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**Densification and fine grain formation mechanisms of BaTiO₃
ceramics consolidated by self-assembly sintering**

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Abstract: In this paper, from the perspective of thermodynamics and kinetics, we have studied the mechanism of balancing the densification and grain growth via co-sintering the micron and nano powders, also known as self-assembly sintering. In the experiment, the 200 nm and 80 nm BaTiO₃ spherical powders were used as models for combination and co-sintering. In terms of thermodynamics, the contact angle method is applied to determine the free energy of the binary particle size system. The surface free energy of 200 nm and 80 nm BaTiO₃ powders are 51.66 J/mol and 203.47 J/mol, respectively. When the powder ratio is 1:1, the surface free energy of the binary particle size system is 127.56 J/mol, which is the reason for the balance between densification and grain growth. In terms of kinetics, the Arrhenius equation was utilized to calculate the apparent activation energy (Q) of the binary particle size system. The results show that the value of Q is 360 kJ/mol at 1000 °C. The fine-grained ceramics with high relative density obtained by this sintering method at a low sintering temperature (1000 °C) can be explained by the relative low value of Q .

Keywords: contact angle; free energy; apparent activation energy; relative density

1.Introduction

Fine-grained ceramics with high relative density have attracted the attention of researchers due to their excellent mechanical properties, high breakdown field strength, excellent dielectric properties and good energy storage properties [1-5]. Since the densification process and grain growth are contradictory, the preparation of fine grained ceramics with high relative density is still a major challenge [3-5]. Up to now, the fine-grained ceramics with relatively high relative density can be obtained by hot pressing sintering, spark plasma sintering, cold sintering, two-step sintering and electric field sintering [6-10]. However, it is difficult to achieve this goal under normal conditions, that is, using a muffle furnace at atmospheric pressure [11-13]. This problem is closely related to the size of the powders. Using micron powders for sintering, the ceramics with high relative density can not be obtained, because of the high sintering window temperature and which being close to the powder melting point [14]. When nano powders are used for sintering, the sintering window temperature is relative low and whose range is narrow [15]. Nano powders can be used to obtain high relative density ceramics, but the grain growth cannot be avoided, and the coarse-grained ceramics are usually formed [15-17]. Generally, the methods, including the hot pressing sintering, spark plasma sintering, cold sintering, two-step sintering and electric field sintering, usually involve sintering equipment and complex microstructure design (such as core-shell structure design) [6-10]. From the perspective of energy saving and convenience, it is of great significance to develop a sintering method that can be used under normal conditions in order to obtain fine-grained ceramics with high relative density [13-15].

As mentioned above, the size of the powders plays a decisive role in the sintering performance. Studies have shown that using the intrinsic properties of powders, such as morphology, size and so on, through the combination of powders with different sizes then co-sintering, the contradiction between densification and grain growth can be balanced [18-24]. Consequently, the fine-grained ceramics with high relative density can be obtained by sintering under conventional conditions [20-24]. For example, J W Oh et.al [21] used the Fe powders with sizes 3 μm and 100 nm to co-sintering. The ceramics with high relative density of 92.5 % and grain size with 4.1 μm can be obtained. H Y Xu et.al [22] utilized the same way to synthesize the Al_2O_3 dense fine-grained ceramics by 3 μm and 220 nm Al_2O_3 powders, whose relative density is 92.2% and grain size is 250 nm. The researchers found that when combining two sizes of powders, the key point is that the sizes must meet the requirements of the close-packed model, because it can maximize the space utilization [23-27]. X Y Zhai et.al [23] and Q Jin et.al [24] have achieved indium tin oxide (ITO) and BaTiO_3 fine-grained ceramics with high relative density under conventional sintering conditions, respectively. They considered that this method is similar to the self-assembly process of colloidal crystal, and named this way as a self-assembly sintering method [24]. What is more, researchers have pointed out the requirements met by the two sizes of powders and their reasonable ratios by the calculations of close packing model, and gave the general conditions for this method [22-24].

