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Structure–property relations of ferroelectric $BaTiO_3$ ceramics containing nano-sized Si_3N_4 particulates

Orapim Namsar [a], Anucha Watcharapasorn [a,b], Sukanda Jiansirisomboon [a,b,*]

[a] Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
[b] Materials Science Research Center, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

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Abstract

Barium titanate/silicon nitride ($BaTiO_3/xSi_3N_4$) powder (when x = 0, 0.1, 0.5, 1 and 3 wt%) were prepared by solid-state mixed-oxide method and sintered at 1400 °C for 2 h. X-ray diffraction result suggested that tetragonality (c/a) of the $BaTiO_3/xSi_3N_4$ ceramics increased with increasing content of Si_3N_4. Density and grain size of $BaTiO_3/xSi_3N_4$ ceramic were found to increase for small addition (i.e. 0.1 and 0.5 wt%) of Si_3N_4 mainly due to the presence of liquid phase during sintering. $BaTiO_3$ ceramics containing such amount of Si_3N_4 also showed improved dielectric and ferroelectric properties.
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Keywords: C. Dielectric properties; C. Ferroelectric properties; D. $BaTiO_3$ and titanates; D. Si_3N_4

1. Introduction

$BaTiO_3$ has become one of the most important electroceramic materials among all the ferroelectric materials [1]. $BaTiO_3$-based ferroelectrics transform from paraelectric phase to ferroelectric phase at Curie temperature ($T_C \sim 130$ °C). This transformation normally causes a complicated stress system in this ferroelectric material, and then results in a generation of internal stresses at room temperature which significantly affect properties of $BaTiO_3$. Therefore, much attention has been paid into development of a new approach to enhance properties of $BaTiO_3$ ceramics. One of the most interesting methods is based on 'nanocomposites concept' [2] by an incorporation nanosized second phases into $BaTiO_3$ ceramic matrix [3–5]. This method has been found to be a promising way to improve mechanical properties and electrical reliability of $BaTiO_3$ matrix. However, there are only a few studies about the electrical properties of $BaTiO_3$-based nanocomposite. In the present study, aims to fabricate new ferroelectric $BaTiO_3$-based ceramics using nano-particle of non-oxide compound, *e.g.* Si_3N_4, using a solid-state mixed-oxide method. The characterization particularly in terms of phase evolution, microstructures changes, dielectric and ferroelectric properties of $BaTiO_3$ ceramics were reported and discussed.

2. Experimental

$BaTiO_3$ powder was prepared by a solid-state mixed-oxide method. The starting chemicals used were $BaCO_3$ (98.5%, Fluka, Buchs, Switzerland) and TiO_2 (99%, Fluka, Buchs, Switzerland). The starting powders were weighed, ball-milled in ethanol for 24 h and dried using an oven drying method. After drying, the mixed powders were calcined at 950 °C for 2 h. For the $BaTiO_3/Si_3N_4$ powders, different percentages by weight (0, 0.1, 0.5, 1 and 3) of nano-sized Si_3N_4 (96%, 30–70 nm, Nano Amor, Los Alamos, USA) powder were mixed with in-house prepared $BaTiO_3$ powder. Each batch of the mixture was prepared using the same procedure mentioned earlier to form $BaTiO_3/Si_3N_4$ powders. Green compacts were formed by uniaxial pressing into disc-shaped pellets. The disc samples were sintered at 1400 °C for 2 h.

Phase characterization of $BaTiO_3/xSi_3N_4$ ceramics was carried out using X-ray diffractometry (XRD, Phillip Model X-pert, Eindhoven, Netherlands). Density of ceramics was determined using Archimedes' method. Microstructures of

* Corresponding author at: Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand.
Tel.: +66 53 941921x631; fax: +66 53 943445.
E-mail address: sukanda@chiangmai.ac.th (S. Jiansirisomboon).

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sintered samples were examined using scanning electron microscopy (SEM, JEOL JSM-6335F, Tokyo, Japan). Average grain size was determined using a mean linear intercept method from SEM micrographs. Dielectric properties were measured at room temperature with a measured frequency of 100 kHz using LCR Hitester (Instek, 821, Tokyo, Japan). Ferroelectric hysteresis (*P–E*) loops were characterized using a computer controlled modified Sawyer–Tower circuit.

