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Bulk dense nanocrystalline $BaTiO_3$ ceramics prepared by novel pressureless two-step sintering method

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Abstract In this paper, we investigate preparation of bulk dense nanocrystalline $BaTiO_3$ ceramics using an unconventional two-step sintering strategy, which offers the advantage of not having grain growth while increasing density from about 73 to above 99.6%. Isothermal and constant grain size sintering have been carried out to high density in pure $BaTiO_3$ system. The kinetics of this method is also discussed, which exploits the different kinetics between densification diffusion and grain boundary mobility. Using this method, bulk dense ceramics with a grain size of 8–10 nm was obtained successfully at a very low sintering temperature.

Keywords Nanocrystalline · $BaTiO_3$ · Two-step sintering · Pressureless · Nanoceramics

1 Introduction

As one of most important electroceramics, perovskite-structured barium titanate, $BaTiO_3$ (BT) has been extensively used in the fabrication of high dielectric constant capacitors, PTC resistors, transducers and ferroelectric memories [1]. It is well known that above the Curie temperature (130 °C), the structure of BT is cubic and paraelectric, below the Curie point, the structure is slightly distorted and three ferroelectric polymorphs with nonzero dipole moment exist depending on temperatures (4 mm tetragonal to mm2 orthorhombic at about 5 °C and finally to 3 m rhombohedral below −90 °C). With the development of microelectronics and communications, miniaturization and integration of ferroelectric components is required. However, the reduction of the physical sizes of ferroelectric materials seems to have a significant effect on their properties and this could have a limitation also for the miniaturization. The most important issue is the extent to which bulk physical properties can be considered for the design of miniaturized thin-layer devices from the micrometer scale to the nanometer scale. Therefore, the size dependent characteristics on the ferroelectric behavior are of great sustained interest both in fundamental and in practical.

Recently, Ferry et al. [2], and Zhao et al. [3], reported the dielectric data of dense BT ceramics with GS from 70 nm to 20 μm fabricated by pseudoisostatic hotpressing (HIP) in a multianvil press at 8 GPa, and 50–1,200 nm fabricated by spark plasma sintering (SPS) with an uniaxial pressure of 100 MPa during sintering respectively. They both found a progressive reduction of tetragonal distortion, Curie temperature and relative dielectric constant on BT ceramics when GS decreases from micrometer to nanometer. The critical size for disappearance of ferroelectricity has been evaluated to be 10–30 nm by Zhao et al. [3] based on their experimental trend. However, the applied pressure above several hundred of MPa to the powders during sintering will affect the distortion (c/a ratio) of the tetragonal unit cell, Curie temperature and permittivity of BT [4–7]. According to the previous works, for an applied pressure of 0.1 GPa, the decrease of the tetragonal strain is about 5%

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of the spontaneous strain. Actually, the Curie temperature of the BT samples prepared by HIP [2] or SPS [3, 8, 9] (≈120 °C) is lower than that obtained for conventionally sintering BT ceramics (typically=125–130 °C) with the same grain size.

In order to get better understanding of the intrinsic size effect in sub-micrometer and nanometer-scale barium titanate ceramics and to meet its real industrial application, sintering processing without any applied pressure is imminently required. The recent development of an unconventional two-step sintering strategy featuring densification without grain growth is deemed particularly exciting as we reported in Nature [10], since it promises to deliver nanoceramics by pressureless sintering.

In this paper, more effort has been done to fabricate bulk dense BT ceramics from submicron down to nanometer size using the two-step sintering method, and the kinetics window of constant-structure sintering for pure BT is also addressed. The finest grain size of fully dense BT ceramics obtained is about 8–10 nm for the first time using pressureless sintering.

