by wet method and dehydration was then carried out in a stream of HF/N_2 at 1000 K. The presence of the orthorhombic phase at room temperature and the first-order transition to the rhombohedral phase around 480 °C and an additional transition at higher temperature (727 °C), giving rise to hexagonal phase [13]. However, Zalkin et al. reported that the hexagonal SmF_3 crystal was prepared by wet method at a low temperature (100 °C–150 °C), and then compounds with hexagonal and orthorhombic symmetry was formed after a high temperature heat treatment (1000 °C–1400 °C) for 1 h [4]. Cao et al. reported that the hexagonal SmF_3 crystal was obtained by solid-solid synthesis at 300–400 °C for 4 h [7]. Wang et al. reported that the hexagonal SmF_3 crystal was obtained by wet method and the compounds with hexagonal and orthorhombic symmetry was formed by heat treatment [14]. It is difficult to think through these mazes of contradictory conclusions. So no answer has been obtained to give this question for structural phase transition process of SmF_3.

With the aim of answering this question, the solid-solid synthesis is used to prepare the single phase of SmF_3 in this study, which can observe precisely gradual changes in crystal growth modes of SmF_3 and help people better understand the structural phase transition process of SmF_3 due to no effect of aqueous solution condition like pH value. Phase identification was carried out by X-ray diffraction (XRD), and studied the refinement structure of these samples by Rietveld analysis. Jade6.0 software was used for calculating the grain size of SmF_3. The microstructure of SmF_3 was characterized by transmission electron microscope (TEM). A possible structural phase transition process of SmF_3 was proposed.

2. Experimental

Raw materials were fine-grained Sm_2O_3 and NH_4HF_2, produced by the Sinopharm Chemical Reagent Co., Ltd., which were both analytical reagents with nominal purities of 98.0 and 98.5 pct, respectively. Samples were prepared by mixing the compounds of Sm_2O_3 and NH_4HF_2 (1:8 mol ratio) together. And then the mixtures were pressured into pellets with diameter of 8 mm using a pressure of 5 MPa. The shaped samples were placed into a horizontal electric furnace. The furnace was closed, and nitrogen flow with 500 mL/min was used to take gaseous

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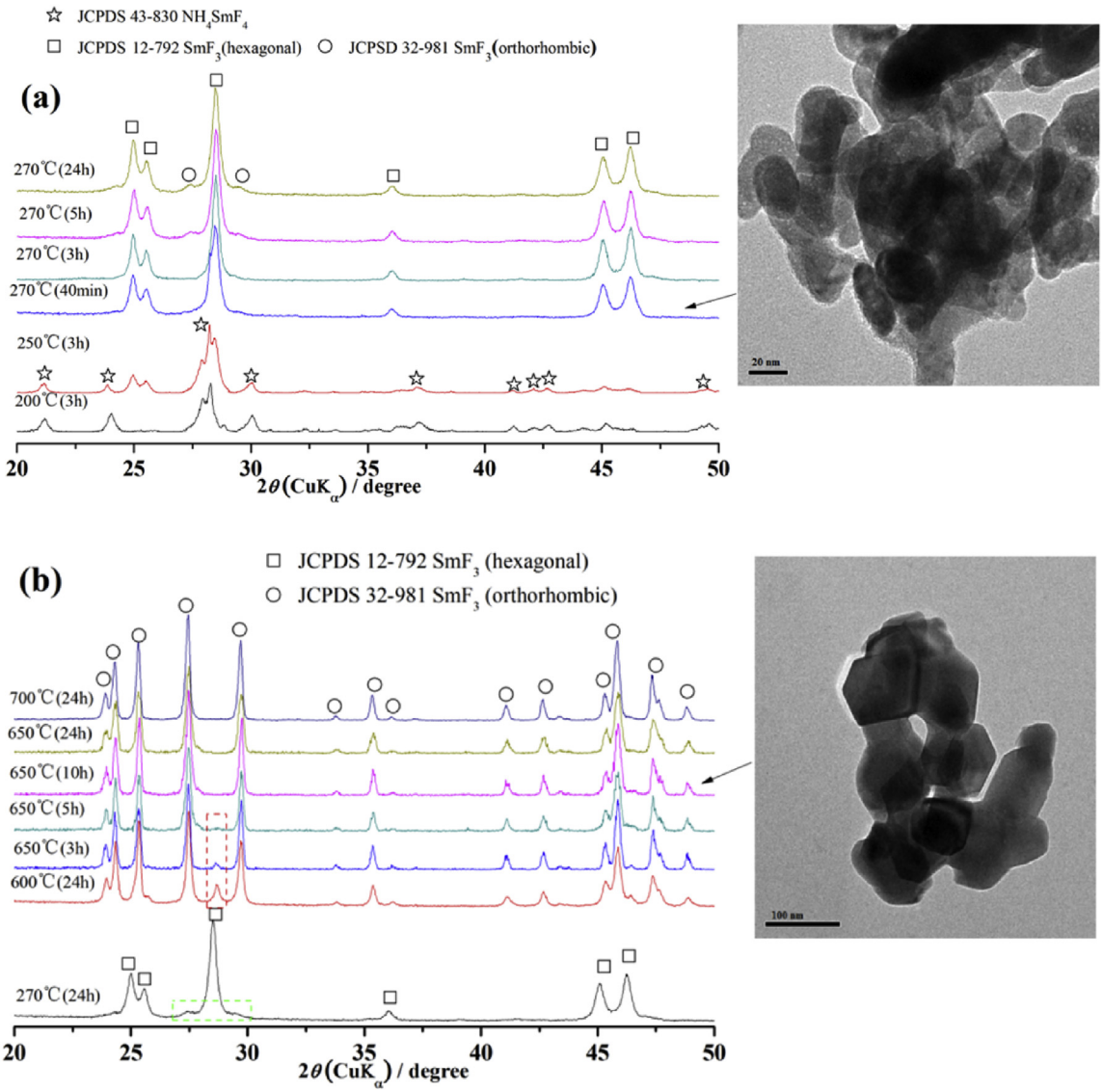

