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Molten salt route of well dispersive barium titanate nanoparticles

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ABSTRACT

Well dispersive barium titanate ($BaTiO_3$) nanoparticles were synthesized by molten salt method using barium hydroxide octahydrate ($Ba(OH)_2 \cdot 8H_2O$), titanium dioxide (TiO_2), and the eutectic salts (NaCl–KCl) as raw materials. The as-prepared samples were characterized by X-ray diffraction, Fourier transform infrared spectrometry, UV–vis diffuse reflectance spectra, and field emission scanning electron microscopy. The present results show that $BaTiO_3$ can be formed at low temperature of 600 °C. The crystallinity of $BaTiO_3$ increases with the temperature rising. SEM images clearly indicate that well dispersive $BaTiO_3$ nanoparticles can also be successfully obtained even at high temperature of 800 °C. Most $BaTiO_3$ nanoparticles display hexagonal outline in shape. The average size of $BaTiO_3$ nanoparticles is around 50 nm. Meanwhile, compared with crystalline TiO_2, amorphous TiO_2 is favorable for the formation of $BaTiO_3$, especially decreasing other undesired phases. In the end, the formation mechanism of well dispersive $BaTiO_3$ nanoparticles is proposed for this molten salt system. Well dispersive $BaTiO_3$ nanoparticles begin to show some sintering ability at low temperature of 900 °C.

1. Introduction

Barium titanate ($BaTiO_3$), with a perovskite structure, is a kind of typical ferroelectric, piezoelectric, and insulating material [1–4]. Due to its outstanding properties, such as high permittivity, low dielectric loss and high dielectric tunable properties, $BaTiO_3$ has widespread applications in multilayer ceramic capacitors (MLCCs), dynamic random access memory, tape, sensors, and thermistors [5–8].

Traditionally, $BaTiO_3$ is prepared by solid state reaction between $BaCO_3$ and TiO_2 under high temperature. Using this method, the as–prepared $BaTiO_3$ is easily agglomerated, which results in poor electrical properties of the sintered ceramics. As the performance of $BaTiO_3$ ceramics significantly depends on the microstructure of the sintered body, much attention has been focused on the synthesis of $BaTiO_3$ nanoparticles. In recent years, wet-chemistry synthesis techniques, including sonochemical synthesis [9], sol–gel [10–12], hydrothermal [13–16], solvothermal [17] and chemical coprecipitation [18,19], have been investigated to prepare $BaTiO_3$ nanoparticles. However, it's still a challenge to synthesize well dispersive $BaTiO_3$ nanoparticles with controlled morphology. In the past decade, the molten salt method has been used to prepare many ceramic materials [20–23]. Above the melting point of the chosen salt, the molten salt forms a liquid phase to act as a solvent for reactant dissolution, diffusion and precipitation. This method is also simple, versatile approach, in which the molten salt can be recovered for utilization by possible recrystallization process. This means that molten salt method has a good prospect of industrial application. Taking advantage of the above molten salt method as well as on the basis of our previous synthesis work [12,24–27], we tried to use the molten salt method to synthesize the well dispersive $BaTiO_3$ nanoparticles.

In this work, molten salt method is employed to prepare $BaTiO_3$ nanoparticles under the wide range of temperatures from 600 to 800 °C. Well dispersive $BaTiO_3$ nanoparticles were obtained. The average particle size is about 50 nm. Well dispersive $BaTiO_3$ nanoparticles begin to show some sintering ability at low temperature of 900 °C. Meanwhile, we propose a mechanism which can well explain the formation of well-dispersed $BaTiO_3$ nanoparticles in the molten salt.

2. Experimental

2.1. Synthesis procedure

The starting materials used in the experiment were all of analytical grade reagents. In a typical procedure, $Ba(OH)_2 \cdot 8H_2O$ and TiO_2 were mixed with NaCl–KCl eutectic salts (50 mol% NaCl + 50 mol% KCl) at a molar ratio of 1:1:20, and ground for 20 min. The mixture was then transferred into a corundum crucible and calcined at different temperatures for 3 h. The crucible was subsequently naturally cooled down to room temperature. Samples were collected and washed with deionized water until no chloride ions were detected by silver nitrate solution, and then dried at 120 °C for 2 h.