At present, the sintering mechanism of the hot pressing sintering, spark plasma sintering, cold sintering, two-step sintering and electric field sintering have been

studied [6, 9, 27-30]. The previous researches conducted from the perspectives of synthesis methods, phase composition, physical changes, chemical changes and properties [6, 9, 27-30]. However, there is a lack of research on the mechanism of the self-assembly sintering method. In this paper, from the ceramic sintering thermodynamics and kinetics, and the view point of the intrinsic properties of powders, we utilized the 200 nm and 80 nm BaTiO₃ powders as a research model, combining them with a ratio of 1:1 to form a binary system and co-sintering. The contact angle is used to study the sintering force (Gibbs Free Energy, G) of the binary particle size system, and the Arrhenius equation is used to study the apparent activation energy (Q), which can explain how to balance the contradiction between the densification of ceramics and the grain growth. We presented a way to study the mechanism of controlling the synthesis of BaTiO₃ dense and fine-grained ceramics by the binary particle size sintering method at a relative low temperature (1000 °C).

2. Experimental Procedures

2.1 Materials

Raw materials of Ba(Ac)₂ (99% purity), TiCl₄ (99% purity), NaOH (99% purity), CH₃CH₂OH (99.7% purity) and HAc (36% purity) were all analytical-grade chemicals. They were purchased from Tianjin Damao Chemical Industry Co., Ltd.

2.2 Preparation of the BaTiO₃ powders particles

The monodispersed BaTiO₃ powders particles with mean size of 200 nm and 80 nm were prepared respectively, and their Ba/Ti is 1:1, using a co-precipitation approach through adjusting the concentration of the precipitant [24]. The morphology

and phase of the as-prepared BaTiO₃ powders particles can be seen in Fig. S1 and Fig. S2. The BaTiO₃ powders particle size distributions and the calculation values of the specific surface area can be seen in Fig. S3 and Supplementary Information.

2.3 Preparation of the BaTiO₃ ceramics

In a typical synthetic process, the large and the small powders particles with weight of 0.5 g were ultrasonically dispersed in absolute ethanol respectively, labeled as A and B suspension respectively. While mechanically stirring the A suspension, the B suspension was slowly added into it. After stirring for 4 h, the C suspension was obtained. The C suspension was evaporated to dry at 50 °C in an oven for 24 h. Then the particles were pressed into pellets with 6 MPa (~8 mm of diameter and ~1.5 mm of thickness), and sintered at 1000 °C for 2-14 h.

2.4 Characterization Methods

The phase structures of the BaTiO₃ powders and ceramics were checked by X-ray diffraction (XRD; angular step interval: 0.02°, Advance, Bruker, Frankfurt, Germany) at room temperature using CuK α radiation ($K\alpha = 1.5418 \text{ \AA}$) in the 2θ range of 20°-70° with a scan rate of 0.1°/s. The microstructure of the BaTiO₃ powders and ceramics were characterized by scanning electron microscope (SEM, Quanta-600, FEI, USA). The particles size and grain size were determined by measuring the grains from the SEM micrograph through a linear intercept method. The surface area of the BaTiO₃ powders was calculated by the particles size distribution of the BaTiO₃ powders obtained through the Laser Particle Size Analyzer (temperature: 25.0 °C, dispersant: water, absorption: 0.01, refractive index: 1.520, Malvern Instruments Ltd,

England). The grain size distribution was calculated by using the analytical software named Nano Measurer. The densities were measured by the Archimedes method using water as the liquid media, and a theoretical density of 6.02 g/cm^3 was adopted for the BaTiO_3 ceramics. The relative density is the ratio of the measured density to the theoretical density. The dielectric properties of the BaTiO_3 ceramics were evaluated by a LCR tester (Model HP4284A, Hewlett-Packard, USA) at 1 kHz ranging from -60 to 130°C . The water contact angle (WCA) and cetane contact angle (CCA) of the BaTiO_3 powders surface were recorded by video contact angle measurement system (DSA25, KRÜSS, Germany). 2 μL of deionized water and cetane were dripped on the dried BaTiO_3 green body with a syringe. The contact angles were measured by software named Drop Shape Analysis. For emission transmission electron microscopy (TEM) measurements, the ceramics were polished by a fine grade of sandpaper, diamond abrasives and argon-ion beam milling (Precision Ion Polishing System 691, Gatan), respectively.

