Microstructural Characterization and Dielectric Properties of Barium Titanate Solid Solutions with Donor Dopants

Yeon Jung Kim,* June Won Hyun, Hee Soo Kim, Joo Ho Lee, Mi Young Yun, S. J. Noh, and Yong Hyun Ahn[†]

*Department of Applied Physics, Dankook University, Yongin 448-701, Korea. *E-mail: yjkim80@dankook.ac.kr*
[†]*Department of Chemistry, GRRC, Dankook University, Yongin 448-701, Korea*

The correlation between the sintering temperature and dielectric properties in the Nb^{5+} and Ta^{5+} doped BaTiO₃ solid solutions have been investigated. The samples were sintered at temperatures ranging from 1250 to 1350 °C for 4 h in air. SEM, XRD and SEM/EDS techniques were used to examine the structure of the samples with particular focus on the incorporation of Nb^{5+} and Ta^{5+} ions into the BaTiO₃ crystal lattice. The X-ray diffraction peaks of (111), (200) and (002) planes of BaTiO₃ solid solution doped with different fractions of Nb^{5+} and Ta^{5+} were investigated. The dielectric properties were analyzed and the relationship between the properties and structure of doped BaTiO₃ was established. The fine-grain and high density of the doped BaTiO₃ ceramics resulted in excellent dielectric properties. The dielectric properties of this solid solutions were improved by adding a small amount of dopants. The transition temperature of the 1.0 mole% Ta^{5+} doped BaTiO₃ solid solution was ~ 110 °C with a dielectric constant of 3000 at room temperature. At temperatures above the Curie temperatures, the dielectric constant followed the Curie-Weiss law.

Key Words: BaTiO₃, Donor dopants, Dielectric properties, Curie-Weiss law

Introduction

Ferroelectric materials, particularly polycrystalline ceramics, have attracted considerable interest for applications in a variety of fields, such as high dielectric constant capacitors, pyroelectric sensors, piezoelectric/electrostrictive transducers, actuators, ferroelectric random access memories, electro-optic devices and positive temperature coefficient thermistors.[1,2] BaTiO₃ was the very first ceramic transducer. The discovery of ferroelectricity in BaTiO₃ ceramics was extremely important because it demonstrated for the first time that ferroelectricity can exist in simple oxide materials, and that it was not always associated with hydrogen bonding. At room temperature BaTiO₃ has tetragonal symmetry with the spontaneously polarization along the c-axis. Its dielectric maximum can be shifted towards room temperature by compositional substitution, and its dielectrics are sensitive to temperature, field strength and frequency, particularly near the Curie temperature. Figure 1 shows the basic structure of BaTiO₃ with Ti^{4+} ion occupying the octahedral coordinated site and the Ba^{2+} ion in the twelve coordinated sites in a high temperature Pm3m cubic symmetry. The ferroelectric phase at room temperature is tetragonal with O^{2-} and Ti^{4+} ions shifting to produce spontaneous polarization. In the ferroelectric state below the Curie temperature, T_C= 120 °C, spontaneous polarization occurs due to the non-centrosymmetric displacement of Ti^{4+} and O^{2-} ions relative to Ba^{2+} ions P4mm.[3] There is self-strain proportional to polarization that is associated with the phase transformation at T_C. The interrelationship between the anomalous electromechanical, structural and thermal properties of BaTiO₃ was modeled phenomenologically by Devonshire.[4] Pure BaTiO₃ is an excellent insulator with a large energy gap (~ 3.05 eV at room temperature) that becomes semiconducting when doped with small quantities of
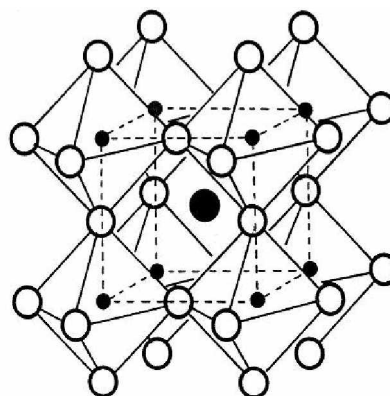
Figure 1. Basic perovskite structure of BaTiO₃ with the Ba^{2-} ion in the center of the cell and Ti^{4+} ions inside the oxygen octahedra.

donor ions. Semiconducting BaTiO₃ can be produced by replacing the Ba^{2+} ion sites with a trivalent ion (e.g. La^{3-}, Sb^{3-}, Y^{3+}), or with a pentavalent ion (e.g. Nb^{5-}, Ta^{5-}) on the Ti^{4+} ion sites.[5,6] This substitution is charge compensated by a valence shift, providing a shallow donor level from which electrons can be excited into the 3d conduction band. When the doping concentration exceeds a certain limit, it changes into an insulator again due to the formation of ionic defects that compensate for the extra charge from the donors. Nb^{5-} and Ta^{5-} are example donor dopants. Because Nb^{5-} and Ta^{5+} ions have different valences to that of Ba^{2+} or Ti^{4+} ions, substitution with Nb^{5-} or Ta^{5+} ions causes charge imbalance and charge compensation requiring the production of electrons, electron holes, or vacancies. The powder processing and sintering conditions have a strong influence on the mechanism of doping, creation of defects, the crystalline structure obtained and finally, the properties of BaTiO₃ ceramics.

