**Research Paper**

# Effects of Nb$^{5+}$ Addition on Microstructure and Dielectric Properties of BaTiO$_3$

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**Abstract** Structural studies on the addition characteristics of Nb ions to BaTiO$_3$ solid solutions were performed by XRD and SEM/EDS technique. The X-ray diffraction peaks of the (111), (200) and (002) planes of Nb-doped BaTiO$_3$ solid solutions with different mole% of Nb were analyzed. We also investigated the relationship between the dielectric and structural properties of Nb-doped BaTiO$_3$. The transition temperatures of BaTiO$_3$ solid solution doped with 0.5mole%Nb and 1.0 mole%Nb were ~116$^o$C and ~87$^o$C, respectively, which were found to be shifted to very low temperature from the transition temperature of pure BaTiO$_3$ (about 125$^o$C). As a result of analysis of 1/K versus T and ln[(1/K)-(1/K$_m$)] versus (T-T$_m$)] of the two compositions used in this experiment, the diffusivity slightly differs from that of pure BaTiO$_3$ at temperatures above Curie temperature. And this characteristic was analyzed by applying the modified Curie-Weiss law.

**Keywords:** Nb-doped BaTiO$_3$, SEM/EDS, Dielectric properties, Modified Curie-Weiss law

## I. Introduction

Ferroelectric BaTiO$_3$ (BT) which has been actively studied since the early 1940's, has been studied extensively in the scientific and industrial fields. The discovery of BT affected every field of applications on ferroelectric materials, especially in the field of lead-free materials. The structure of BT in at high temperature Pm3m cubic phase, and at room temperature is tetragonal phase. In the ferroelectric state below the Curie temperature, a spontaneous polarization arises due to the noncentrosymmetric displacement of Ti$^{4+}$ and O$^{2-}$ ions relative to Ba$^{2+}$ ions P4mm [1-3]. It is known that pure BT is an insulator with a large energy gap (~3.05 eV at room temperature) and becomes semiconducting when slightly doped with donor ions [4,5].

Adding a suitable impurity to BT can move its dielectric maximum temperature to room temperature. It is also possible to improve the sensitivity of temperature, electric field strength and frequency around the Curie temperature. By adding a strictly and appropriately selected impurity to BT, its transition temperature can be shifted to room temperature. In addition, sensitivity to temperature, electric field intensity, and frequency can be improved near room temperature and Curie temperature.

The purpose of this paper is to investigate the effect of the 5-valent (Nb$^{5+}$) donor dopant on the microstructure and

dielectric properties of Nb-doped BT (BTNb) ceramics based on our previously reported research data [6]. In addition, this study is to develop lead-free environment-friendly ceramic composition which is indispensable in the electronic material industry.

## II. Experimental Procedure

BTNb ceramics were prepared by using the raw materials of BaO, TiO$_2$, and Nb$_2$O$_5$ oxides. The powders are doped by Nb$_2$O$_5$ with an amount from 0.5?1.0mole% of dopant ions. The optimum sintering temperature in this experiment was 1300°C. In the case of BT, it is known that charge imbalance occurs when Ba/Ti is substituted with Nb$^{5+}$ because it has a different valence from that of Ba$^{2+}$ and Ti$^{4+}$ ions.

$$2BaO + Nb_2O_5 \rightarrow 2Ba_{Ba} + 2Nb_{Ti} + 6O_o + \frac{1}{2}O_2(g) + 2e' \quad \text{(Eq.1)}$$
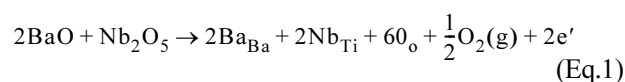
The Nb is an example of a donor dopant. As a consequence, a reduction in the titanium valence (Ti$^{4+}$ to Ti$^{3+}$) is produced, and structures like Ba$^{2+}$(Ti$_{1-2x}$$^{4+}$ + 4Nb$_x$$^{5+}$ + 5Ti$_x$$^{3+}$)O$_3$ could appear. This is similar to the study of the addition of other low/high valence dopants (Dy$^{3+}$, La$^{3+}$, Mn$^{2+}$, Sb$^{3+}$, Ta$^{5+}$, Y$^{3+}$) to BT [7-10]. X-ray diffraction patterns obtained on a laboratory diffractometer with Cu$K\alpha$ radiation confirmed the formation of perovskite phases with no evidence of any impurities. Dielectric

