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

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ABSTRACT

A $\text{Ba}_{0.9}\text{Bi}_{0.1}\text{TiO}_3$ solid solution was prepared by substituting 0.1 mole % Bi_2O_3 at the Ba^{2+} sites in BaTiO_3 , and its dielectric properties were investigated. The $\text{Ba}_{0.9}\text{Bi}_{0.1}\text{TiO}_3$ 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 BaTiO_3 , pyrochlore $\text{Bi}_2\text{Ti}_2\text{O}_7$ was observed in $\text{Ba}_{0.9}\text{Bi}_{0.1}\text{TiO}_3$ at approximately 27.1° . Overall, the perovskite structure was well formed. The $\text{Ba}_{0.9}\text{Bi}_{0.1}\text{TiO}_3$ 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 BaTiO_3 .

Keywords: $\text{Ba}_{0.9}\text{Bi}_{0.1}\text{TiO}_3$, 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 BaTiO_3 is suitable for meeting this requirement, and it has the potential to be actively used in these fields. As shown in Fig. 1, BaTiO_3 consists of Ti^{4+} at octahedral coordination sites and Ba^{2+} at 12-coordinated sites in a high-temperature $\text{Pm}3\text{m}$ cubic symmetry. Spontaneous polarization occurs owing to noncentrosymmetric displacement in the ferroelectric state below 120°C . As BaTiO_3 is a relatively simple compound, it is easy to synthesize it using appropriate impurities or additives such as La^{3+} , Sb^{3+} , Nb^{5+} , Ta^{5+} , Co^{2+} , and Ni^{2+} . Thus, it is possible to fabricate an efficient dielectric with a high electric field strength and frequency-dependent properties. In this respect, BaTiO_3 is an excellent electronic material with various advantages over other materials [1–5].

In this study, $\text{Ba}_{0.9}\text{Bi}_{0.1}\text{TiO}_3$ was synthesized by substituting Bi^{3+} in BaTiO_3 , 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 $\text{Ba}_{0.9}\text{Bi}_{0.1}\text{TiO}_3$ solid solution was prepared by synthesizing BaO , TiO_2 , and Bi_2O_3 with a purity of 99.9 % or higher. The mole fractions of BaO , TiO_2 , and Bi_2O_3 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 $\text{Ba}_{0.9}\text{Bi}_{0.1}\text{TiO}_3$ solid solution, which was synthesized by sintering at 1310°C for 5 h. The ionic radius of Bi^{3+} (153 pm) is half of that of Ba^{2+}

Figure 1. Perovskite BaTiO_3 with the Ba^{2+} at the center of the cell and Ti^{4+} inside the oxygen octahedra.

(255 pm); hence, a charge imbalance of cations may occur. The formation and atomic ratio of the perovskite structure of the $\text{Ba}_{0.9}\text{Bi}_{0.1}\text{TiO}_3$ 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 $\text{Ba}_{0.9}\text{Bi}_{0.1}\text{TiO}_3$ solid solution were obtained using an LCR meter. They were measured as a function of temperature at frequencies of 10^2 – 10^5 Hz and a heating rate of $4^\circ\text{C}/\text{min}$.

Figure 2. XRD patterns of (a) pure BaTiO₃ and (b) Ba_{0.9}Bi_{0.1}TiO₃ solid solutions.

3. Results and discussion

Crystallographically pure BaTiO₃ crystals have two phases: tetragonal and cubic. Figure 2 shows the XRD results of BaTiO₃ and Ba_{0.9}Bi_{0.1}TiO₃. The (222) pyrochlore phase was not observed. However, (110) perovskite, which is an evidence of the perovskite structure, was clearly observed. Therefore, the specimens calcined at 1180 °C and sintered at 1310 °C for 5 h formed a stable perovskite structure at the current level and satisfied the appropriate heat treatment conditions. However, in the specimen substituted with Bi₂O₃, the XRD intensity corresponding to pyrochlore Bi₂Ti₂O₇ was observed at approximately 27.1°. Phases at approximately 35° and 49° could not be clearly identified. However, these phases were observed in previous studies. In particular, when more than 0.15 mole % Bi³⁺ was substituted in BaTiO₃, pyrochlore Bi₂Ti₂O₇ was more clearly observed in XRD data. Therefore, a stable perovskite structure can be obtained if the substitution amount of Bi³⁺ is adjusted to approximately 0.1 mole %. It was speculated that it was sintered to a high density at 1310 °C and Ba_{0.9}Bi_{0.1}TiO₃ had a stable (A₁A₂)BO₃ 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 BaTiO₃ with other ions strongly affects its physical properties, such as dielectric, piezoelectric, and pyroelectric properties. Figure 3 shows the EDS results of pure BaTiO₃ and Ba_{0.9}Bi_{0.1}TiO₃. The EDS spectrum of pure BaTiO₃ was typical. The atomic percentages of Ba²⁺, Ti⁴⁺, and O²⁻ 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}TiO₃ clearly showed that the substitution of Bi³⁺ was related to inhomogeneous particles. In this case, the atomic percentages of Ba²⁺, Ti⁴⁺, and O²⁻ 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 %) Bi³⁺ was observed. This was due to the nonuniform distribution of Bi³⁺ and the separation of the sample, resulting in a partial nonferroelectric region in the BaTiO₃ specimen. However, there was no significant change in dielectric properties. There was a relatively large difference between the atomic compositions of pure BaTiO₃ and Ba_{0.9}Bi_{0.1}TiO₃. It has been reported that the addition or substitution of impurities strongly affects the crystallization 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 Bi³⁺ (153 pm) is 60 % of that of Ba²⁺ (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, Ba²⁺ can be substituted

Figure 3. EDS spectra of (a) pure BaTiO₃ and (b) Ba_{0.9}Bi_{0.1}TiO₃ solid solutions.

