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Dielectric properties of barium titanate ceramics with different materials powder size

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Abstract

The dielectric properties of barium titanium ceramics fabricated with nano-size fine powders (about 40 nm) are compared with that fabricated with micro-size coarse powders (about 2 μm). Three kinds of ceramics were fabricated; one using pure nano-size fine powders, the other using pure micro-size coarse powders, and the third using the combination of both. The sintering temperature of the ceramics with pure nano-size fine powders is 150 °C lower than that with pure micro-size coarse powders. For the same sintering conditions, the relative density of the ceramics is increases with the amount of nano-size fine powders. The grain size of the ceramics body with pure micro-size coarse powder is about 5 μm, but that of pure nano-size fine powder is about 1 μm. The room temperature dielectric constant of the ceramics increases with the increasing of the amount of nano-size fine powder. For pure nano-size fine powders, the room temperature dielectric constant is about 5000, and that of micro-size coarse powders is about 2200.

Keywords: A. Sintering; C. Dielectric properties; D. $BaTiO_3$ and titanates; E. Capacitors; Nano-powders

1. Introduction

Barium titanate ($BaTiO_3$) ceramics have been extensively studied during the last few decades in order to its understanding dielectric and ferroelectric properties [1–7]. The dielectric characteristics of $BaTiO_3$ ceramic depend on the microstructure, especially the grain size [8–13]. In $BaTiO_3$ ceramic the relative permittivity increases with the decrease of grain size down to 0.8 μm. A pronounced maximum $\varepsilon_r \approx 5000$ at grain size 0.8–1 μm was found, which decreases with continuous grain size reduction, because no 90° domain wall can exist at the grain size less than 0.8 μm [14]. Zhang et al. [15] showed that, as the grain size decreases, the transition temperature T_C and the relative permittivity decreases and the transition becomes diffuse. The size reduction is also interesting for reducing the loss tangent. It is known that, the motion of 90° domain walls is one of the sources of dielectric losses. In small-grained ceramics, the wall motion is limited by the pinning effect of grain boundaries [16], which may reduce the value of loss tangent.

In general, the conventional preparation route of $BaTiO_3$ ceramics is solid-state reaction between oxides and carbonates at high temperature. In the solid-state reaction preparation route the properties of $BaTiO_3$ ceramics depends on the characteristics of raw materials; such as purity, particle size distribution etc., in which the particle size is the most importance factor. From the results of Carter [17], the reaction rate of the particles is proportional to $1/r^2$, where r is the radius of the particles, so the sintering temperature of solid-state reaction can decrease with the decreasing of particle size. Recently, high-purity, nano-scale size ultrafine powders of $BaTiO_3$ has been synthesized by many low temperature wet chemical routes such as sol–gel [18–24]. Sol–gel method has the advantages of low cost, high purity, fine grain size, easier compositional

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control and short fabrication cycle, but its through-put is very low. In this study we use the attrition milling to fabricate the $BaTiO_3$ nano-powder and the influence of starting materials particle size on the sintered $BaTiO_3$ ceramics dielectric properties are under discussion.

2. Experimental

In this study the barium titanate powders were prepared by solid-state reaction. Barium carbonate $BaCO_3$ and titanium dioxide TiO_2 with the rutile structure, were milled together in water with zirconia balls; the mixing powders were dried in an oven at 120 °C. Then, the mixture was calcined at 1000 °C for 2 h in air. The crystal phase of the calcined powders was examined by XRD. After that, the calcined powders were divided into two parts, one was crushed by the conventional ball milling with zirconia balls, and the other was milled by attrition milling with zirconia balls. The obtained powders were analysed by Laser Particles Analyzer (Beckman, Coulter LS230). Different size powders were mixed together with the (μm size/nm size) ratio equal to (100/0), (75/25), (50/50), (75/25) and (0/100). The powders were isostatically pressed at 200 MPa and sintered in air at temperatures 1250–1350 °C, with a heating/cooling rate of 3 °C/min and sintering time of 2 h. Density measurements were carried out in water with Archimedes method. Scanning Electron Microscopy (JEOL, JSM-5610LV) was used to evaluate microstructures on polished and thermally etched samples. XRD were conducted to determine lattice constant of the $BaTiO_3$ ceramics. Finally, dielectric constants were measured on silver-electroded discs from room temperature to 180 °C using Hioki-3532-50 LCR meter and an oven.

