

Preparation and property of BaTi₂O₅ ceramics by arc-melting and spark plasma sintering

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Abstract In the present study, a new procedure, arc-melting followed by spark plasma sintering, was employed to prepare BaTi₂O₅ ceramics with high relative density and large dimension. Single-phased BaTi₂O₅ powders were synthesized from BaCO₃ and TiO₂ powders by arc-melting, and then the BaTi₂O₅ powders were densified by spark plasma sintering at different temperatures (1273–1473 K) and pressures (20–50 MPa). Single-phased BaTi₂O₅ ceramic was obtained at and below 1423 K, however, it tended to decompose at elevated temperatures. Considering the upper-bound decomposing temperature, we further enhanced the densification of BaTi₂O₅ ceramics by increasing the sintering pressure, and a high relative density of 92.1 % was achieved at 50 MPa. The permittivity of the BaTi₂O₅ ceramics was 28.7 at 1 MHz, and increased with the measuring temperature, reaching a maximum value of 191 at the Curie temperature of ~740 K.

Keywords BaTi₂O₅ ceramics · Arc-melting · Spark plasma sintering · Dielectric property

1 Introduction

Ferroelectric materials in perovskite structure, for instance, BaTiO₃ (BT), PbTiO₃ (PT) and PbZr_{1-x}Ti_xO₃ (PZT) etc., have been extensively studied for their high dielectric constant, good piezoelectric and ferroelectric properties [1–5]. However, these materials have drawbacks such as low Curie

temperature for BT ($T_c \approx 403$ K) or environmentally-unfriendly element like Pb in PT and PZT. The development of new lead-free ferroelectric materials is thus required from the viewpoint of the protection of environment and the availability at higher working temperatures.

Barium dititanate (BaTi₂O₅), an environmentally-friendly ferroelectric material [6, 7], began to attract much attention recently due to the significant dielectricity and ferroelectricity with a relatively higher Curie temperature ($T_c \approx 750$ K), which is supposed to be a promising ferroelectric material available at high working temperatures. Unfortunately, BaTi₂O₅ was reported to be easily decomposed into BaTiO₃ and Ba₆Ti₁₇O₄₀ [8–10], and difficult to synthesize by the conventional solid-state reaction. Although the processes of sol-gel [11, 12], hydrothermal reaction [13], containerless processing [14], rapid cooling [15, 16], floating zone [17, 18], arc-melting [19] have been developed to prepare single-phased BaTi₂O₅ in forms of micro-powders, nano-belts, glass spheres, needle-like or rod-like crystals, both the densification and dimension of those products are not satisfied. For the purpose of practical and wider applications, dense and large-scaled BaTi₂O₅ ceramics should be produced, especially as the target materials for further preparing BaTi₂O₅ films by physical vapour deposition. Up to now, few studies on BaTi₂O₅ ceramics with large dimension and high densification have been reported. Beltran et al. [20] prepared single-phased BaTi₂O₅ ceramics by pressureless sintering the sol-gel-derived powders below 1200°C, which showed a low relative density caused by pores. Polycrystalline BaTi₂O₅ bulks were obtained by Tu et al. [19] via hot-press sintering, but small cracks were observed. Li et al. [21, 22] and Xu et al. [23, 24] prepared BaTi₂O₅ bulks with B₂O₃, ZrO₂, KF additives, and the relative density can be increased to a certain extent. However, the electrical or electromechanical properties of the products, including

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bulks and films prepared from the bulks, would be degraded by the non-ferroelectric dopants. Single-phased BaTi_2O_5 ceramics with a high relative density of $\sim 95\%$ without any additives have been prepared by Akishige et al. [25] using the sol–gel-derived nanopowders. However, sol–gel method may be not suitable for mass-production due to the complicated processes required for chemical reaction. In the present study, a new procedure, arc-melting followed by spark plasma sintering, was then employed to prepare single-phased BaTi_2O_5 ceramics with high relative density and large dimension. The influences of preparation process on the phase, density and microstructure of the BaTi_2O_5 ceramics were elaborately investigated, and the dielectric property was also introduced.

