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Sintering of nanocrystalline $BaTiO_3$

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Abstract

Two-step sintering method was employed to consolidate nano-size $BaTiO_3$ powders. The two-step sintering method comprises the initial heating at relatively higher temperatures and the following low-temperature sintering for a long period of heating. Pressed green bodies of $BaTiO_3$ were first heated to 1300 °C to achieve an intermediate density (>75% of theoretical density), then cooled down and held at 1100 °C for 0–20 h until they became fairly dense. Slight grain growth progressed during the second step, whereas the density significantly increased. The average grain size of dense ceramics was around 1 μm. The dielectric constant of $BaTiO_3$ was much greater than that of the normal sintering method. Furthermore, Dy-doped $BaTiO_3$ showed much smaller grain sizes than the undoped $BaTiO_3$, which is comparable with the conventional sintering behavior of $BaTiO_3$.

Keywords: A. Sintering; D. $BaTiO_3$; Nano-powder

1. Introduction

$BaTiO_3$ is a well known ferroelectric material with high permittivity (>1000), and one of the most widely used ceramic materials in the electric industry, especially in multilayer ceramic capacitors (MLCC). $BaTiO_3$ ceramic has been extensively studied due to its high dielectric constants with the high insulating resistivity [1]. Electrical properties of $BaTiO_3$ strongly depend on microstructures as well as chemical compositions. Kinoshita and Yamaji [2] reported that the relative permittivity can be increased up to 5000, if polycrystalline $BaTiO_3$ of 1.1 μm grain size is achieved. Thus, a fine grain is essential to achieve optimum dielectric properties.

The microstructure of $BaTiO_3$ can be controlled by two approaches. One way uses additives to prohibit the grain growth. Some additives have been reported to effectively prevent discontinuous grain growth [3–5]. It is well known that additives such as Dy, Nb and Ca act as a grain growth inhibitor. Another way uses novel processing techniques to tailor the microstructure. In general, it is known difficult to prepare dense $BaTiO_3$ ceramics with fine grains via a conventional sintering process. Nano-size particles, due to the tendency to form agglomerates, can lead to microstructures with defects that cannot be eliminated during sintering [6]. Therefore, techniques such as pressure assisted sintering, or compacting of the powders at enormous pressures of up to 8 GPa at elevated temperatures or at ambient temperatures followed by sintering in common furnaces are employed [7,8].

Recently, a two-step sintering method has been proposed to achieve the densification of ceramic bodies without significant grain growth by Chen and Wang [9]. To succeed in two-step sintering, they suggested that a sufficiently high starting density should be obtained during the first step. When the density is greater than 70%, pores in Y_2O_3 become subcritical and unstable against shrinkage, which is induced by capillary action. These pores can be filled as long as grain-boundary diffusion allows it, even if the particle network is frozen as it is clearly in the second step [10,11].

In this study, effects of two-step sintering on the microstructure development of nano-size $BaTiO_3$ powders will be discussed as well as the dielectric properties. Furthermore, effects of Dy-doping on microstructure structure will be investigated as well.

2. Experimental procedure

Nano-sized $BaTiO_3$ powders were prepared using the liquid mix method developed by Pechini [12]. Dy-doped

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sample compositions as well as undoped $BaTiO_3$ were prepared by calcinations of an organometallic solution containing precisely determined amounts of the metallic components as described in the previous work [13]. Solutions were calcined in air at 600 °C for 30 min. The calcined powders were pressed into rectangular bars at 300 MPa. In normal sintering process, the specimens were then sintered at 1200 °C for 1–5 h. In the so-called two-step sintering process, the heating schedule comprises two stages, the fairly high-temperature initial heating and the followed lower temperature sintering. The pressed green body of $BaTiO_3$ was first heated to 1300 °C to achieve an intermediate density and then cooled down and held to sinter at 1100 °C for 0–20 h until it became fairly dense. The effect of two-step sintering process on the microstructure development was investigated for the as-fired surface of the sintered body using a scanning electron microscope (Hitachi S2150). Particle sizes were determined from the microstructure of a field emission scanning electron microscope (Jeol LTD JSM890) and X-ray diffraction analysis (Rigaku Rotaflex D/MAX System). The dielectric constant was measured over the temperature range from −55 to 145 °C using a capacitance measurement system (Sanders & Associates).