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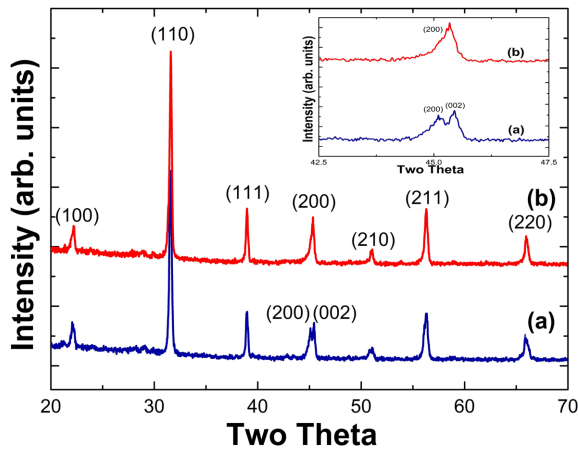E-mail: yjkim80@dankook.ac.kr

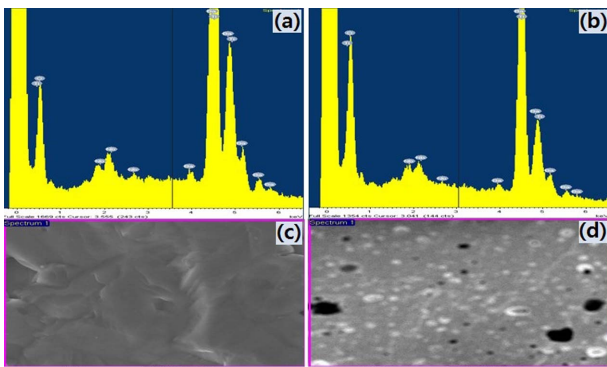**Figure 1. XRD patterns of (111), (200) and (002) plane of Nb-doped BaTiO₃. (a) 0.5 mole%Nb (b) 1.0 mol%Nb.**



**Figure 2. SEM/EDS spectrum of Nb-doped BaTiO₃. (a, c) 0.5 mole%Nb (b, d) 1.0 mol%Nb.**



**Figure 3. Frequency dependence of dielectric constant and loss of Nb-doped BaTiO₃.**

constants and losses were measured at a temperature increase rate of 4°C/min from 20°C to 300°C, and the frequency range was 10 Hz to $10^6$ Hz.

## III. Results and Discussion

Pure BT has two phases, tetragonal and cubic. Fig. 1 shows the X-ray diffraction peaks of (111), (200) and (002) planes of BTNb. The observed diffraction peaks did not show evidence of phase coexistence, but by analyzing the diffusion of the XRD peaks, it is possible to know characteristics of the phases different from those of pure BT by doping Nb ions. This XRD measurement results strongly indicate the formation of two BT phases. Analysis of 002 (tetragonal), 200 (tetragonal) and 200 (cubic) observed at 43~48° confirmed tetragonal and cubic phases. As shown in the inserted figure in Fig. 1, the (002) and (200) peaks of the sample doped with 0.5mole%Nb exhibit a tetragonal phase, while the (200) peak of the sample doped with 1.0 mole%Nb identifies the cubic phase.