2 Experimental procedure

The experimental process for preparing BaTi_2O_5 ceramics is outlined in Fig. 1. Micropowders of BaCO_3 (99 % in purity and $\sim 1\ \mu\text{m}$ in diameter) and TiO_2 (98 % in purity and $\sim 2\ \mu\text{m}$ in diameter with rutile phase) were used as the starting materials, whose morphology are shown in Fig. 2(a) and (b), respectively. The reagents were weighed in a molar ratio of 1:2 ($\text{BaCO}_3:\text{TiO}_2$) and ball-milled for 12 h with absolute ethanol to mix them thoroughly. The mixture was dried at 353 K for 10 h and pressed into discs of 10 mm in diameter. The discs were melted in an electric arc furnace (Diavac ACM-S01) filled with Ar of 2.5 kPa, and then the button-like pellets were obtained after arc-melting successively for four times at the output power of 3000 W. The pellets were further ground into powders (Fig. 2(c)), put into a graphite

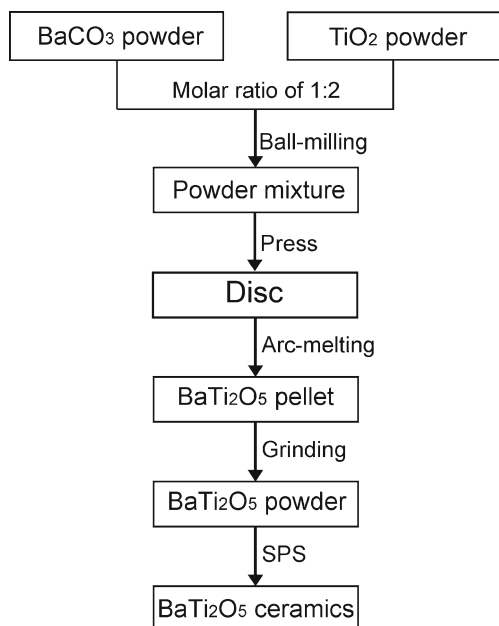


Fig. 1 Flow chart for the preparation of BaTi_2O_5 ceramics

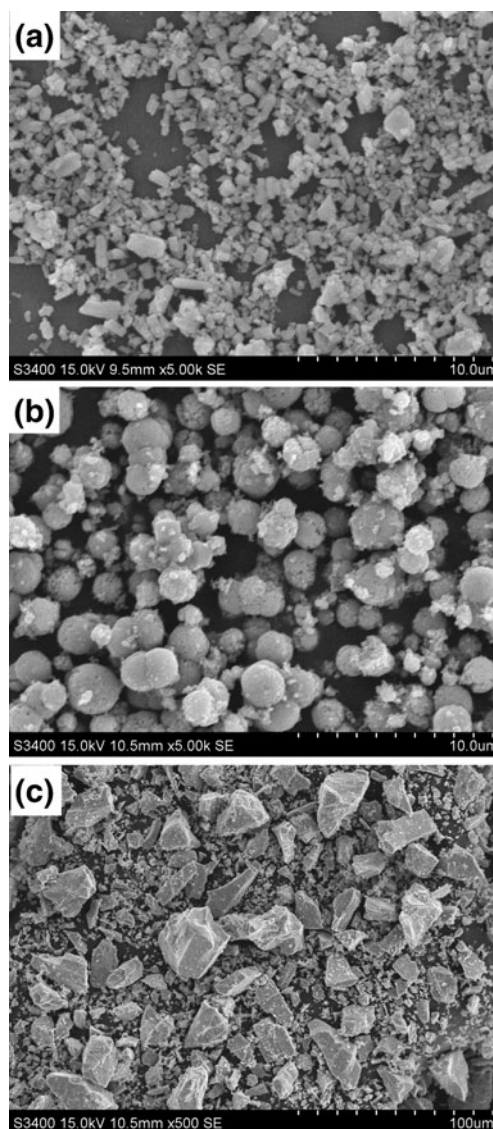


Fig. 2 SEM images of (a) BaCO_3 powders, (b) TiO_2 powders and (c) arc-melted powders

die and then sintered in vacuum by spark plasma sintering (SPS, Sumitomo SPS-1050) with a heating rate of 100 K/min. The sintering temperature was changed from 1273 to 1473 K, and the holding time was kept at 10 min. During the sintering process, an axial load ranging from 20 to 50 MPa was applied to the mould, respectively, until the specimens were cooled down to room temperature. Finally, BaTi_2O_5 ceramics of 20 mm in diameter and ~ 4 mm in height were obtained after annealing in air for 12 h.

