Influence of Bismuth Oxide on Dielectric Properties of Barium Titanate Solid Solution

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ABSTRACT
A Ba0.9Bi0.1TiO3 solid solution was prepared by substituting 0.1 mole % Bi2O3 at the Ba2+ sites in BaTiO3, and its dielectric properties were investigated. The Ba0.9Bi0.1TiO3 solid solution was sintered at 1310 °C for 5 h. The stable formation of the perovskite structure was confirmed through X-ray diffraction, energy-dispersive X-ray spectroscopy, and field emission scanning electron microscopy. Unlike pure BaTiO3, pyrochlore Bi2Ti2O7 was observed in Ba0.9Bi0.1TiO3 at approximately 271 °C. Overall, the perovskite structure was well formed. The Ba0.9Bi0.1TiO3 solid solution showed typical dielectric properties and followed the modified Curie–Weiss law. In addition, the curve of the dielectric constant vs. temperature showed an extremely gradual change compared to the phase transition behavior of BaTiO3.

Keywords: Ba0.9Bi0.1TiO3, Dielectric properties, Phase transition, Modified Curie–Weiss law

1. Introduction
The requirement for ecofriendly electric and electronic materials, particularly multilayer ceramic capacitors, is increasing in the fields of information technology and artificial intelligence. Ecofriendly BaTiO3 is suitable for meeting this requirement, and it has the potential to be actively used in these fields. As shown in Fig. 1, BaTiO3 consists of Ti4+ at octahedral coordination sites and Ba2+ at 12-coordinated sites in a high-temperature Pm3m cubic symmetry. Spontaneous polarization occurs owing to noncentrosymmetric displacement in the ferroelectric state below 120 °C. As BaTiO3 is a relatively simple compound, it is easy to synthesize it using appropriate impurities or additives such as La3+, Nb5+, Ta5+, Co2+, and Ni2+. Thus, it is possible to fabricate an efficient dielectric with a high electric field strength and frequency-dependent properties. In this respect, BaTiO3 is an excellent electronic material with various advantages over other materials [1–5].

In this study, Ba0.9Bi0.1TiO3 was synthesized by substituting Bi3+ in BaTiO3, and the effects of the substitution on perovskite structures and dielectric properties were analyzed. The substitution mechanism was examined because it strongly affects defect generation, crystal structure, and overall dielectric properties.

2. Experimental details
The Ba0.9Bi0.1TiO3 solid solution was prepared by synthesizing BaO, TiO2, and Bi2O3, with a purity of 99.9 % or higher. The mole fractions of BaO, TiO2, and Bi2O3 were 13.7997, 7.9900, and 2.3298, respectively. Calcination was carried out in 10 intervals at 1150–1200 °C. The powder synthesized at 1180 °C was stably calcined, and it had the highest perovskite content. Sintering was performed using this powder. The specimen used for characterization was a disk-shaped Ba0.9Bi0.1TiO3 solid solution, which was synthesized by sintering at 1310 °C for 5 h. The ionic radius of Bi3+ (153 pm) is half of that of Ba2+ (255 pm); hence, a charge imbalance of cations may occur. The formation and atomic ratio of the perovskite structure of the Ba0.9Bi0.1TiO3 solid solution were observed using X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), and field emission scanning electron microscopy (FESEM), which are general-purpose analytical methods. The capacitance and dielectric loss of the Ba0.9Bi0.1TiO3 solid solution were obtained using an LCR meter. They were measured as a function of temperature at frequencies of 102–105 Hz and a heating rate of 4 °C/min.

Figure 1. Perovskite BaTiO3 with the Ba2+ at the center of the cell and Ti4+ inside the oxygen octahedra.

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was typical. The atomic percentages of Ba strongly affects its physical properties, such as dielectric, piezoelectric, and Ba clearly identified. However, these phases were observed in previous studies. The pyrochlore phase Bi had a stable (A$_1$A$_2$)O$_3$ complex perovskite structure. Consequently, the dielectric properties over a wide temperature range can be improved.

