

Phase and Microstructural Transformation of BaTiO₃ Powder Synthesized by Solid-State Reaction

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Abstract: BaTiO₃ powder with small particle size and high tetragonality was synthesized by a sanding solid-state phase method with domestic submicron BaCO₃ and TiO₂ as raw materials. We also studied the effects of calcination temperature, heating rate and holding time on the average particle size and tetragonality of BaTiO₃. The results show that the reaction mechanism for the synthesis of BaTiO₃ by solid phase reaction can be divided into two stages: when the calcination temperature is lower than 900 °C, BaCO₃ and TiO₂ first form cubic phase BaTiO₃. When the calcination temperature rises to 900 °C, the cubic phase BaTiO₃ begins to transform into a tetragonal phase. Ultrafine BaTiO₃ powder with a particle size of 180.7 nm and a tetragonality (*c/a*) of 1.0086 is prepared at a calcination temperature of 900 °C, a heating rate of 5 °C/min, and a 5 h incubation. This work provides a good research idea for the preparation of high performance BaTiO₃ powder used for ultra-thin MLCC.

Key words: barium titanate; solid state reaction; phase transformation; microstructure

As a dielectric and ferroelectric material, BaTiO₃ (BTO) has been applied in many microelectronic devices: multilayer ceramic capacitors (MLCCs), embedded capacitance for printed circuit boards, positive temperature coefficient (PTC) thermistors and electroluminescent display^[1-3]. As the miniaturization of electronic products has been put forward, MLCCs with smaller size and higher capacity are increasingly required. In order to achieve high capacity in a small volume, a greater number (exceed 1000 pieces) and thinner (below 1 μm) green sheets of MLCCs are required^[4-6]. Thus, small BTO particles with high tetragonality (*c/a*) and minuscule size are desired.

Recently, there are lots of methods to synthesize nano-sized BTO powders, such as solid-state reaction (SSR), hydrothermal synthesis^[7-9], processes via a sol-gel route^[10,11], and a method starting from oxalates^[12,13]. Among the aforementioned synthetic routes, SSR is regarded as an inferior route, whose final product is usually coarse and seriously agglomerative due to the high calcination temperature. Compared with SSR, finer and more homogeneous BTO powders are

much easier to obtain via other chemistry synthetic routes. However, relatively high cost and various unavoidable lattice defects make them still not particularly admirable. Therefore, there are a number of researches to explore the improved SSR process to prepare fine BTO powders with narrow size distribution. Kong et al^[14] reported that the BTO powders could be obtained by calcination at 800 °C for 2 h with a prior ball mill of the starting mixture. Yanagawa et al^[15] reported that the well dispersed BaTiO₃ powders with an average primary particle size less than 200 nm and lattice tetragonality up to 1.010 could be successfully prepared by using a laboratory-sized vibration ball mill. In addition, the introduction of organic additives such as nylon, bovine serum albumin^[16], glycine^[16] and carbon black^[17] was also reported as an effective approach that helps to obtain well-dispersed BTO with small size. Nevertheless, it is apparent that the relevant researches on preparing BTO nanoparticles only focus on exploring improved SSR processes to obtain BTO nanoparticles with high tetragonality whereas the explanation of formation of

Received date: February 18, 2019

Foundation item: Priority Academic Program Development of Jiangsu Higher Education Institutions (GRCK2017042411005977); Research Fund of Low Cost Fabrication of GaN Power Devices and System Integration, China (JCYJ20160226192639004); Research Fund of AlGaIn HEMT MEMS Sensor for Work in Extreme Environment, China (JCYJ20170412153356899); Research Fund of Reliability Mechanism and Circuit Simulation of GaN HEMT, China (2017A050506002)

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tetragonal BTO nanoparticles via SSR appear is missed.

In this work, the influence of calcining temperature, dwelling time and heating rate on the structure, morphology and phase transformation was investigated.