3. Results and discussion

Fig. 1 shows the morphology of the calcined $BaTiO_3$ powders at 600 °C for 30 min. The primary particles were of round shape with a uniform size about 17 nm and were heavily agglomerated. This result is similar to the particle size calculated from the half-width of the XRD peaks of (1 1 0) planes using Scherrer's equation [14], which supports that the estimated particle sizes are in good agreement with the observation through the FE-SEM photographs. Thus, thermal decomposition of polymerized solution

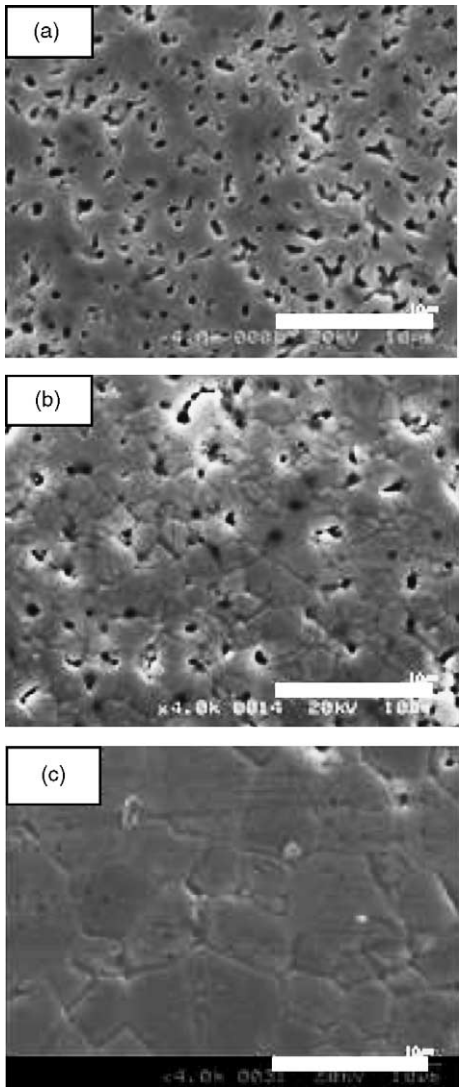

Fig. 2. The microstructure of $BaTiO_3$ sintered at 1200 °C for various sintering times: (a) 1 h, (b) 3 h and (c) 5 h.

