Glass synthesis and particle size control of BaTiO₃ by designing different calcinations modes

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Different calcinations techniques are adopted to investigate influences of the calcinations modes on the synthesis of BaTiO₃ powders. Two step calcinations (TSC), in which the samples are first heated to a higher temperature (T₁) and then cooled quickly down to a low temperature (T₂) for staying, can retard the grain growth and accelerates the phase transformation effectively. Using BaO, TiO₂ and B₂O₃ oxides as precursors, the spherical BaTiO₃ powders with a particle size of 15–20 nm can be achieved based on TSC technique. A detailed investigation upon the possible particle growth mechanism of TSC is also carried out in this paper. The optimized T₁ can accelerate the phase transition rate while the optimized T₂ can refrain the particle growth depending upon the transition of the particle growth mechanism.

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1. Introduction

BaTiO₃, which has a perovskite-type structure is one of the most widely studied lead-free ferroelectric materials [1,2]. It has far reaching applications in the electronics industry for high-K dielectrics, piezoelectric transducers, PTC thermistors, dynamic RAM, and is mostly used to make multilayer ceramic capacitors (MLCC) [3,4]. The structures and dielectric properties of BaTiO₃ materials are strongly influenced by the particle size [5–8]. Moreover, with the rapid development of electronic device miniaturization, high performance of BaTiO₃ nano-particles is necessary [9]. Traditionally, BaTiO₃ powders are usually prepared by the conventional solid-state reaction, in which an equi-molar mixture of oxides is heating at temperature higher than 1200 °C. In recent years, wet-chemistry synthesis techniques, such as hydrothermal method, sol–gel process, combustion synthesis, microwave heating, and micro-emulsion process, have been applied to synthesize BaTiO₃ nano-crystals. However, these synthesis routes also suffer from various unsettled problems, including inferior crystal structure, poor stoichiometry and non-uniform microstructure and low yields, as well as complex process, or high cost of vessels [10–14]. So it’s still a challenge to synthesize well dispersive BaTiO₃ nano-particles with controlled morphology.

The method of crystallization of a glass is believed to be effective for the preparation of powders, which can avoid the above questions related to the conventional solid-state reaction and produce the powders with desirable characteristics. The merits of the glass crystallization method are that the crystallization occurs at relatively low temperatures and the particle size can be controlled by the choice of heating temperature and time. Although it has been well-known that glass ceramics can be obtained by the glass crystallization method, powders are seldom prepared using this process. Several researchers have successfully applied the glass procedure to synthesize BaTiO₃ powders [15,16]. A few others have investigated BaO–TiO₂–B₂O₃ glasses system with the same purpose [17]. A limitation of these studies is that the particle size of the prepared BaTiO₃ powders is large and usually in micro-scale. For instance the particles synthesized by Kusumoto et al. are about 1–3 µm. This makes the particle size control become highly desirable when the glass method is applied for BaTiO₃ powders synthesis.

When the glass crystallization method is used to fabricate BaTiO₃ powders, B₂O₃ is usually employed as glass forming additive. The mixed precursors, such as B₂O₃/BaO/TiO₂ or B₂O₃/BaCO₃/TiO₂, are usually calcinated at a relatively high temperature firstly and then cooled with a fast cooling rate. So, the calcinations technology should play a critical role in particle size control. However, up to the present time, no one has designed any system of significant particle growth suppression based on various calcinations technology and glass synthesis. So, in the present study, different regimes are envisaged to reveal the role of various calcinations procedure on synthesis and particle control of the BaTiO₃ powders and a detailed investigation on particle control mechanism under glass conditions is reported.
2. Experimental procedure

The BaTiO₃ nano-powders were prepared as follows. All the chemical reagents used in this research were analytical grade. The starting materials BaO, TiO₂ and B₂O₃ were weighed according to the molar ratio to 3B₂O₃/5BaO/2TiO₂, 3B₂O₃/3BaO/2TiO₂ and 2B₂O₃/1BaO/1TiO₂, respectively. The mixtures were homogeneously mixed in anhydrous alcohol medium using ball milling with 4 h. After ball milling, the mixture was dried and then reground using agate mortar. Heat treatment was then carried out in the temperature range of 600–900 °C for different holding time in a muffle furnace. After heat treatment, the powders were first washed using glacial acetic acid to remove the residual B₂O₃, and then washed by absolute ethyl alcohol. The obtained powders were then dried at 80 °C and characterized. To reveal the role of various calcinations technology on synthesis of the powders, the oxide precursors were handled by different ways. (a) Single step calcinations (SSC): the sample was calcinated by a conventional method, in which the calcinations was conducted at temperatures between 700 and 850 °C for 5 h in air with a heating ramp of 10 °C min⁻¹. The schematic diagram illustrating the single step calcinations (SSC) was shown in Fig. 1(a). (b) Modified single step calcinations (MSSC): The calcinations procedure was similar to that of SSC. However, after the desired temperature was achieved, the sample was quickly cooled to room temperature in air with no holding for a time at the desired temperature. The schematic diagram illustrating MSSC was shown in Fig. 1(b). (c) Two step calcinations (TSC): two step calcinations (TSC) consisted of: (1) heating at 10 °C min⁻¹ to T₁, (2) holding for 0 min at T₁, (3) cooling at 50 °C min⁻¹ to T₂, and (4) holding up to different time at T₂. The schematic diagram illustrating TSC was shown in Fig. 1(c).