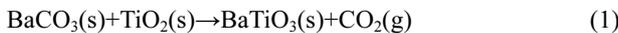
1 Experiment

1.1 Sample preparation

Stoichiometric quantities of rutile TiO₂ (Xin Fu Titanium Dioxide, Ningbo, China, $D_{50} \approx 566.8$ nm), standard BaCO₃ (Sinopharm Chemical Reagent, Shanghai, China, $D_{50} \approx 992.0$ nm) were used as raw materials, and triethanolamine (Sinopharm Chemical Reagent, Shanghai, China) was used as dispersant. Compared to the conventional ball milling, sand milling with high energy input and the use of smaller grinding media (the diameter is generally smaller than 1 mm) can offer more mechanical activity to the particles^[18]. Therefore, the particle size of the raw material was greatly reduced by sanding in a sand mill (NT-1L) for 4 h with zirconia balls (purity 99.99%, ϕ 0.1 mm) in deionized water. The homogenization of mixture was performed by ball milling for 4 h at 40 Hz in polyethylene bottles with zirconia balls (purity 99.99%, ϕ 0.6 mm) in deionized water. The mass ratio of powder, solvent and milling media was 1:4:4. After drying and sieving, the mixed powder of BaCO₃ and TiO₂ was obtained. Then, the powder was placed in a furnace (LHT 02/17/LB Speed, Nabertherm, Lilienthal, Germany) to fabricate BTO powders.

1.2 Characterization

Solid-state reaction to prepare BTO is based on the reaction below:



The reaction between BaCO₃ and TiO₂ was studied by means of simultaneous thermogravimetric analysis (TGA, STA 499 F3, Netzsch, Bavarian, Germany) and differential scanning calorimetry (DSC, Discovery, USA). The mixtures were isothermally held at different temperatures from 800 °C to 950 °C with temperature steps of 50 °C and heating rate of 5 °C/min. Dry argon was used as purge gas at speed of 0.02 L/min. The second type of TGA experiments was carried out by heating rate of 2 and 8 °C/min, and followed by an isothermal holding at 900 °C under a 0.02 L/min flow of dry argon. The phase composition and crystallographic analyses of calcined powders were performed by X-ray diffraction (XRD-9KW, Cu K α radiation, Smartlab, Rigaku, Tokyo, Japan). The XRD measurements were acquired at 2θ from 15° to 75°, and the scanning rate was set at 5°/min. The in-situ XRD measurements were performed with stage DHS 1100 and temperature control unit TCU 100. The temperature went down from 900 °C to 25 °C at controlled cooling rate of 10 °C/min. The morphologies of BTO were characterized by field emission scanning electron microscope (FESEM, Meilin SEM, ZEISS, Oberkochen, Germany). The average grain size D_g was obtained by averaging over 200 grains and using Image J software. The particle size distribution of the materials was

determined by a laser diffraction-scattering particle size analyzer (DLS, BI-200SM, Brookhaven, Holtsville, USA). Each sample was tested more than 20 times to ensure the accuracy of results.

2 Results and Discussion

2.1 Formation of initial cubic phase

The first derivative of the mass loss with respect to time (dw/dt , usually denoted as DTG), DSC and TG of the BaCO₃, TiO₂ and triethanolamine mixture is presented in Fig.1. As shown in Fig.1, three endothermic peaks can be easily observed. In particular, the first peak located at 538 °C is corresponding to the liquid-gas transition of triethanolamine. The second and third peaks located at 633 and 839 °C are corresponding to different stages of the reactions between BaCO₃ and TiO₂. In terms of mass (as shown in Fig.1b), there is a loss of 3% including the loss of triethanolamine ($\approx 1\%$) around 664 °C. Between 664 °C and 914 °C, the mass loss is approximately 13%. So the overall mass loss corresponding to reaction (1) is about 15%.