The crystal structure of the samples was identified by X-ray diffractometer (XRD, Rigaku Ultima III) with $\text{Cu K}\alpha$ radiation. Scanning electron microscopy (SEM, Hitachi S-3400) was used to examine the microstructure, and the density of the samples was determined according to the Archimedes' principle. The room-temperature permittivity

and dielectric loss were measured in air with an impedance analyzer (HP 4194) over a frequency range between 100 Hz and 1 MHz. The dielectric property as a function of temperature (300–823 K) were measured using an LCR meter (HP 4284A).

3 Results and discussion

Figure 3(a) and (c) show the XRD patterns of the raw powder mixture and arc-melted powders, respectively. The standard pattern of BaTi_2O_5 (JCPDS 34–0133) is also presented for comparison as shown in Fig. 3(b). The diffraction peaks corresponding to BaCO_3 and TiO_2 can not be observed in the XRD patterns of the arc-melted powders, and both the peak position and relative intensity are well consistent with those of JCPDS 34–0133, indicating that BaCO_3 and TiO_2 have reacted completely to form BaTi_2O_5 . This proves that arc-melting is an effective technique for the synthesis of BaTi_2O_5 powders, although single-phased BaTi_2O_5 is usually hard to obtain [8–10].

As mentioned in literatures [26], BaTi_2O_5 is in-fact a metastable phase, which may form as the first product from the reaction between BaCO_3 and TiO_2 . But it can only exist stably in a narrow temperature range between 1493 K and 1503 K [26], and will be easily decomposed into BaTiO_3 and $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ if cooled down slowly to room-temperature. As a result, single-phased BaTi_2O_5 is difficult to obtain by the conventional solid-state reaction due to the fairly low cooling rate. On the contrary, arc-melting is a non-equilibrium synthesis technique, which can preserve BaTi_2O_5 phase in the synthesized state by the extremely high-speed cooling. Therefore, the decomposition of BaTi_2O_5 will be effectively restrained when cooled from the arc-melted temperature and as a result single-phased BaTi_2O_5 powders can be obtained.

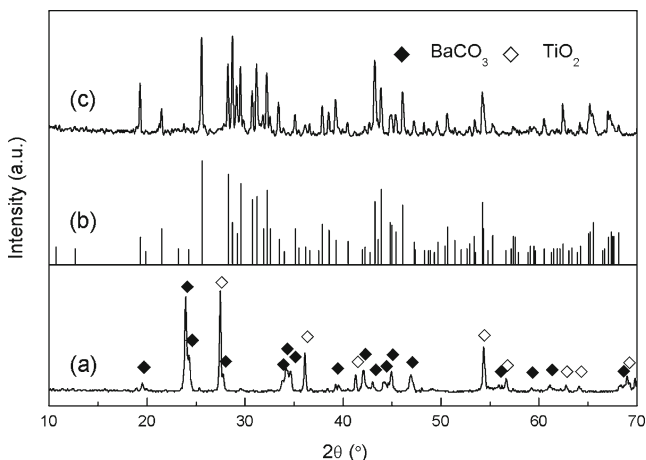


Fig. 3 XRD patterns of (a) raw powder mixture, (b) JCPDS 34–0133 and (c) arc-melted powders

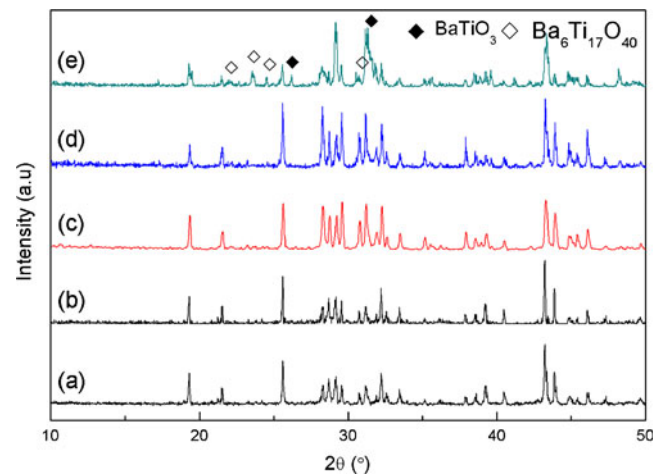


Fig. 4 XRD patterns of the BaTi_2O_5 ceramics sintered at (a) 1273 K, (b) 1323 K, (c) 1373 K, (d) 1423 K and (e) 1473 K