3. Results and discussions

Fig. 1 shows the XRD pattern of $BaCO_3$ and TiO_2 mixture after calcined at 1000 °C. It was found that the tetragonal $BaTiO_3$ is the unique crystal phase in the calcined powder, and these powders will be used as the raw materials in the future research works.

Fig. 2(a) and (b) shows the particle size distribution of the powders after being crushed by the conventional ball milling and that by the attrition milling, respectively. It found that the particle size of the powders crush by the conventional ball mill was about 2 μm, and that crush by the attrition milling was about 40 nm.

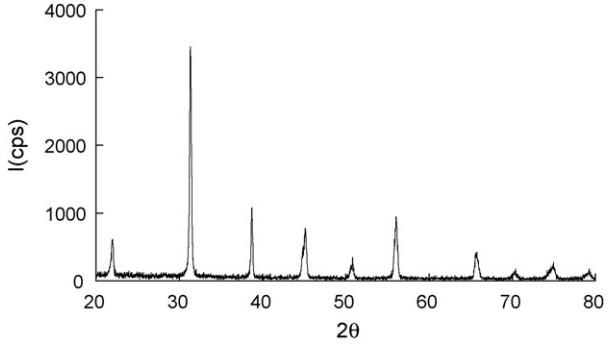
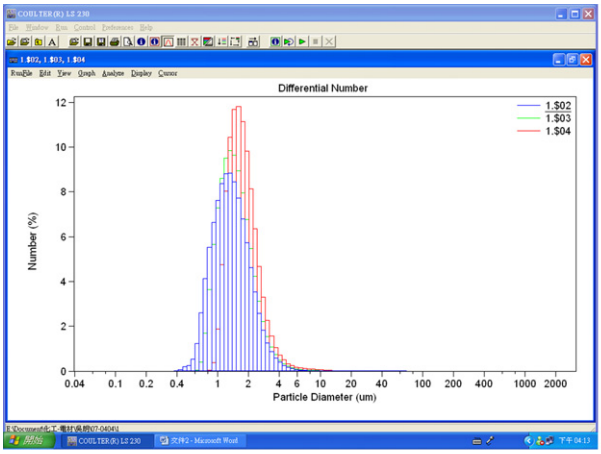
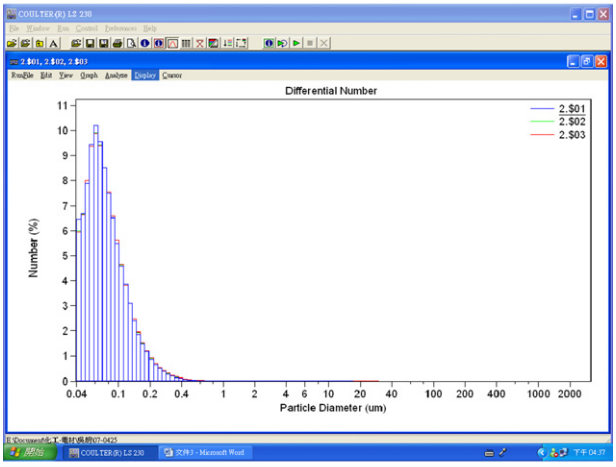


Fig. 1. XRD of $BaCO_3$ and TiO_2 mixture after calcined at 1000 °C.



(a)



(b)

Fig. 2. Particle size distribution after crush by (a) conventional ball mill and (b) attrition mill.

Table 1 shows the compositions used in this study, in which C represented the micro-size coarse powder fabricated by conventional ball mill, and F represented the nano-size fine powder fabricated by attrition milling. The number was the amount of the powder, such as (C75/F25) representing the mixing of 75 wt% micro-size coarse powders and 25 wt% nano-size fine powder.

