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Direct synthesis of barium zirconate titanate (BZT) nanoparticles at room temperature and sintering of their ceramics at low temperature

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Abstract

Using tetrabutyl titanate, zirconium nitrate and barium octahydrate as the raw materials, BZT nanoparticles with a grain size of ~10 nm were directly synthesized at room temperature. With low energy consumption and without any contamination produce, the synthesis process is green, environmental-friendly, convenient and efficient. The graingrowth of the as-prepared nanoparticles annealed at different temperatures was checked, and a rapid graingrowth starting at 600 °C was observed. The sintering characteristics were also studied and it was found that an adapted sintering aid was very important for the sintering of the BZT nanoparticles at low temperature. Here, adding the useful active liquid of Bi_2O_3–Li_2O as the sintering aid results in obtaining the dense BZT ceramics with the relative density of 96% even sintering at the temperature as low as 900 °C for 2 h.

Keywords: A. Sintering; BZT; Nanopowder; Direct synthesis

1. Introduction

Barium titanate (BT) based materials are very important for the modern industry of electrical and electronic devices. They have ferroelectric, thermoelectric, and piezoelectric properties when they assume the tetragonal structure [1], and can be widely used in capacitors, positive temperature coefficient resistor, dynamic random access memories(DRAM), electromechanics, and nonlinear optics [2–4]. Barium zircornate titanate ($BaZr_yTi_{1-y}O_3$, BZT) is an important species of this family with potential applications such as piezoelectric transducers, DRAM, tunable microwave devices, and electrical energy storage units [5–8]. With the increase of zirconium content of BZT materials, the three transition points and the three corresponding ε_r maxima move closer together and, finally, coalesce into a single broad maximum at y=0.10 [9]. After moving the broad maximum near room temperature, a high dielectric constant can be obtained, and thus, BZT with the composition can be generally be adopted in Y5V multilayer ceramic capacitors (MLCC) [10,11]. When fabricated under a suitable process, the ceramics can have high dielectric constant over 10^4, while keeping a high breakdown voltage value which is suitable for high voltage applications [12]. BZT materials are often sintered into dense ceramics at a high temperature over 1300 °C. After adding sintering aids such as ZnO–Li_2O, the sintering temperature can be lowered to around 1250 °C [10]. It is hard to obtain a dense BZT ceramics sintering at low temperature below 960 °C (silver's melting point), but is very useful technically for multiple layer ceramic capacitors (MLCC) with magnetism-free device. Fortunately, the grain size of the ceramic powders decreases, and the sintering temperature decreases theoretically, especially for nanoparticles. Here, we report a direct synthesis route to BZT (for example $BaZr_{0.1}Ti_{0.9}O_3$ in this study) nanoparticles at room temperature, which is similar to that of BT nanoparticles [13]. Their sintering characteristics at low temperature are also studied.

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2. Experimental procedure

The method is evolved from direct synthesis from solution (DSS) [14] and is carried out in an enclosed system. The analytical reagents barium octahydrate ($Ba(OH)_2 \cdot 8H_2O$), zirconium nitrate pentahydrate ($Zr(NO_3)_4 \cdot 5H_2O$) and tetrabutyl titanate ($Ti(OC_4H_9)_4$) are adopted as starting raw materials to prepare the BZT nanoparticles. The titanium and zirconium (ZT) solution is obtained by dissolving 30.6 g Ti $(OC_4H_9)_4$ and 4.3 g $Zr(NO_3)_4 \cdot 5H_2O$ into 50 ml ethanol absolute. The alkali slurry is prepared by ball milling 31.6 g $Ba(OH)_2 \cdot 8H_2O$ in 100 ml ethanol for 4 h. The ZT solution is added into the alkali slurry in the jar, pH value is adjusted by ammonia, and then resealed for another 18 h milling at the rate of 200 rpm, after that, homogenous white slurry is obtained. The white slurry is air-dried and BZT nanoparticles are synthesized. All the procedures are operated at room temperature. The dry pressed disks with the as-prepared nanoparticles were annealed or sintered at different temperatures for the study on sintering characteristics through observing the grain-growth and sintering shrinkages. In order to study the role of the sintering aids, the mixture of Li_2O–Bi_2O_3 was added to the as-prepared BZT powders with 3 wt%, and dry pressed into disks, then sintered at 900 °C for 2 h.