3. Results and discussion

Phase characteristics of $BaTiO_3/xSi_3N_4$ ceramics were revealed by X-ray diffraction patterns in Fig. 1. $BaTiO_3$ ceramic showed only tetragonal phase. A small amount of $Ba_2TiSi_2O_8$ phase started to appear for ceramic containing 1–3 wt% Si_3N_4 samples. This phase was likely to be the result of reaction between $BaTiO_3$ matrix and SiO_2 phase. The latter could be originally present in the starting powders or from decomposition of Si_3N_4 particles heated under oxidizing atmosphere [6] as in this experiment. Similar reaction product was also observed in $BaTiO_3$–SiC system when their mixtures were heated above 1300 °C [5].

The effect of the Si_3N_4 content on the unit cell of $BaTiO_3$ ceramic is shown in Fig. 2.

The incorporation of Si_3N_4 nanoparticles led to a reduction in lattice parameter of *a* and *c*, with a slight increase in tetragonality (*c*/*a*). The distortion of the unit cell could be partly due to the substitution of Si into Ti position. Based on the ionic radius of Si^{4+} ion ($r_{si}^{4+} = 0.40$ [7]), it would preferentially substitute Ti ($r_{Ti}^{4+} = 0.605$ [7]) sites rather than Ba^{2+} ($r_{Ba}^{2+} = 1.35$ [7]) site.

The density values of $BaTiO_3/xSi_3N_4$ composites are listed in Table 1. Although the density of $BaTiO_3$ was rather low, its value was close to a range of relative density values (i.e. ~90–99%) reported for $BaTiO_3$ ceramics sintered at about 1400 °C [5,8–10]. Addition of small amount of Si_3N_4 caused an apparent increase in density. This was most likely to be due to the effect of liquid phase sintering. Since 0.1 wt% and 0.5 wt% Si_3N_4 were too small to cause any large change in melting point of $BaTiO_3$, the second phase $Ba_2TiSi_2O_8$ which had much lower melting point than $BaTiO_3$ could form liquid at grain boundaries of $BaTiO_3$ and enhanced the densification rate. Further increasing Si_3N_4 content however caused a decrease in density. The result indicated that Si_3N_4 content had significant effect on densification of $BaTiO_3$ ceramics. Similar results have been observed in glassy phase-$BaTiO_3$ system which showed that the densification of $BaTiO_3$ depended not only on the amount of glass addition but also on the glass former content [11]. Moreover, Lee et al. reported that adding SiO_2 sintering aids more than 0.3 mol% into $(Ba_{0.96}Ca_{0.04})(Ti_{0.85}Zr_{0.15})O_3$ ceramics lead to decrease in density, indicating that densification of $(Ba_{0.96}Ca_{0.04})(Ti_{0.85}Zr_{0.15})O_3$ ceramics was strongly dependent on SiO_2 content [12]. According to the liquid phase sintering theory [13], a proper quantity of liquid phase present in liquid phase sintered ceramic is an important factor to control densification of the ceramic.

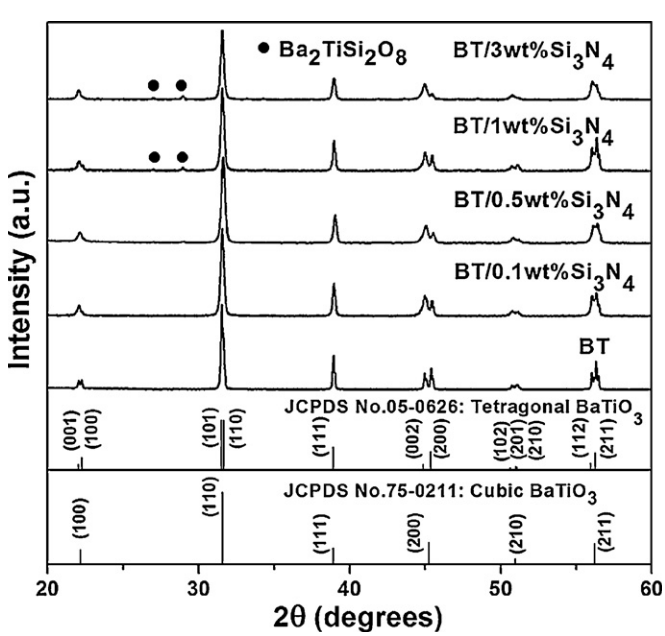

Fig. 1. XRD patterns of $BaTiO_3/xSi_3N_4$ ceramics.