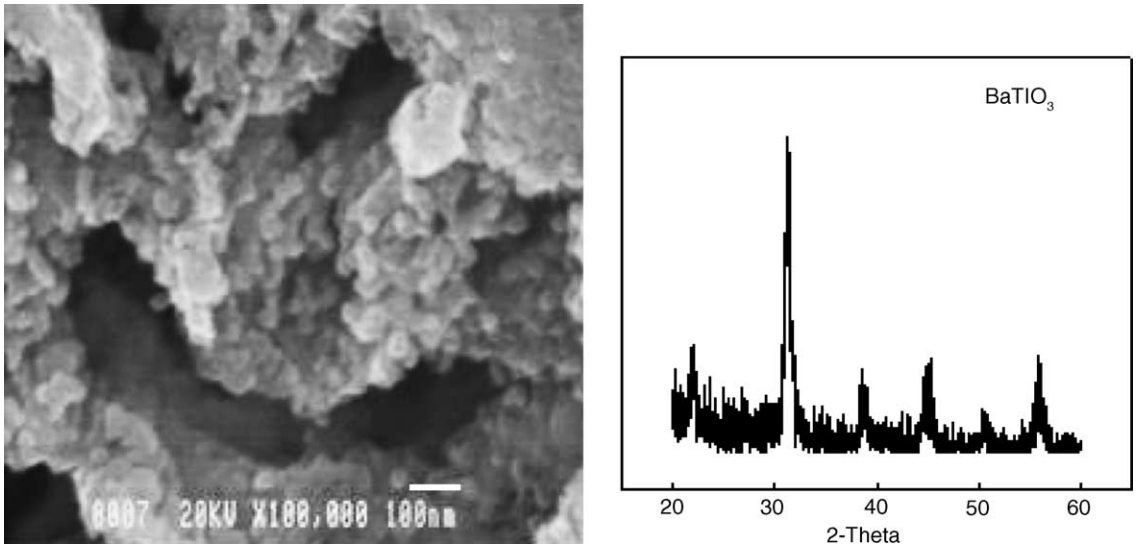

Fig. 1. FE-SEM micrographs and XRD patterns of $BaTiO_3$ powder.

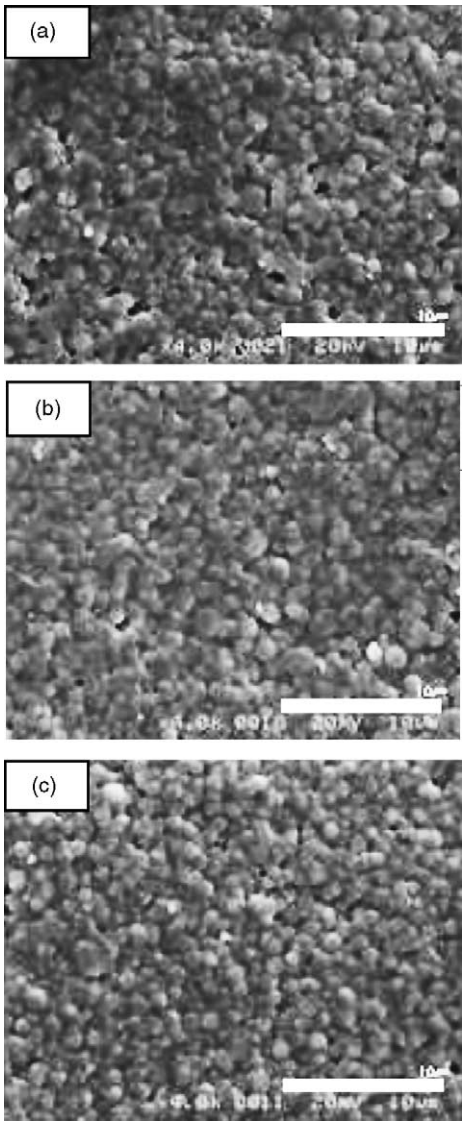

Fig. 3. The microstructure of $BaTiO_3$ which was first heated to 1300 °C and held at 1100 °C for various times: (a) 0 h, (b) 5 h and (c) 20 h.

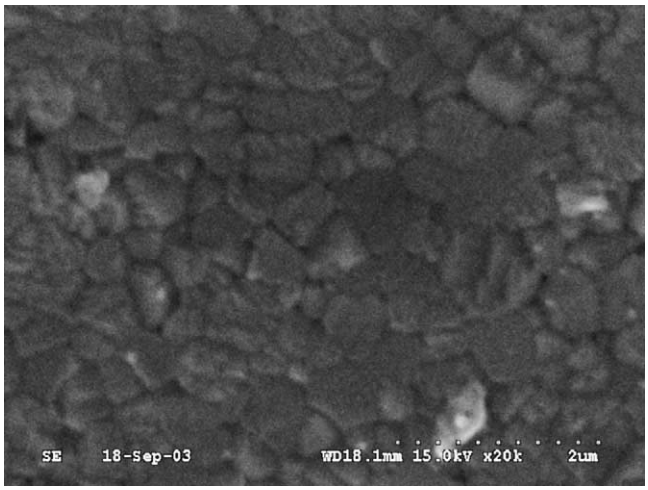

Fig. 5. The microstructure of $BaTiO_3$ doped with 1 mol% Dy (first heated to 1300 °C, and then held at 1100 °C for 20 h).

prepared by Pechini method can be an applicable experimental technique to prepare nano-size $BaTiO_3$ powders.

