

Sintering behaviors and dielectric properties of nanocrystalline barium titanate

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Received 15 August 2005; received in revised form 12 December 2006; accepted 7 January 2007

Abstract

Nanometer-scale barium titanate (BaTiO_3) powders were prepared via a process consisting of chemical dispersion and physical grinding/mixing. Sintering behaviors, microstructures as well as their correlations to dielectric properties of nano- BaTiO_3 sintered at the temperatures ranging from 1100 to 1300 °C for various time spans were investigated. It was found that specific control on sintering condition is required for the nano- BaTiO_3 powders to achieve desired microstructure, crystalline phase and dielectric properties of devices. The BaTiO_3 sample sintered at 1100 °C for 6 h possesses relatively small grain sizes (about 140 nm), high density (about 95% T.D.) and distinct room-temperature dielectric properties (dielectric constant = 8000; dielectric loss = 5×10^{-3}). Hence, in addition to the saving of thermal budget, the adoption of nano-scale ceramic powders in conjunction with appropriate sintering process may dramatically improve the dielectric properties of devices.

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Keywords: Nano- BaTiO_3 ; Sintering; Dielectric properties

1. Introduction

Barium titanate (BaTiO_3) is a versatile ceramic material for the fabrication of various electronic devices, e.g., self-controlled heaters, color TV degaussers, fuel evaporators, varistors, air-conditioning equipment, etc., due to its unique electrical properties [1]. One of the common applications of BaTiO_3 is the dielectric layer for multilayer ceramic capacitors (MLCC) [2,3]. However, the dielectric properties of BaTiO_3 are affected by many physical features such as grain size, crystalline structure, purity, sintering density, etc [4]. The relationship of dielectric properties of BaTiO_3 ceramics to grain sizes is an interesting phenomenon from both scientific and application view points. There have been many studies investigating the influence of grain sizes on the dielectric properties of BaTiO_3 ceramics. For bulk BaTiO_3 , most of the studies aimed at the samples with grain sizes about in the range of 1–50 μm and a decrease of dielectric constants with the increase of grain sizes were observed [5–12]. For instance, Arlt and Hennings reported that the BaTiO_3 with fine (1 μm) and coarse (50 μm) grain structures possess the dielectric constants of 4800 and 1200 at the

room-temperature, respectively [5]. Herard et al. found that the dielectric constants of BaTiO_3 is in the range of 1500–2700 when its grain size was 10 μm [6]. On the other hand, the BaTiO_3 with about 1 μm grain size was found to exhibit dielectric constant about 3500–5000 [7]. Effects of internal stresses [8] and the increase of 90°-domain wall density [9–12] were proposed to explain the change of dielectric properties with grain sizes of BaTiO_3 samples.

In addition to affect the dielectric properties, the crystal structures of BaTiO_3 are also known to affect the dielectric properties. Among all phases, the tetragonal BaTiO_3 is desired for the optimization of dielectric properties [13–16]. Zhu et al. showed that the hydrothermally synthesized tetragonal BaTiO_3 possesses better sintering behaviors and higher dielectric constants in comparison with the cubic BaTiO_3 [15]. However, the tetragonal BaTiO_3 might be difficult to form when nano-scale powders (<100 nm) are adopted for sample preparation [15,16]. Further, the powder preparation method was found to affect the phase type of BaTiO_3 . Burtrand [17] showed that cubic BaTiO_3 forms after sintering at 1100 °C for 2 h. However, the cubic phase may transform to tetragonal phase at 1200 °C when the BaTiO_3 powders was prepared by hydrothermal process [16,17].

This work studied the dispersion and sintering behaviors of nanometer-scale BaTiO_3 powder in an attempt to form tetragonal BaTiO_3 at nanometer-scale with desired dielectric properties.

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The densification process at different sintering temperatures and time spans as well as the relationships between grain sizes, crystallization behaviors, microstructure changes and dielectric properties were investigated.