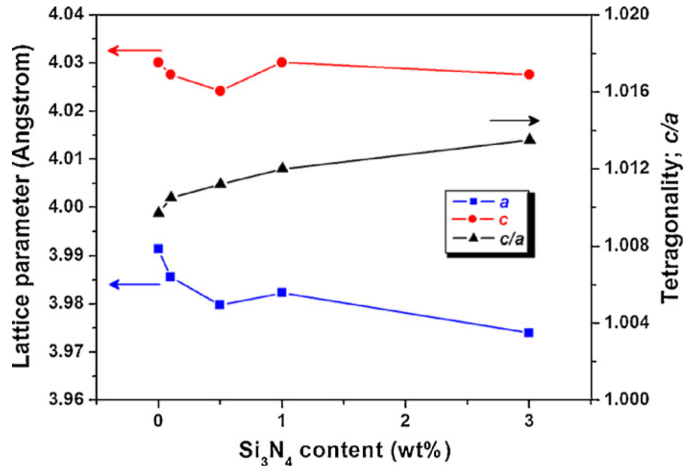

Fig. 2. Lattice parameter and tetragonality of $BaTiO_3/xSi_3N_4$ ceramics.

SEM micrographs of thermally etched surfaces for $BaTiO_3/xSi_3N_4$ ceramics are shown in Fig. 3. Equiaxed grains were observed for all samples. An increase in Si_3N_4 concentration dramatically increased the grain size of $BaTiO_3/xSi_3N_4$ ceramics as listed in Table 1. The extensive grain growth as well as the presence of flat content areas between grains could be associated with liquid-phase formation as mentioned earlier. From the study of Rase and Roy [14], the SiO_2–$BaTiO_3$ system also contained several low-melting point compounds besides $Ba_2TiSi_2O_8$. The existence of these liquid phases therefore gave rise to observed grain growth during sintering [15,16]. For samples containing 0.1 and 0.5 wt% Si_3N_4, the presence of liquid phase seemed to enhance densification by allowing pores to diffuse and be removed at grain boundaries, hence producing dense grain structure with improved density. However, adding more Si_3N_4 resulted in pore coalescence into the size as large as some of the grains. These large pores inhibited densification of grains and caused the samples to possess rather low density.

Table 1
Physical, dielectric and ferroelectric properties of $BaTiO_3/xSi_3N_4$ ceramics.

Si_3N_4 content (wt%)	Relative density (%)	Average grain size (μm)	Dielectric props.		Ferroelectric props.		
			ε_r^a	$\tan\delta^a$	P_r (μC/cm^2)	E_c (kV/cm)	R_{sq}
0	77.8	2.14 ± 0.53	3023	0.0364	3.72	4.55	0.59
0.1	96.5	12.61 ± 1.55	3279	0.0102	5.08	4.82	0.61
0.5	92.0	20.13 ± 2.79	3036	0.0131	4.67	5.02	0.62
1	89.4	22.07 ± 4.49	2225	0.0321	4.40	6.53	0.63
3	85.1	33.07 ± 5.84	1465	0.0339	3.17	8.06	0.70

Note: Dielectric data obtained at a frequency of 100 kHz; superscript *a* indicates room temperature, ε_r is dielectric constant; $\tan\delta$ is dielectric loss; P_r is remanent polarization; E_c is coercive field and R_{sq} is loop squareness.

The room temperature dielectric constant and loss of sintered ceramics measured at 100 kHz are listed in Table 1. The maximum dielectric constant was obtained for ceramic with 0.1 wt% Si_3N_4 addition. This could be resulted from its higher density compared to the other samples. The fall-off of dielectric constant in sample with higher Si_3N_4 content was due to lower sample density together with a higher amount of $Ba_2TiSi_2O_8$ and other secondary phases present in the samples.