The as-prepared $BaTiO_3$ nanoparticles were pressed into pellets of 25 mm in diameter and about 1 mm in thickness at a pressure of

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20 MPa, using 8 wt.% PVA (polyvinyl alcohol solution) as a binder. The pellets were sintered at 900 °C in air for 3 h and cooled down to room temperature in furnace naturally.

2.2. Characterization

The phase of the as-prepared samples were characterized by X-ray diffraction (XRD, XD-3A, Japan), using Cu Kα radiation. FTIR spectra of the samples were characterized by Fourier transform infrared spectrometry (FTIR, Bruker Equinox 55, Germany), using KBr as a binding material in the range of 400–4000 cm^{-1}. The amounts of Na, K and Cl incorporated and Ba/Ti atomic ratio in the typical product were measured by X-ray fluorescence spectrometry (XRF, SRS-3400, Germany). UV–vis spectrum of the typical sample was recorded by a UV–vis spectrophotometer (JASCO, V-550, Japan). The morphology was detected by field emission scanning electron microscopy (FE-SEM, HITACHI S-4800, Japan). The average and distribution sizes of $BaTiO_3$ nanoparticles were calculated from $BaTiO_3$ scanning electron images by the software of Nano Measurer. The microstructure of the sintered $BaTiO_3$ sample was studied by scanning electron microscope (SEM, Quanta 450, America).

3. Results and discussion

3.1. Crystal phases of the as-prepared samples

Fig. 1 shows the XRD patterns of the as-prepared samples calcined at different temperatures. $BaTiO_3$ phase is detected at 600 °C, while $BaCO_3$ phase can be also found, just as those of other sol–gel techniques [10–12], $BaCO_3$ is usually coexisted with $BaTiO_3$ phase. As the temperature increases, the peaks of $BaCO_3$ disappear. A dominant $BaTiO_3$ phase is obtained at 800 °C. According to JCPDS card (31–0174), the as-prepared $BaTiO_3$ phase has a cubic perovskite structure. Compared to traditional solid state synthesis, the molten salt method decreases the synthesis temperature of $BaTiO_3$ greatly. This result indicates that the molten salts acting as solvent can enhance the diffusion of reactants and accelerate the rate formation of $BaTiO_3$.

3.2. FTIR spectra of the typical samples

To trace $BaCO_3$ possibly existed in the samples, the FTIR spectra of the typical samples are shown in Fig. 2. Two weak absorption peaks at around 1430 and 850 cm^{-1} reveal the existence of minimal $BaCO_3$, while the wide absorption band between 480 and 700 cm^{-1} is the characteristic vibration frequency of TiO_6 octahedra [11]. With an increase in reaction temperature, no apparent absorption peaks for $BaCO_3$ are observed. The FTIR results strongly confirm the above analysis of XRD patterns, i.e., $BaCO_3$ can be found at low calcined temperature, and then disappears at high calcined temperature.

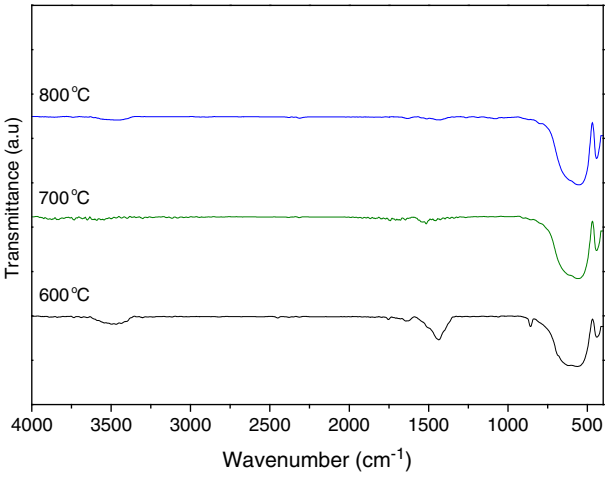

Fig. 2. FTIR spectra of $BaTiO_3$ prepared at different temperatures.