Fig. 2 shows the SEM photographs of the $BaTiO_3$ samples sintered at 1200 °C for various sintering times, 1, 3 and 5 h, respectively. Significant densification and grain growth progressed as the sintering time increased. The specimen sintered for 5 h exhibited the average grain sizes about 5–6 μm, where the bulk density was 5.6 g/cm^3 (>93% of the theoretical density). However, the sintered specimen for 1 h showed smaller grain sizes with poor sintering densities (83% of the theoretical density). This result represents the normal densification process of ceramic bodies, indicating that there is no densification without grain growth. It was reported that the driving forces for densification and grain growth are comparable in magnitude, both being proportional to the reciprocal grain size in this final-stage sintering [15,16]. Thus, this has greatly hampered efforts to produce dense materials with nano-size grain structure.

Fig. 3a–c show the microstructure development of $BaTiO_3$ specimen prepared by the two-step sintering, which was

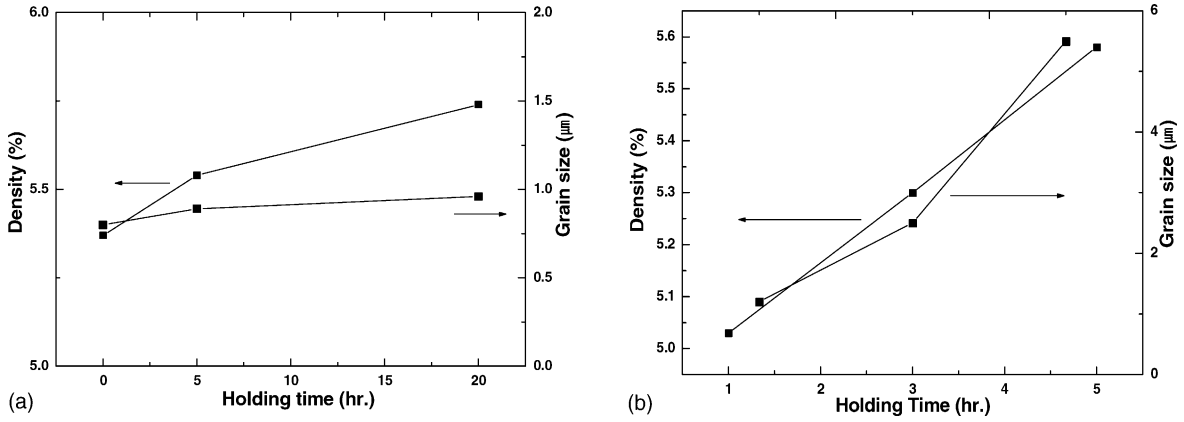

Fig. 4. The sintered density of $BaTiO_3$ compacts and grain size as a function of holding time: (a) two-step sintering process, (b) normal sintering process.

