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Short communication

Preparation of barium hafnate fine powders by oxalate method

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Abstract

Barium hafnate ($BaHfO_3$) precursor was prepared by mixed barium nitrate and hafnium (IV) chloride with ammonium oxalate aqueous solution. Barium hafnate powders were obtained by decomposition of the precipitate precursor at 800 °C for 2 h. As a dispersant, polyethylene glycol (PEG6000) was used in the precipitation reaction and the influence of dispersant dosage on particle size was studied. X-ray diffraction analysis (XRD) showed the powders was pure cubic $BaHfO_3$ without impurities. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) demonstrated that the size distribution was uniform, and the average grain size was about 50 nm.

Keywords: Barium hafnate; Powders; Preparation; Oxalate method

1. Introduction

The perovskite-type oxides are widely researched for their unique properties such as ferroelectricity, superconductivity, catalytic activity, and thermoelectricity [1–4]. Recently more and more interests arose in the perovskite-type alkaline earth hafnates such as barium hafnate ($BaHfO_3$) and strontium hafnate ($SrHfO_3$). Due to their high density, relative high light output [5,6] and high effective atomic number, $BaHfO_3$ and $SrHfO_3$ materials appear as promising candidates for new solid-state scintillators when activated with rare earths (for example Ce^{3+} ion), which have potential large impact on high-energy nuclear medical applications such as computer tomography (CT) and positron emission tomography (PET) [7].

However, it is difficult to obtain $BaHfO_3$ single crystals for its melting point in excess of 2800 °C. So efforts are turned to fabricate transparent ceramics, for which fine powder is a key factor.

For preparation of monophasic $BaHfO_3$ powders from $BaCO_3$ and HfO_2 by conventional solid-state reaction, the stoichiometry must be precisely controlled, and the reactive temperature is relatively high. Zhang and Evetts synthesized homogeneous $BaHfO_3$ powders from the precursors yielded by spray drying method and then calcined at 1150 °C for about 20 h [8]. Ji et al. had acquired the Ce^{3+}-doped nanosized $MHfO_3$ (M = Ba, Sr or Ca) by nitrate–EDTA combustion method [9]. The combustion process is not easy to be controlled and not friendly to the environment for the releasing some nitride gases. To our knowledge, few investigations have been reported to prepare $BaHfO_3$ by oxalate method. This oxalate method has several advantages, including simple experimental procedure, environmental friendship, controllable particle size, chemical homogeneity and mass product. Lots of perovskite-type powders have been prepared by this oxalate method [10–12]. However, powder agglomeration happened inevitably by this method.

The objective of this job is to synthesize $BaHfO_3$ fine powders by oxalate method. To lessen the powder agglomeration, dispersant was used during the precipitation. The influence of the precipitation parameters and dispersant content on the morphology and particle size distribution was evaluated.

2. Experimental procedure

The starting materials were barium nitrate ($Ba(NO_3)_2$) (99.9%), hafnium (IV) chloride $HfCl_4$ (99%), diammonium oxalate monohydrate ($(NH_4)_2C_2O_4 \cdot H_2O$) (99.5%), ammonia (∼25%) and polyethylene glycol 6000 (PEG6000). 1.0 L aqueous solution containing $Ba(NO_3)_2$, $HfOCl_2$ (hydrolyzed from $HfCl_4$) with a molar ratio of Ba:Hf equal to 1:1 was

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prepared with a concentration of 0.2 mol/L for total cations. PEG6000 (molar ratio of PEG6000 to total cations: 0, 0.2%, 0.5%, 0.8%, 1.0%, 1.5%) was added into it. These solutions were respectively added with 0.37 L $C_2O_4(NH_4)_2$ (0.3 mol/L) aqueous solutions when stirred in a water bath of 65 °C. To ensure a complete precipitation, $C_2O_4(NH_4)_2$ was 10% in excess of the stiochiometric amount. The experiment was conducted at pH 7, which was adjusted by the addition of appropriate amounts of ammonia. The precipitate was firstly separated by filtration and washed with de-ionized water to remove chloride and nitrate ions. Then, it was washed with absolute alcohol to decrease the agglomerate strength. After dried at 80 °C in the vacuum drying chamber, and ball milled, the precipitate was calcined at 800 °C for 2 h in the muffle furnace, with a heating rate of 5 °C/min.

The precipitate precursor was characterized by thermo-gravimetric and differential thermal analysis (TG-DTA) (Netzsch STA-449c, Germany) under air flow at a heating rate of 10 °C/min. X-ray powder diffraction was performed on a Japan Rigaku K/max-γA X-ray diffractometer (Model D/MAX-2550 V, Rigaku Industrial Corporation, Japan) with Cu Ka radiation (1.54178 Å). The morphology of the powder was observed with scanning electron microscopy (JSM-6390, JEOL, Japan) and transmission electron microscopy (Model JEM2010, JEOL, Japan).