2. Experimental

High purity, amorphous BaTiO₃ powder (Seedchem, Australia) with Ba/Ti=0.915, average size = 100 nm, and specific area = 9.18 m²/g was utilized as the raw material of experiment. Aqueous BaTiO₃ solution was prepared via a combination of chemical dispersion and physical grinding/mixing processes. The Na⁺ salt of poly(methacrylic acid) (PMAA-Na) was adopted as the chemical dispersant. The raw BaTiO₃ powder was mixed with 3 wt.% PMAA-Na in DI water before milling. The physical grinding/mixing was carried out by a laboratory mill (MiniZeta 03, NETZSCH-Feinmahltechnik GmbH) containing 3 mm ZrO₂ milling balls. The balls/powder ratio was fixed at 1:1 and the milling was carried out at 3600 rpm/min for 15 min. It was dried subsequently at 100 °C for 24 h. After being deagglomerated by using agate mortar and sieved through a 100 mesh, appropriate amounts of powder was dry-pressed to form disk-like samples of 10 mm in diameter and 3 mm in thickness at an uniaxial pressure of 150 MPa. The capacitor samples were subsequently sintered at 1100–1300 °C for various time spans.

After sintering, the density of sample was measured by the Archimedes method [18]. Grain sizes, morphology and element distribution of sintered bodies were examined by scanning electron microscopy (SEM, Hitachi 4700) attached with energy dispersive spectroscopy (EDS, STUW 3.3). Intercept method was used to calculate the average grain sizes of samples from the SEM images [16]. The phase constitutions and the dielectric properties of the sintered samples were acquired by an X-ray diffractometer (Siemens D5000) operating at 40 kV with $\lambda = 0.1542$ nm and an impedance analyzer (HP 4194A) at a frequency of 1 kHz, respectively.

3. Results and discussion

3.1. Microstructures

Figs. 1 and 2 show the morphology and particle size distribution of the BaTiO₃ particles subjected to the chemical dispersion and physical grinding/mixing process. The average size of BaTiO₃ particles was about 76 nm and no aggregation was observed. This evidenced that the PMMA-Na salt is an appropriate chemical dispersant for the preparation of aqueous nano-BaTiO₃ solution.

The microstructures of BaTiO₃ sintered in the temperatures ranging from 1100 to 1300 °C for 6 h are depicted in Fig. 3(a)–(c). The grain sizes of BaTiO₃ evolve as follows: at 1100 °C, 140 nm; at 1200 °C, 900 nm; at 1300 °C, 70 μ m. The SEM morphology observation in conjunction with the results of density measurement shown in Fig. 4 indicate that both the densities of sintered body and grain sizes of BaTiO₃ increase with the sintering temperatures. Further, the results presented in Figs. 3 and 4 reveal three distinct densification processes for

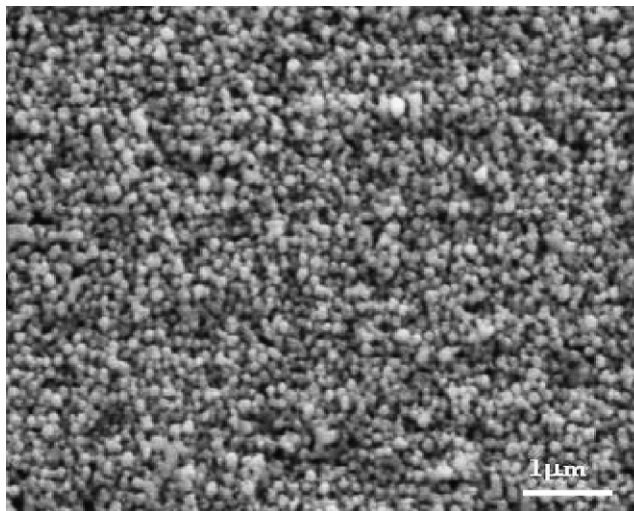


Fig. 1. SEM micrograph of nano-sized BaTiO₃ powders subjected to chemical dispersion and physical grinding/mixing process.

nano-BaTiO₃ particles at different sintering conditions. When sintering temperatures were below 1100 °C, densification and grain growth are both insignificant that, in essential, no sintering occurred. For the samples sintered in between 1100 and 1200 °C for less than 6 h, a rapid densification takes place with a relatively slow grain growth. When sintering times exceeded for 5 h at 1300 °C, grain growth prevailed and a slight desintering phenomenon occurred as indicated by a very little density decrease of samples sintered for more than 6 h (see Fig. 4). As suggested by previous study [19,20], the desintering phenomenon might be caused by gas releasing and/or abnormal grain growth during sintering.