3. Results and Discussion

3.1 Effect of the powders ratios on the composition and morphology of the BaTiO_3 ceramics

Fig. 1 shows that the ceramics obtained by different ratios of the BaTiO_3 powders are tetragonal perovskite. The XRD peak shifts to high angle, which indicates that the unit cell decreases with the increase of the ratio of 200 nm BaTiO_3 powders, which is related to the decrease of grain size. In addition, the degree of the XRD peak intensity gradually weakened from 44° to 46° . Generally speaking, for the

pure tetragonal phase BaTiO_3 ceramics, the integrated area of the diffraction peak of (200) crystal plane is larger than that of the (002) crystal plane. As the grain size decreases, the difference in the integrated area of the diffraction peaks between the two becomes small, displaying that the content of tetragonal phase decreases gradually. Researches show that the phase transition and cell distortion of the ceramics are affected by composition and grain size [16, 17]. Because the composition of the as-obtained ceramics is BaTiO_3 , the phase change and cell distortion are mainly affected by the grain size [16]. According to the grain size effect, with the grains becoming smaller, the internal stress caused by the grain distortion would be enhanced, and the cell distortion dose not occur easily, leading to the phase transform from the tetragonal to the cubic [9, 16, 17]. Therefore, when the grain size decreases, the tetragonal phase decreases with increasing 200 nm powders. For the further explanation, the grain size changes are discussed in detail below.

Fig. 1 XRD patterns of the BaTiO_3 ceramics obtained by different ratios of the BaTiO_3 powders. The ratio of 0:1 represents the ratio of 200 nm powders to 80 nm powders. Other ratios have the same meanings.

Fig. 2 displays the dielectric properties of ceramics. As the ratio of the 200 nm

powders increases, the relative density decreases continuously, the overall dielectric permittivity decreases due to the reduction of the relative density (Table I). The value of maximum dielectric permittivity (ϵ_{max}) decreases with the grain size decreasing. Furthermore, the relative density decreases as the ratio of the 200 nm powders increases, resulting in an increase in the $\tan\delta$. Due to the grain size effect, the sharpness of the Curie peak of the samples becomes low gradually with the decreasing grain size [16, 17].

Fig. 2 (a) The dielectric permittivity and (b) the dielectric loss of the samples obtained by different ratios of the BaTiO₃ powders.

Fig. 3 shows the morphologies of the BaTiO₃ ceramics obtained by different ratios of the BaTiO₃ powders. With the increase of the ratios of 200 nm BaTiO₃ powders, the large grain size decreases from 2656 nm to 216 nm. What is more, the relative density decreases with the increase of the proportion of 200 nm BaTiO₃ powders. That means the powder ratio has a significant effect on the relative density and grain size of the ceramics (Table I). The results show that the sintering activity of the system changes with the different ratios of the powders, leading to great difference

in grain size and relative density. Due to the influence of space packing effect and surface free energy, increasing the proportion of 200 nm BaTiO₃ powders can reduce the space packing effect and surface free energy, which reduces the sintering force, hinders the grain boundary diffusion and grain boundary migration. Finally, it makes the ceramics difficult to densification and the grains difficult to grow. On the contrary, the addition of 80 nm BaTiO₃ powders can improve the sintering activity and promote the densification and grain growth. However, excessive 80 nm BaTiO₃ powders result in too small curvature and high sintering activity, causing the grain boundary migration and abnormal grain growth. That is not conducive to the preparation of fine-grained ceramics. When the sintering activity of BaTiO₃ powders is balanced, whih the powder ratios being appropriate, the densification process and grain growth are balanced. Consequently, when the ratio is 1:1, the fine-grained BaTiO₃ ceramics with grain size of 252 nm and relative density of 92% can be achieved at relative low temperature 1000 °C. The reasons for adopting this sintering method to obtain fine-grained ceramics with higher relative density are as follows:

(1) The space packing effect: the 80 nm powders can fill in the voids formed by the 200 nm powders to improve the space utilization due to the decrease of Gibbs free energy, thereby increasing the relative density of the ceramics.

(2) The surface free energy: Generally, under the certain sintering conditions, the sintering force is determined by the surface energy of the powders. The 200 nm powders with low surface free energy have low sintering force, and 80 nm powders with high surface free energy correspongding high sintering force. When the ratio of

the two is appropriate, the sintering force of the system can be balanced.

(3) The apparent activation energy: The apparent activation energy determines the sintering temperature. The lower the apparent activation energy is, the lower the sintering temperature is.

As the space packing effect is well known, the surface free energy and the apparent activation energy are discussed in details below.

Fig. 3 SEM micrographs of the BaTiO₃ ceramics obtained by different ratios of the BaTiO₃ powders: (a) 0:1, (b) 1:1, (c) 5:1 and (e) 1:0.

Table I. Summary of parameters of the BaTiO₃ ceramics by different ratios of the BaTiO₃ powders.