All the samples are characterized at room temperature by XRD on a Philips X-ray diffractometer (XRD Model: X'Pert-Pro MPD) using CuKα radiation (40 kV, 30 mA). The microstructures of the samples are observed by scanning electron microscopy (SEM) on a Hitachi field-emission SEM (Model: SU-4800).

3. Results and discussions

BZT nanoparticles can be prepared by the DSS method using isopropoxides as raw materials in isopropanol–water system [15] at 70 °C. Due to the high price and instability of isopropoxides in damp air, here we replace zirconium isopropoxdie with $Zr(NO_3)_4 \cdot 5H_2O$ as starting raw materials. Without introducing any contamination and with low energy consumption, the synthesis process is green, environmental-friendly, convenient and efficient. In order to check the sintering characteristics, the dry pressed disks with the as-prepared nanoparticles were annealed or sintered at different temperatures. Their crystalline structures were checked by XRD as shown in Fig. 1.

It is confirmed that the as-prepared nanoparticles have perfect perovskite structures. Although the peaks of impurity phase at 24° and 33° are indexed as $BaCO_3$, they disappear after suitably being annealed at a temperature over 700 °C. The small amount of $BaCO_3$ in the as-prepared samples possibly derives from the raw material barium hydroxides which can react with CO_2 in the air during its storage. The $BaCO_3$ can be synthesized into the perovskite structure while it releases CO_2 at a temperature as low as 500–700 °C because the decrease of $BaCO_3$ phase was clearly observed.

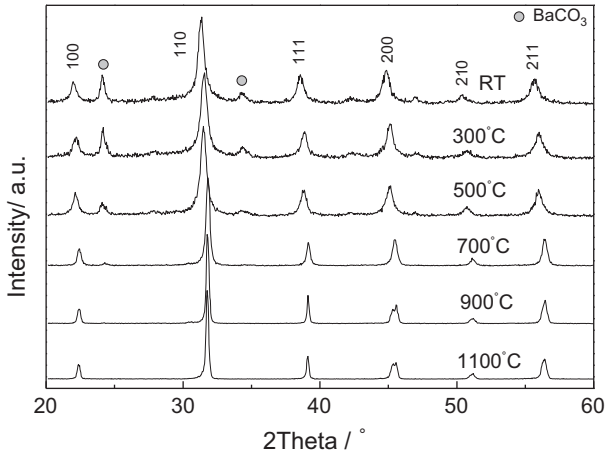

Fig. 1. XRD profiles of the directly synthesized BZT nanopowders annealed at different temperatures.

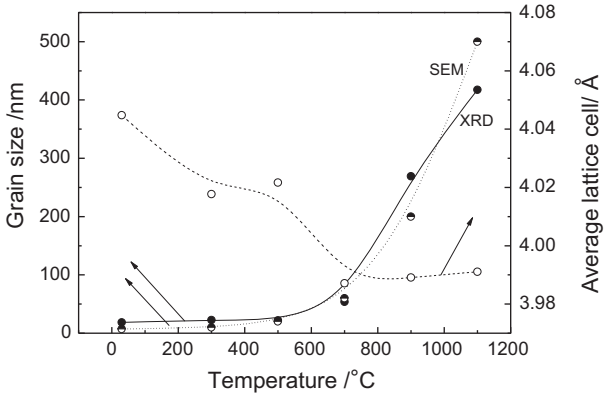

Fig. 2. The annealing temperature dependencies of grain size and lattice cell of the directly synthesized BZT nanopowders.

The grain size of $BaTiO_3$ nanoparticles can be estimated by Scherrer's equation [16], and also can be checked by SEM directly. Fig. 2 shows the grain size increases with annealing temperature by these two methods. The lattice cell parameters estimated by XRD are also shown here. The results of the grain size estimated by the SEM agree with that of XRD as shown in Fig. 2.

The lattice cell parameters can also be estimated by XRD as shown in Fig. 2. They decrease with annealing temperature at first, and tend to become constant at a temperature over 800 °C. Because of the involvement of water during the synthesis of the as-prepared nanoparticles, hydrogen interstitial can be inducted into the lattice of the perovskite as

$$H_2O \rightarrow V''_{Ba} + 2H^{\bullet}_i + O^{\times}_O. \quad (1)$$

Therefore, the lattice expands. When annealed at higher temperature, the hydrogen atom is extracted, hence the interstitial is eliminated and the lattice restores. The size effect of nanoparticles is another reason of the lattice expansion in as-prepared nanoparticles. Due to the ratio of surface to bulk

increase, the lattice band is weakening, and the lattice expands slightly in nanomaterials.