This study examined the effects of pentavalent donor

dopants on the microstructure and dielectric properties of doped BaTiO₃ ceramics with the ultimate aim of developing an environment-friendly, lead-free ceramic capacitor in the electronic device industry.

Experimental Procedure

Reagent-grade oxide powders of BaO, TiO₂, Nb₂O₅ and Ta₂O₅ with purity better than 99% were used as starting raw materials. The powders were doped with Nb₂O₅ and Ta₂O₅ at concentrations ranging from 0.5 ~ 1.0 mole%. The completion of the reactions and structure of the material was confirmed by X-ray diffraction (XRD) using a laboratory diffractometer with Cu radiation. The calcined powders were reground with the addition of a few drops of PVA and cold-pressed into pellets, approximately 5 mm thick and 12 mm in diameter. The pellets were first heated to 500 °C in an alumina crucible for 1 h in to drive off the PVA, and then sintered at 1250 ~ 1350 °C for 4 h in an alumina crucible to form highly densified ceramics. The XRD patterns confirmed the formation of perovskite phases with no evidence of impurities. The fractured surface of sintered pellets were examined by scanning

electron microscopy (SEM). Temperature dependence of the dielectric constant and loss were measured at various frequencies (0.1 to 1000 kHz) at a heating rate of 4 °C/min by using an LCR meter, an environment chamber, and a control unit and its interface. Prior to the dielectric measurements, the specimens were poled by applying a DC field of approximately 15 kV/cm while cooling from well above the transition to a temperature well below.

Results and Discussion

Microstructure and XRD Analysis. Modification of the BaTiO₃ solid solution by the addition of Nb⁵⁺ and Ta⁵⁺ has marked effects on the basic properties of ceramics, such as dielectric constant, pyroelectric coefficient, and densification. Powders obtained after calcination were fine-grained, which influenced the consolidation, densification and sintering behavior significantly. Small amounts of additives to the base composition increased the sintered density. The density of Nb⁵⁺ and Ta⁵⁺ doped BaTiO₃ (sintered at 1300 °C for 4 h) is approximately 85 ~ 88% of the theoretical density. Scanning electron micrographs of fracture surface of the 1.0 mole%
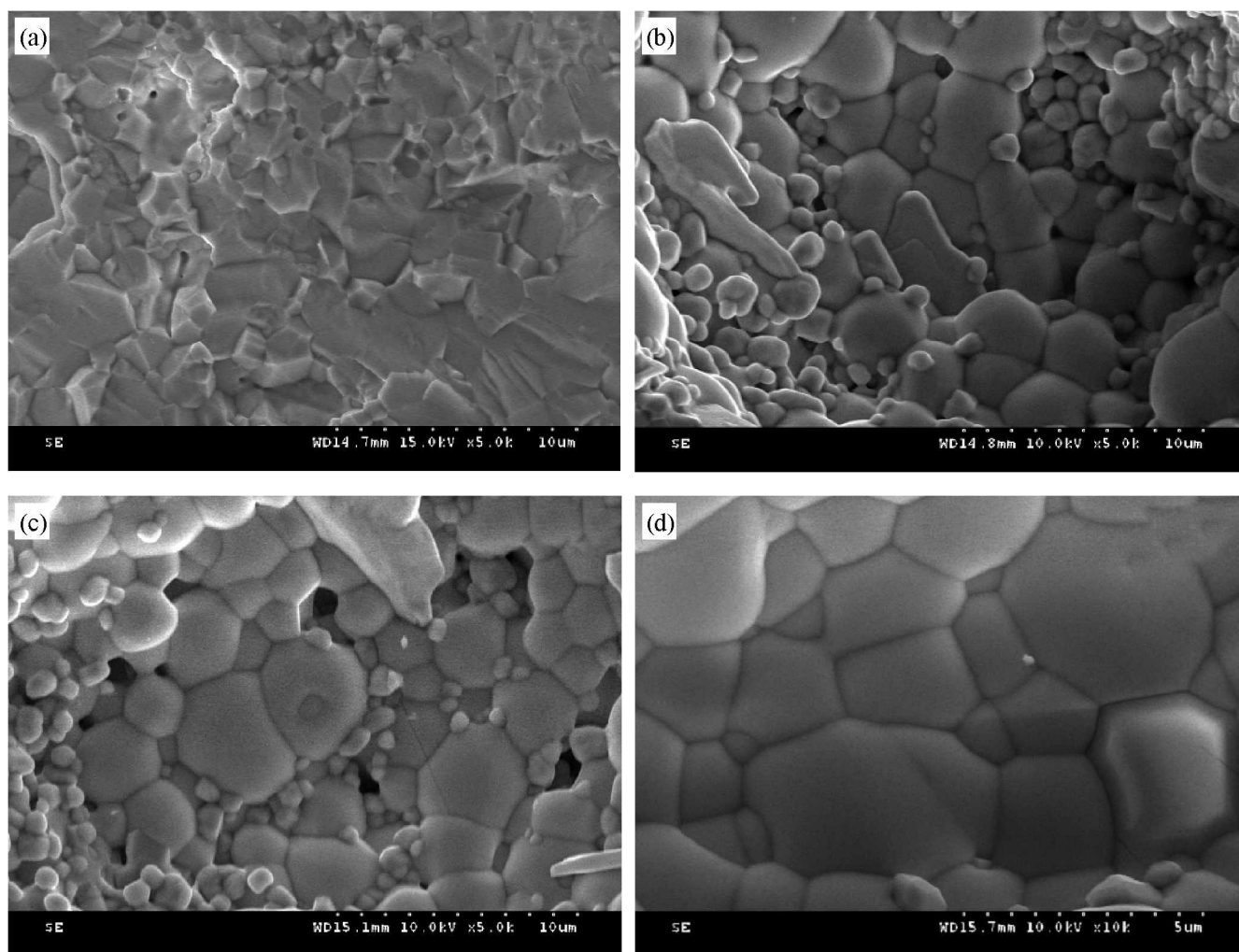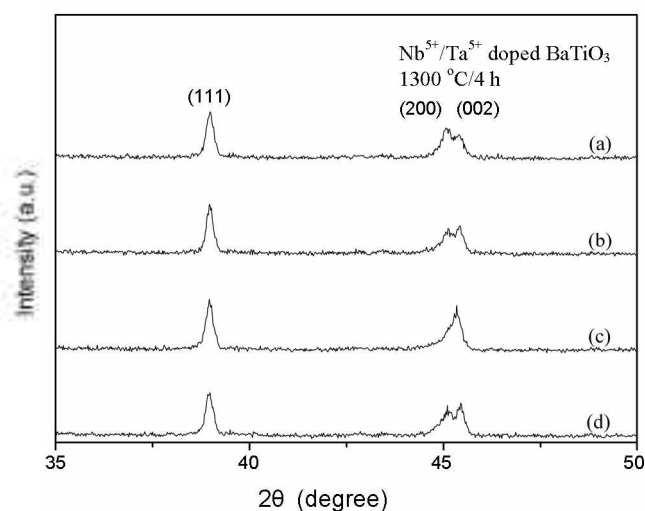