Fig. 1. XRD patterns and TEM micrographs of samples were obtained. (a) Compounds with Sm_2O_3 and NH_4HF_2 (1:8) versus temperature from 200 to 270 °C. (b) The hexagonal and orthorhombic SmF_3 crystal versus temperature from 270 to 700 °C.

products (NH_3, H_2O) and provide an inert atmosphere, and then passed through an absorbed gas bottle (aqueous solution of KOH) for avoiding harmful gas pollution to laboratory environment.

The phase composition of samples was identified using an X-ray diffraction (XRD) with CuKα radiation (Rigaku D/max-A, Tokyo, Japan). XRD data for Rietveld analysis were collected at 25 °C over a 2θ range 10°–90° with a step interval of 0.02° and a counting time of 2 s per step. The diffraction data were refined using the GSAS program of the Rietveld analysis. Diamond software was used for drawing the crystal structures of single phase of SmF_3. The grain size of SmF_3 was calculated by the Jade6.0 using X-ray diffraction patterns as data sources, which is based on the Debye-Scherrer equation [15].

$$D = \frac{K\lambda}{\beta COS\theta} \tag{1}$$

Where D is grain size (nm); K is a constant; λ denotes the wavelength of X-ray (nm); β represents the half-value breadth, $\beta=(B^2-b^2)^{1/2}$ in which B is an original half-value breadth of the diffracted peak; θ designates diffraction angle (rad). Si powder was used as a standard sample for eliminating the effect of equipment, which $b = 0.14468–1.7859 \times 10^{-3}\cdot(2\theta)+1.7148 \times 10^{-5}\cdot(2\theta)^2$. The microstructures of these samples were observed with TEM (JEM-2010, JEOL, Japan).

3. Results and discussion

Compounds with Sm_2O_3 and NH_4HF_2 (1:8) versus temperature from 200 to 270 °C, in which the XRD patterns and TEM micrograph of samples are shown in the Fig. 1 (a). NH_4SmF_4 is known as the intermediate product in the preparation process (Eq. (2)). No NH_4SmF_4 is observed in the XRD patterns measured between 40 min and 24 h at 270 °C. It means that the NH_4SmF_4 is vanished at 270 °C, when the holding time exceeded 40 min, as shown in the following Eq. (3).

$$Sm_2O_3 + 5NH_4HF_2 = 2NH_4SmF_4 + NH_3 + 2NH_4F + 3H_2O \tag{2}$$

$$NH_4SmF_4 = SmF_3 + NH_3 + HF \tag{3}$$

In the meantime, the peaks of orthorhombic SmF_3 crystal (circle) were appeared, when the holding time exceeded 5 h, it agrees with the results of Wang et al. [14], who determined that the hexagonal SmF_3 crystal was formed firstly at low temperature, and then transited into the