We can study the sintering characteristics from mass transfer and grain growth. A rapid graingrowth at a temperatures over 600 °C is observed, and a remarkable grain size increases even at a temperature as low as 300 °C as shown directly in Figs. 2 and 3. The grain size of the sample annealed at 500 °C is double that of the as-prepared sample and that at 900 °C is 20 times higher as shown in Fig. 3(a), (b) and (c). It is indicated that the as-prepared nanoparticles start mass transfer, and have grain boundary migration even at very low temperature such as 300–500 °C, thus, sintering can happen at this time theoretically. However, even we sinter our sample at 1100 °C, and we cannot obtain the dense ceramics as shown in Fig. 3(d). The grain size increases as great as ~500 nm, but there are many pores in the sample. During sintering, there are several changes such as the grain size and grain shape due to graingrowth, and the porosity becomes smaller with the elimination of the pores. If the grain grows more rapidly than the elimination of the pores in the samples during sintering, dense ceramics could never be obtained. Due to the unavoidable agglomerations of nanoparticles, the inter-aggregate pores are eliminated slowly during sintering, and thus, many pores would remain in the samples. Therefore, only improving the activity of the powders is not enough for a good sintering, and the elimination of the pores should be sped up at the same time. The necessary conditions to obtain the dense ceramics at a certain temperature are, (1) mass transfer should take place so a sufficiently high temperature should be needed and (2) grain boundary migration should be slower than the elimination rate of the pores, that is the graingrowth should not be too fast [17]. Under these conditions, a suitable soaking time for the dense ceramics decreases with the sintering temperature. In our samples, even at a temperature as low as 300–500 °C, the graingrowth can be observed and thus the mass transfer can take place. We should speed up the elimination rate of the pores and slow down the graingrowth. An effective means to achieve these conditions is adding an active sintering aid. At first, the surface tension should decrease and then active liquid produced by the sintereing aid could jam into the inter-aggregate pores and speed up the elimination rate of the pores. Because active liquid is a secondary phase, a pinning effect could play a role in slowing down the graingrowth and the migration of the grain boundary.

It is important to choose a suitable active liquid because other effects may take place, such as it may lead to mass transfer in liquid phase and enhance the graingrowth. The active liquid, in which a composition can decrease the graingrowth while speeding up the elimination of the pores, is suitable for sintering aids. Here, for example, Bi_2O_3 is suitable for $BaTiO_3$ based materials. Based on them, Bi_2O_3–Li_2O is adopted and the sintering temperature (900 °C) is chosen up to the melting point of Bi_2O_3 slightly. The microstructure of the ceramics sintered at 900 °C for 2 h with the active liquids is shown in Fig. 4.

According to the formula of $BaZr_{0.1}Ti_{0.9}O_3$, the molecule weight is estimated at 237.6 and the average lattice cell parameter at 4.02 A, thus, the theoretical density of BZT is estimated at 6.08 g/cm^3. It is revealed that the ceramic grains are homogenous with the size about 1 μm from Fig. 4. The porosity of the ceramics is small and the relative density is ~96% as measured using Archimedes measurement. In other