To better understand the reaction occurring in the SSR process, the extent of reaction α is introduced in this study, and it can be calculated as^[19]

$$\alpha = \frac{\omega_0 - \omega_t}{\omega_0 - \omega_\infty} \quad (2)$$

where ω_0 is the initial mass, ω_t is the mass at time t , and ω_∞ is the theoretical mass corresponding to reaction (1). The extent

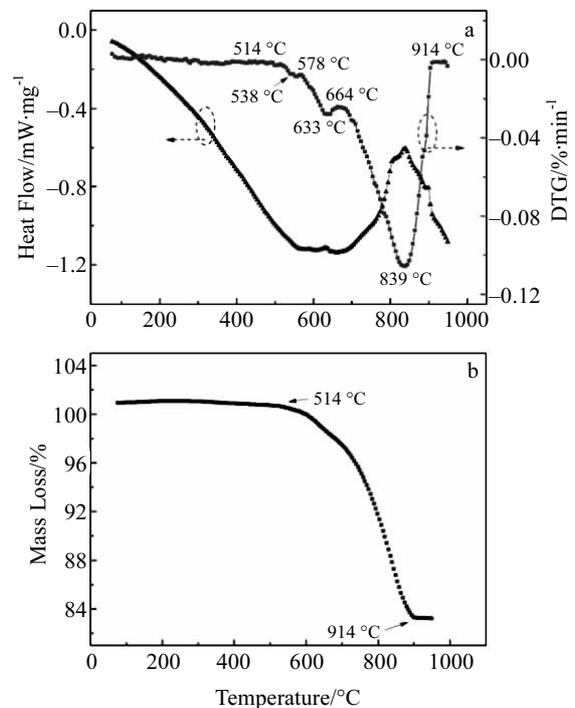


Fig.1 DTG-DSC curves (a) and TG curve (b) of BaCO₃-TiO₂ mixtures

of reaction of BTO at different target temperatures is presented in Fig.2. The second mass loss located at 633 °C is corresponding to the direct chemical reaction between BaCO₃ and TiO₂ at the interface, indicating the beginning of reaction (1)^[16,20]. According to Fig.1a, the reaction of forming BTO is finished at 914 °C, so when the target temperature is 800 and 850 °C, the process of forming BTO still need 90 and 20 min to complete, respectively. It should be noted that the extent of reaction at 850 °C is higher than that at 800 °C, due to a more active mixture at higher temperature.

Fig.3 shows the XRD patterns of BTO powders calcined at different temperatures and for different time (800 °C for 90 min,

850 °C for 20 min and 900 °C for 0 min). According to JCPDS (79-2263) card, cubic BTO phase is the major phase for all samples and no trace of other side products is observed. During the scanning region of $2\theta \sim 45^\circ$, there is no presence of split peaks and it further proves the formation of pure cubic BTO phase.

2.2 Influence of the heating rate on the initial cubic phase

From the above results, it can be noted that the higher temperature can accelerate the formation of BTO. Additionally, it is also interesting to explore the effect of another temperature parameter (heating rate) on the reaction (1). As shown in Fig.4, the reactions with various heating rates all result in pure cubic BTO, indicating that the heating rate is not an effective