EDS is typically used to find the abundance of a particular element present in a material. Crystals doped with Nb in BT cause charge imbalance due to the different oxidation states. Fig. 2 shows SEM/EDS images of BTNb sintered at 1300°C for samples containing 0.5 mole%Nb
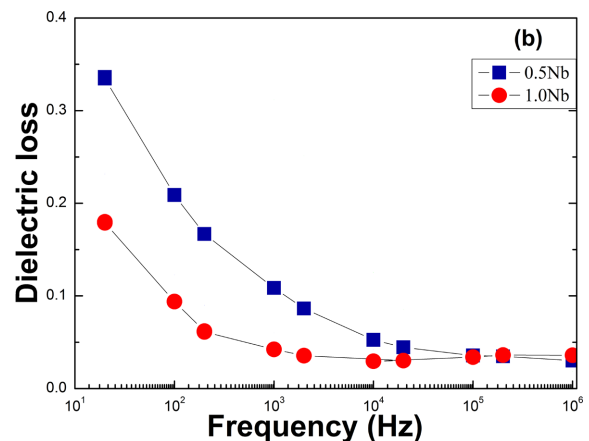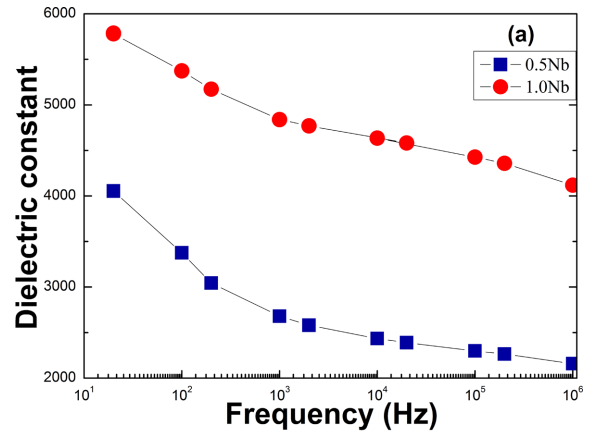
and 1.0 mole%Nb, consisting of spherical particles with a visually broad particle size distribution in the SEM image. Observations of the EDS spectrum show that the Nb ion is associated with a portion of the sample with elongated and needle-shaped grains. The corresponding EDS spectrum indicates that the regions rich in Nb 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 and its segregation in the local parts of the samples (in Fig. 2). Iso-valent impurities in BT ceramics do not significantly affect conductivity, but off-valent impurities are known to significantly affect ferroelectric behavior and conductivity. Although only few regions rich in Nb were detected by EDS, their influence on the micro-structural uniformity was negligible, as reported in reference [11].

Fig. 3(a, b) show the frequencies dependence of the dielectric constant and loss of BTNb. As shown in Fig. 3(a), the dielectric constant decreased sharply up to $10^3$ Hz, but gradually decreased at higher frequencies. However, unlike 0.5 mole%BTNb, the slope of decrease of dielectric constant is relatively slow in 1.0 mole%BTNb. The dielectric constant of BT ceramics is high at lower frequencies and decreases rapidly with increase frequency. This means that as the frequency increases, more energy is
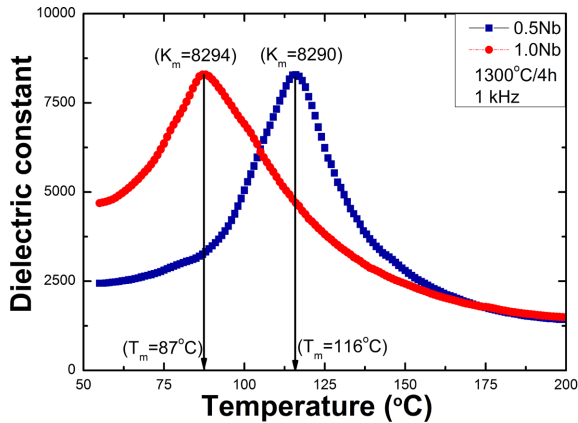
**Figure 4. Temperature dependence of dielectric constant of Nb-doped BaTiO₃.**

supplied to orientation the dipole. The dielectric constants obtained after initially obtaining large values at low frequencies in two compositions are constant at $f \geq 10^2$ kHz. As shown in Fig. 3(b), the frequency dependence of the dielectric loss is similar to that of the dielectric constant. Increasing the frequency for both compositions reduces the dielectric constant and loss, but slightly increases the dielectric loss at high frequencies ($f > 10^2$ kHz). It is indicated that the Curie temperature of BT ceramic with the Nb doping concentration in the range of 0.5~1.0 mole% was similar to that of the pure BT ceramic.

The effect of the appropriate additive on the dielectric behavior of BTNb can be analyzed via dielectric constant versus temperature curves. The microstructure characteristics observed with the additive type directly affect the dielectric properties of BTNb. Fig. 4 shows that the change of the dielectric constant with the temperature of BTNb with various compositions shows that Nb has a noticeable influence on the dielectric properties. The variation of dielectric constant with temperature is also related to the tolerance factor of perovskite materials. The tolerance factor t of perovskite structure can be calculated from the following Eq.2.

$$t = \frac{B_O + R_A}{\sqrt{2(R_B + R_O)}} = \frac{R_{O(2-)} + R_{Ba(2+)}}{\sqrt{2R_{Ti(4+)} + R_{Nb(5+)} + R_{O(2-)}}} \cong 1.1{\sim}1.3$$

(Eq.2)