Figure 2. SEM micrographs of fracture surfaces at sintered (a) 1250 °C (b) 1270 °C (c) 1285 °C (d) 1300 °C of 1.0 mole% Ta⁵⁺ doped BaTiO₃ ceramics.
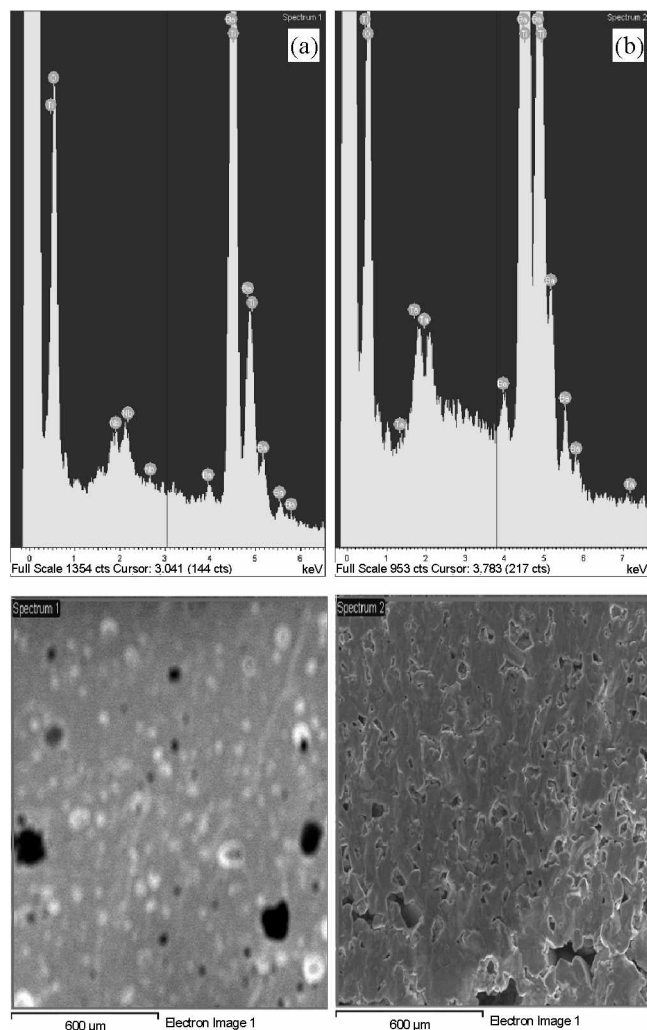
Figure 3. SEM/EDS spectrum of (a) 1.0 mole% Nb^{5-} and (b) 1.0 mole% Ta^{5+} doped BaTiO₃ ceramics sintered at 1300 °C.