2 Experimental procedure

High purity BT nanocrystalline powders used here were synthesized by a modified oxalate precipitation method as described previously [11]. The starting materials used were barium acetate ($Ba(CH_3COO)_2$), tetrabutyl titanate ($Ti(OC_4H_9)_4$), oxalic acid ($H_2C_2O_4$) as precipitator and alcohol as a media solution. The precursor was calcined at different temperature (650∼750 °C) to produce pure nanocrystalline BT powders. The mean particle size was from 30 nm to less than 10 nm depending on the calcining temperatures. The Ba/Ti atomic ratio was within 1±0.003 for all the powders. The nanocrystalline powders were pre-milled and pressed into disks (10 mm in diameter and 1.0 mm thickness). After isostatic pressing at 200 MPa to achieve a relative density of 46%, the green compacts were sintered using various two-step firing schedules. Typically, the sample was heated at 10 °C/min to a higher temperature T_1 (920–1,250 °C), then immediately cooled, at 30 °C/min, to a lower temperature T_2 (1,150–850 °C) for isothermal sintering with dwell times of 4∼20 h.

The crystalline structures of the powders and ceramic samples were determined by a Rigaku Powder X-ray diffractometer using *Cu* K_α radiation. The microstructures of the ceramics were investigated using a Zeiss CSM-950 scanning electron microscopy (SEM) and transmission electron microscopy (TEM, JEM-2010F). In the Archimedes method for density measurements, distilled water was used as the displacement liquid and the estimated accuracy was within ±0.01 g/cm^3.

3 Results and discussion

3.1 Pressureless two-step sintering

To our knowledge, unconventional two-step thermal processing without applied pressure was used to prepare nano/submicro grained BT ceramics for the first time. In two-step sintering, the sample is heated first to a higher temperature, T_1, to obtain grain size of G_1 (with density of ρ_1), and then sintered at a lower temperature T_2 for some time (thermal cycle as shown in Fig. 1 insert) to reach full density. During the second step sintering, density improved from a lower value (73–87%) to better than 99.6% without any grain growth. Table 1 gives some successful results for the constant-structured sintering during the second step. The contrast of microstructure development in normal versus two-step sintering can be seen in Fig. 1. This two-step schedule is very different from the conventional practice for sintering of ceramics. Usually, in normal sintering, the nano-sized BT green compacts are heated in a first cycle at a predetermined rate, and held at desired temperature until the highest densification level is reached. The grain size in that way increases continuously as density increases. The grain size achieved for the dense BT ceramic body sintered at 1,200 °C/2 h (97%) by normal sintering is 1.2 μm, the grain growth process accelerates as usual in the final stage of sintering where the relative density exceeds 85%. In two step process, a sufficiently high starting density has been obtained during the first stage. The surface free energy remains so higher that it delivers more energy to complete densification during the second stage. In BT system, the critical density obtained at T_1, which is required for producing dense ceramics during the second step sintering, is about 73%. This is essentially the same value as for Y_2O_3 (about 75%) [10]. Figure 1 shows that the grain size in T_2 remains

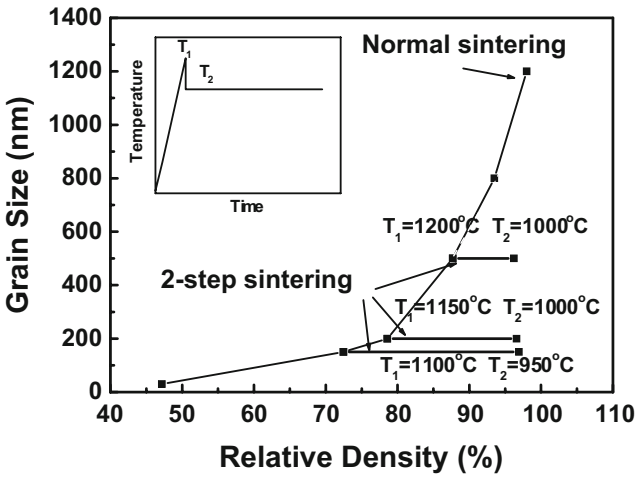

Fig. 1 Grain size versus density for the $BaTiO_3$ specimens sintered by two-step and by normal sintering

Table 1 Two-step sintering of $BaTiO_3$ (10 and 30 nm powders) reaching high density without grain growth.