The substitution of the A and B sites of pure BaTiO$_3$ with other ions strongly affects its physical properties, such as dielectric, piezoelectric, and pyroelectric properties. Figure 3 shows the EDS results of pure BaTiO$_3$ and Ba$_{0.9}$Bi$_{0.1}$TiO$_3$. The EDS spectrum of pure BaTiO$_3$ was typical. The atomic percentages of Ba$^{2+}$, Ti$^{4+}$, and O$^{2-}$ were 18.95 (58.14 wt %), 18.09 (19.36 wt %), and 62.96 % (22.50 wt %), respectively. However, the EDS spectrum of Ba$_{0.9}$Bi$_{0.1}$TiO$_3$ clearly showed that the substitution of Bi$^{3+}$ was related to inhomogeneous particles. In this case, the atomic percentages of Ba$^{2+}$, Ti$^{4+}$, and O$^{2-}$ were 38.25 (69.71 wt %), 25.35 (17.21 wt %), and 33.12 % (7.270 wt %), respectively, and approximately 3.280 % (5.810 wt %) Bi$^{3+}$ was observed. This was due to the nonuniform distribution of Bi$^{3+}$ and the separation of the sample, resulting in a partial nonferroelectric region in the BaTiO$_3$ specimen. However, there was no significant change in dielectric properties. There was a relatively large difference between the atomic compositions of pure BaTiO$_3$ and Ba$_{0.9}$Bi$_{0.1}$TiO$_3$. It has been reported that the addition or substitution of impurities strongly affects the crystalization kinetics of a solid solution. This effect can be interpreted as follows: Generally, the diffusion dynamics of the elements that constitute each oxide during the heat treatment process are significantly affected by the presence of charge compensation defects. As the atomic radius of Bi$^{3+}$ (153 pm) is 60 % of that of Ba$^{2+}$ (255 pm), charge imbalance was observed during the experiment in this study owing to the difference in the oxidation state. In terms of the ionic radii of two ions at an A site, Ba$^{2+}$ can be substituted by Bi$^{3+}$ in the perovskite lattice. Furthermore, low-valence ions are substituted by high-valence ions. Thus, Ba$_{0.9}$Bi$_{0.1}$TiO$_3$ is synthesized as a defect in the charge and structure. The substitution of Ba$^{2+}$ with Bi$^{3+}$ causes a charge compensation reaction and changes the pore concentration of the crystal because of the difference in the atomic radii and valences. As stated earlier, approximately 3.280 % (5.810 wt %) Bi$^{3+}$ was detected in Ba$_{0.9}$Bi$_{0.1}$TiO$_3$. At this atomic percentage, the effect of Bi$^{3+}$ on microstructural uniformity is not a major problem. Figures 4(a)-(c) show the surface micrographs of BaTiO$_3$, Ba$_{0.9}$Bi$_{0.1}$TiO$_3$, and Ba$_{0.9}$Sb$_{0.1}$TiO$_3$, respectively. In polycrystals, the number of pores and impurities decreases because of heat treatment at high temperatures, and crystal grains generally grow. As shown in Fig. 4(c), the particle size of the sintered Ba$_{0.9}$Sb$_{0.1}$TiO$_3$ solid solution was approximately 2.0 μm, indicating a relatively dense particle arrangement. However, as shown in Fig. 4(b), sintered Ba$_{0.9}$Bi$_{0.1}$TiO$_3$ consisted of dense and relatively small grains. This implied that the particle size was slightly smaller than that of BaTiO$_3$ systems with a donor dopant [6,7]. In complex structured perovskites, the energy required to stably bind displaced ions of different ionic radii and valences at each lattice site is associated with the formation of compensatory defects. On the basis of the XRD results shown in Fig. 2, it was judged that Ba$_{0.9}$Bi$_{0.1}$TiO$_3$ sintered at 1310 °C had relatively normal grain growth and a uniform microstructure. The presence of chemically heterogeneous systems in Ba$_{0.9}$Bi$_{0.1}$TiO$_3$ specimens was different from that in Nb$^{5+}$-substituted and Ta$^{5+}$-substituted BaTiO$_3$ systems but quite similar to that in recently reported Sb$^{5+}$-substituted Ba$_{0.9}$Sn$_{0.1}$TiO$_3$ systems [3].

