

XRD studies on phase formation and the crystallite structure of BaTiO₃ synthesized by HBM: the effect of calcination temperature

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Barium titanate (BaTiO₃, or BT) powders were synthesized via a solid state reaction of BaCO₃-TiO₂ by combining a high-energy ball milling (HBM) technique and a calcination method. Using X-ray diffraction (XRD) methods with a Rietveld refinement, the effects of calcination temperature on the phase formation and crystallite structure of BT powders were studied. It is found that by means of HBM the synthesis temperature for obtaining BT single phase is decreased to 960 °C, which is much lower than that required by the conventional solid-state reaction process, and the crystallite structure of BT is in the (pseudo)cubic form. As the calcination temperature is increased to 980 °C, the structure of BT crystallites transforms from the (pseudo)cubic to the tetragonal form. With an increase in the calcination temperature, both the tetragonality (*c/a*-1) and crystallite size are increased.

Key words: Barium titanate, Crystallite structure, XRD, Rietveld refinement, High-energy ball milling.

Introduction

Barium titanate (BaTiO₃ or BT) is one of classical ferroelectric ceramics, which has been widely utilized in the electronics industry. The initial BT powder has always been studied widely because of its importance for producing ceramics with fine-grained and dense microstructures [1-5]. Conventionally, BT powders were synthesized by a solid-state reaction of BaCO₃-TiO₂ at temperatures higher than 1200 °C [1]. However, with this method the size of BT obtained was too large to prepare ceramics with excellent physical properties. In order to obtain BT powders with a nanometre size, various methods have been utilized, such as hydrothermal [2], electrospinning [3], sol-gel [4], a solid-state reaction in water vapour atmosphere [5], etc. High-energy ball milling (HBM) is a simple and efficient method for making various nanocrystalline powders [6]. Kong and co-workers have shown that with the HBM technique, single-phase ceramic powders can be produced by calcining the milled mixture at a temperature much lower than that required in the conventional solid-state reaction process [7]. The calcination temperature is a very important factor for the development of the solid state reaction of raw powders. The optimum calcination temperature for obtaining single phase BT is different for the different parameters of synthesis [8-11]. Also, the influence of the calcination temperature on the structure of BT crystallites varies with a change of the synthesis methods [12-13]. So,

it is necessary to investigate the effects of the calcination temperature on the phase formation and crystallite structure of BT for the specified synthesis technique.

The Rietveld refinement method uses the least-squares approach to refine a theoretical line profile until it matches the measured profile of an X-ray diffraction curve [14]. In order to judge the quality of the final structural refinement, reliability index parameters are used. The weighted profile residual factor (*R_{wp}*), the expected residual factor (*R_{exp}*), and the goodness of fit (*Sig*) are defined respectively as:

$$R_{wp} = \sqrt{\frac{\sum w_i(I_{io} - I_{ic})^2}{\sum w_i I_{io}^2}} \quad (1)$$

$$R_{exp} = \sqrt{\frac{N - P}{\sum w_i I_{io}^2}} \quad (2)$$

$$Sig = R_{wp}/R_{exp} \quad (3)$$

where *I_{io}* is the experimental intensity; *I_{ic}* is the calculated intensity; *w_i* = 1/*I_{io}*; *N* and *P* are the number of data points and the number of fitting parameters, respectively. By repeated refining, an *R_{wp}* with a value of less than 15% and a *Sig* with a value between 1.1~1.3 confirm the goodness of refinement. By using X-ray Rietveld refinement, the information about microstructural parameters, and crystallite structure parameters can be obtained.

In this study, BT powders were prepared from a mixture of BaCO₃ and TiO₂ by combining HBM and a calcination method. By using XRD with the Rietveld refinement, the effects of the calcination temperature on the phase formation and crystallite structure of BT powders were studied in detail.