Figure 4. XRD patterns of (111), (200) and (002) plane of BaTiO₃ ceramic doped with different fractions of Nb_2O_5 and Ta_2O_5. (a) 1.0 mole% Ta^{5-} (b) 0.5 mole% Ta^{5-} (c) 1.0 mole% Nb^{5-} (d) 0.5 mole% Nb^{5-}.

Ta^{5+} doped BaTiO₃ solid solution sintering at various temperatures are shown in Figure 2 and show increasing grain size with increasing sintering temperature. The sample sintered at 1250 °C showed smaller grain size (< 1.0 μm) where as large grain sizes (1.5 ~ 3 μm) were observed for the samples sintered at 1300 °C as shown in Figure 2. When dopants substitutes Ba^{2+} and Ti^{4+}, the differences in radii and valence of Nb^{5+} and Ta^{5+} dopants, Ba^{2+} and Ti^{4+} will lead to variance in the vacancy concentration in crystals in order to compensate the charge. As observed, the solid solutions sintered at 1300 °C showed a dense microstructure with enlarged grains which are substantially free from pores. There are two microstructure regions that differ in grain size and phase composition. Some residual porosity is evident after 4 hours sintering but no evidence was found for the growth of abnormally large grains. The outstanding feature in these specimens is the presence of a non homogeneous phase composition throughout the specimens.[8] Nb^{5+} and Ta^{5-} doped BaTiO₃ ceramics exhibited normal grain growth, a fairly uniform microstructure and homogeneous distribution of additives. In Nb^{5+} and Ta^{5-} doped BaTiO₃ ceramics, the average grain size ranges from 1.5 ~ 3 μm.

The corresponding EDS spectrum indicates that the regions rich in Nb^{5+} ions were associated with non homogeneous grains. The presence of non-ferroelectric regions leads to a decrease in dielectric constant due to the non-uniform distribution of Nb^{5+} and its segregation in the local parts of the samples (in Figure 3). Isovalent impurities in BaTiO₃ ceramics do not significantly affect the bulk electrical conductivity, while off-valent impurities affect both the ferroelectric behavior and the conductivity. In many carriers the addition of impurities can significantly affect the crystallization kinetics of ceramics, since the diffusion kinetics during the sintering process can be greatly affected by the presence of impurities or charge-compensation defects. Dopants have a considerable effect on the properties of BaTiO₃. However, in addition to the variety of functions that a dopant can display, an analysis of the role of the dopant is rather complicated. Nb^{5-} and Ta^{5+} at lower concentrations enhances grain growth thereby improving the properties. On the other hand, they inhibit grain growth and alter the electrical properties at levels close to or above the dopant solubility in BaTiO₃.[9] Ta^{5+} has a prominent influence on grain growth and can enhance grain growth. Indeed, the major role of both donor cations (Nb^{5-} and Ta^{5+}) is their ability to influence the grain boundary mobility because charge compensation has an important effect. Substitution by Nb^{5-} produces charge imbalance due to its different oxidation state. In terms of the ionic radius, Nb^{5-} can substitute for Ti^{4+} at the B-site perovskite lattice. Therefore, an ion with a higher valence state substitutes for an ion with the lower valence state resulting in charge imbalance and the creation of a defect structure of BaTiO₃. All doped BaTiO₃ samples investigated had a tetragonal phase in the P4mm space group. Unit cell refinement showed that the tetragonality of BaTiO₃ was changed by introducing Nb^{5-} and Ta^{5-}. In addition to the above equilibrium mechanisms, segregation of the Ti-rich phase with incorporated Nb^{5-} can be also expected in BaTiO₃ based ceramics. Although only few regions rich in Nb^{5-} were detected by EDS, their influence on the microstructural uniformity was negligible, as reported in reference.[10] When Nb^{5-} and Ta^{5+}

1270   *Bull. Korean Chem. Soc.* **2009**, Vol. 30, No. 6

Yeon Jung Kim et al.

(a)