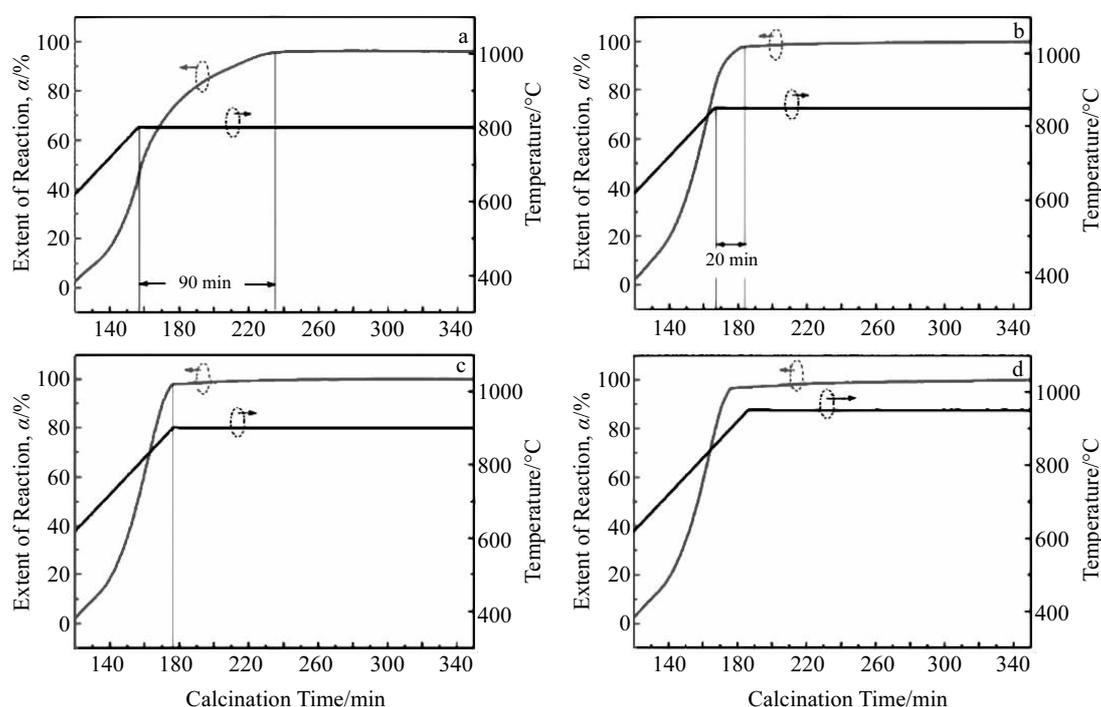


Fig.2 Extent of reaction for BTO formation calcined at 800 °C (a), 850 °C (b), 900 °C (c), and 950 °C (d) with a heating rate of 5 °C/min

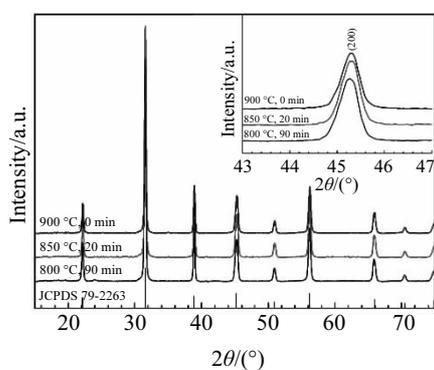


Fig.3 XRD patterns of initial BTO calcined at different temperatures with heating rate of 5 °C/min

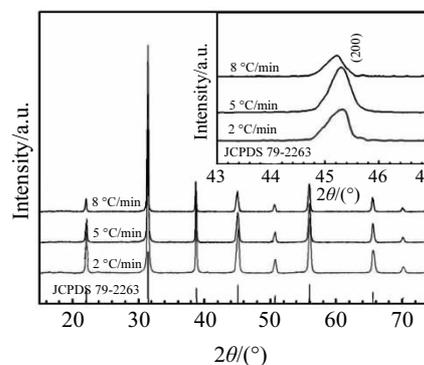
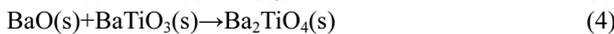


Fig.4 XRD patterns of BTO calcined at 900 °C for 0 min with heating rate of 2, 5 and 8 °C/min

parameter of the final product.

Based on the thermogravimetric and differential thermal analysis of mixtures of BaCO₃ and TiO₂, the formation of BTO with a constant heating rate could be divided into two reaction steps^[21], as shown in Fig.5^[22].

The first step located around 650 °C or even lower temperature (500~600 °C) in some active powders can be attributed to the direct chemical reaction at the interface of BaCO₃ and TiO₂, as shown in Eq. (1)^[23,24]. The second step including several complicated reactions are located at higher temperature (839 °C), and the mass loss of this step is two to three times higher than that of the first step, indicating that the formation of BTO mainly occurs in this step. According to the investigations of Hsiang et al^[25], the reactions occurring in the second step can be separated into three reactions including the decomposition of BaCO₃, the formation of intermediate phase Ba₂TiO₄, and the formation of the pure BaTiO₃ via a complex material transportation, as proposed in Eqs. (3), (4) and (5):



The formation of BaTiO₃ mainly occurs in the temperature interval between 820 and 900 °C. With a different heating rate of 2, 5 and 8 °C/min, the soaking time is 40, 16 and 10 min, respectively. The difference among soaking time is to balance the influence of heating pattern on the formation of BTO. There are a great number of aggregations appearing in BTO powders, as shown in Fig.6, and the characteristics of powder are listed in Table 1, where D_g is the average grain size.