Sintering condition		Relative density (%)		Final grain size (nm)
First-step	Second step	ρ_1	ρ_2	
980 °C[a]—0 min	900 °C—4 h	78	97	70
1,100 °C—0 min	900 °C—20 h	73	96	150
1,100 °C—0min	950 °C—20 h	73	97	150
1,150 °C—0min	900 °C—20 h	78	96	200
1,150 °C—0 min	950 °C—20 h	78	97	200
1,150 °C—0 min	1,000 °C—20 h	78	97	200
1,180 °C—0 min	950 °C—20 h	83	97	300
1,180 °C—0 min	1,000 °C—20 h	83	97	300
1,200 °C—0 min	900 °C—20 h	87	96	500
1,200 °C—0 min	1,000 °C—20 h	87	96	500
1,200 °C—0 min	1,100 °C—10 h	87	97	500

[a] 10 nm powder

unchanged, while the density continues to improve, in contrast to normal sintering when both proceed concurrently.

It is found that the temperature T_2 required for the second step decreased with the increasing grain size (G_1). However, if T_2 is too low, then sintering proceeds for a while and then becomes exhausted. On the other hand, if T_2 is too high, grain growth still occurs in the second step. Figure 2 shows the kinetic, processing window of T_2 as a function of grain size G_1 for reaching full density without grain growth. Solid symbols are temperature and grain-size (after T_1 firing) conditions of successful second-step sintering runs for BT. Open symbols above the upper boundary are conditions that showed grain growth in the second step, whereas open symbols below the lower boundary are ones that did not reach full density in the second-step sintering.

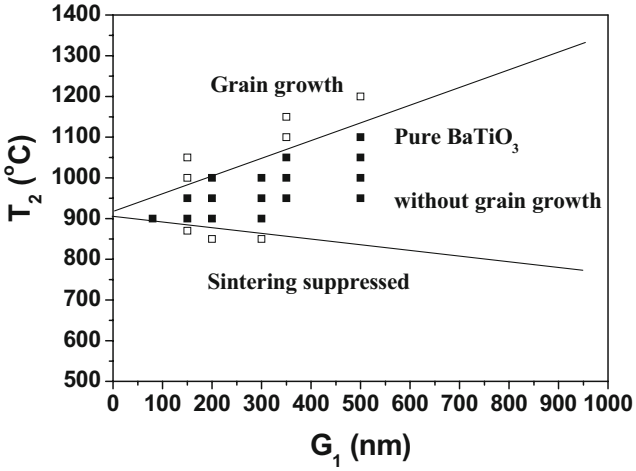

Fig. 2 Kinetic window for second-step sintering without grain growth for $BaTiO_3$. *Full symbols* indicate successful runs; *open symbols* unsuccessful ones with either grain growth (*upper*) or poor density (*lower*)

The feasibility of densification without grain growth relies on the suppression of grain-boundary migration while keeping grain-boundary diffusion active. To achieve densification without grain growth, grain boundary diffusion needs to be maintained while the grain boundary migration suppressed. It seems likely that grain boundary migration involves additional kinetic processes other than grain boundary diffusion, and if such processes require a higher activation energy, then grain boundary migration can be suppressed at lower temperature despite active grain boundary diffusion. The most likely candidates for such step are the movement of nodal points or nodal lines on the grain boundary, such as four-grain junctions, pore-grain boundary junctions, or three-grain junctions (lines) [12]. The structures of these nodal points and lines may be special and they could become stabilized by prior high temperature treatment, rendering them difficult to alter to