Fig. 5 plots the relative density and grain size versus sintering time of nano-BaTiO₃ sintered at 1100 °C. After 6 h sintering, the sample exhibits a relatively high densification (about 95% T.D.) with a moderate grain growth that the average grain size of BaTiO₃ sample increases from about 80 to 140 nm. This indicates that for the sintering of nano-BaTiO₃ powders, grain growth occurs earlier in comparison with conventional process

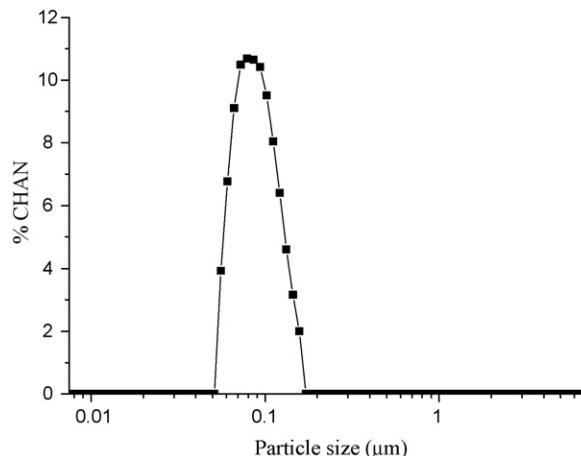


Fig. 2. Particle size distribution of nano-BaTiO₃ powder subjected to chemical dispersion and physical grinding/mixing process.

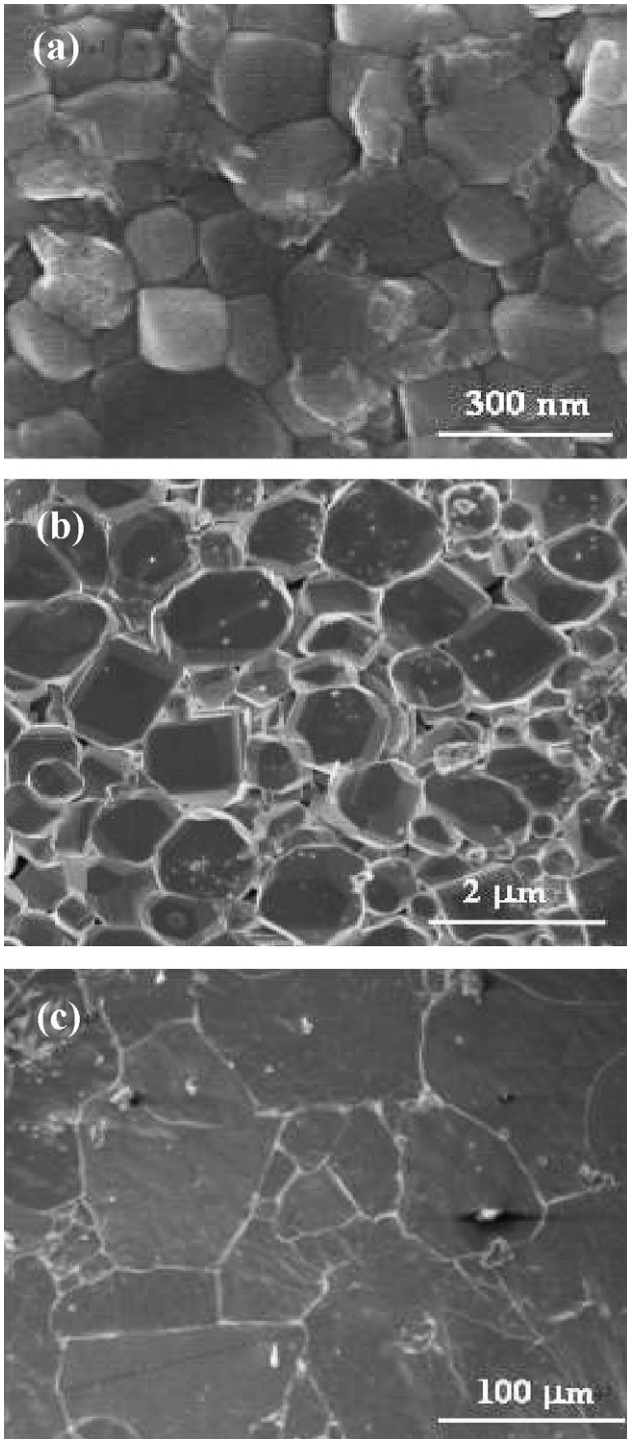


Fig. 3. SEM micrographs of BaTiO₃ sintering at (a) 1100 °C, (b) 1200 °C and (c) 1300 °C for 6 h.

that the apparent grain growth usually occurs at the end of sintering [18]. The occurrence of grain growth at the early stage of sintering was attributed to large specific surface area (SSA) of nano-BaTiO₃ powders. The nano-particles tended to reduce the surface energy of sample by eliminating the total surface area. Interface-driven processes such as grain boundary diffusion and surface diffusion dominated the mass transport at the early stage of sintering and hence a premature grain growth was observed.