(b)
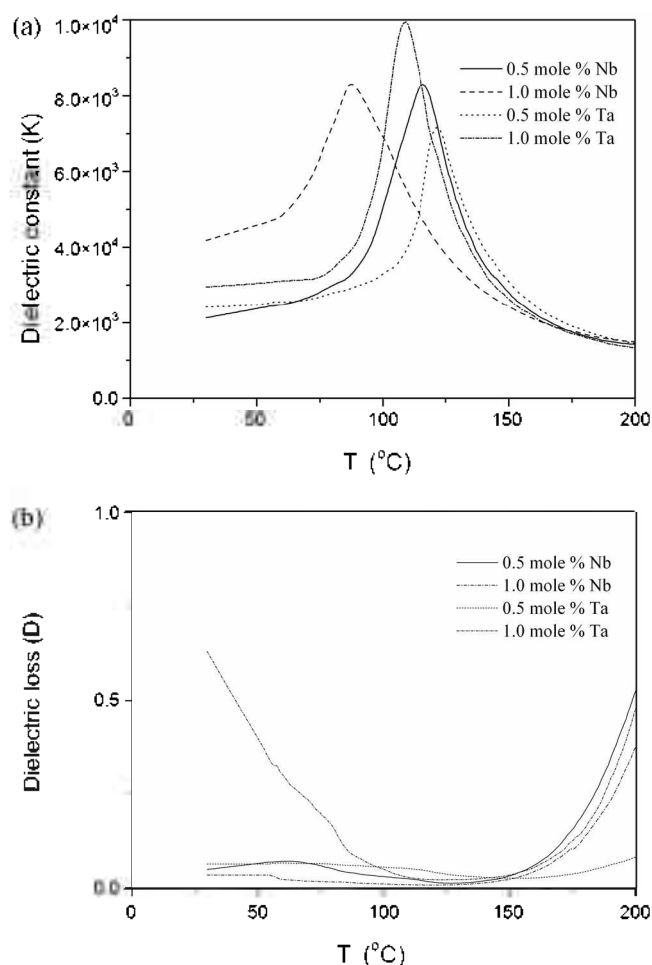
Figure 5(a, b). Dielectric constant and loss of Nb^{5+} and Ta^{5+} doped and $BaTiO_3$ as a function of temperature.

substitutes for Ba^{2+} and Ti^{4+}, the differences in the radii and valence of Nb^{5+}, Ta^{5+}, Ba^{2+} and Ti^{4+} will lead to variations in the vacancy concentration in the crystals in order to compensate for the charge. Generally, the energy needed to incorporate a dopant ion into an individual lattice site in complex oxides is related to distortions (different in ionic radii), and to the formation of compensating defects during the incorporation of aliovalent ions (different in valence). Therefore, the solubility at the two different lattice sites of $BaTiO_3$ is influenced by the energy required to form compensating defects. However, no energy is needed for the dopants to concentrate at the grain boundaries. Therefore, there is a high concentration of Nb^{5+} and Ta^{5+} ions at or near grain boundaries that restrict abnormal grain growth during sintering, which promotes the formation of $BaTiO_3$ with fine grains and high density. The microstructure of $BaTiO_3$ ceramic doped with Nb^{5+}, Ta^{5+} at different concentrations (sintered at 1300 °C) was examined. Ta^{5+} doped $BaTiO_3$ sintered at 1300 °C had a fairly uniform microstructure with normal grain growth. EDS detected some Nb^{5+} or Ta^{5+} rich regions. The additive rich phases were formed in local regions due primarily to insufficient homogenization of the starting powders. For the polygonal grains, EDS did not show the presence of Nb^{5+}, while there was a considerable quantity of Nb^{5+} in the irregular grains. The presence of a
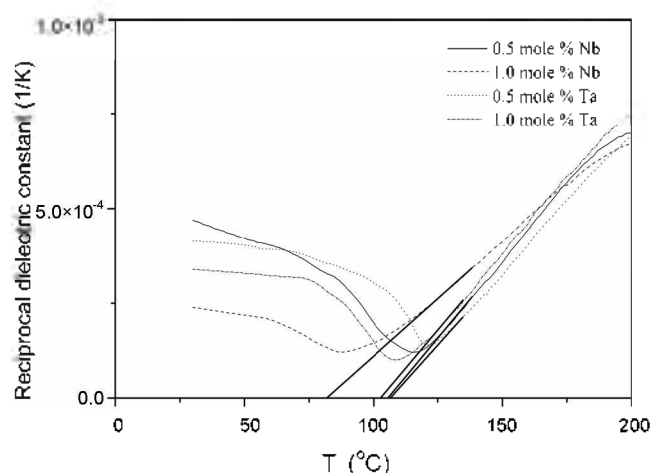
Figure 6. Temperature dependence of the reciprocal dielectric constant in the vicinity of the transition temperature of $BaTiO_3$ ceramics sintered at 1300 °C, which were measured at 1 kHz.

chemically inhomogeneous system in Nb^{5+} doped $BaTiO_3$ samples causes a decrease in the dielectric constant that is different from Ta^{5+} doped $BaTiO_3$ ceramics.

Figure 4 shows the XRD peaks of the (111), (200) and (002) planes of $BaTiO_3$ ceramic doped with different fractions of Nb_2O_5 and Ta_2O_5. The X-ray diffraction pattern showed a tetragonal perovskite structure for Nb^{5+} and Ta^{5+} doped $BaTiO_3$ ceramics. No evidence of the precursor phase BaO, TiO_2, Nb_2O_5 and Ta_2O_5 was detected by XRD. In each case, the observed diffraction peaks showed no evidence of phase coexistence. However, an analysis of peak broadening shows that the two compositions behave quite differently. In general, there are two phases of $BaTiO_3$, tetragonal and cubic. From the measurements, the strongest reflections apparent in most of the XRD patterns indicate the formation of two $BaTiO_3$ phases. The tetragonal and cubic phases were identified by an analysis of the 002 (tetragonal), 200 (tetragonal), 200 (cubic) peaks at $43 \sim 48°$ in the range 2θ. Splitting of the (002) and (200) peaks indicates a tetragonal phase, while a single (200) peak confirms a cubic phase.