3. Results and discussion

The TG–DTA curves of the dried $BaHfO_3$ precursor are shown in Fig. 1. It can be seen that two main stages of weight loss corresponded to two endothermic peaks at 177.2 °C and about 407–720 °C. Weight loss from 20 °C to 177.2 °C is about 15%, which might be ascribed to the evaporation of adsorbed water. Weight loss from 200 °C to 800 °C is about 28.4%, which might be attributed to releasing of CO_2 and evaporation of crystal water. The two nearly overlapped endothermic peaks at 407 °C and 442 °C might result from the nonsynchronous decomposition of hydrated barium oxalate and hafnium oxalate. The exothermic peak at 327 °C corresponded to a small weight loss was ascribed to the decomposition of the PEG6000. The other exothermic peak at 602 °C was attributed to the crystallization of the $BaHfO_3$. Yamamura et al. [12], Fang et al. [13] and Marin et al. [14] reported the preparation of $BaC_2O_4{\cdot}0.5H_2O$ and $BaTiO(C_2O_4){\cdot}4H_2O$ by the oxalate method. Analogically, we suppose that the present precursor consists of $BaC_2O_4{\cdot}xH_2O$ and $HfO(C_2O_4){\cdot}yH_2O$, as shown by equation

$$[HfO]^{2+} + Ba^{2+} + 2[C_2O_4]^{2-} + (x+y)H_2O$$
$$= Ba(C_2O_4)\cdot xH_2O + HfO(C_2O_4)\cdot yH_2O$$

So the decomposition reaction can be described as follows:

$$Ba(C_2O_4)\cdot xH_2O + HfO(C_2O_4)\cdot yH_2O + O_2$$
$$= BaHfO_3 + 4CO_2 + (x+y)H_2O$$

After the precursor calcined at 800 °C for 2 h, the pure crystalline $BaHfO_3$ was obtained, as shown in Fig. 2. The phase composition of the particles can be identified to cubic system (*Pm*3*m* space group) and the crystallization was sufficient that can be judged from the sharp peaks.

SEM micrographs of the $BaHfO_3$ powders after being calcined at 800 °C for 2 h in muffle furnace were shown in Fig. 3. The particle size of the powders prepared without dispersant (Fig. 3a) and those with 0.8% PEG6000 as dispersant (Fig. 3b) were about 300 nm and 150 nm respectively. And it can be found that the particle size distribution of the sample (b) with dispersant was narrower than that of the sample (a) without dispersant. These indicate that 0.8% of the dispersant PEG6000 decreased the agglomeration.

The variation of particle size with the dosage of PEG6000 was plotted in Fig. 4. It was found that when the dispersant dosage was 1%, the particle size was the smallest. When the dispersant molecules were adsorbed on the surface of precursor particles, the steric effect and electronic repulsion helped to disperse the particles. With the increase of dispersant the particle size decreased. As the dispersant content was over

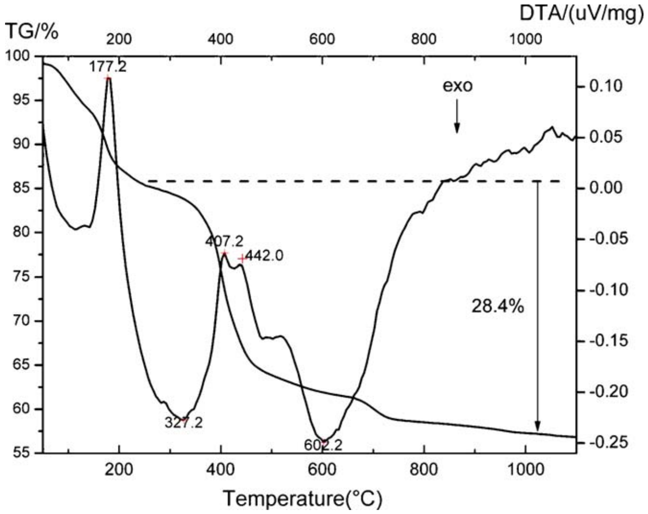

Fig. 1. TG–DTA curve of the precursor.

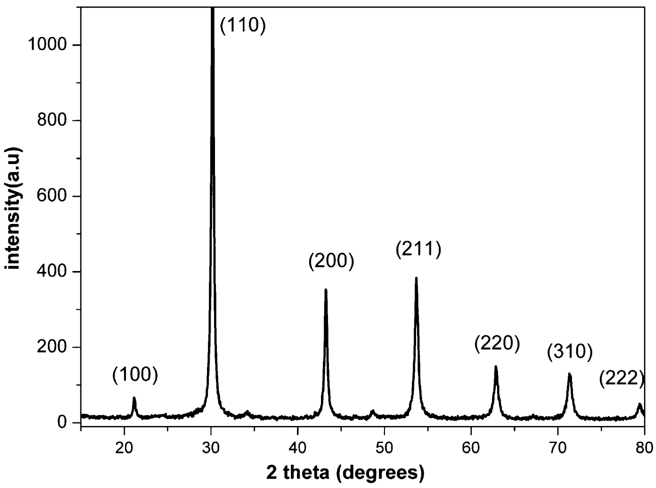

Fig. 2. XRD patterns of the as-prepared powders calcined at 800 °C for 2 h.