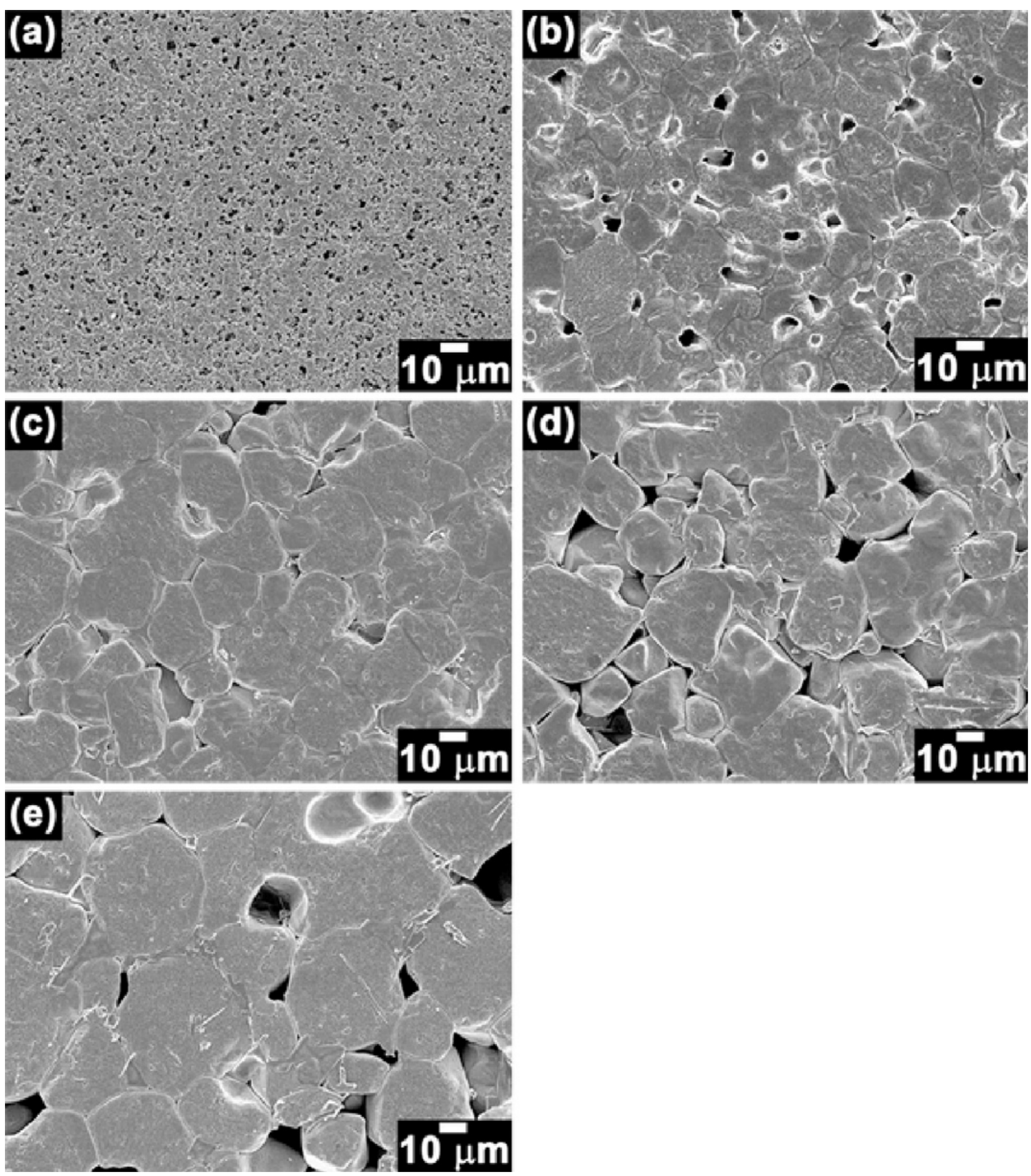

Fig. 3. SEM images of surfaces of $BaTiO_3/xSi_3N_4$ ceramics, where (a)–(e) represent $x = 0$, 0.1, 0.5, 1 and 3 wt%, respectively.