Figure 4. FESEM micrographs of (a) pure BaTiO₃, (b) Ba_{0.9}Bi_{0.1}TiO₃, and (c) Ba_{0.9}Sb_{0.1}TiO₃ solid solutions.

tuted by Bi³⁺ in the perovskite lattice. Furthermore, low-valence ions are substituted by high-valence ions. Thus, Ba_{0.9}Bi_{0.1}TiO₃ is synthesized as a defect in the charge and structure. The substitution of Ba²⁺ with Bi³⁺ 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 %) Bi³⁺ was detected in Ba_{0.9}Bi_{0.1}TiO₃. At this atomic percentage, the effect of Bi³⁺ on microstructural uniformity is not a major problem. Figures 4(a)-(c) show the surface micrographs of BaTiO₃, Ba_{0.9}Bi_{0.1}TiO₃, and Ba_{0.9}Sb_{0.1}TiO₃, 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}TiO₃ 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}TiO₃ consisted of dense and relatively small grains. This implied that the particle size was slightly smaller than that of BaTiO₃ 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}TiO₃ 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}TiO₃ specimens was different from that in Nb⁵⁺-substituted and Ta³⁺-substituted BaTiO₃ systems but quite similar to that in recently reported Sb³⁺-substituted Ba_{1-x}Sb_xTiO₃ systems [3].

The dielectric constant and dielectric loss of BaTiO₃, Ba_{0.9}Bi_{0.1}TiO₃, and Ba_{0.9}Sb_{0.1}TiO₃ were measured at frequencies of 10²–10⁵ 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 10³ Hz, the dielectric constant of Ba_{0.9}Bi_{0.1}TiO₃, which required more energy for the rotation of dipoles in polycrystals,

Figure 5. Frequency dependence of dielectric properties of BaTiO₃, Ba_{0.9}Bi_{0.1}TiO₃, and Ba_{0.9}Sb_{0.1}TiO₃ solid solutions.

decreased more rapidly than that of BaTiO₃ and Ba_{0.9}Sb_{0.1}TiO₃. This was accompanied by a rapid increase in the dielectric loss. These dielectric properties of Ba_{0.9}Bi_{0.1}TiO₃ were considered to be caused by the Bi₂Ti₂O₇ pyrochlore phase generated in polycrystals by the substitution of Ba²⁺ 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, Bi_{Ba} → Bi_{Ba}^{*} + e' and Bi_{Ba} → Bi_{Ba}^{*} + (1/2)V_{Ba}^{''}. In this process, Bi_{Ba}^{*} is the ionized Bi²⁺ donor, V_{Ba}^{''} is the double ionized barium vacancy, and e' is the electron. In the case of substitution with a low Bi²⁺ concentration, as in this study, compensation occurs via Bi_{Ba} → Bi_{Ba}^{*} + e'. At high Bi³⁺ concentrations, compensation occurs via Bi_{Ba} → Bi_{Ba}^{*} + (1/2)V_{Ba}^{''}, similar to other trivalents. This may imply that there are numerous crystal defects in the crystal structure of Ba_{0.9}Bi_{0.1}TiO₃ 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 6 shows the plot of $\ln[(1/K)-(1/K_m)]$ vs. $\ln(T-T_m)$ for Ba_{0.9}Bi_{0.1}TiO₃, where K is the dielectric constant, K_m is the maximum dielectric constant, T is the temperature, T_m 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, Ba_{0.9}Bi_{0.1}TiO₃ did not exhibit perfect diffusion ferroelectricity. The modified Curie–Weiss quadratic equation, $1/K = 1/K_m + [(T-T_m)^\gamma / (2K_m\delta^2)]$, 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 Ba²⁺ 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 Ba_{0.9}Bi_{0.1}TiO₃ could be expressed in terms of γ . In addition, γ of Ba_{0.9}Bi_{0.1}TiO₃ 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 Ba_{0.9}Bi_{0.1}TiO₃ solid solution as a function of temperature. Substitution with Bi³⁺ at a low concentra-

Figure 6. Plot of $\ln[(1/K)-(1/K_m)]$ vs. $\ln(T-T_m)$ for Ba_{0.9}Bi_{0.1}TiO₃ solid solution. The inset shows the reciprocal of the dielectric constant of Ba_{0.9}Bi_{0.1}TiO₃ vs. temperature.

tion of 0.1 mole % had a relatively stable effect on intrinsic dielectric phenomena, such as the Curie temperature and phase transition, because only partial nonuniformity existed. This variation in basic dielectric properties has been actively studied by numerous researchers on the basis of the physical change in Ba_{0.9}Bi_{0.1}TiO₃ created by substituting/doping the A and B sites of BaTiO₃. The atypical phase transition and dielectric characteristics of Ba_{0.9}Bi_{0.1}TiO₃ obtained in this study were similar to the phase transition and dielectric characteristics of Ba_{0.9}Sb_{0.1}TiO₃ reported in previous studies [4]. Therefore, the phase transition temperature of BaTiO₃ can be decreased and diffusivity can be increased while widening the phase transition temperature range.

4. Conclusions

A Ba_{0.9}Bi_{0.1}TiO₃ 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 Ba_{0.9}Bi_{0.1}TiO₃ 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 Ba_{0.9}Bi_{0.1}TiO₃ 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 Ba_{0.9}Bi_{0.1}TiO₃ decreased and its dielectric loss increased. At frequencies higher than 10³ Hz, this increase and decrease were faster than those for BaTiO₃. However, Ba_{0.9}Bi_{0.1}TiO₃ 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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