, where $R_A$ is the ionic radius of A-site atom (cube corner), $R_B$ is ionic radius of B-site atom (body center) and $R_O$ ionic radius of the oxygen atom (face center). This value is slightly smaller than that of pure BT at t = 1.6, but is an appropriate value for growing into a perovskite structure. Pure BT is a typical ferroelectric with first order phase transitions. However, the BTNb ceramics shows some diffuse phase transition characteristics although it differs from perfect relaxor. The Nb ions lead to the formation of core-shell structure, with BT core and Ti⁴⁺ modified BT shell [12]. Since the BTNb samples exhibit a

different dielectric behavior it is for expected that the Curie constant would be very sensitive to the type and concentration of additive. In a BTNb sample where a chemically inhomogeneous system is formed, the overall dielectric behavior is two different microstructure regions. Addition of Nb to pure BT increased the dielectric constant but the dielectric constant at room temperature was relatively low. When the amount of Nb added to BT was increased from 0.5 mole%Nb to 1.0 mole%, the dielectric constant increased from 2340 to 4660 at room temperature. Although not shown in Fig. 4, the dielectric loss at room temperature was 0.069 for samples with 0.5mole%Nb and 0.0348 for samples with 1.0mole%Nb, showing very stable characteristics. This trend of the effect of adding donor ions to BT is similar to that reported by other research groups. In addition, a characteristic tetragonal-cubic phase transition was observed from the ferroelectric phase in the paraelectric phase of BT. In addition, the phase transition from the cubic phase to the tetragonal phase was analyzed in the paraelectric phase of BT. This property of BT with Nb added results from the fact that more crystal defects are produced in the crystal structure and that the Nb ion exchanges Ti⁴⁺ ions at the B site of ABO₃ (higher
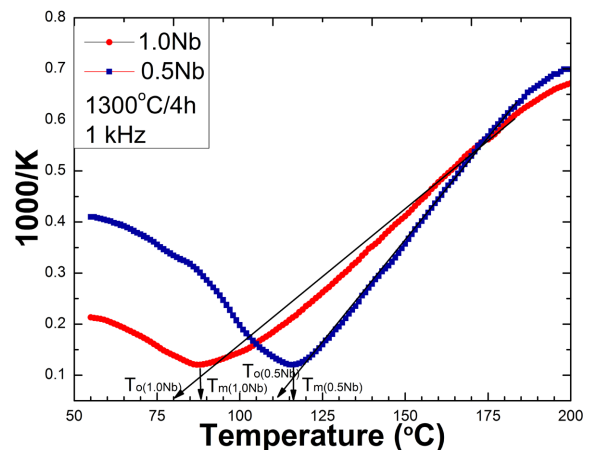


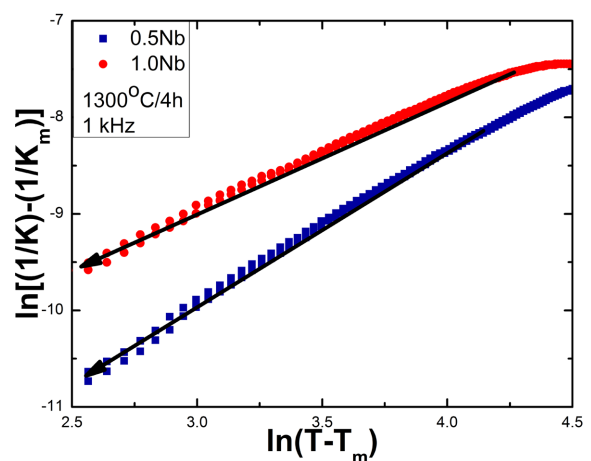**Figure 5. Temperature dependence of reciprocal dielectric constant of Nb-doped BaTiO₃.**



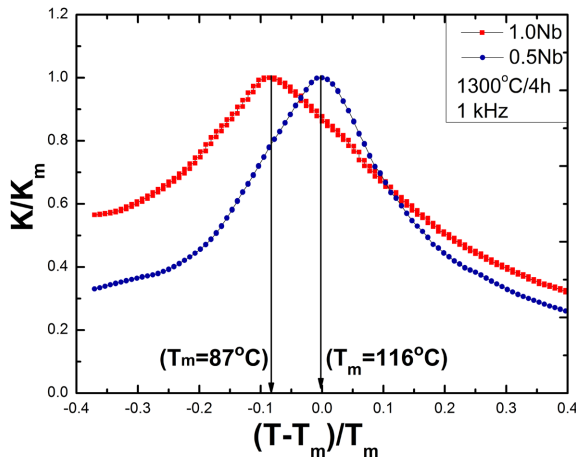**Figure 6. Plot of ln[(1/K)-(1/Kₘ)] as a function of ln(T-Tₘ) for Nb-doped BaTiO₃.**