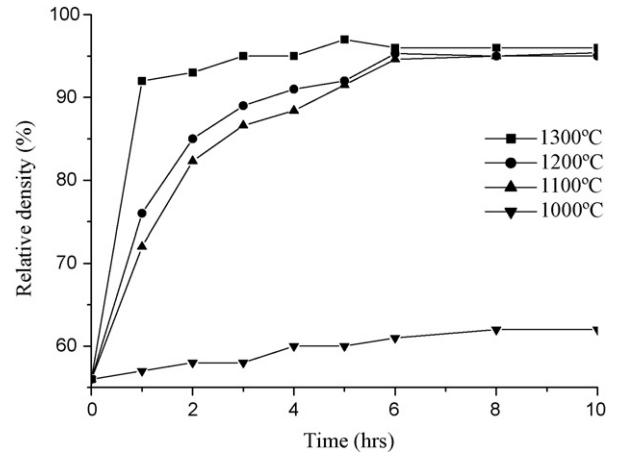


Fig. 4. Relative density change vs. sintering times at different temperatures.

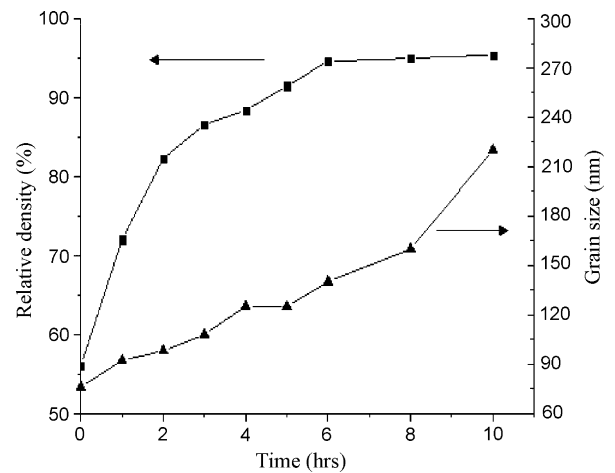


Fig. 5. The relative density and grain size vs. sintering time of sample sintered at 1100 °C.

3.2. Phase constitution

Fig. 6 presents the X-ray diffraction (XRD) patterns for the samples sintered at temperatures ranging from 1000 to 1300 °C

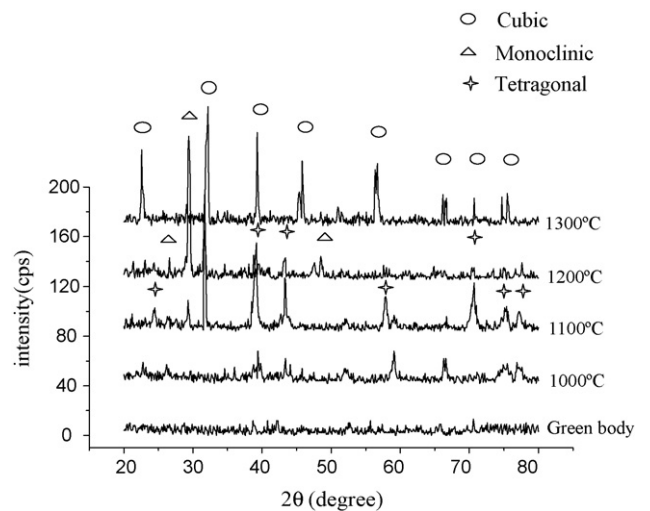


Fig. 6. The XRD patterns for the BaTiO₃ sintered at different temperatures.