According to Table 1, D_{50} decreases with increasing of heating rate, while D_{50h} (half width of D_{50}) keeps constant, indicating a lower shift of particle distribution or the reduction of particle size. We define a factor A_g to present hard agglomeration of grains, which can be considered as a representative of the agglomeration of particles, calculated as $A_g = D_{50h}/D_g$. The ideal value of A_g is 1, which means one particle only contains one grain. The value of A_g decreases from 3.82 to 2.37 with the increase of heating rate from 2 °C/min to 8 °C/min, which can be ascribed to various time consumptions during the heating process. The reaction of BaCO₃ and TiO₂ occurs mostly in the heating process from 820 °C to 900 °C, but the

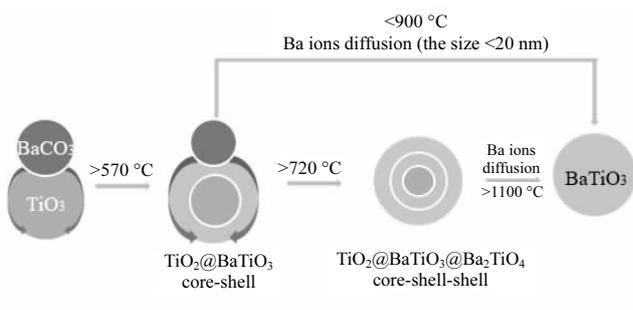


Fig.5 Schematic of the solid-state reaction to synthesize BaTiO₃^[22]

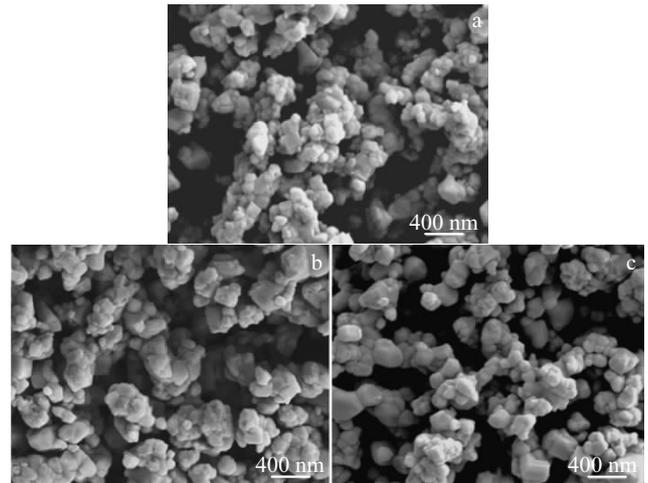


Fig.6 FESEM images of c-BTO powders calcined at 900 °C with heating rate of 2 °C/min (a), 5 °C/min (b), and 8 °C/min (c)

Table 1 Characteristics of c-BTO and t-BTO calcined at 900 °C with different heating rates and holding time

Heating rate/ °C·min ⁻¹	Holding Time/h	D_g / nm	D_{50} / nm	D_{50h} / nm	$A_g =$ D_{50h}/D_g
2	0	140.9	499.5	249.7	3.82
	5	229.0	458.2	244.3	2.00
	10	155.7	382.1	228.5	2.45
5	1	155.8	457.2	252.2	2.93
	3	163.7	377.6	212.5	2.30
8	5	180.7	353.5	216.7	1.96
	0	158.9	377.3	232.5	2.37
	5	203.0	533.6	301.0	2.63

effects of BaCO₃ decomposition on the morphology of sample cannot be neglected. There is enough time to form hard agglomeration among grains at the heating rate of 2 °C/min.