**Figure 7. Plot of (T-T$_m$)/T$_m$ versus K/K$_m$ of BaTiO$_3$ doped with 0.5 mole%Nb and 1.0 mole%Nb.**

coordination number). Therefore, the addition of Nb to pure BT reduces the local disorder around the Ba$^{2+}$ atom and also has a minor effect on the local structure of Ti$^{4+}$. The conclusions of Fig. 1 (XRD) and Fig. 4 (dielectric constant) data confirm that the dielectric behavior of pure BT and BTNb is due to the presence of tetragonal crystals at room temperature and phase transition from tetragonal to cubic at Curie temperature. Fig. 4 shows that the effect of the dopant is expressed and affects the change of the phase transition temperature. Fig. 4 also shows that Nb addition affects the phase transition temperature of BT and that the phase transition temperature shifts to low temperature when the addition amount is increased.

Fig. 5 shows the change of the reciprocal dielectric constant with temperature of 0.5 mole% BTNb and 1.0 mole% BTNb ceramics. Since the two compositions doped with Nb are not uniformly distributed, they have a small effect on inherent dielectric parameters such as Curie temperature. For BTNb, a continuous dielectric response is observed in the transition region where the paraelectric phase region significantly reduces the dielectric constant. The diffusion characteristics of BTNb can be analyzed by the Curie-Weiss law [13-16].

$$\frac{1}{K} = \frac{1}{K_m} + \left(\frac{T - T_m}{C}\right)^\gamma \qquad (Eq.3)$$

, where K is the dielectric constant , K$_m$ is the maximum dielectric constant, T is the temperature, T$_m$ is the dielectric constant maxima temperature, C is the Curie constant, and γ is the critical exponent. This means that as the amount of Nb added to BT increases, the degree of diffusivity changes, which is represented by the critical exponent γ. Therefore, it is possible to analyze the diffusivity of the ferroelectric by examining the critical exponent γ. Generally, the critical exponent γ of the perfect normal ferroelectric is 1, but the critical exponent γ of the perfect relaxor is 2. The dielectric constant of relaxors near the Curie region is governed by a modified Curie-Weiss

quadratic equation $\frac{1}{K} = \frac{1}{Km} + \frac{(T - T_m)^\gamma}{2Km\delta^2}$, where δ is the diffuseness parameter. The plots of ln[(1/K)-(1/K$_m$)] as a function of ln(T-T$_m$) for BTNb ceramic are shown in Fig. 6. The value of the critical exponent γ is obtained from the slope of the fitting curve using Eq. 3. It is observed that the γ value of samples is decreased with the increasing of Nb contents. It is may be due to the increase of grain size with an increase of Nb content and is confirmed by SEM/EDS data. Fig. 7 shows the correlation between (T-T$_m$)/T$_m$ versus K/K$_m$ of BT doped with 0.5 mole%Nb and 1.0 mole%Nb. A number of researchers have reported that the occurrence of this diffusion is explained by a change in the local composition that leads to different micro-regions, each region having a slightly different T$_C$ for the phase transition [17].

## IV. Conclusions

In this paper, a comparative study was conducted on the microstructure and dielectric properties of BTNb ceramics. The crystal structure of BTNb showed smaller tetragonality. The analytical results showed that abnormal grain growth was inhibited by increasing Nb$^{5+}$ concentration. The dielectric constant of 1.0 mole%BTNb reaches to 4660 at room temperature. The Curie temperature for all investigated samples is lower compare to pure BT ceramics. A linear decrease of dielectric constant with frequency up to $10^2$ kHz has been noticed in all specimens. A dissipation factor is independent of frequency greater than 10 kHz for 0.5 mole% BTNb ceramics. The transition temperatures of 0.5 mole% BTNb and 1.0 mole%BTNb were ~116ºC and ~87ºC, respectively. As a result of analysis of 1/K versus T and ln[(1/K)-(1/K$_m$)) versus (T-T$_m$)] of the two compositions used in this experiment, the diffusivity slightly differs from that of pure BT at temperatures above Curie temperature.

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