Table 1
The EDS analysis of Ba:Ti ratio of samples sintered at different temperatures for 6 h

Sintering temperatures (°C)	Ba:Ti ratio
1100	1:1.12
1200	1:1.76
1300	1:1.14

for 6 h. At the temperatures below 1000 °C, tetragonal BaTiO₃ phase remains insignificant. However, the tetragonal BaTiO₃ becomes the dominant phase at 1100 °C and, when the sintering temperature is raised to 1200 °C, most of tetragonal phase evolves into the monoclinic phase. After the 1300 °C-sintering, the BaTiO₃ is overwhelmed by the cubic phase. The XRD pattern for the sample sintered at 1200 °C indicates that diffraction peaks corresponding to tetragonal phase are relatively weak in comparison with those corresponding to monoclinic phase. Table 1 shows the Ba:Ti ratio obtained by using the EDS attached to SEM. The higher Ba:Ti ratio $\approx 1:1.76$ indicates that the stoichiometry of monoclinic phase is likely BaTi₂O₅. It was hence concluded that the phase constitution for the sample sintered at 1200 °C is monoclinic BaTi₂O₅ mixed with a relatively small amount of tetragonal BaTiO₃.

Previous studies reported that the BaTi₂O₅ might form in the surface reaction layer and also in the bulk of BaTiO₃ pellets when the BaO-TiO₂ samples were sintered in oxygen-rich ambient at high temperatures [21,22]. It was also found that the BaTi₂O₅ is of paraelectric [10] and, when monoclinic BaTi₂O₅ is present in BaTiO₃, it would shift the capacitor sample from ferroelectric to paraelectric and hence decrease its dielectric constant [23,24].

3.3. Dielectric properties

Figs. 7–9 present the 1 kHz dielectric constants and dielectric losses versus the grain sizes of BaTiO₃ sintered at 1100, 1200 and 1300 °C, respectively. It can be seen that for the samples sintered at 1100 and 1200 °C, the dielectric constant first

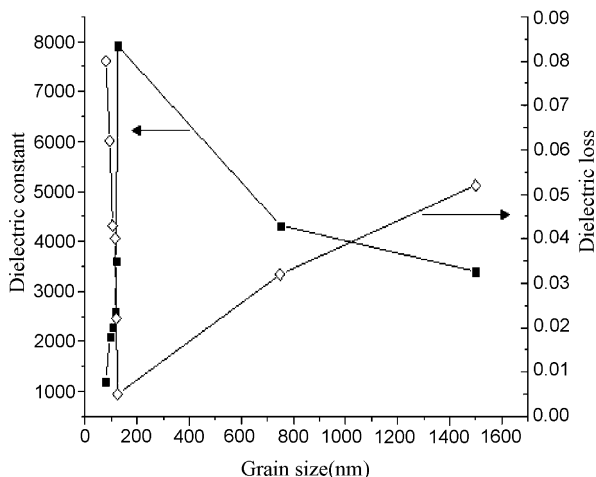


Fig. 7. 1 kHz dielectric constant and dielectric loss vs. grain sizes of nano-BaTiO₃ sintered at 1100 °C.

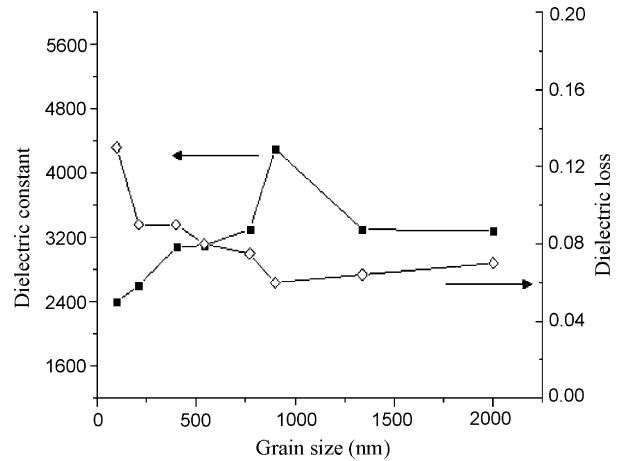


Fig. 8. 1 kHz dielectric constant and dielectric loss vs. grain sizes of nano-BaTiO₃ sintered at 1200 °C.

increases with the increase of grain sizes then decreases with the further increase of grain sizes and vice versa for the dielectric loss. The highest dielectric constant about 8000 and the lowest dielectric loss about 5×10^{-3} were achieved in the sample sintered at 1100 °C for 6 h with grain size about 140 nm. As to the samples sintered at 1300 °C, the dielectric constant decreases and dielectric loss increases monotonically with the increase of grain sizes, which is in the same trend as reported by previous studies relating to micro-scale BaTiO₃ [5].