Further calculating from the slow XRD scanning (with steps of $2\theta=0.02^\circ$ at 6 s per step), the lattice parameters of the arc-melted BaTi_2O_5 powder are obtained. They are $a=1.69119$ nm, $b=0.39314$ nm, $c=0.94147$ nm and $\beta=103.075^\circ$, which is in accord with those reported in the literatures [17].

The arc-melted BaTi_2O_5 powders with single-phase were then densified by spark plasma sintering (SPS) at temperatures of 1273–1473 K, respectively, under the pressure of 20 MPa for 10 min. The crystalline phase of the as-sintered samples is shown in Fig. 4 as a function of sintering temperature. All the samples sintered at and below 1423 K show similar XRD patterns to the arc-melted powders, and the patterns are well consistent with the standard pattern of BaTi_2O_5 . With the increasing of sintering temperature, the diffraction peaks grow sharper and higher, indicating better crystallization at the elevated temperatures. Further increasing the sintering temperature to 1473 K, BaTiO_3 and

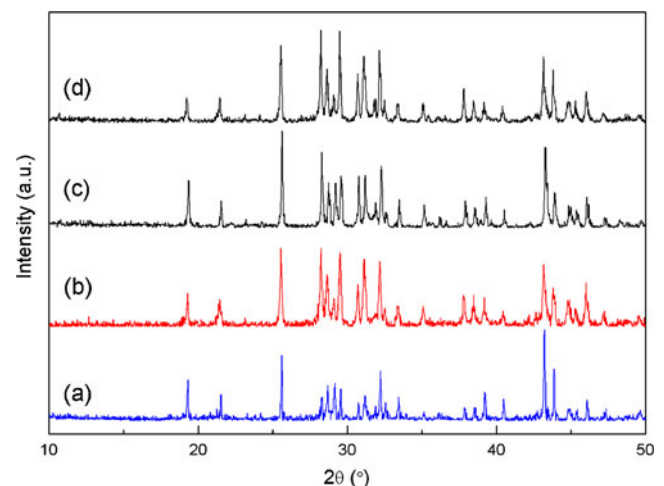


Fig. 5 XRD patterns of the BaTi_2O_5 ceramics sintered at (a) 20 MPa, (b) 30 MPa, (c) 40 MPa and (d) 50 MPa

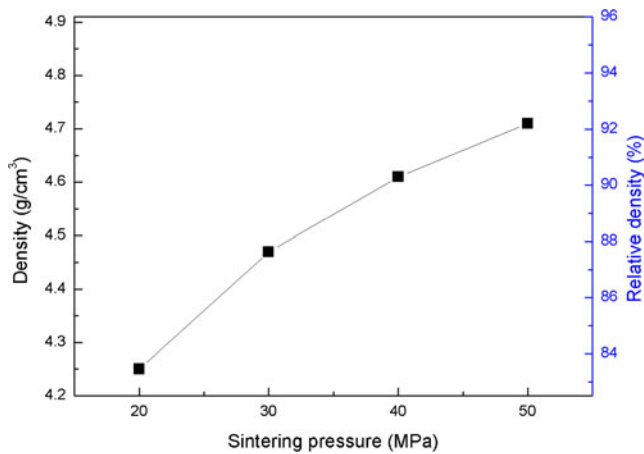


Fig. 6 Pressure dependence of density and relative density of BaTi₂O₅ ceramics prepared by SPS at 1423 K

Ba₆Ti₁₇O₄₀ impurity phases begin to be discerned besides the main BaTi₂O₅ phase (Fig. 4(e)) caused by the decomposition of BaTi₂O₅ [8–10]. Therefore, the spark plasma sintering temperature should not exceed 1423 K in order to obtain single-phased BaTi₂O₅ ceramics.