Phase analysis of as-received powder was conducted by an X-ray diffractometer (XRD, Rigaku D/max-RB). To track the evolution of the particle size, the obtained powders were also characterized by SEM (SEM, JSM-6700F, JEOL, Japan) equipped with an energy dispersive X-ray (EDS) spectrometer for product morphology at an accelerating voltage of 5 kV. After the obtained products were dispersed in ethanol aided by ultrasonic treatment, the TEM image and electron diffraction pattern of the sample were taken by transmission electron microscopy (JEM, 2010) with an accelerating voltage 200 kV.

3. Results and discussions

3.1. Single-step calcinations (SSC)

Fig. 2 exhibits the XRD patterns of the oxide precursors calcinated at 700–850 °C by single step calcinations (SSC). It is easily found that the low content of BaO and B₂O₃ impedes the BaTiO₃ formation from glass. The precipitation of BaTiO₃ crystallites from the glasses is realized in the composition range around 3B₂O₃/5BaO/2TiO₂, which is consistent to the reports by Kusumoto et al. [15]. For 3B₂O₃/5BaO/2TiO₂ sample, Fig. 2 also indicates the calcinations temperature plays an important role on the control of the crystalline phase. Pure BaTiO₃ phase cannot be obtained below 750 °C. On the other hand, depending upon the calcinations temperature, the habit of BaTiO₃ crystals tends to change. The XRD patterns appear cubic for samples prepared at 750 °C but are tetragonal for samples prepared at 800 °C. This implies that pure BaTiO₃ with tetragonal structure can be synthesized by SSC at temperatures higher than 800 °C. Besides, the diffraction peak of TiO₂ also can be observed in the 800 °C sample. This suggests that formation probability of (Ba–B) types of compounds might increase with the increased temperature and further lead to a small amount of titanium dioxide remained in the final product.

3.2. Modified single-step calcinations (MSSC)

Fig. 3 exhibits the XRD patterns of the oxide precursors (3B₂O₃/5BaO/2TiO₂ sample) obtained by modified single step calcinations (MSSC). The detailed calcinations process is presented in Fig. 1(b). T₁ is taken from 650 to 950 °C. T₂ is as low as room temperature. The holding time at T₁ is 0 min. At a lower calcinations temperature, the diffraction peaks of BaB₂O₄ and TiO₂ appear in the patterns besides the peaks of BaTiO₃. The amounts of BaTiO₃ phase increase with temperature increasing. When the temperature is higher than 950 °C, pure BaTiO₃ with tetragonal structure is generated. In comparison with Fig. 2, the structure evolution
process confirmed by XRD patterns suggests that large amounts of BaTiO$_3$ cannot be obtained at temperatures lower than 800°C. The BaTiO$_3$ synthesis temperature of the MSSC is 200°C higher than that of the SSC. This implies both the phase transformation and the particle growth of BaTiO$_3$ under glass conditions depend heavily on both the calcinations time and temperature.

3.3. Two step calcinations (TSC)

XRD patterns of the oxide precursor calcinated by TSC are exhibited in Fig. 4. T1 is chosen as 850 and 800°C, respectively while T2 is chosen as low as 700°C. The previous research on MSSC (Fig. 3) indicates that obvious impurities are left at 850°C although BaTiO$_3$ has been shown to be the dominated phase in the product. However, Fig. 4 suggests the above impurities can be eliminated effectively with the help of staying the sample for a period of tens of hours at a lowered temperature. For example, pure BaTiO$_3$ can be obtained in 2 h when the sample is first heated up to 850°C and then cooled to 700°C. Further decreasing T1 to 800°C, similar results are obtained when the calculations time is prolonged more than 5 h. It seems that TSC, from which the decreased efficiency of phase transformation can be compensated by delaying the holding time at relatively low temperature, can lower the formation temperature of pure BaTiO$_3$ phase in a degree. Moreover, higher T1 could result in a shorter calculations time necessary for obtaining pure BaTiO$_3$ phase.