The dielectric constant and dielectric loss of BaTiO$_3$, Ba$_{0.9}$Bi$_{0.1}$TiO$_3$, and Ba$_{0.9}$Sb$_{0.1}$TiO$_3$ were measured at frequencies of 10$^2$–10$^5$ Hz to analyze the frequency dependence of these properties. The results are shown in Fig. 5. As the frequency increased, the dielectric constant decreased and the dielectric loss increased. At frequencies higher than 10$^5$ Hz, the dielectric constant of Ba$_{0.9}$Bi$_{0.1}$TiO$_3$, which required more energy for the rotation of dipoles in polycrystals,
decreased more rapidly than that of BaTiO₃ and Ba₈₂Sb₁₀TiO₃. This was accompanied by a rapid increase in the dielectric loss. These dielectric properties of Ba₈₂Sb₁₀TiO₃ were considered to be caused by the Bi₂Ti₂O₇ pyrochlore phase generated in polycrystals by the substitution of Ba³⁺ with Bi³⁺. The absolute value of the dielectric constant decreased in the case of Bi³⁺ substitution compared to Sb³⁺; however, the frequency stability improved. This phenomenon in the BaTiO₃ system has been reported by several other researchers [8–10]. In general, when trivalent ions, such as Bi³⁺, La³⁺, and Sb³⁺, are substituted in BaTiO₃ systems, they occupy Ba²⁺ sites because of similar ionic radii and electronegativities. Therefore, Bi³⁺ located at the A site of perovskite BaTiO₃, which is Ba²⁺ site, attempts to maintain charge balance. Hence, electron and/or barium vacancies occur, for example, Bi₂–→Bi³⁺+e⁻ and Bi₂–→Bi⁴⁺+(1/2)V²⁻Ba. In this process, Bi²– is the ionized Bi²⁺ donor, V²⁻ is the double ionized barium vacancy, and e⁻ is the electron. In the case of substitution with a low Bi⁴⁺ concentration, as in this study, compensation occurs via Bi₂–→Bi³⁺+e⁻. At high Bi³⁺ concentrations, compensation occurs via Bi₂–→Bi⁴⁺+(1/2)V²⁻Ba, similar to other trivalents. This may imply that there are numerous crystal defects in the crystal structure of Ba₈₂Sb₁₀TiO₃ and shows that Bi³⁺ partially substitutes Ba²⁺ at the A site of ABO₃. Therefore, when Bi³⁺ substitution occurs in pure BaTiO₃, under suitable conditions, the local disorder around Ba²⁺ atoms is reduced. Moreover, the local structure of Ti⁴⁺ is affected to a certain extent [11,12].

Figure 5 shows the plot of ln[(1/K)-(1/K₀)] vs. ln(T-Tₘ) for Ba₈₂Sb₁₀TiO₃, where K is the dielectric constant, K₀ is the maximum dielectric constant, T is the temperature, Tₘ is the dielectric constant maximum temperature. A dielectric reaction that continuously decreased the dielectric constant in the phase transition region was observed. This showed a certain degree of singularity, which was different from that of pure BaTiO₃. In other words, unlike BaTiO₃, Ba₈₂Sb₁₀TiO₃ do not exhibit perfect diffusion ferroelectricity. The modified Curie–Weiss quadratic equation, 1/K = 1/K₀ + [(T-Tₘ)²/(2K₀δ²)], was used to examine the characteristic diffusion phenomenon, where δ is the diffusion parameter and γ is the critical index [9,10,13]. The substitution of Ba³⁺ with Bi³⁺ made it possible to maintain the ferroelectric phase over a wide temperature range and changed the degree of δ, thereby making γ larger than 1. The diffusivity of Ba₈₂Sb₁₀TiO₃ could be expressed in terms of γ. In addition, γ of Ba₈₂Sb₁₀TiO₃ slightly decreased as the sintering temperature increased (data not shown in this report). It has been reported that this dielectric diffusion phenomenon is due to the change in the local composition caused by the formation of multiple microdomains within the crystal structure [8–10]. The inset in Fig. 6 shows the change in the reciprocal dielectric constant of the Ba₈₂Sb₁₀TiO₃ solid solution as a function of temperature. Substitution with Bi³⁺ at a low concentra-

4. Conclusions

A Ba₈₂Sb₁₀TiO₃ solid solution was prepared by substituting 0.1 mole % Bi₂O₃ at the Ba²⁺ sites in BaTiO₃, and its dielectric properties were investigated. The solid solution was stably prepared by sintering at 1310 °C for 5 h. XRD analysis showed that unlike pure BaTiO₃, pyrochlore Bi₂Ti₂O₇ was observed in Ba₈₂Sb₁₀TiO₃ at approximately 27.1°. The perovskite structure was well formed. The dielectric properties were analyzed using the modified Curie–Weiss law. The dielectric properties of Ba₈₂Bi₁₀TiO₃ were slightly different from those of BaTiO₃. The plot of the dielectric constant vs. temperature showed stable changes over a wide temperature range, unlike the phase transition behavior of pure BaTiO₃. As the measurement frequency increased, the dielectric constant of Ba₈₂Bi₁₀TiO₃ decreased and its dielectric loss increased. At frequencies higher than 10⁶ Hz, this increase and decrease were faster than those for BaTiO₃. However, Ba₈₂Bi₁₀TiO₃ showed stable dielectric properties over a wide temperature range. In the future, the close physical relationship between pyrochlore Bi₂Ti₂O₇ and the dielectric properties, which was observed after Bi³⁺ substitution in BaTiO₃, should be analyzed.

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