Dielectric properties. A simple way of determining the dielectric constant is to measure the capacitance of a parallel plate capacitor containing the ferroelectric substance as the dielectric.[11] The dielectric displacement vector $\overrightarrow{D}$ represents the total surface charge density induced in the dielectric

$$\overrightarrow{D} = \epsilon_0 \overrightarrow{E} + \overrightarrow{P} = (1 - \chi)\epsilon_0 \overrightarrow{E} \qquad (1)$$

where ϵ_0, $\overrightarrow{E}$, $\overrightarrow{P}$, and χ is the permittivity of a vacuum, electric field, polarization and dielectric susceptibility, respectively. Figure 5(a) shows the temperature dependence of the dielectric constant as a function of the Nb^{5+} and Ta^{5+} doping concentration. This indicates that the Curie temperature of the $BaTiO_3$ ceramic with a Ta^{5+} doping concentration ranging from 0.5 to 1.0 mole% was similar to that of the pure $BaTiO_3$ ceramic. The highest value of dielectric constant at room temperature $(K_{25°C} \sim 4000)$ and the greatest change of permittivity in
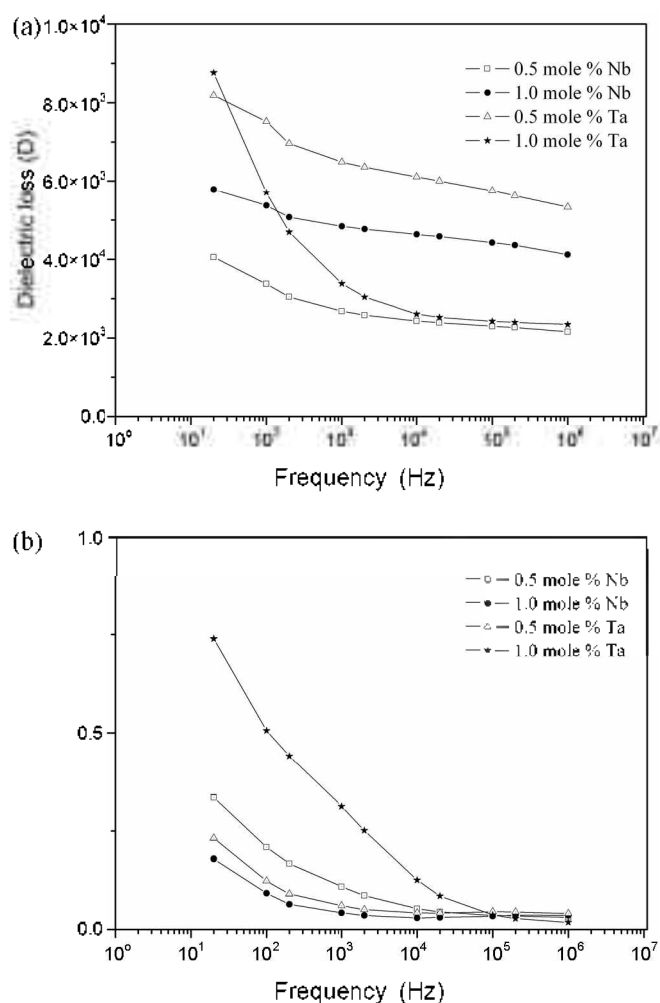
Figure 7. Frequency dependence of the (a) dielectric constant and (b) loss of doped BaTiO₃ ceramics samples sintered at 1300 °C.

function of frequency was observed in 1.0 mole% Nb^{5+} doped BaTiO₃ ceramics. Dielectric constant in 1.0 mole% Ta^{5+} doped BaTiO₃ at room temperature is ~ 3000. The dielectric constant reached 9800 at a Ta^{5+} concentration of 0.5 mole %. A characteristic tetragonal-cubic phase transition, from a ferroelectric to paraelectric phase of BaTiO₃ was observed. In general, the dielectric constant *vs.* temperature response and a sharp phase transition, from ferroelectric to paraelectric phase at Curie temperature, are observed for Nb^{5+} doped BaTiO₃ and Ta^{5+} doped BaTiO₃ solid solutions. The dielectric constant, insulation resistance, and breakdown field strength are important engineering parameters for high voltage ceramic capacitors. The maximum voltage withstanding ability of a ceramic capacitor is governed mainly by the microstructure of the ceramic, such as uniformity and average grain size.[12] Hence, fine grains would promote a high-density microstructure. The domains can be oriented using an externally applied electric field during the course of polarization. Orientation of the domains will lead to strain in the dielectric ceramics. The change in dielectric constant with temperature for the samples at various compositions (Figure 5a) confirmed Nb^{5+} and Ta^{5+} to have a significant effect on the dielectric properties.