Fig. 5 shows the scanning electron microscopy micrographs recorded for BaTiO$_3$ particles prepared under various conditions. Obvious duplex microstructure can be seen in the MSSC sample (Fig. 5(b)) in spite of no staying at high temperature. This trend becomes more obvious in the SSC sample (Fig. 5(a)). Large number of very small particles are less than 100 nm in size while the relatively large particles size, which are regular squares in shape, are in range of 500–1000 nm. In comparison with Fig. 5(a) and (b), no obvious large particles except the aggregated spherical nanoparticles, which are in the scale of about 10 nm, are found in Fig. 5(c). This implies TSC can restrain the abnormal particle growth effectively.

In order to investigate the influence of temperature T2 upon the phase transformation, T1 is still kept as 850°C while T2 is lowered to 600 and 650°C, respectively. At the same time the holding time at T2 is arranged from 5 to 25 h. XRD patterns of the corresponding samples are presented in Fig. 6(a) and (b). It is easily found from Fig. 6 that the diffraction peaks intensities of impurities weaken and BaTiO$_3$ phase contents increase with the holding time increasing. When the holding time is increased beyond 20 h, pure BaTiO$_3$ phase is obtained in all samples. The comparison between Figs. 6 and 4 indicates efficiency of TSC can also benefit from the temperature of the second calcinations step (T2). Higher T2 can shorten the calculations time necessary for obtaining pure phase effectively while lower T2 tends to lengthen the time for pure phase.

The results of EDS result and TEM observations on the products prepared by TSC are given in Fig. 7. Peaks of the elements are detected in the EDS pattern. EDS characterization shows that the body of the nano-wire is exclusively composed of Ba, Ti and O with the ratio of Ba to Ti approximately equal to 1:1, conforming to the chemical formula of BaTiO$_3$. For further clarity, the simultaneous measurements of both Ti and Ba in the as-prepared samples by ICP-AES (Leeman Labs Inc. Profile, American) are also explored and the result is shown in Table 1. The calibration solutions used in this study are prepared by dissolving 0.5 mg products in 5 ml HCl for 2 h. Table 1 indicates the ICP results are consistent to the EDS measurement. Fig. 7(b) and (c) shows the TEM image of the sample, which shows obvious agglomerates of very fine crystals. From electron diffraction image shown in the inset of Fig. 7(b), both alternatively bright and dark rings and diffraction spots are observed. The alternatively bright and dark diffraction rings are originated from the long range ordered structure of the grain crystals. Further observations, the area corresponding to point A shown in Fig. 7(b) is enlarged and the enlarged TEM image and the corresponding selected area electron diff-
fraction result are given in Fig. 7(c), which indicate the spherical single crystal particles are well dispersed with an average size of 20–30 nm, which was agreed with the results of XRD calculation.

Based on the above observations, we know that pure BaTiO$_3$ phase cannot be obtained at 850 °C in MSSC (Fig. 4) and 700 °C in SSC (Fig. 2). However, under TSC conditions, pure BaTiO$_3$ phase can be obtained within 10 h with $T_1$ and $T_2$ chosen as 800 and 700 °C, respectively. With $T_1$ increase to 850 °C, the corresponding holding time at $T_2$ is shortened to be only 2 h. This indicates TSC has an advantage over MSSC and SSC when BaTiO$_3$ powders are synthesized from glass. TSC can lower the synthesis temperature of BaTiO$_3$ effectively under equivalent conditions. In order to improve phase transformation fraction, the calcinations temperature ($T_2$) needs lowering to an extent that no interruption to the phase transformation occurs.

### 3.4. Investigations on TSC

For quantifying the ratio of the BaTiO$_3$ phase, the following equation is used:

\[
\text{ratio} \left( \% \right) = \frac{\sum I_{\text{BaTiO}_3}(hkl)}{\sum I_{(hkl)}}
\]

Here $I_{\text{BaTiO}_3}(hkl)$ are the intensities of the diffraction peaks of BaTiO$_3$ while $I_{(hkl)}$ are the intensities of all the displayed diffraction peaks, respectively [18,19]. Fig. 8 shows the variation in BaTiO$_3$ phase content with synthesis temperature. Note that the phase transformation of TSC starts above 600 °C and is completed at about 700 °C while no remarkable changes in the phase transformation of MSSC occur. The phase transformation fraction of MSSC reaches only 40% at 850 °C. In comparison with MSSC, the change of the phase transformation fraction of SSC with the calcinations temperatures at an almost constant rate up to about 99% at 850 °C demonstrates that the phase change depends on the holding time besides the calcinations temperature.