The amounts of Na, K and Cl incorporated and Ba/Ti atomic ratio in the typical sample calcined at 800 °C were measured by XRF. The atomic ratio of Ba, Ti, Na, K, and Cl in the sample is 1.018:1:0.080:0.004:0.010. Compared with K and Cl, the amount of Na is relatively high. The reason may be that Na^+ can easily incorporate in $BaTiO_3$ due to its small ionic radius.

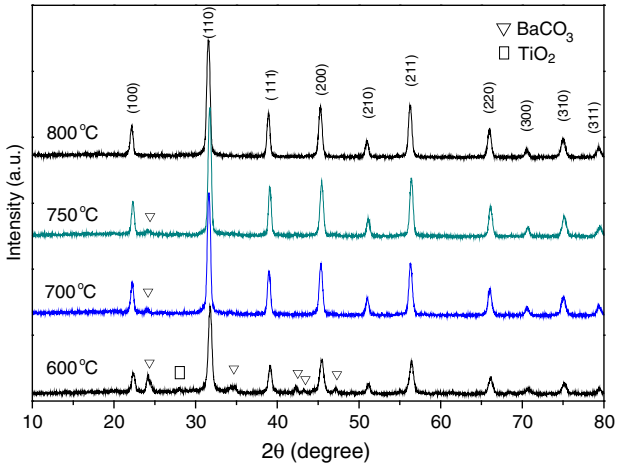

Fig. 1. XRD patterns of $BaTiO_3$ synthesized by molten salt method (Ba precursor: $Ba(OH)_2 \cdot 8H_2O$, Ti precursor: TiO_2 obtained by alkoxide-hydrolysis).

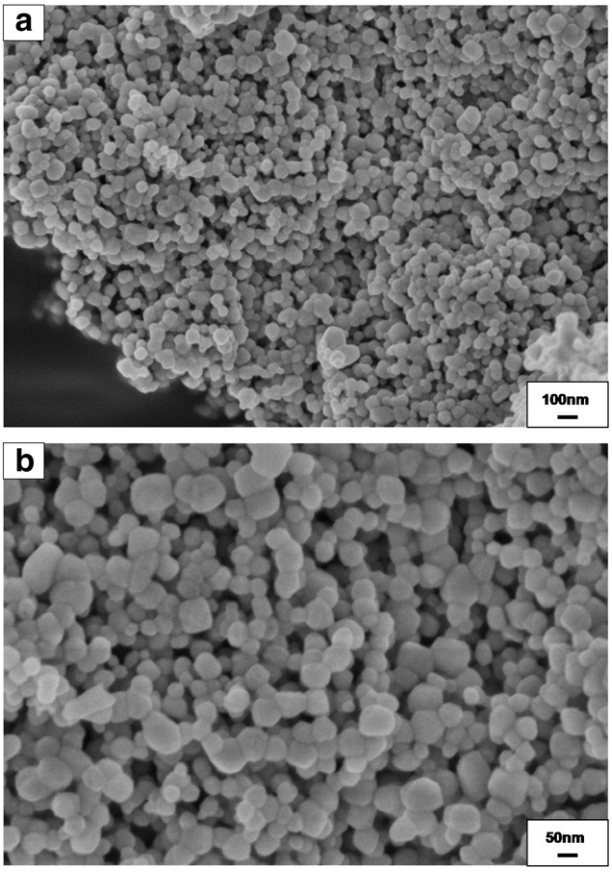

Fig. 3. SEM images of $BaTiO_3$ nanoparticles prepared by molten salt method at 800 °C (Ti precursor: TiO_2 obtained by alkoxide-hydrolysis).