Possibility of ferroelectric bismuth and nitrogen co-doped barium titanate

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The possibility of bismuth (Bi) and nitrogen (N) co-doped barium titanate (BaTiO₃) as a ferroelectric material was investigated by calculation and experiment. From first principles calculations, it was found that Bi and N co-doped BaTiO₃ has a higher spontaneous polarization than undoped BaTiO₃ since dopant Bi and N ions contribute to the enhancement of covalent interactions between cations and anions. Because it was revealed that the ferroelectricity of BaTiO₃ can be improved by co-doping of Bi and N, we demonstrated the synthesis of (Ba,Bi)Ti(O,N)₃ powder by annealing (Ba,Bi)TiO₃ in NH₃ gas. The tetragonal distortion of (Ba,Bi)Ti(O,N)₃ was smaller than that of BaTiO₃, which may be due to A-site and O-site vacancies in the perovskite lattice introduced during NH₃ annealing.

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1. Introduction

Conventional research on ferroelectric materials has focused on perovskite-type oxides (ABO₃), and dielectric and ferroelectric properties have been controlled by constituent elements,⁴-⁷ microstructure,⁴-⁷ and defects.⁴-¹² One of the most important factors for the dielectric and ferroelectric properties is the bonding state between cations and oxide ions, in other words, previous studies have changed the bonding state to control the properties. In the example of SrTiO₃, when the Ti is partially substituted with Nb¹³ or oxygen vacancies are introduced,¹⁴ the soft mode frequency increases because of the covalency change between B-site and O ions, and then the dielectric property decreases. In the case of BaTiO₃, it is well-known that Ba substitution with Pb causes the enhancement of the ferroelectricity due to the enhancement of the covalency between A-site and O ions.¹⁵-¹⁷ While many previous studies have examined the effects of cation substitution, we have been focusing on the effects of anion (oxygen-site) substitution on dielectric and ferroelectric properties since the covalency should be controlled by anion substitution. Recently, we have successfully fabricated strontium titanium oxynitride (N-doped SrTiO₃) single crystal and reported that the dielectric permittivity increased with the amount of dopant nitrogen.¹⁸ The increase in the permittivity seems to be due to a change in the covalency between Ti ion and anion by nitrogen doping.

In this study, we focused on barium titanium oxynitride (N-doped BaTiO₃) system. Substitution with N having a small electronegativity increase the covalent bonding between the anion and the cation, possibly enhancing the ferroelectricity of BaTiO₃. In BaTiO₃ system, the substitution ions that enhance the ferroelectricity are known to be only Pb²⁺, Bi⁵⁺ and Sn²⁺ in A-site,¹⁹,²⁰ and it is interesting whether nitrogen plays a role in enhancing the ferroelectricity. However, since N³⁻ and O²⁻ have different valences, it is considered that oxygen vacancies are generated with N doping, and the structure represented by BaTiO₃–N₂O/3 may be stable. Generally, oxygen vacancies in perovskite-type structure suppress the ferroelectricity, and therefore an idea to reduce the number of oxygen vacancies is required. In this study, we attempted to fabricate Bi and N co-doped BaTiO₃ [(Ba,Bi)Ti(O,N)₃] to suppress the generation of oxygen vacancies. (Ba,Bi)TiO₃ was fabricated by partially nitriding (Ba,Bi)TiO₃. In addition, the effects of Bi and N co-doping on the spontaneous polarization of BaTiO₃ were examined using first-principles calculations.

2. Calculation procedure

First-principles calculations were carried out using the Vienna Ab-initio Simulation Package.²¹,²² The density functional theory calculation was performed using projector augmented wave method²³ and the generalized gradient approximation with PBEsol exchange–correlation potential.²⁴ The plane-wave cutoff energy was 500 eV and
the k-point mesh was $3 \times 3 \times 3$. A BaTiO$_3$ model consisting of $2 \times 2 \times 2$ supercell (8 perovskite unit cells) was constructed shown in Fig. 1(a), and then an atom of the 8 barium atoms was replaced with a bismuth atom to express Bi-doped BaTiO$_3$, which corresponds to Ba$_{0.875}$Bi$_{0.125}$TiO$_3$ [Fig. 1(b)]. In addition, an atom of the 24 oxygen atoms was replaced with a nitrogen atom to express Bi and N co-doped Ba$_{0.875}$Bi$_{0.125}$TiO$_2$N$_{0.125}$. When modeling Ba$_{0.875}$Bi$_{0.125}$TiO$_2$N$_{0.125}$, positions of Bi and O atoms can take various arrangements. As a result of the geometry optimization, the model with the minimum total energy was the one in which Bi and O were located closest to each other. Therefore, we adopted the nearest neighbor model shown in Fig. 1(c) for Ba$_{0.875}$Bi$_{0.125}$TiO$_2$N$_{0.125}$. Geometry optimization was performed using the conjugate-gradient technique based on the Hellmann–Feynman theorem, so that the symmetry of BaTiO$_3$ ($P4mm$) did not change by substitutions with Bi and N. The partial charge density was calculated and visualized using VESTA software. Moreover, the Born effective charges were calculated using density-functional perturbation theory (DFPT) to estimate the spontaneous polarization.