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Materials and Experimental Methods

Raw materials of BaCO₃ (purity >99%) and TiO₂ (purity >99%) powders were dried at 100 °C for 24 h to eliminate moisture and then weighed according to their stoichiometric composition. The milling operation was carried out in a Fritsch Vario-Planetary high-energy ball milling system in air. Raw materials with a total mass of 20 g were put in a tungsten carbide vial with a volume of 250 ml and milled for 1 h. The mass ratio of balls and raw materials was about 12 : 1. The rotation speed of the disk was 300 rpm and that of the vials was 450 rpm. The milled powders were subsequently calcined for 2 h at temperatures between 700–1300 °C.

The crystallite structure was investigated by X-ray diffraction (XRD, Rigaku D/Max 2550) using CuK_α ($\lambda = 0.154056$ nm). Data were collected in the 2θ range of 20–80° with a scanning step of 0.02°. Receiving soler slits (0.3 mm), scattering slit (1 degree) and variable divergence slits were used. The Rietveld refinement was completed by utilizing the program of MAUD (Materials Analysis Using Diffraction), which combines the Rietveld method and a Fourier transform analysis [15]. It should be noted that the Cagliotti parameters, instrumental asymmetry and Gaussianity parameters for the instrument have been corrected using a standard sample of CeO₂. The unit cell parameters and average crystallite size of BT powders were refined.

Results and Discussions

Fig. 1 shows the XRD pattern of the as-milled powders. It is noticed that the diffraction peaks are all attributed to BaCO₃ and TiO₂, indicating that no reaction had yet been triggered during the milling process. The BaCO₃ and TiO₂ phases are consistent with JCPDS No. 71-2394 and 71-1166 [16], respectively.

In order to investigate the phase evolution of the milled powders with increasing calcination temperature, the powders

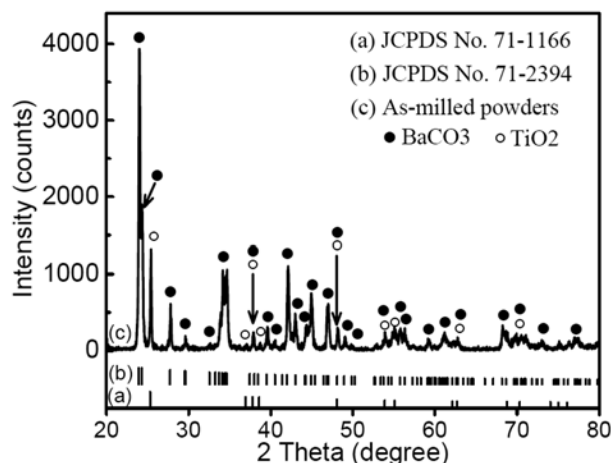


Fig. 1. XRD pattern of the as-milled powders and JCPDS numbers of 71-2394 and 71-1166.

prepared from the HBM technique were calcined for 2 h in air at various temperatures from 700 °C to 1300 °C. Fig. 2(a) shows the XRD peaks of the powders by heat treatment between 700 °C and 960 °C. When the milled powders were calcined at 700 °C for 2 h, the BT phase already appeared, accompanied by unreacted BaCO₃ and TiO₂. The BT phase could be matched with JCPDS No. 79-2263 [16]. With an increase in the calcination temperature to 800 °C, the intensity of the BT peaks was further enhanced, and that of the BaCO₃ and TiO₂ phases were further decreased. Moreover, an intermediate phase with a composition of Ba₂TiO₄ (JCPDS No. 35-0813 [16]) is detected. According to the earlier studies of Ref. [1], the Ba₂TiO₄ phase was formed as follows:



For the powders calcined at 900 °C, the phases in the mixture are similar to that for the powders calcined at 800 °C. On increasing to 940 °C, the diffraction peaks can be almost all attributed to the BT phase with some weak peaks for the Ba₂TiO₄ phase. For the powders annealed at 960 °C, only peaks belonging to the BT single phase were detected and the starting materials and inter-