Sample	Mean grain size (nm)	Density (g/cm ³)	Relative Density	ϵ_{max}	ϵ_r	$\tan\delta$
0:1	2656	5.659	94%	3332	2685	0.027
1:1	252 (78%)/18 (22%)	5.538	92%	2692	2192	0.049
5:1	242 (83%)/28 (17%)	5.059	84%	2436	1802	0.055
1:0	216	4.515	75%	2078	1422	0.086

3.2 The surface free energy

As mentioned above, the sintering force of ceramics is determined by the surface free energy of BaTiO₃ powders [31, 32]. By measuring the contact angle (CA) at room temperature, the surface free energy of BaTiO₃ powders at room temperature can be determined to qualitatively explain the influence of 80 nm and 200 nm powders on the sintering force. The CA method is often used to measure the contact angle between powder and specific liquid, and then the corresponding surface free energy can be obtained through calculation [33, 34]. The dispersion force (γ_l^d) and the polarity force (γ_l^p) of specific liquid are required to test the contact angle of powders, whose specific data are shown in Table II [33, 34].

Table II. Surface energy components of water and hexadecane

Liquid	γ_l^d (mJ/m ²)	γ_l^p (mJ/m ²)	γ_l (mJ/m ²) *
Water	21.8	51.0	72.8
Cetane	27.3	0	27.3

*The γ_l means the surface free energy of specific liquid.

Fig. 4 demonstrates the WCA and CCA of 80 nm and 200 nm BaTiO₃ powders. The WCA (11.3 ° and 13.5 °) of 80 nm BaTiO₃ powder are large, and the CCA (57.0 ° and 57.6 °) are small, indicating that they has strong hydrophilicity. But the CA of 200 nm BaTiO₃ powders show the opposite results, and whose WCA is larger than that of the CCA, displaying strong hydrophobicity. In general, the hydrophilic powders have high surface free energy. Consequently, from the qualitative point of view, the 80 nm BaTiO₃ powders have larger surface free energy than that of the 200 nm BaTiO₃ powders. Additionally, the penetration time of the water droplets in 80 nm BaTiO₃ powders was short (0.47 s), while it was long (7.02 s) at the 200 nm BaTiO₃ powders.

The penetration time of cetane droplet at the 80 nm BaTiO₃ powders and the 200 nm BaTiO₃ powders are 1.79 s and 2.24 s, respectively. The results of penetration time test show that the 80 nm BaTiO₃ powders have strong hydrophilicity, and the 200 nm BaTiO₃ powders have strong hydrophobicity, which is consistent with the contact angle test results. These also prove the 80 nm BaTiO₃ powders with large surface free energy and the 200 nm ones with relatively small surface free energy. When the two are mixed to form a binary particle size system, the difference of the surface free energy between them is easy to induce self-assembly [35]. According to Owens Wendt equation (1), we can quantitatively determine the surface free energy of the binary particle size system [33].

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s^d \gamma_l^d)^{1/2} - 2(\gamma_s^p \gamma_l^p)^{1/2} \quad (1)$$

Where, the surface free energy of solid-liquid interface is represented by γ_{sl} , the surface free energy of solid and liquid are γ_s and γ_l respectively, γ_s^d and γ_s^p mean the dispersion force and the polarity force of the solid respectively. By combining the equation (1) with the young's equation ($\gamma_s = \gamma_{sl} + \gamma_l \cos\theta$), we can get the equation (2) as follow:

$$\frac{\gamma_l(\cos\theta + 1)}{2(\gamma_l^d)^{1/2}} = (\gamma_s^p)^{1/2} \frac{(\gamma_l^p)^{1/2}}{(\gamma_l^d)^{1/2}} + (\gamma_s^d)^{1/2} \quad (2)$$

Where, θ is the CA, whose schematic diagram is shown in Fig. 5.

Fig. 4 CA images of the 80 nm BaTiO₃ powders: (a) start (water), (b) end (water), (c) start (hexadecane) and (d) end (hexadecane), CA images of the 200 nm BaTiO₃ powders: (e) start (water), (f) end (water), (g) start (hexadecane) and (h) end (hexadecane).

Fig. 5 Schematic diagram of the contact angle.