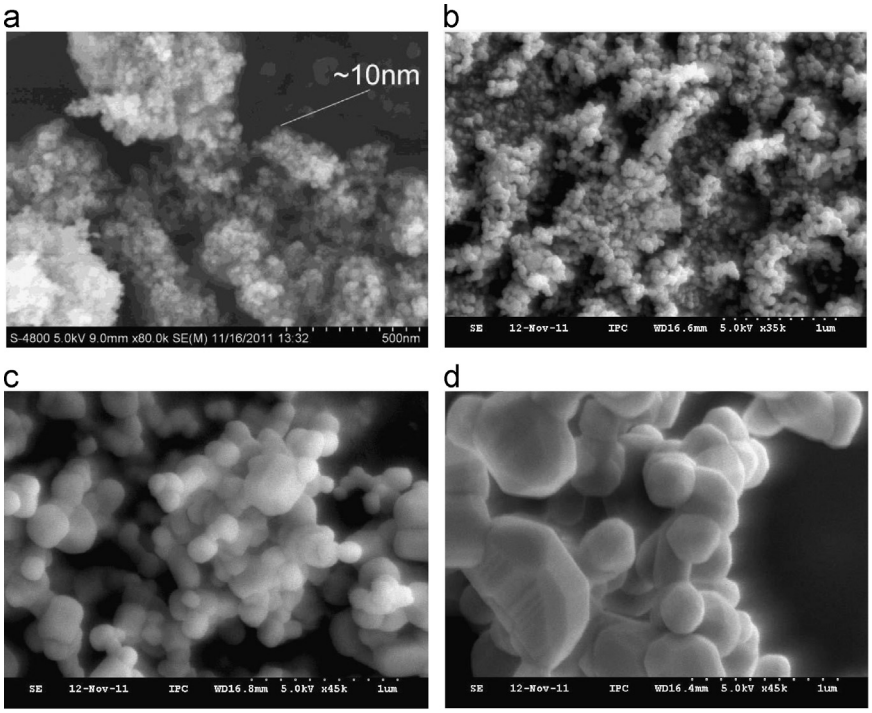

Fig. 3. SEM of BZT nanopowders annealing at different temperatures: (a) as-prepared BZT nanopowders ~10 nm, (b) annealed at 500 °C ~20 nm, (c) annealed at 900 °C ~200 nm, and (d) sintering at 1100 °C ~500 nm.

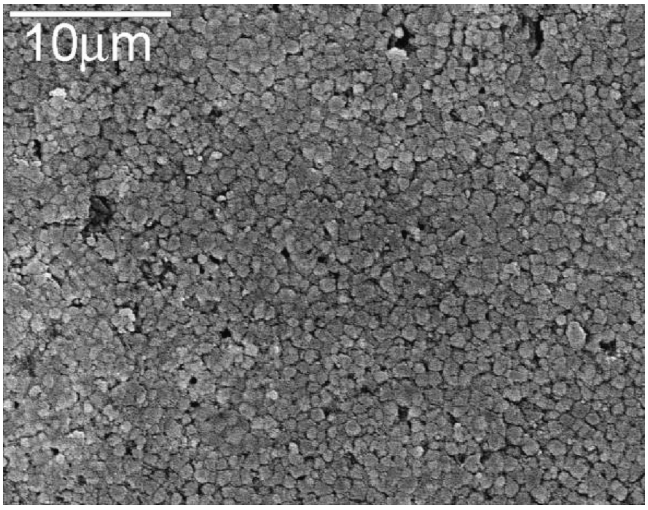

Fig. 4. The microstructure of the ceramics sintered at 900 °C for 2 h with Bi_2O_3–Li_2O sintering aid.

words, the sintering aids have a good effect and our BZT nanoparticles can be sintered well as dense ceramics at a temperature as low as 900 °C for 2 h with Bi_2O_3–Li_2O sintering aids. On the other hand, the ceramics sintered at 1100 °C without sintering aids have only a relative density of ~73%.

4. Conclusions

Similar to $BaTiO_3$, perfect perovskite BZT nanoparticles can also be directly synthesized at room temperature. The whole process is easy to operate without any pollution to the environment. Nanoparticles with the grain size of ~10 nm can be obtained using ethanol absolute as assistant agent. The graingrowth of the nanoparticles was observed even at a temperature as low as 300–500 °C, and increased rapidly at a temperature over 600 °C, although the dense ceramics can hardly be obtained at the sintering temperature as high as 1100 °C. To obtain dense ceramics at a certain temperature, mass transfer should take place so that a high enough temperature should is got and at the same time the grain boundary migration should be slower than the elimination rate of the pores, so that the graingrowth should not be fast. After the sintering aid Bi_2O_3–Li_2O was added, the surface tension was decreased and the inter-aggregate pores were jammed out, thus the elimination rate of pores was increased and, in the mean while, the pinning effect of the active liquid phase can slow down the graingrowth. Therefore, dense ceramics with relative density of 96% can be obtained even sintering at the temperature as low as 900 °C for 2 h. Above all, the nanoparticles prepared by direct synthesis method can have outstanding properties for various applications.

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