2.3 Transformation from c-BTO to t-BTO

XRD patterns of BTO calcined at 900 °C for 5 h with different heating rates from 2 °C/min to 8 °C/min are presented in Fig.7. The 2θ of 43~47° is chosen. The peak splitting of the (200) plane in this region indicates the existence of tetragonal phase^[26,27]. The BTO calcined at 900 °C for 5 h matches well with the tetragonal phase (JCPDS 76-0744). Structure refinement indicates that the t-BTO calcined at 2, 5 and 8 °C/min exhibits the crystal structure with high tetragonality, in which the relative c to an axis ratio (c/a) is 1.0082, 1.0086 and 1.0084, respectively. Compared with Fig.3 and Fig.4, where only cubic BTO is presented after calcining at 900 °C for 0 h, t-BTO appears when held at 900 °C for 5 h, indicating that the transformation of c-t BTO occurs during the heating process.

In-situ XRD patterns of BTO calcined at 900 °C for 5 h during cooling is presented in Fig.8. The c-t transformation can

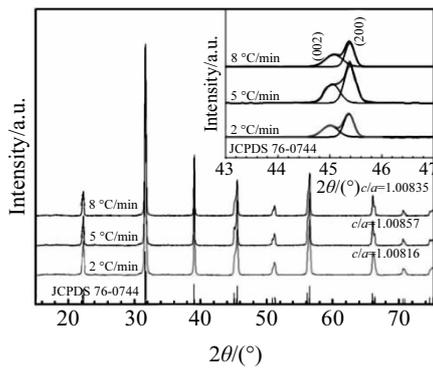


Fig.7 XRD patterns of t-BTO powders calcined at 900 °C for 5 h with heating rate of 2, 5 and 8 °C/min

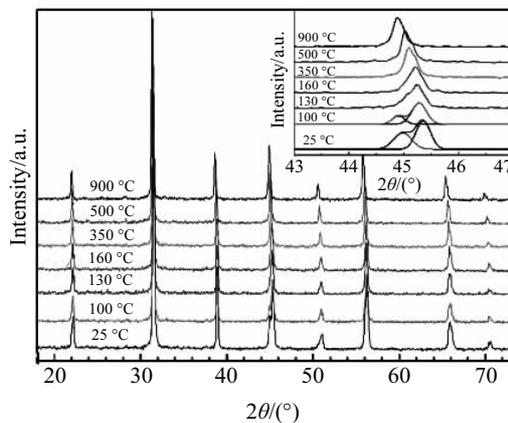


Fig.8 In-situ XRD patterns of BTO powder calcined at 900 °C for 5 h during cooling

be clearly observed from 900 °C to 25 °C. Above 350 °C, only c-BTO is observed. When the temperature decreases to 160 °C, the crystal structure with low tetragonality is observed. As the temperature drops to 25 °C, the split peak in the 2θ of 44°~46° has formed completely, indicating the formation of t-BTO.

Fig.9 presents the FESEM images of BTO calcined at 900 °C for 5 h with different heating rates. The agglomeration of particles is observed. The characteristics of t-BTO calcined at 900 °C for 5 h are listed in Table 1. It suggests that the A_g of t-BTO does not decrease monotonously with the increment of the heating rate. When the heating rate is 5 °C/min, A_g achieves the minimum value and increases as the heating rate further increases.

Fig.10 presents XRD patterns of BTO calcined at 900 °C for 0~5 h with a heating rate of 5 °C/min. From the enlarged view of 43°~47°, the c-t transformation occurs and the tetragonality increases as the dwell time increases. After holding at 900 °C for 3 h, the c/a value increases to 1.0086.

The agglomeration of t-BTO calcined at 900 °C for 1, 5 h

with a heating rate of 5 °C/min can be observed in Fig.11, showing that A_g decreases as the holding time increases. On the other hand, D_g increases from 155 nm to 180 nm. Combining XRD patterns with particle size distribution, 180 nm and less agglomerative BTO powder with high c/a value of