Regarding of the upperbound decomposing temperature of BaTi₂O₅ ceramics (1423 K), the arc-melted powders were further consolidated at elevated sintering pressures. The XRD patterns of the BaTi₂O₅ ceramics obtained by SPS at 1423 K under the pressures of 20–50 MPa are shown in Fig. 5. Only the characteristic diffraction peaks of BaTi₂O₅ can be observed, indicating that all the samples are in single-phase and the sintering pressure has no prominent influence on crystal phase. The density and relative density of the BaTi₂O₅ ceramics as a function of sintering pressure are illustrated in Fig. 6. We can see that the density of the ceramics increases with sintering pressure, so does the relative density. The sintering pressure can effectively enhance

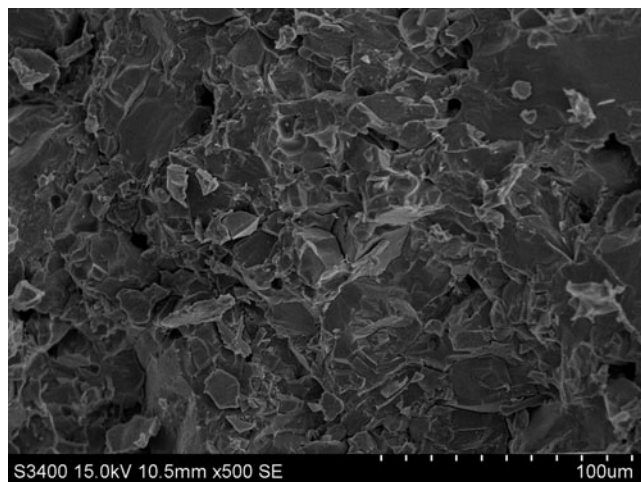


Fig. 7 SEM image of the BaTi₂O₅ ceramic prepared by SPS at 1423 K-50 MPa

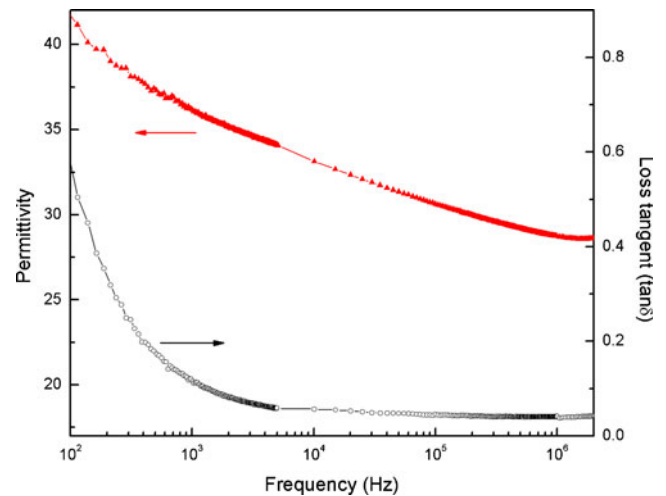


Fig. 8 Permittivity and dielectric loss of the BaTi₂O₅ ceramic prepared by SPS at 1423 K-50 MPa

the densification of BaTi₂O₅ ceramics, since the pressure exerted on the powders is beneficial to the contact and diffusion between particles. At 20 MPa, the relative density is relatively lower (83.5 %), but it increases remarkably when the sintering pressure is elevated. The density reaches 4.71 g/cm³ at 50 MPa, corresponding to high densification (relative density 92.1 %). A higher relative density could be predicted if the sintering pressure is further elevated, but under the bearing capacity of the graphite die. As compared with the BaTi₂O₅ ceramics prepared by SPS from the sol-gel-derived nanopowders [25], the value of relative density in our work is a little lower, probably due to the bigger particle size and wider size distribution in the arc-melted powders. Smaller particle size means larger specific surface and more surface energy, which will enhance the densification of BaTi₂O₅ ceramics.