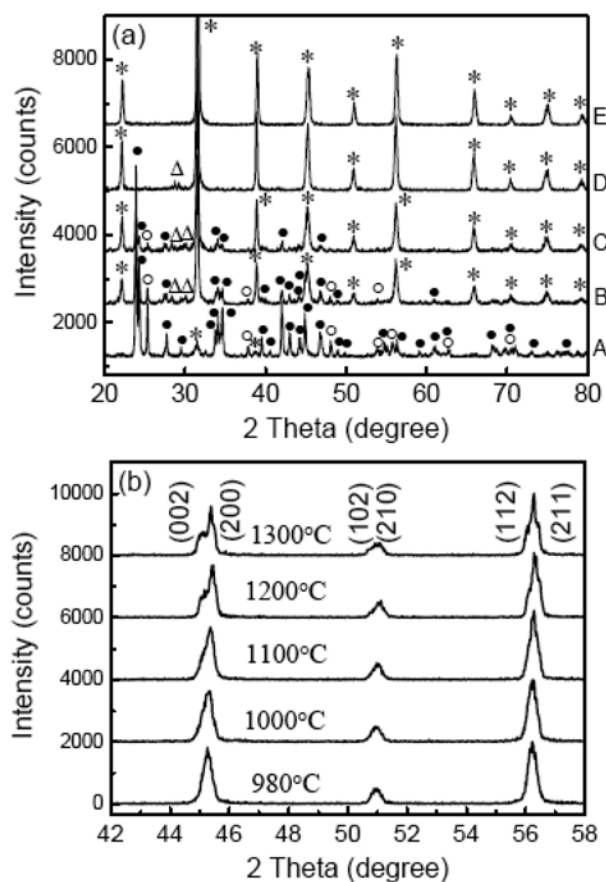
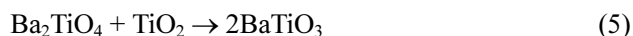


Fig. 2. (a) XRD patterns of the milled powders calcined at temperatures of 700 °C (A), 800 °C (B), 900 °C (C), 940 °C (D), 960 °C (E) for 2 h [•BaCO₃, o TiO₂, * BaTiO₃, Δ Ba₂TiO₄]; (b) XRD patterns of the milled powders calcined at temperatures from 980 °C to 1300 °C for 2 h.

mediate phase disappeared completely. The disappearance of Ba₂TiO₄ could be attributed to the reaction described as follows [1]:



Using the conventional solid-state reaction of BaCO₃-TiO₂, the temperature for synthesizing the BT single phase was higher than 1200 °C [1]. Here, the temperature (960 °C) at which the BT single phase was obtained is significantly lower than that required by the conventional solid-state reaction process. The low formation temperature for BT is believed to be beneficial from the refined powders as a result of HBM [7]. As the calcination temperature was increased from 980 °C to 1300 °C, only the BT phase appeared in the XRD pattern. It is noticed that the diffraction peaks at $2\theta = 45.5^\circ$, 51.0° , 56.3° are widened gradually and finally split with an increase in the calcination temperature (Fig. 2(b)), which implies that the tetragonal structure of the BT phase is formed well at the higher calcination temperature.

In order to investigate the evolution of the crystallite structure of the BT phase calcined at different temperatures, the Rietveld refinement of the full XRD pattern including all reflections from $2\theta = 20^\circ$ to 80° was carried out for the powders calcined at 960, 980, 1000, 1100, 1200, and 1300 °C. The background was described by a 5-order polynomial function. An anisotropic peak-broadening model was selected as Popa LB, and the size-strain model used Popa rules. A 8-order harmonic correction was used for the preferred orientation in order to obtain smaller values of R_{wp} . After repeated refinement, the R_{wp} values for all the samples are all less than 15%. A typical result of Rietveld refinement is shown in Fig. 3. It can be seen that the calculated XRD profile agrees well with the experimental data across the whole range of measured angles.

The lattice parameters calculated by Rietveld refinement from the diffraction data as a function of temperature are shown in Fig. 4(a). It is found that the BT phase for