Besides, Nb^{5+} and Ta^{5+} ions in BaTiO₃ will replace Ti^{4+} to form solid solution. Though this replacement will not change the structure form of the original BaTiO₃, however it will more or less distort the crystalline lattice which lead to shift the Curie peak to lower temperature and give effect on the dielectric property of the ceramic material. The addition of Nb^{5+} leads to an increase in the dielectric constant but the dielectric constant at room temperature was quite low, ranging from 2000 to 3000. Considering the influence of dopants and their concentration on the properties of BaTiO₃, it is clear that the properties are also strongly dependent on the grain size, which is affected by the process of powder preparation. Overall, it is possible to establish a certain relationship between the structure and properties of doped BaTiO₃. First, the introduction of a dopant in pure BaTiO₃ affects the crystal structure by changing the tetragonality of the crystal lattice. Nevertheless, this change is rather small. Nb^{5+} ions have a larger effect than Ta^{5+} ions. This is a result of the creation of various types of defects, higher concentrations of defects in the crystal structure, as well as the Nb^{5+} ion exchanges for Ti^{4+} ions at the B site of ABO₃ (higher coordination number), which influences the total effect of the dopant. The introduction of dopants alters the charge balance in the crystal lattice of BaTiO₃ because an ion with a higher valence substitutes for an ion with a smaller valence state. The local structure around Ba^{2+} and Ti^{4+} atoms remained rhombohedral. A slight amplitude increase in the Fourier transform first peak compared with the undoped sample can be related to a decrease in local disorder. Therefore, the addition of Nb^{5+} and Ta^{5+} induces a decrease in local disorder around the Ba^{2+} atoms, and has a rather small influence on the local structure of Ti^{4+}. Finally, the dielectric behavior of pure and doped BaTiO₃ confirmed the presence of a tetragonal phase at room temperature and phase transition from a tetragonal to cubic phase at the Curie temperature. This is in agreement with the results obtained by XRD. The dopants influenced the change in the temperature of the phase transition. A higher concentrations of dopants decreased the Curie temperature. Owing to that the volume fraction of shell-core structure for different BaTiO₃ grain is different, which will give rise to diffuse the Curie point to a broad temperature range, as a result, to flatten the dielectric constant peak of the material. In Nb^{5+} and Ta^{5+} doped BaTiO₃ ceramics two different microstructure regions (in Figure 3), where a chemically inhomogeneous systems are formed, together with a considerable amount of cubic phase the already existing at temperature below transition temperature, govern overall dielectric properties.

Figure 6 shows the change in the reciprocal dielectric constant (1/K) with temperature in the vicinity of the transition temperature of Nb^{5+} and Ta^{5+} doped BaTiO₃ ceramics sintered at 1300 °C. 1.0 mol% of the additive has a small effect on the intrinsic dielectric parameter, such as the Curie temperature because it was not distributed uniformly in the samples. A flat dielectric response in the transition zone was observed for Nb^{5+} doped BaTiO₃ in which the para-electric regions reduce the dielectric constant significantly. The dielectric behavior above the Curie temperature can be characterized by Curie-Weiss law:[6]

$$K = \epsilon_0 + \frac{C}{T - T_0} \qquad (2)$$

where C is the Curie constant and T_0 is the Curie-Weiss temperature, which is close to the Curie temperature. Generally, $T < T_C$ in the case of a first-order phase transition. On the other hand, $T = T_0$ for a second-order phase transition. The dielectric data clearly showed a first-order phase transition and excellent Curie-Weiss behavior. The Curie constant obtained for this sample was $1.8 \times 10^5\,^\circ$C, which is in good agreement with the value reported for pure BaTiO₃ [1]. According to the Curie-Weiss law, $1/K$ temperature curves were fitted and the corresponding Curie constants were calculated. Regardless of the type of additive, there were no deviations from Curie-Weiss law detected. This exception of the Curie constant in Nb₂O₅ doped specimens ($1 < C < 2.36$) to that ones calculated in Nb^{5+} or Ta^{5-} doped BaTiO₃ ($1 < C < 2.33$) might be due to the synergistic effect of Nb^{5-} and Ti^{4-} ions during the sintering of BaTiO₃. Ta^{5-} ions lead to the formation of a core-shell structure, with a BaTiO₃ core and Ti^{4-} modified BaTiO₃ shell.[12] Nb^{5-} ions segregating at grain boundaries act as grain growth inhibitors. Since the doped BaTiO₃ samples exhibited a different dielectric behavior, it was expected that the Curie constant would be quite sensitive to the type and concentration of the additive.[13]