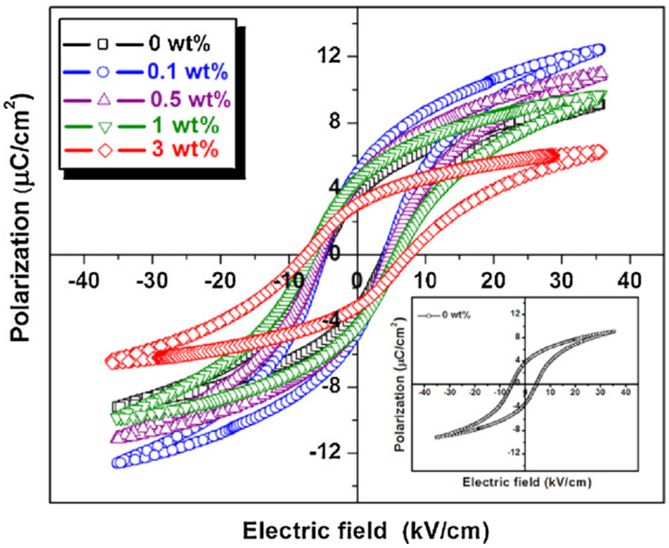

Fig. 4. *P–E* hysteresis loops of $BaTiO_3/xSi_3N_4$ ceramics measured at a frequency of 50 Hz.

The dielectric loss in $BaTiO_3/xSi_3N_4$ ceramics investigated in this study was found to have nearly the same value. The slightly lower dielectric loss in 0.1 and 0.5 wt% Si_3N_4 containing samples could be attributed to their relatively high density.

Ferroelectric properties of $BaTiO_3/xSi_3N_4$ ceramics in terms of *P–E* hysteresis loops plotted as a function of Si_3N_4 content are shown in Fig. 4. The values of remanent polarization (P_r) and coercive field (E_c) are also listed in Table 1. $BaTiO_3$ ceramic showed a slim ferroelectric loop with 4.55 kV/cm of E_c, 3.72 μC/cm^2 of P_r and 0.59 of loop squareness (R_{sq}). This result resembled with work of Chaisan et al. [17] whose $BaTiO_3$ sample showed a ferroelectric loop with 4.63 kV/cm of E_c, 7.78 μC/cm^2 of P_r and 0.49 of R_{sq}. These loops seemed to be typical hysteresis loop for $BaTiO_3$ ceramic [1]. Addition of 0.1 wt% Si_3N_4 enhanced ferroelectric activity such that the value of P_r increased while E_c remained nearly the same. This seemed to be the effect of large grain and high density of this sample. A further increase in Si_3N_4 reduced the value of P_r with corresponding increase in E_c, indicating that energy loss also increased in agreement with dielectric measurement. In these samples, both low density and the presence of secondary phase seemed to play a role in this reduced ferroelectric behaviour. Although, substitution of Si^{4+} into Ti^{4+} sites could also affect ferroelectric properties, its influence as isovalent ionic substitution was less than that of physical and microstructural aspects of these ceramics. In this study, therefore, Si_3N_4 could be used as additive to effectively change densification behaviour and microstructure of $BaTiO_3$ ceramics which, in turn, improved its dielectric and ferroelectric properties.

4. Conclusions

Monolithic $BaTiO_3$ and $BaTiO_3/xSi_3N_4$ ceramics were prepared by a simple solid-state mixed oxide method. $BaTiO_3$ ceramic was identified by X-ray diffraction method as a material with a perovskite structure having tetragonal phase. Addition of Si_3N_4 in $BaTiO_3$ ceramics resulted in a slightly smaller unit cell size while tetragonal structure was maintained. The grain size and density of $BaTiO_3/xSi_3N_4$ ceramic increased for the samples containing small amount of Si_3N_4. The enhancement was mainly due to the presence of liquid phase in the Si_3N_4 added. For small addition of Si_3N_4, both dielectric and ferroelectric properties were also improved, which was contributed to high density and better microstructural homogeneity of ceramic samples.

Acknowledgements

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