The density of sintered $BaTiO_3$ ceramics is shown in Fig. 3. For sinter at 1250 °C the density of (C50/F50), (C25/F75) and (F100) compositions can reach 96% of the theoretical density,

Table 1
The compositions used in this study

No.	wt% of μm size powder	wt% of nm size powder
C100	100	0
C75/F25	75	25
C5/F5	50	50
C25/F75	25	75
F100	0	100

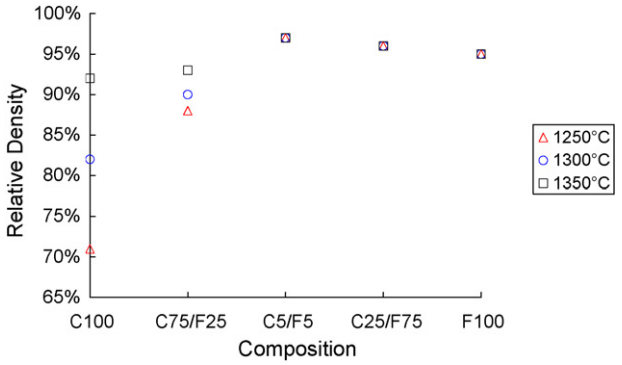


Fig. 3. The density of ceramics after sintering.

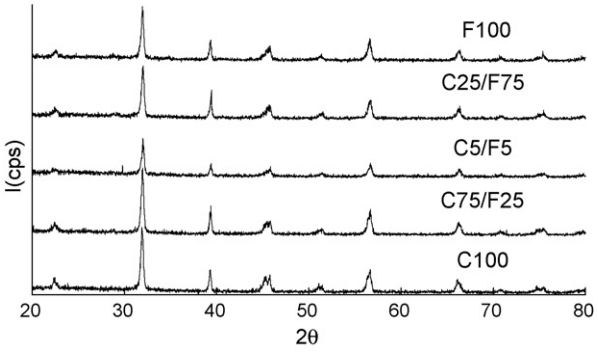


Fig. 4. The XRD of sintered ceramics with maxima density.

but that of (C100) and (C75/F25) was lower than 90% of the theoretical density. The density of (C50/F50), (C25/F75) and (F100) compositions is nearly constant with the increase of sintering temperature, but that of (C100) and (C75/F25) increases with the sintering temperature. From the results of Fig. 3, it found that the sintering temperature of (C50/F50), (C25/F75) and (F100) compositions was 1250 °C, but the sintering temperature of (C100) and (C75/F25) was much higher. For pure micro-size coarse powder composition (C100), the optimum sintering temperature may be equal to 1400 °C. In comparison with (C100) and (F100) composition, it was found that the sintering temperature of ceramic with pure nano-size fine powder was 150 °C lower than that with pure micro-size coarse powder. The density of (F100) composition was lower than that of (C50/F50) and (C25/F75) compositions, that is because the porosity of (F100) composition was larger than that of (C50/F50) and (C25/F75) compositions, as shown in Fig. 5.

The XRD patterns of sintered ceramic with maxima density are shown in Fig. 4. It was found that the crystal structure of all the compositions was tetragonal perovskite $BaTiO_3$, but the tetragonality (c/a) varies with the raw material particle size. The (c/a) ratio of (C100) composition was the largest and it will decrease with the increase of the amount of fine powders. As shown in Table 2, the crystal structure changes from tetragonal to pseudo-cubic with the increases of the amount of nano-size fine powders. The same results were also observed at the paper of Kwon and Yoon [25].

Table 2
The c/a ratio of ceramics with maxima density

Composition	c/a
C100	1.01
C75/F25	1.009
C50/F50	1.007
C25/F75	1.003
F100	1.003

Fig. 5 shows the SEM of sintered ceramics. It was found that the grain size of (C100) and (C75/F25) composition are nearly equal to 5 μm, but that of (C50/F50), (C25/F75) and (F100) was nearly equal to1 μm.

The room temperature dielectric constant of sintered ceramics measured at 1 kHz was shown in Fig. 6. The dielectric constant of (C100) and (C75/F25) composition is around 2200 at room temperature due to the large grain size, but the room temperature dielectric constant of other compositions was around 5000. The dielectric constant at room temperature increases with nano-size fine powders content, but the maximum of dielectric constant occurs at the (C25/F75) composition, not at the F100 composition. That is because the porosity of (F100) is larger than that of (C25/F75) composition.