Fig. 6a shows the CA values of the 80 nm and the 200 nm BaTiO₃ powders. Substituting the CA values and the values of the γ_l^d and γ_l^p in Table II into the equation (2) and then linear fitting, the γ_s values of the 80 nm and the 200 nm BaTiO₃ powders are 70.06 and 44.47 mJ/m², respectively (Fig. 6b). According to the thermodynamics, the total surface free energy (Gibbs free energy, G) of the system is the sintering force. For 1 mol spherical particles with radius R , the following equation is satisfied:

$$N = \frac{3M}{4\pi R^3 \rho} = \frac{3V_m}{4\pi R^3} \quad (3)$$

Where M is the molecular weight of the BaTiO₃ powders, ρ is its density, and V_m is its molar volume. According to the equation (4), the total surface area (S_A) of the BaTiO₃ powders is obtained.

$$S_A = 4\pi R^2 N = \frac{3V_m}{R} \quad (4)$$

When the temperature and pressure are determined, the G satisfies the following equation (5):

$$G = \frac{3\gamma_s V_m}{R} \quad (5)$$

According to equation (5), the G values of the 80 nm and the 200 nm BaTiO₃ powders

are 203.47 J/mol and 51.66 J/mol, respectively. When the powder ratio is 1:1, the G value of the system is 127.56 J/mol. Furthermore, we measured the particle size of the BaTiO₃ powders by the method of a laser particle size analyzer, and found that the specific surface area of the 80 nm and 200 nm BaTiO₃ powders are 10.2802 m²/g and 4.5953 m²/g, respectively (Fig. S3 and Supplementary Information). The G values of the 80 nm and the 200 nm BaTiO₃ powders obtained by the experimental results are 167.81 J/mol and 47.61 J/mol, respectively. The G value of the binary particle size system is 107.71 J/mol (the details in Supplementary Information). The experimental and the calculated results display that the sintering force of the binary particle size system provided by the surface free energy is much higher than that of the 200 nm BaTiO₃ powders only. Compared with the 80 nm BaTiO₃ powders only, the sintering force is relatively small, thus balancing the densification and grain growth.

Fig. 6 (a) comparison of contact angle between the BaTiO₃ powders

and (b) γ_s^d , γ_s^d , γ_s^p and γ_s of the BaTiO₃ powders.

3.3 The apparent activation energy

By studying the surface free energy of BaTiO₃ powders, it can be found that the

G is relatively low, indicating that sintering cannot proceed spontaneously. It needs to be triggered at a certain sintering temperature before sintering can proceed. The sintering temperature is usually determined by the apparent activation energy of the system, so low-temperature sintering can be illustrated by calculating the apparent activation energy. Determining the sintering mechanism is the prerequisite for calculating the apparent activation energy [37]. Generally, the ceramic sintering mechanisms are divided into solid phase sintering and liquid phase sintering. Since the binary particle size self-assembly system does not introduce a liquid phase sintering aid, it may be a solid phase sintering mechanism. To illustrate it, TEM was used to characterize the ceramics obtained at different dwelling times (Fig. 7). With the extension of the dwelling times, the BaTiO_3 particles evolve from quasi-spherical into polyhedral grains with obvious grain boundaries gradually. Simultaneously, the pores gradually decreased until disappeared, indicating that the ceramic densification is enhanced. In addition, the proportion of small size grains gradually decreases, and the proportion of large size grains increases, eventually forming uniform size grains. The results show that the 80 nm BaTiO_3 powders promote the mass transfer process, then trigger the external growth of the 200 nm BaTiO_3 powders, leading to reduce the number of pores and complete the densification. During the whole sintering process, only solid phase powder participated, and no liquid phase was found in TEM characterization. Therefore, it is a typical solid phase sintering, which conforms to the evaporation-condensation mass transfer mechanism. This mass transfer mechanism means that the binary system BaTiO_3 powders have different vapor pressures due to

the different radii of curvature of the surface and neck, which makes the gas phase with a mass transfer trend. Because the small size powders are interstitial in the gap formed by the large size powders, there is a positive radius of curvature on the surface of the large one, and there is a negative radius of curvature (sintering neck) at the junction of the large and small powders. The substance can migrate and condense from the convex surface to the concave surface (sintering neck) by evaporation, so that the sintering neck is gradually filled [20-22, 36]. Additionally, the size of small size grains are quite different from that of large ones, so that the size of large ones grows slowly, thereby balancing the contradiction between densification and grain growth.

Fig. 7 TEM micrographs of the ceramics with the powders ratios of 1:1 sintered

at 1000 °C for 2 h to 14 h: (a, b) 2 h, (c, d) 6 h, (e, f) 10 h and (g, h) 14 h.