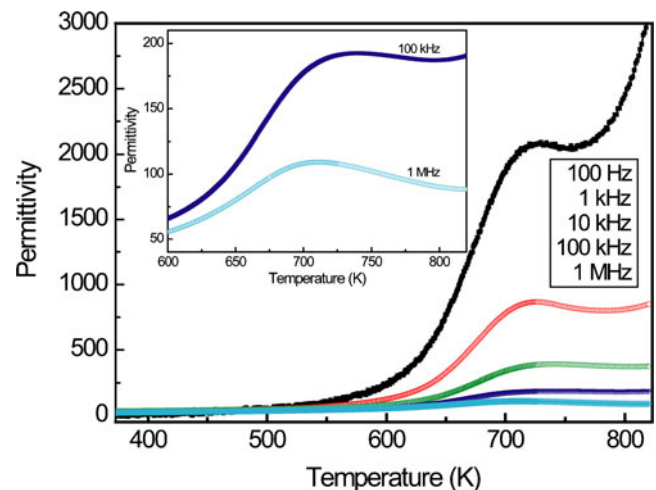


Fig. 9 Temperature dependence of permittivity of the BaTi₂O₅ ceramic prepared by SPS at 1423 K-50 MPa

Figure 7 shows the SEM image of fracture surface of the BaTi₂O₅ ceramic sintered at 1423 K and 50 MPa with a relative density of 92.1 %. The sample exhibits a nearly dense texture with a few tiny pores, and the grains grow completely and connect tightly with each other. As compared with other sintering processes such as hot-press or pressureless sintering, spark plasma sintering is a non-conventional powder consolidation method, which is characteristic of the extremely high heating speed (100 K/min) and short sintering time (10 min). As a result, the grain growth will be effectively restrained, which makes the densification of BaTi₂O₅ ceramics easier and a high relative density can thus be obtained.

Figure 8 depicts the frequency dependence of dielectric properties at room temperature of the BaTi₂O₅ ceramic, which was prepared by SPS at 1423 K and 50 MPa. Since the permittivity and dielectric loss will change rapidly at a low frequency range due to the resistivity component or leakage loss [19], the true dielectric properties should be evaluated at higher frequencies. At 1 MHz, the permittivity and dielectric loss of the BaTi₂O₅ ceramic are 28.7 and 0.041, respectively.

The dielectric properties of the BaTi₂O₅ ceramics were also measured as a function of temperature from 300 to 823 K in a frequency range of 100 kHz~1 MHz, which are shown in Fig. 9. The permittivity increases with the measuring temperature and reaches a maximum value of 191 at ~740 K and 100 kHz, indicating a high Curie temperature (T_C) of 740 K. BaTi₂O₅ ceramic can be regarded as a composite material consisting of air and grains, and the permittivity will be degraded by the air [23]. As a result, the value of the measured permittivity here is higher than that of polycrystalline BaTi₂O₅ ceramics (ϵ' =130) prepared by pressureless sintering [20] with a high porosity.

On the other hand, as indicated in the literatures [15–17, 20], T_C of BaTi₂O₅ varies with the fabrication conditions. For example, BaTi₂O₅ crystals prepared in air shows a higher Curie temperature of 752 K; By contrast, the crystals prepared in a reducing atmosphere show a diffuse phase transition near T_C =703 K due to the oxygen vacancies [15]. The existence of those mobile oxygen vacancies appears to induce a decreased T_C and broaden the phase transition, as observed in PLZT [27]. In the present study, BaTi₂O₅ ceramics were prepared by SPS in vacuum followed by annealing in air. The crystal defects such as oxide vacancies would form during this process and remain in the samples even if they were subjected to oxidization. Therefore, the as-prepared BaTi₂O₅ ceramics have a medium Curie temperature (T_C =740 K).

4 Conclusions

BaTi₂O₅ powders with single phase were synthesized from BaCO₃ and TiO₂ powders by arc-melting, and then consolidated by spark plasma sintering at optimum temperature and

pressure to prepare BaTi₂O₅ ceramic with high relative density and large dimension. Single-phased BaTi₂O₅ ceramics can be obtained at and below 1423 K, but it tends to decompose at elevated temperatures. The sintering pressure has no prominent influence on the crystalline phase, whereas it effectively enhances the densification process. At 1423 K and 50 MPa, BaTi₂O₅ ceramics with a large dimension of 20 mm and a high relative density of 92.1 % can be obtained, whose permittivity and dielectric loss are 28.7 and 0.041 at 1 MHz, respectively. The permittivity increases with the measuring temperature, and reaches a maximum value of 191 at the Curie temperature of ~740 K.

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