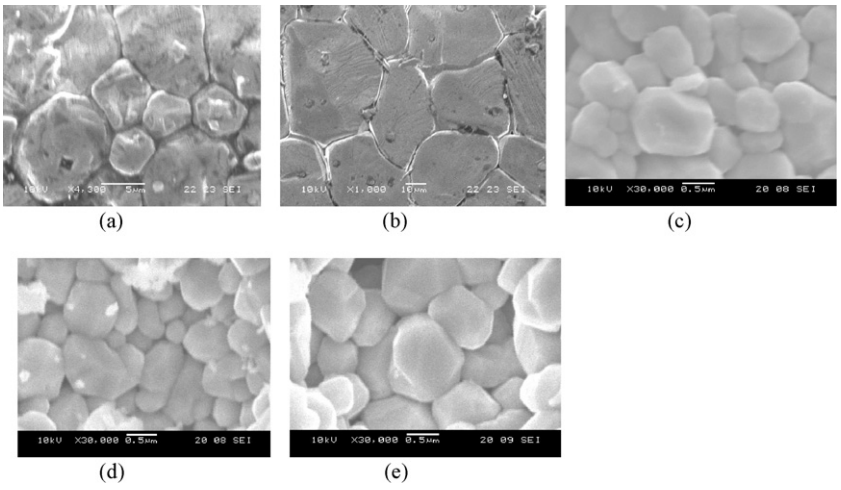


Fig. 5. SEM of sintered ceramics (a) C100, (b) C75/F25, (c) C5/F5, (d) C25/F75 and (e) F100.

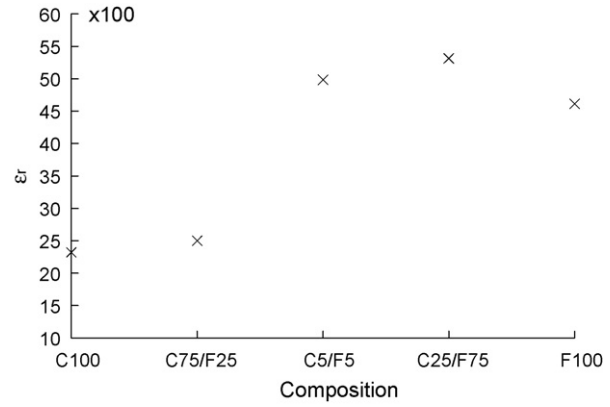


Fig. 6. Room temperature dielectric constant of sintered ceramics.

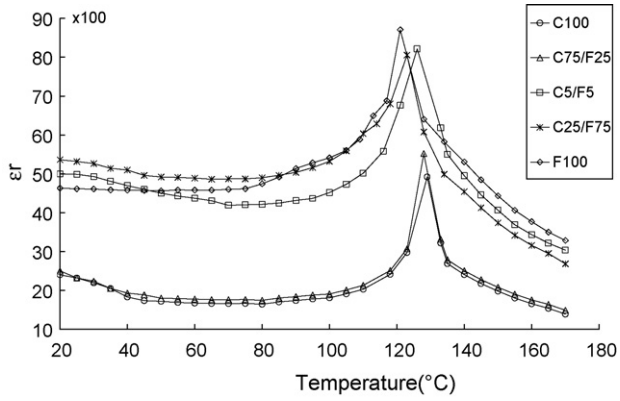


Fig. 7. Dielectric constant vs. temperature of sintered ceramics.

Fig. 7 shows the temperature dependence of dielectric constant. The ferroelectric phase transition temperature (T_c) of (C100) and (C75/F25) compositions is 130 °C. Although some authors have proposed that T_c increases with the decrease of grain size, but in this study the T_c decreases with decreasing of grain size, as proposed by Zhang et al. [15] and Lee and Auh [26].

4. Conclusions

The crystal structure and dielectric characteristics of $BaTiO_3$ ceramic depend on the particle size of raw materials. When the particles size of raw material become finer, the crystal structure changes from tetragonal to pseudo-cubic. The sintering temperatures of the ceramics using nano-powders as raw material are 150 °C lower than that using pure coarse powders. For the same sintering conditions, the relative density of the ceramics increased with the amount of nano-powders. For pure nano-powders, the room temperature dielectric constant is about 5000, and that of coarse powders is about 2200. The ferroelectric phase transition temperature decreases with decreasing of grain size.

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