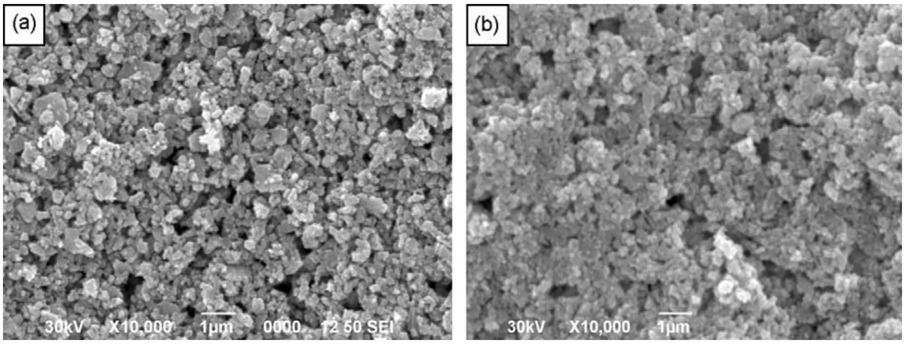

Fig. 3. SEM micrographs of the $BaHfO_3$ samples: (a) without dispersant, (b) with 0.8% PEG6000 as dispersant.

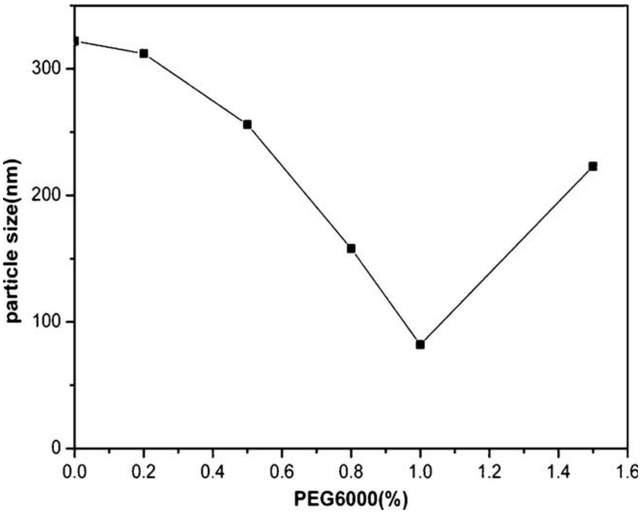

Fig. 4. Variation of particle size with the dispersant PEG6000.

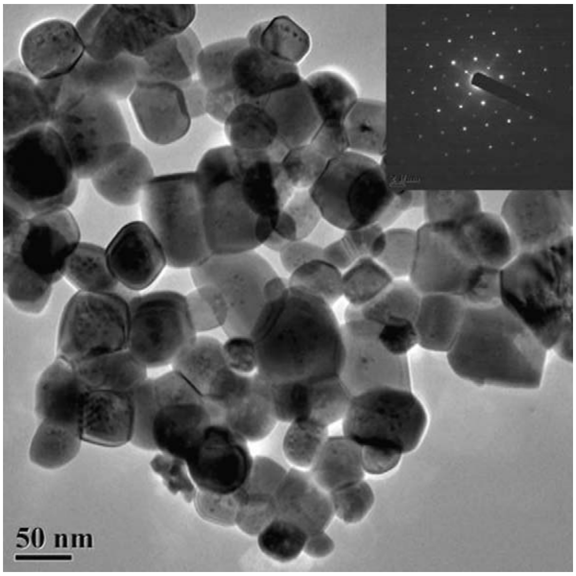

Fig. 5. TEM micrograph and SAED pattern of the $BaHfO_3$ powders prepared with 1.0% PEG6000.

1.0%, the bridging flocculation may occur and then the powder agglomeration increased.

The TEM micrograph and selected area electron diffraction pattern of the $BaHfO_3$ powders prepared with 1.0% PEG6000 is presented in Fig. 5. The grain size is about 40–50 nm, and is well dispersed. The selected area electron diffraction (SAED) shows the phase composition of the microcrystal is cubic system, in agreement with XRD results (Fig. 2).

4. Conclusions

Homogeneous and fine barium hafnate ($BaHfO_3$) powders with the cubic structure were successfully prepared by the oxalate method. The influence of dispersant (PEG6000) dosage on the particle size was studied and it was found that about 1% PEG6000 was effective to prepare $BaHfO_3$ nano-particles with small agglomeration. The $BaHfO_3$ phase was first formed at about 600 °C by this method. The oxalate method offered a simple way for the preparation of narrow size distribution $BaHfO_3$ fine powders.

Acknowledgements

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