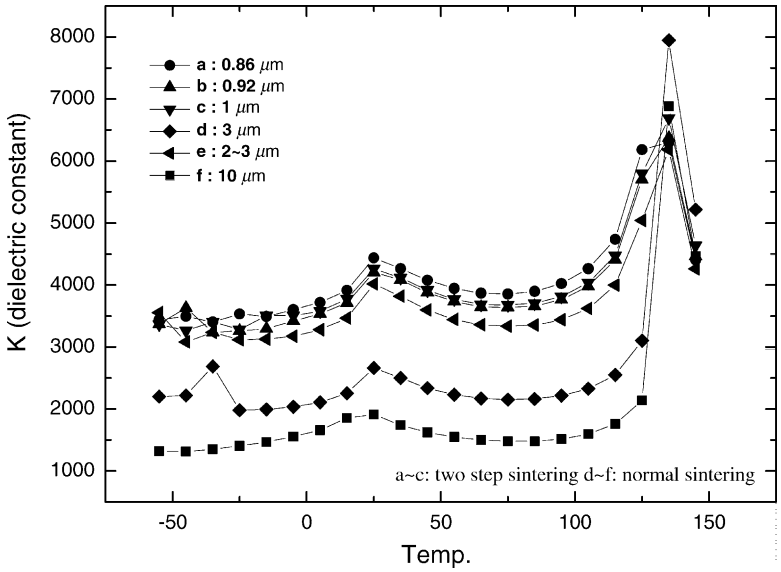

Fig. 6. The temperature dependence of dielectric constant in various grain sizes.

initially heated up to 1300 °C and cooled down, followed by sintering at 1100 °C for various times, 0, 5 and 20 h, respectively. The fast heating up to 1300 °C resulted in a fairly high density(89%) without further sintering process and the grain size was ~0.85 μm as shown in Fig. 3a. The sintering process (20 h) followed by the initial heating yielded the high bulk density greater than 95% as shown in Fig. 3c. However, it should be noted that the second step sintering does not accompany the grain growth normally occurring in most densification processes. Chen and Wang [9] reported that the lack of grain growth in the second-step sintering has important implications for kinetics. Grain coarsening creates a powerful dynamic that constantly refreshes the microstructure. This evolution can be a source of enhanced kinetics. Even without grain growth, enhanced kinetics has also been suspected in cases when microstructure evolution is otherwise robust. Because the second-step sintering proceeds in a 'frozen' microstructure, it should have slower kinetics. Yet the slower kinetics is sufficient for reaching fairly high density, while providing the benefit of suppressing grain growth [9].

Fig. 4a and b show the sintered density and grain size of $BaTiO_3$ specimen as a function of sintering time. In the two-step sintering process, a slight grain growth was observed after 20-h heating, whereas the density significantly increased from 5.3 to 5.7 g/cm^3. However, in the normal sintering process, unlike the two-step process the grain size increased from 1 to 6 μm as the sintering time increased from 1 to 5 h and the density changed from 5.0 to 5.6 g/cm^3. It was thus confirmed that the two-step sintering process could suppress the grain growth effectively and increase density significantly.

Fig. 5 shows a microstructure of the $BaTiO_3$ specimen doped with 1 mol% of Dy, which was sintered using the two-step process. Dy-doped $BaTiO_3$ exhibited a signification reduction in grain size. The average grain size of dense ceramics ranged from 200 to 400 nm and the bulk density was ~5.6 g/cm^3 (>93% of the theoretical density). It is well known that $BaTiO_3$ doped with small amount of donor impurities (>0.5 mol%) yields cation vacancy compensation and results in the material being fine-grained (1–2 μm) [17]. Yamaji et al. [3,18] also reported that Dy is an effective additive for retarding grain growth. They obtained sintered samples with 1.2 μm grain size by doping 0.4–0.8 mol% Dy.

Fig. 6 shows dielectric constants as a function of temperature for various grain sizes. The specimen with grain sizes of 0.8 μm exhibits the highest permittivities for the temperature range below the Curie point. As the grain size increased, the permittivities decreased at the most of temperature studied. This result is in good agreement with the previous reports that the contribution of residual stresses in individual grains causes substantially untwined structure as grain size decreases [19–21].

4. Conclusions

Two-step sintering can effectively suppress the grain growth in $BaTiO_3$, leading to a fine-grained microstructure. The sample sintered in two-step sintering showed a slight grain growth with relatively high densities (5.3–5.7 g/cm^3) and an average grain size of ~1 μm. Dy-doped $BaTiO_3$ specimens showed the microstructure development with fine grains (200–400 nm), which was smaller than that of the undoped $BaTiO_3$. It was also confirmed that dielectric constant is strongly dependent on the grain size. As the grain size increased, the permittivities decreased at most of temperatures studied.