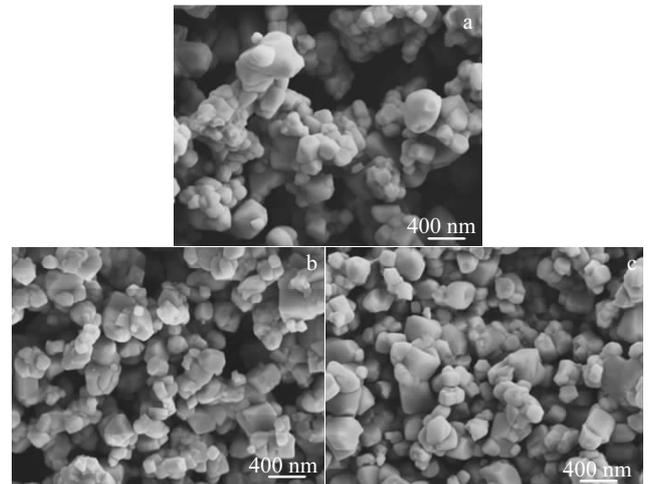


Fig.9 FESEM images of t-BTO powders calcined at 900 °C for 5 h with different heating rates of 2 °C/min (a), 5 °C/min (b) and 8 °C/min (c)

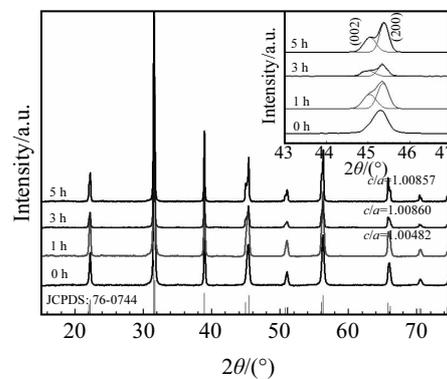


Fig.10 XRD patterns of BTO powders calcined at 900 °C for 0, 1, 3 and 5 h with a heating rate of 5 °C/min

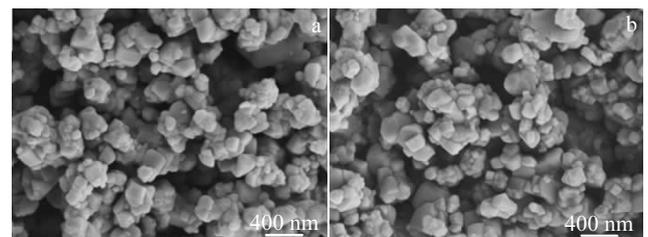


Fig.11 FESEM images of BTO powders calcined at 900 °C with a heating rate of 5 °C/min for 1 h (a) and 5 h (b)

1.0086 can be obtained by calcining at 900 °C for 5 h with a heating rate of 5 °C.

3 Conclusions

1) In SSR of t-BTO powders with calcination temperature higher than 900 °C, the reaction of BaCO₃ and TiO₂ is completed during heating process.

2) The c-BTO is produced at first with a completed reaction and the t-BTO is transformed from c-BTO.

3) The c-t transformation happens during the cooling down process accompanied with an increase of *c/a* value and a growth of grains size.

4) When BTO is calcined at 900 °C with the heating rate of 5 °C/min, the BTO has fine grain (180.7 nm) and a high *c/a* value (1.0086) after heat holding for 5 h.

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固相反应法合成 BaTiO₃ 粉末的相变和微观结构的转变

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摘要: 以国产亚微米级 BaCO₃ 和 TiO₂ 为原料, 采用砂磨固相法合成粒径小、四方性高的 BaTiO₃ 粉体, 同时研究煅烧温度、升温速率及保温时间对 BaTiO₃ 平均粒径和四方性的影响。结果表明, 通过固相反应合成 BaTiO₃ 的反应机理可分为两个阶段: 当煅烧温度低于 900 °C 时, BaCO₃ 和 TiO₂ 首先形成立方相的 BaTiO₃, 当煅烧温度升至 900 °C 时, 立方相 BaTiO₃ 开始向四方相转变。在升温速率为 5 °C/min, 煅烧温度为 900 °C 保温 5 h 时, 制备出粒径为 180.7 nm, 四方性 (*c/a*) 为 1.0086 的超细 BaTiO₃ 粉体。该工作为制备超薄层 MLCC 用高性能 BaTiO₃ 粉体提供了较好的研究思路。

关键词: BaTiO₃; 固态反应; 相变; 微观结构

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