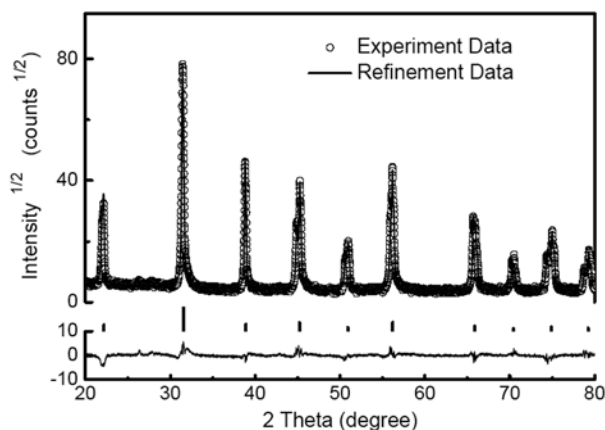


Fig. 3. Typical results of the Rietveld refinement of the XRD pattern for BT powder calcined at 1300 °C for 2 h. Vertical bars show the positions of the Bragg reflections for BT. The observed-calculated difference pattern is depicted at the bottom of figure.

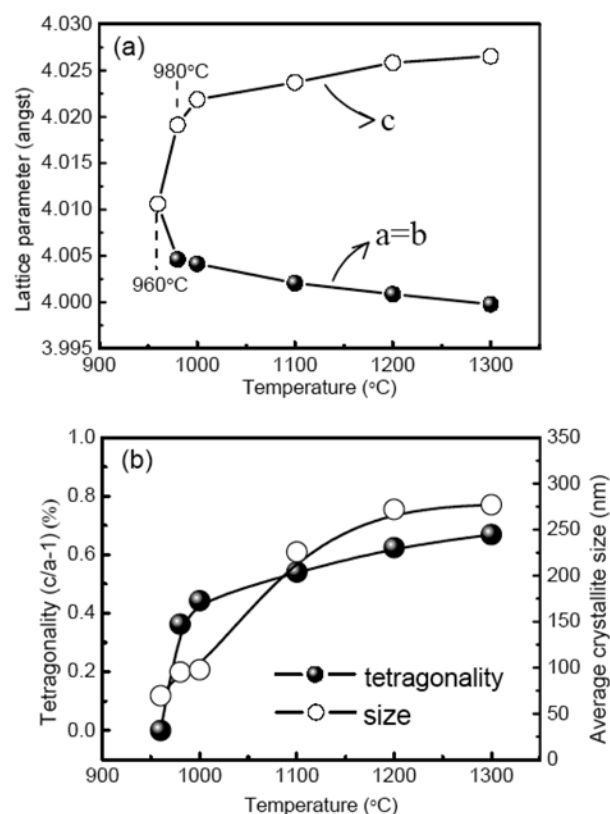


Fig. 4. Change in lattice parameters (a), tetragonality and average crystallite size (b) as a function of calcination temperature.

the powders calcined at 960 °C could be indexed according to a (pseudo)cubic structure with space group Pm-3m, consistent with JCPDS file number 79-2263 [16]. The result of the Rietveld refinement gave the lattice parameters of the BT phase as $a = b = c = 401.061$ pm. When the calcination temperature was increased to 980 °C, the a and b were decreased to 400.461 pm and c was changed to 401.915 pm. This implies that the crystallite structure of BT evolves as tetragonal phase. With an increase in the temperature, the lattice parameters $a = b$ are decreased, and the parameter c is increased.

Fig. 4(b) shows the tetragonality ($c/a-1$) and average crystallite size as a function of calcination temperature. Because of the decrease of a and the increase of c , the tetragonality is increased with an increase in the calcination temperature. It can also be found that the average crystallite size is increased with an increase in the calcination temperature. The variation of the tetragonality of BT powders as a function of calcination temperature is the same as that of the crystallite size with an increase in the calcination temperature. This means that the tetragonality of the synthesised BT powders by the HBM technique is closely related to the average crystallite size. A similar result has also been reported for BT powders obtained by a sol-gel method [17]. Further work is needed to explore the precise mechanism responsible for the relation between the crystallite structure and size.

Conclusions

In conclusion, the effects of calcination temperature on phase formation and crystallite structure of BT powders were studied using the X-ray Rietveld method. For the BT powders synthesized with the HBM technique, the temperature to obtain a BT single phase is decreased to 960 °C, which is significantly lower than that required by the conventional solid-state reaction process. With an increase in the calcination temperature, the structure of BT crystallites transforms from the (pseudo)cubic to the tetragonal form, and the tetragonality ($c/a-1$) and crystallite size are increased.

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