3. Experimental procedure

We synthesized oxide (Ba,Bi)TiO$_3$ powder and partially nitrided it to produce oxynitride (Ba,Bi)Ti(O,N)$_3$ powder. BaCO$_3$ (Nippon chemical industrial, 99.86%), TiO$_2$ (Toho titanium, 99.9%), and Bi$_2$O$_3$ (Kojundo Chemical, 99.9999%) powders were weighed at a ratio of Ba$_{0.92}$Bi$_{0.08}$TiO$_3$, and the mixture was milled in ethanol. The milled powder was calcined at 1000 °C in an alumina crucible for 1 h to obtain oxide Ba$_{0.92}$Bi$_{0.08}$TiO$_3$ powder. The oxide powder was annealed in gaseous ammonia (NH$_3$) at 1000 °C using a tubular electric furnace. The flow rate of NH$_3$ gas was 0.1 L/min, and the annealing time was 4 h. The crystal structures of the obtained oxide and partially-nitrided samples were evaluated by powder X-ray diffraction (XRD) with Cu K$_\alpha$ ray (Rigaku RINT-2000). The chemical compositions were characterized using a X-ray fluorescence (XRF) spectrometer (Bruker, M4 TORNADO) equipped with a Rh tube, operating at 50 kV and 300 μA. The dopant nitrogen ions in the oxynitride samples were semi-quantitatively measured by X-ray photoelectron spectroscopy (XPS) with Al K$_\alpha$ ray (PerkinElmer, 5500MT). The constant pass energy was 23.5 eV.

4. Results and discussion

First-principles calculations were performed to understand the doping effect of Bi and N in BaTiO$_3$. Figure 2 shows total and projected density of states for BaTiO$_3$, Ba$_{0.875}$Bi$_{0.125}$TiO$_3$, and Ba$_{0.875}$Bi$_{0.125}$TiO$_2$N$_{0.125}$. In BaTiO$_3$ (Fig. 2), oxygen 2p orbital gives the primary contribution to the valence band (VB) and the top of VB was created by O 2p orbital. The bottom of conduction band (CB) was formed by Ti 3d orbital. This orbital gave the main contribution to CB at around the lowest portion. Ti 3d orbital also contributed to the valence state. The overlap of Ti 3d and O 2p orbitals indicates the covalent interaction between Ti and O ions. In Ba$_{0.875}$Bi$_{0.125}$TiO$_3$ (Fig. 3), the fermi energy ($E_F$) was located near the top of VB. The position of $E_F$ was located near to the top of VB by $2p$ orbital. The band gap of oxynitride is narrower than that of oxide since the energy level of N 2p orbital is higher than that of O 2p orbital. The same trend was applicable to the calculations of N-doped BaTiO$_3$. The overlapped N 2p and Ti 3d orbitals in VB should...
contribute to the covalency between Ti and N ions. It is noted that the bands due to Ti 3d and O 2p orbitals in VB expanded by N doping. This suggests that N doping also affected the covalent interaction between Ti and O ions.

Figure 5 indicates partial charge density distribution of Ba, Bi, Ti, O and N orbitals constituting the VB. In BaTiO$_3$ [Fig. 5(a)], Ti and O ions formed a weak covalent bonding while Ba ion is almost ionic. It is well known that the covalent bonding between Ti and O ions is closely related to the ferroelectricity of BaTiO$_3$. In Bi-doped BaTiO$_3$ [Fig. 5(b)], the covalent interaction between Ti and O ions was reduced. As is already explained, the Bi 6s
orbital contributed to the covalency between A-site and O ions, however, the doped electrons suppress the covalency between Ti and O ions. The displacement of Bi ion along [001] direction increased, however, the displacement of Ti ion decreased by Bi doping. In Bi and N co-doped BaTiO3 [Fig. 5(c)], N ion was more strongly hybridized with Bi and Ti ions. The displacement of Ti ion was enhanced, and the charge density around N and O ion was biased. The displacement of Bi ion was also larger than that of Bi-doped BaTiO3. It is noted that the local symmetry of Bi and N co-doped BaTiO3 should be different from the that of non-doped BaTiO3, however, the calculation was performed under $P4_2/mnm$ symmetry because the average structure of the synthesized powder had the same symmetry as non-doped BaTiO3. The spontaneous polarizations in [001] of BaTiO3 and Ba$_{0.875}$Bi$_{0.125}$TiO$_{2.875}$N$_{0.125}$ calculated by DFPT were 0.313 and 0.454 C/m$^2$, respectively. It was cleared that the ferroelectricity of BaTiO3 can be increased by co-doping with Bi and N ions.