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References

[1] D.H. Yoon, B.I. Lee, $BaTiO_3$ properties and powder characteristics for ceramic capacitors, J. Ceram. Process. Res. 3 (2002) 41–47.
[2] K. Kinoshita, A. Yamaji, Grain-size effects on dielectric properties in barium titanate ceramics, J. Appl. Phys. 47 (1976) 371–373.
[3] A. Yamaji, Y. Enomoto, K. Kinoshita, T. Murakami, Preparation, characterization, and properties of Dy-doped small-grained $BaTiO_3$ ceramics, J. Am. Ceram. Soc. 60 (1977) 97–101.
[4] M. Kahn, Preparation of small-grained and large-grained ceramics from Nb-doped $BaTiO_3$, J. Am. Ceram. Soc. 54 (1971) 452–454.
[5] V.S. Tiwari, N. Singh, D. Pandey, Structure and properties of (Ba, Ca)TiO_3 ceramics prepared using (Ba, Ca)CO_3 precursors: 1. Crystallographic and microstructural studies, J. Am. Ceram. Soc. 77 (1994) 1813–1818.
[6] J.R. Groza, Nanosintering, Nanostruct. Mater. 12 (1999) 987–992.
[7] S.C. Liao, Y.J. Chen, B.H. Kear, W.E. Mayo, High pressure/low temperature sintering of nanocrystalline alumina, Nanostruct. Mater. 10 (1998) 1063–1079.
[8] M.J. Mayo, Nanocrystalline ceramics for structural application: processing and properties, in: Nanostructure Materials, Kluwer Academic Publishers, The Netherlands, 1998, pp. 361–385.
[9] I.W. Chen, X.H. Wang, Sintering dense nanocrystalline ceramics without final-stage grain growth, Nature 404 (2000) 168–171.
[10] P.L. Chen, I.W. Chen, Sintering of fine oxide powder: I. Microstructural evolution, J. Am. Ceram. Soc. 79 (1996) 3129–3141.
[11] P.L. Chen, I.W. Chen, Sintering of fine oxide powder: II, J. Am. Ceram. Soc. 80 (1997) 637–645.
[12] M. Pechini, Barium titanium citrate, barium titanate and processes for producing the same, US Patent 3,330,697 (1967).
[13] R.K. Sharma, N.H. Chan, D.M. Smyth, Solubility of TiO_2 in $BaTiO_3$, J. Am. Ceram. Soc. 64 (1981) 448–451.
[14] B.D. Cullity, Diffraction under nonideal conditions, in: Elements of X-Ray Diffraction, second ed., Addison-Wesley Publishing Company, Inc., USA, 1978, pp. 99–106.
[15] C.P. Cameron, R. Raj, Grain-growth transition during sintering of colloidally prepared alumina powder compacts, J. Am. Ceram. Soc. 71 (1988) 1031–1035.
[16] V.V. Skorokhod, A.V. Ragulya, Features of nanocrystalline structure formation on sintering of ultra-fine powders, in: Nanostructure Materials, Kluwer Academic Publishers, The Netherlands, 1998, pp. 387–404.
[17] J. Nowotny, Nonstoichiometry and related properties of ceramics interfaces, in: Science of Ceramic Interfaces II, Elsevier, Amsterdam, 1994, pp. 1–31.
[18] Y. Enomoto, A. Yamaji, Preparation of uniformly small-grained $BaTiO_3$, Ceram. Bull. 60 (1981) 566–570.
[19] W.R. Buessem, L.E. Cross, A. K Goswami, Phenomenological theory of high permittivity in fine-grained barium titanate, J. Am. Ceram. Soc. 49 (1966) 33–36.
[20] W.R. Buessem, L.E. Cross, A. K Goswami, Effect of two-dimensional pressure on the permittivity of fine and coarse-grained barium titanate, J. Am. Ceram. Soc. 75 (1992) 2926–2929.
[21] G. Arlt, D. Hennings, G. de With, Dielectric properties of fine-grained barium titanate ceramics, J. Appl. Phys. 58 (1985) 1619–1625.