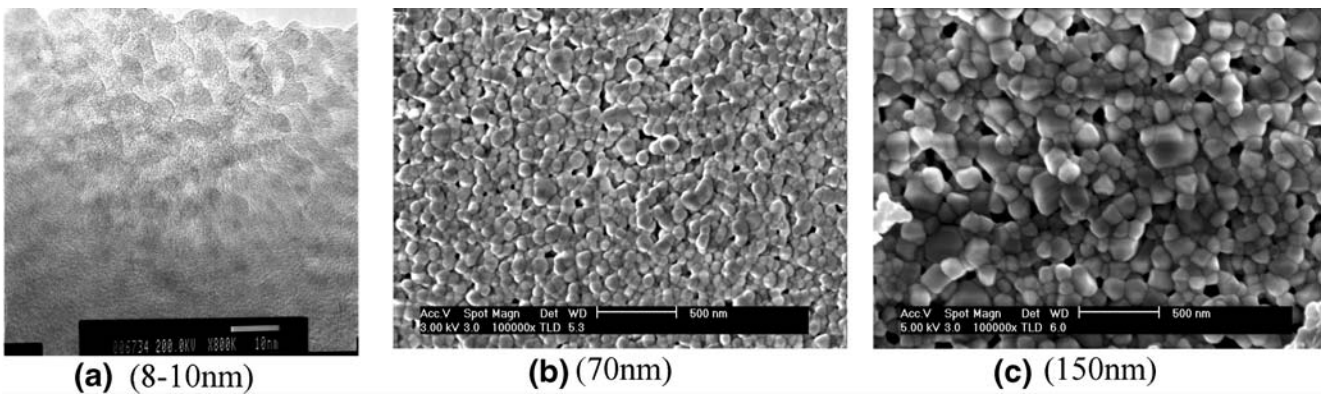

Fig. 3 TEM and SEM micrographs of dense $BaTiO_3$ ceramics prepared by two-step sintering (**a**) 8–10 nm (TEM) (T_1=920 °C/0 min, T_2=850 °C/20 h) (**b**) 70 nm (SEM) (T_1=980 °C/0 min, T_2=900 °C/4 h) (**c**) 150 nm (SEM) (T_1=1,100 °C/0 min, T_2=900 °C/20 h)

accommodate the subsequent movement of migrating grain boundary at low temperatures. Empirically, this may be modeled by assigning mobility to the nodal point (line), whose ratio to grain boundary mobility decreases with increasing temperature. In fact, Czubayko's studies of high-purity zinc have shown that grain-boundary migration can be severely hampered by the slow mobility of grain junctions at lower temperatures, the latter having a higher activation energy [13].

Furthermore we noted that the upper boundary line has a positive slope. This is reasonable since the driving force for grain growth decreases with the grain size, so a higher temperature is needed. Figure 2 also shows a lower-bound temperature, below which sintering is exhausted before full density is achieved. This suggests that grain boundary diffusion itself can be suppressed at lower temperatures. Interface kinetics in very fine grain polycrystals is sometimes limited due to difficulties in maintaining sources and sinks to accommodate point defects [14–17]. This effect should diminish at larger grain sizes, allowing the kinetic window to extend to lower temperatures.

3.2 Dense nanocrystalline BT ceramics

Employing the two-step sintering strategy without applied pressure, a series of high density bulk BT ceramic samples with grain size ranging from submicro-scale to nano-scale have been successfully prepared. Figure 3 shows some microstructures for the dense BT samples by two-step sintering. The finest grain size of dense BT ceramics (99.6% of theoretical density) obtained so far is around 8–10 nm (Fig. 3(a)). It was derived from starting powders with an initial size less than 10 nm, and cold-die-pressed at 2 GPa to 61% relative density, then two-step sintered using T_1=920 °C and T_2=850 °C (20 h). To our knowledge, it is the first time to achieve fully dense nanocrystalline BT ceramics in such small grain size. Another fine grain BT ceramic, B (70 nm, density of 97%), was obtained using 10 nm powder, isostatic pressed at 200 MPa and then two-step sintered using T_1=980 °C and T_2=900 °C (4 h) (Fig. 3(b)). While the ceramic C (150 nm, density of 96%), was obtained using 30 nm powder, isostatic pressed at 200 MPa and then two-step sintered using T_1=1,100 °C and T_2=900 °C (20 h) (Fig. 3(c)). With the benefit the simplicity of this approach, a systematical investigation on the nature size effect explorations of dense BT materials on tetragonal distortion, phase transition, Curie temperature and dielectric properties as well as mechanical properties are currently in progress, and will be reported in another paper.

4 Conclusions

Two-step pressureless sintering was used to sinter $BaTiO_3$ ceramics to high density with unprecedentedly fine grain size, by suppressing grain growth in the final stage of densification. The processing window for successful second step sintering to achieve high density without grain growth was identified for $BaTiO_3$. It shares the same feature as the one previously determined for undoped and doped Y_2O_3. Dense BT ceramics with grain size ranging from 8 to 500 nm were successfully achieved at a very low sintering temperature (900 °C) by two step sintering. The finest grain size of dense BT ceramics (99.6%) obtained so far is about 8 nm for the first time.

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