To find how effectively the calcinations time would enhance phase transformation, Fig. 9 (a) displays the relations between the holding time and phase transformation. For comparison, the phase transformation data for both TSC and SSC after the similar holding time are presented. For all the samples the fraction of phase transformation accelerates with increased holding time. For TSC, the displayed data shown in Fig. 9 (a) indicates that the phase transformation is temperature dependent and the fraction of phase transformation keeps an almost linear increase with the prolonged time when the temperature $T_2$ is equal to 700 °C. For completing the total phase transformation, the necessary holding
time at T2 for 850–700 °C sample is about 5 h while that for 850–650 °C sample should be increased up to 25 h. The relative low phase transformation data is observed in SSC. The isothermal phase transformation fractions with the holding time ranging from 0 to 25 h are given in Fig. 9 (a). The general feature of SSC is the phase transformation fraction increases rapidly at short annealing time and then continues to grow at a very low rate. This trend is very similar to the results reported by other researchers [20]. The very fast phase transition in the first 5 or 10 h implies a process with low activation energy dominates in this stage. At longer annealing time, the phase transformation fraction exhibits a leveling-off trend and approaches a limiting data. This indicates contributions of the holding time upon the phase transformation are limited under SSC conditions.

Under different conditions, such as TSC, and SSC, contributions of the holding time to the phase transformation can be described as below:

\[ D = \alpha_2 - \alpha_1 \]  

Here, \( \alpha_2 \) denotes the maximum phase transformation fraction obtained at 25 h (or 5 h for 850–700 °C sample of TSC) shown in Fig. 9 (a) while \( \alpha_1 \) denotes the corresponding phase transformation fraction of MSSC shown in Fig. 8. Fig. 9 (b) displays the \( D \) values obtained under various conditions. It is easily found that the \( D \) values of TSC are much larger that of SSC, which indicates T1 in TSC is very important to the full phase transformation. In comparison with SSC, TSC can improve the phase transformation more effectively.

Dependence of the average particle size on the calcinations temperatures under different calcinations conditions is shown in Fig. 10. The average particle size (\( D \)) of BaTiO\(_3\) powders was
determined from both the XRD patterns according to the Scherrer equation and SEM observations. Line 1, 2 and 3 correspond to the lowest temperature for obtaining BaTiO$_3$ phase versus various calcinations techniques. Most obviously, the calcinations temperature $T_1$ play a vital role in particle size evolution of BaTiO$_3$ powders during TSC operations. In comparison with SSC, TSC with $T_1$ equal to 850°C can restrain the abnormal particle growth significantly.

The plots of $\ln D$ versus $1/T$ are shown in Fig. 11. A straight line is plotted according to the Scott equation given below under the condition of homogeneous growth of the particles, which approximately describes the growth rate of the particles during calcinations:

$$D = C \exp \left( \frac{E}{RT} \right)$$  \hspace{1cm} (3)

where $D$ is the crystal size, $C$ a constant (=177.67), $E$ the activation energy for the particle growth, $R$ the ideal gas constant and $T$ the absolute temperature. There exists a linear relationship between $\ln D$ and $1/T$. Accordingly, $E$ value could be derived from the slope of the straight line. It can be seen that the growth of BaTiO$_3$ particles depends heavily on $T_1$. There are two distinct regions for TSC with $T_1$ equal to 850°C while no big difference in activation energy is found for the rest lines. This implies the growth mechanism of TSC with $T_1$ equal to 850°C might undergo a possible transition when the temperature $T_2$ is increased higher than 650 °C, which indicates a possible transition of the particle growth mechanism [21]. The particle growth is mainly controlled by diffusion mechanism when the temperature $T_2$ is lower than 650 °C while an interfacial reaction controlled mechanism becomes dominated when the temperature $T_2$ is higher than 650 °C. So, the size increment of the particles at low temperature is dependent on the diffusion while at high temperature an interfacial reaction controlled mechanism would result in the particle growth and morphologies transition. When the temperature $T_1$ is increased up to higher than 900°C, only a single growth mechanism, interfacial reaction controlled mechanism, is able to work. So no turning point is observed. This suggests both $T_2$ and $T_1$ in TSC should be controlled as low as possible in order to obtain fine BaTiO$_3$ powders.

4. Conclusions

BaTiO$_3$ powders had been prepared successfully by TSC route using BaO, TiO$_2$ and B$_2$O$_3$ as precursors. TSC is proved to be a novel technique used to suppress the abnormal particle growth that usually occurs due to the longer annealing time or higher calcinations temperature. The essential part of this technique is
high-temperature heating ($T_1$) followed by structural freezing via rapid cooling to a constant temperature ($T_2$) levels off the particle growth but does not stop the phase transformation. In order to make sure the efficiency of TSC, the residual phase-transformation fraction from the first calcinations step should be completed by maintaining the sample at the low temperature for enough time. Moreover, fine microstructure only can be obtained by controlling both the first and second temperature ($T_1$ and $T_2$) as low as possible. Compared with SSC method, TSC cannot only retard the grain growth, but also enhance the phase transformation more effectively. The well-defined spherical BaTiO$_3$ nano-particles with a particle size of 15–20 nm were successfully synthesized by TSC method.

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