Since first-principles calculations show that the ferroelectricity of BaTiO3 can be enhanced, we examined whether Bi and N co-doped BaTiO3 can be fabricated. At first, oxide (Ba,Bi)TiO$_3$ precursor was prepared by a conventional method, and the obtained powder was partially nitrided to produce oxynitride (Ba,Bi)Ti(O,N)$_3$. Figure 6 indicates the XRD patterns of the obtained oxide and oxynitride powders. Before nitriding treatment, Ba$_2$TiO$_4$ was contained as an impurity phase in addition to the
perovskite phase. Since Bi has a different valence from Ba, Bi-doped BaTiO$_3$ is unstable from the viewpoint of charge balance, and may have a perovskite phase containing cationic vacancies. As shown in Fig. 6, after nitriding treatment, the impurity of Ba$_2$TiO$_4$ disappeared, and then single-phase perovskite compound with a tetragonal structure ($P4mm$) was obtained. It is considered that the charge balance was maintained by the introduction of nitrogen into the perovskite structure, and the perovskite structure was stabilized. Figure 7 shows the XRF patterns of oxide and oxynitride powders. The peaks attributed to Bi were found in both patterns, however, Bi was estimated to have decreased by 43% after nitriding. This is attributable to the fact that Bi was metallized and evaporated as a result of the NH$_3$ decomposition reaction in nitriding treatment. Bi evaporation was found to be one of the problems to overcome in fabricating (Ba,Bi)Ti(O,N)$_3$ system. It is necessary to perform the synthesis at a lower temperature to avoid Bi evaporation. Figure 8 shows XPS N 1s signals of undoped BaTiO$_3$ and (Ba,Bi)Ti(O,N)$_3$. The N 1s peak at 398 eV was attributed to adsorbed nitrogen on the particle surface, and the peak at 394.5 eV to the N$_3^-$ state of the Ti–N bond,$^{39}$ which meant the substituted nitrogen. It was confirmed that the oxygen in the perovskite lattice was substituted with nitrogen. Table 1 indicates the lattice parameters of the BaTiO$_3$, (Ba,Bi)TiO$_3$ and (Ba,Bi)Ti(O,N)$_3$ powders. The DFPT calculation showed that spontaneous polarization was increased by the co-doping of Bi and N, and it was expected that the tetragonal distortion of (Ba,Bi)Ti(O,N)$_3$ was larger than that of BaTiO$_3$, however the experimental result differed unfortunately. It is considered that the smaller tetragonal distortion of (Ba,Bi)Ti(O,N)$_3$ is due to A-site and O-site vacancies in the perovskite structure, i.e., the tetragonal distortion is suppressed by electrostatic repulsion between the cation vacancy and the anion or between the anion vacancy and the cation. It is important to find other fabrication methods or conditions for increasing the substitution amount of Bi and N in order to obtain larger tetragonal distortion. However, since the tetragonal distortion of (Bi,Ba)Ti(O,N)$_3$ is larger than that of (Ba,Bi)TiO$_3$, the N doping effect on the tetragonal distortion was clearly observed.

5. Conclusions

In this study, the possibility of Bi and N co-doped BaTiO$_3$ as a ferroelectric material was investigated by calculation and experiment. From first-principles calculations, it was found that Bi and N co-doped BaTiO$_3$ has a higher spontaneous polarization than undoped BaTiO$_3$ since dopant Bi and N ions contribute to the enhancement of covalent interactions between cations and anions. The ferroelectricity of BaTiO$_3$ is possible to be improved by co-doping of Bi and N. We also examine the possibility of (Ba,Bi)Ti(O,N)$_3$ synthesis. Single phase oxynitride (Ba,Bi)Ti(O,N)$_3$ powder was obtained by nitriding treatment of an oxide precursor. During the nitriding treatment in NH$_3$, the amount of dopant Bi was reduced, and therefore the tetragonal distortion of (Ba,Bi)Ti(O,N)$_3$ was smaller than that of BaTiO$_3$. In further work, we will try other methods and conditions to increase the amount of dopant Bi and N.

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