The sintering temperatures for conventional BaTiO₃ process usually exceed 1300 °C. The results above clearly indicate that, in addition to the upgrading of dielectric properties, the sintering temperature for nano-BaTiO₃ is 200 °C lower than that for conventional process. The reduction of sintering would be a merit of thermal budget for the BaTiO₃ device fabrication.

During the sintering of nano-BaTiO₃, the voids might be rapidly eliminated at the early stage of sintering due to the mass transport processes driven by the large SSA of nano-particles. A relatively dense sintered body thus might achieve prior to the apparent coarsening of grains, resulting in distinct dielectric properties as shown in Fig. 7. Fig. 7 also shows that when the

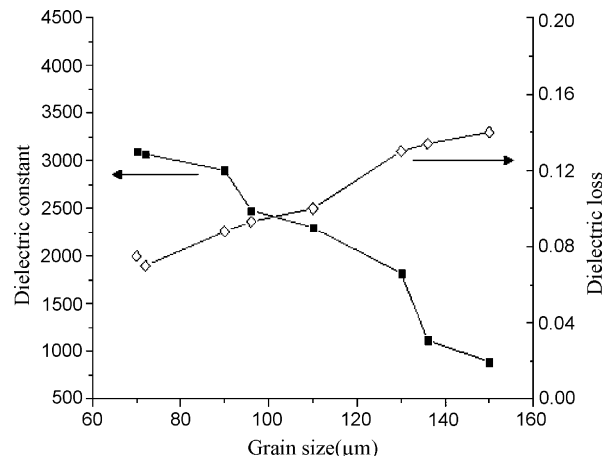


Fig. 9. 1 kHz dielectric constant and dielectric loss vs. grain sizes of nano-BaTiO₃ sintered at 1300 °C.

grain sizes exceed 200 nm, the dielectric constants decrease and dielectric losses increase with the increase of grain sizes. Though further grain growth implies denser sintered body, the grain sizes become micro-scale and the samples exhibit the dielectric properties similar to those of conventional BaTiO₃ samples [9,11,12]. The results above evidence that the adoption of nano-BaTiO₃ powder for device fabrication requires specific control on the sintering condition so as to obtain desired dielectric properties.

A comparison of Figs. 7 and 8 shows that the dielectric properties of 1200 °C-sintered BaTiO₃ are inferior to those of 1100 °C-sintered BaTiO₃ though they exhibit a similar trend of property change with the grain sizes. The decrease of dielectric constant of 1200 °C-sintered BaTiO₃ was attributed to the presence of monoclinic BaTi₂O₅ phase as indicated by XRD and EDS analyses. As stated previously, BaTi₂O₅ is paraelectric [10] and its presence reduces the spontaneous polarization and thus deteriorates the overall dielectric performance of the capacitor sample [23,24].

4. Conclusions

This work presents the preparation of nano-scale BaTiO₃ powder via a combination of chemical dispersion and physical grinding/mixing process. The sintering behaviors, microstructure and dielectric properties of capacitor samples based on such a nano-scale BaTiO₃ powder were investigated accordingly. It was found that distinct room-temperature dielectric properties (dielectric constant = 8000; dielectric loss = 5×10^{-3}) could be achieved in the sample sintered at 1100 °C for 6 h, which possesses relatively small grain sizes about 140 nm and high density (about 95% T.D.). This clearly demonstrated that good dielectric properties could be obtained by a relatively low temperature sintering when nano-scale ceramic powders were adopted. Experimental analyses revealed that due to the large SSA of nano-scale powder, interface-driven mass transport processes shifts the grain growth to the early stage of nano-BaTiO₃ sintering in comparison with conventional process. XRD analysis indicated that the sintering condition also affects the phase structure of BaTiO₃ samples. The tetragonal phase constituted the structure of samples sintered at 1100 °C, while the monoclinic and cubic phases were dominant in samples sintered at

1200 and 1300 °C, respectively. The stoichiometry of monoclinic phase was found to be BaTi₂O₅ and its paraelectric feature deteriorated the dielectric properties. Specific control on the sintering condition is hence required to obtain desired crystalline phase structure and dielectric properties when nano-BaTiO₃ powders are adopted for device fabrication.

Acknowledgements

This work was supported by the National Science Council of the Republic of China under contract no. NSC94-2216-E-009-026. The authors also acknowledge the Materials and Chemical Engineering Research Laboratories at Industrial Technology of Research Institute (ITRI), Taiwan, for their assistance in sintering process and dielectric property measurement.

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