Figure 7(a,b) shows the frequency dependence of the dielectric constant and loss for Nb^{5+} and Ta^{5+} doped BaTiO₃ ceramics at room temperature. At a frequency of 1 kHz, the dielectric constant increased from 2500 to 5000 and the dielectric loss decreased from 0.125 to 0.052 with increasing Nb^{5+} content from 0.5 to 1 mole%. For each sample, the dielectric constant and loss decreased with increasing frequency. However, the dielectric loss increased slightly at high frequency. The trend is similar to that reported by other groups. It should be noted that 1.0 mole% Ta^{5+} doped BaTiO₃ showed a higher dielectric constant and lower dielectric loss, highlighting its suitability in electro-optics device applications. The observed microstructure along with the type of additive have a direct influence on the dielectric properties of doped BaTiO₃. The highest dielectric constant at room temperature and largest change in dielectric constant as a function of frequency was observed in the 0.5 mole% Ta^{5+} doped BaTiO₃ ceramics. The dielectric constant in the 0.5 mole% Ta^{5-} doped BaTiO₃ samples at room temperature was 3500. In the Nb^{5-} doped BaTiO₃ sample, where a chemically inhomogeneous system was formed, the overall dielectric behavior was governed by two different microstructure regions, as shown in Fig. 2, which led to a decreasing dielectric constant compare with the same one in the Ta^{5-} doped BaTiO₃ ceramics. The lowest dielectric constant of only 2500 was noticed in the 0.5 mole% Nb^{5+} doped BaTiO₃ samples. Due to the presence of Nb^{5+} rich regions, a significant part of the sample exhibited non-ferroelectric behavior. In all samples investigated, the dielectric constant after an initially large value at low frequency reached a constant value at $f \geq 10$ kHz. Regarding the loss factor, the largest dielectric loss and greatest change in the function of frequency was detected in Ta^{5+} doped BaTiO₃ (Figure 7b). The influence of the appropriate additive on the dielectric

behavior of doped BaTiO₃ was analyzed by plotting the dielectric constant as a function of temperature, as shown in Fig. 4a. In general, the dielectric constant vs. temperature response and a sharp phase transition from ferroelectric to paraelectric phase at the Curie temperature were observed for both Nb^{5+} and Ta^{5-} doped BaTiO₃ samples. In the Nb^{5-} doped BaTiO₃ samples, the overall dielectric behavior was governed by the two different microstructure regions, a chemically inhomogeneous systems and a considerable amount of paraelectric phase that already existed at temperatures below the Curie temperature.

Conclusions

The microstructure and dielectric properties of BaTiO₃ ceramics doped with Nb^{5+} and Ta^{5-} were examined. The results show that at a Nb^{5+} and Ta^{5+} concentration of 0.5 mole%, abnormal grain growth was inhibited and the lattice parameters of the grain increased to a maximum because of the lowest vacancy concentration. In addition, the fine-grain and high density of BaTiO₃ resulted in excellent dielectric properties. The dielectric behavior of doped BaTiO₃ is in agreement with the presence of the tetragonal structure observed by XRD. The influence of the dopants as well as powder processing was rather significant. The dielectric constant was 3000 at room temperature. These results indicate that the introduction of dopants such as Nb^{5-} and Ta^{5+} did not cause significant changes to the local structure around Ti^{4+} atoms, and according to the results published in the literature, the local structure is similar to that of a pseudocubic (rhombohedral) phase. The highest dielectric constant at room temperature and greatest change in dielectric constant as a function of temperature were observed in Nb^{5-} and Ta^{5+} doped BaTiO₃, which was characterized by the fairly uniform microstructure with a homogeneous distribution of the additive. The Curie temperature for all samples investigated was lower than that of pure BaTiO₃ ceramics. A linear decrease in the dielectric constant with frequency up to 1000 kHz was observed in all specimens. A slight shift in the Curie temperature to a lower temperature than that for pure BaTiO₃ was observed in all samples investigated.

References

1. Moulson, A. J.; Herbert, J. M. *Electroceramics*; Wiley Press: New York, 2003.
2. Uchino, K. *Ferroelectric Devices*; Marcel Dekker, Inc.: New York, 2000.
3. Kay, H. F.; Vousden, P. *Phil. Mag.* **1949**, *40*, 1019.
4. Devonshire, A. F. *Phil. Mag.* **1949**, *40*, 1040, and *Phil. Mag.* **1951**, *42*, 1065.
5. Buchanan, R. C. *Ceramic Materials for Electronics Processing*,

Properties, and Applications; Marcel Dekker Inc.: 1991.
6. Lines, M. E.; Glass, A. M. *Principles and Applications of Ferroelectrics and Related Materials*; Clarendon Press: Oxford, 1977.
7. Makovec, D.; Samardzijia, Z.; Drofenik, M. *J. Am. Ceram. Soc.* **2004**, *87*, 1324.
8. Mitic, V.; Paunovic, V.; Zivkovic, L.; Stojanovic, B. *Proc. of Sintering 2003*; Pennsylvania, 2003; p 757.

9. Frenkel, M.; Frey, M. H.; Payne, D. A. *J. Synshrotron Rad.* **1999**, *6*, 515.
10. Mitic, V.; Paunovic, V.; Vracar, L.; Zivkovic, L. *Transactions of the Materials Research Society of Japan*, **2004**, *29*(4), 1163.
11. Trainer, M. *Am. J. Phys.* **2001**, *69*(9), 966.
12. Chiang, S. K.; Lee, W. E.; Readey, D. W. *Am. Ceram. Bull.* **1987**, *66*(8), 1230.
13. Vittayakorn, N. J. *Appl. Sci. Res.* **2006**, *2*(12), 1319.