The Arrhenius equation is used to calculate the apparent activation energy. For the process of solid phase sintering, the grain growth process follows the following relationship [38]:

$$G^N - G_0^N = tK_0 e^{-\frac{Q}{RT}} \quad (6)$$

Where G is the average grain size of the ceramic, G_0 is the initial grain size, N is the grain growth kinetic index, t is the holding time, K_0 is the constant related to atom migration, and Q is the apparent activation energy, R represents Avogadro's constant, T is the sintering temperature. When the sintering starts, the powders have not yet become grains. It can be considered that $G_0=0$, substituting it into the equation (6), the following equation can be obtained [38]:

$$n \log G = \left(\log K_0 - 0.434 \frac{Q}{RT} \right) + \log t \quad (7)$$

Equation (7) shows that under isothermal conditions, the grain size has a linear relationship with the dwelling time. Substituting the values of grain size into equation (7), $n=3$ can be obtained. Therefore, equation (7) can be rewritten as:

$$\log \left(\frac{G^3}{t} \right) = \log K_0 - \frac{0.434Q}{R} \left(\frac{1}{T} \right) \quad (8)$$

Then substituting the values of grain size into equation (8), the value (360 kJ/mol) of Q can be calculated by linear fitting (Fig. 8). Hotta Y [36] reported that using 150 nm BaTiO₃ powders for traditional sintering, the Q value of the system is 840 kJ/mol. It is more than twice that of the binary particle size self-assembly way. Even if the size of BaTiO₃ powders is refined to 140 nm by ball milling, the Q value calculated by the traditional sintering method is 420 kJ/mol, which is 80 kJ/mol higher than that of the binary particle size self-assembly way. Thus, the fine-grained ceramics with high relative density can be obtained at a lower sintering temperature due to the low apparent activation energy.

Fig. 8 Arrhenius equation linear fitting diagram.

Fig. 9 is a comparison diagram of the synthetic routes of BaTiO₃ ceramics by traditional sintering method and binary particle size self-assembly sintering method. Only using pure 200 nm BaTiO₃ powders for sintering through the traditional sintering method, it is difficult to obtain dense ceramics at 1000 °C due to insufficient sintering force and high apparent activation energy. The binary particle size self-assembly sintering method uses 80 nm BaTiO₃ powders to improve the sintering force and reduce the apparent activation energy, which can balance the contradiction between densification and grain growth. So, fine-grained BaTiO₃ ceramics with relative high relative density can be prepared under low sintering temperature.

Fig. 9 Schematic diagram of the comparison of the two routes.

4. Conclusion

In this work, we take the 200 nm and 80 nm BaTiO₃ powders as the research model for combination and co-sintering. When the powder ratio is 1:1, the fine-grained ceramics (252 nm) with high relative density (92%) can be obtained. The TEM characterization confirmed that the synthesis process satisfies the solid-phase sintering mechanism. The contact angle method is applied to determine that the surface energy of the binary particle size system is 127.56 J/mol, which can play a role in grain boundary diffusion without causing grain boundary migration. The intermediate surface energy is an important reason for balancing the densification and grain growth. The value of the apparent activation energy (Q) with 360 kJ/mol at 1000 °C can be calculated by the Arrhenius equation. The relative low Q is the reason why the ceramics can be sintered at a relative low temperature (1000 °C).

Conflicts of interest

There are no conflicts of interest to declare.

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Figures

Figure 1

XRD patterns of the BaTiO₃ ceramics obtained by different ratios of the BaTiO₃ powders. The ratio of 0:1 represents the ratio of 200 nm powders to 80 nm powders. Other ratios have the same meanings.

Figure 2

(a) The dielectric permittivity and (b) the dielectric loss of the samples obtained by different ratios of the BaTiO₃ powders.

Figure 3

SEM micrographs of the BaTiO₃ ceramics obtained by different ratios of the BaTiO₃ powders: (a) 0:1, (b) 1:1, (c) 5:1 and (e) 1:0.

Figure 4

CA images of the 80 nm BaTiO₃ powders: (a) start (water), (b) end (water), (c) start (hexadecane) and (d) end (hexadecane), CA images of the 200 nm BaTiO₃ powders: (e) start (water), (f) end (water), (g) start (hexadecane) and (h) end (hexadecane).

Figure 5

Schematic diagram of the contact angle.

Figure 6

Please see the Manuscript Doc file for the complete figure caption.

Figure 7

TEM micrographs of the ceramics with the powders ratios of 1:1 sintered at 1000 °C for 2 h to 14 h: (a, b) 2 h, (c, d) 6 h, (e, f) 10 h and (g, h) 14 h.

Figure 8

Arrhenius equation linear fitting diagram.

Figure 9

Schematic diagram of the comparison of the two routes.

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