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## The Effect of MgO and Rare-Earth Oxide on Formation Behavior of Core-Shell Structure in BaTiO<sub>3</sub>

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The formation mechanism of the core-shell structure of a BaTiO<sub>3</sub>(BT)–MgO–Ho<sub>2</sub>O<sub>3</sub>-based system was studied. Mg reacted with BT at low temperatures and showed poor diffusivity compared with Ho. The core-shell structure was considered to be formed by the suppression of the diffusion of Ho into the core region by Mg. Also, replacement modes of Mg and Ho in perovskite were investigated. Lattice parameters were determined at temperatures higher than the Curie temperature in order to avoid crystal structure change. It was confirmed that Mg dissolved in Ti site, and Ho dissolved in both Ba and Ti sites. This indicates that Mg ions act as acceptors and Ho ions act as both donors and acceptors in the shell phase.

**KEYWORDS:** barium titanate, magnesium, holmium, rare-earth oxide, BaTiO<sub>3</sub>–MgO–Ho<sub>2</sub>O<sub>3</sub>, core shell, lattice parameter at high temperatures, acceptor, donor

### 1. Introduction

It is well known that temperature-stable dielectrics based on BaTiO<sub>3</sub> (BT), which are commonly used as multilayer ceramic capacitors (MLCs) of EIA X7R specification, have core-shell structures. The core-shell structure consists of a tetragonal ferroelectric unreacted core and a nonferroelectric modified shell. We previously showed that nonreducible BT–MgO–Ho<sub>2</sub>O<sub>3</sub>-based ceramics, developed for X7R MLCs with nickel electrodes, exhibit the core-shell structure.<sup>1)</sup> It was confirmed that the shell phase was composed of dopants and BT, and the core phase was almost pure BT.

In recent years, the technology for fabricating MLCs with large capacitance and small size has advanced rapidly. Dielectric layers of 3 μm thickness are now possible. To produce such thin-dielectric-layer MLCs with highly reliable electrical characteristics, an understanding of the core-shell formation behavior during the sintering process is important to the control of dielectric microstructure. The formation mechanism of the core-shell structure of a BT–Nb<sub>2</sub>O<sub>5</sub>-based system has been reported by many authors.<sup>2–4)</sup> However, the formation mechanism of that of rare-earth oxide and alkaline-oxide codoped BT is not clear yet. On the other hand, it is well known that the resistance degradation of dielectrics under DC electric field is strongly dependent on the ratio of donor dopants to acceptor dopants.<sup>5)</sup> Obviously, as the dielectric layer thickness is reduced, the field stress in the ceramic material increases at a constant applied voltage. Therefore, it is necessary to clarify the solubility modes of dopants in the shell phase to improve the reliability of high-capacitance MLCs with nickel electrodes.

The purpose of this study is to determine the influence of MgO and Ho<sub>2</sub>O<sub>3</sub> on the formation behavior of the core-shell structure, and to investigate the replacement modes of Mg and Ho in perovskite.

### 2. Experimental

Reagent-grade BaCO<sub>3</sub>, MgCO<sub>3</sub>, TiO<sub>2</sub> and SiO<sub>2</sub>, and 99.9%Ho<sub>2</sub>O<sub>3</sub> were used as raw materials. To examine the reaction process of dopants with BT, a series of Mg-doped BT, Ho-doped BT, and BT–MgO–Ho<sub>2</sub>O<sub>3</sub>–BaSiO<sub>3</sub> samples were prepared. BaSiO<sub>3</sub> was used as a sintering aid. The samples were prepared by the conventional method as follows. BT was precalcined at 1200°C after BaCO<sub>3</sub> and TiO<sub>2</sub> were mixed in equimolar ratios. The obtained particle size of BT was about 0.4 μm. BaSiO<sub>3</sub> was also precalcined at 1000°C. Additives and BT were weighed, mixed by ball milling and then dried. Powder with an organic binder was pressed into disks and after the binder was burned out, the disks were fired at various temperatures in a low oxygen atmosphere controlled by H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O. The microstructures of the ceramics were observed by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX), and the distribution of elements was measured by electron probe microanalysis (EPMA). The ceramics were crushed and ground into powder, and then the sample was characterized by powder X-ray diffraction (XRD) analysis and differential scanning calorimetry (DSC).

In order to analyze solubility modes of Mg and Ho in perovskite, the samples were prepared according to following formulae, Ba(Ti<sub>1–x</sub>Mg<sub>x</sub>)O<sub>3–x</sub>: (B-site replacement model) and (Ba<sub>1–x</sub>Ho<sub>x</sub>)(Ti<sub>1–x</sub>Ho<sub>x</sub>)O<sub>3</sub>: (both A- and B-site replacement model) ( $x < 0.1$ ). The raw materials, BaCO<sub>3</sub>, MgCO<sub>3</sub>, TiO<sub>2</sub> and Ho<sub>2</sub>O<sub>3</sub>, were mixed and then calcined at 1250°C. Identification of precipitated phases was performed by powder XRD analysis. In order to avoid crystal structure change, high-temperature powder XRD analysis was also carried out at temperatures higher than the Curie temperature. The solubility modes were examined by monitoring the behavior of the lattice parameters at 300°C. The lattice parameters were determined precisely using the whole-powder-decomposition

method (WPPD) program.<sup>6)</sup> The measurement system and method are described in detail by Ohsato *et al.*<sup>7)</sup> The microstructure of the sintered samples were also examined.

### 3. Results and Discussion

#### 3.1 Formation mechanism of core-shell structure

Figure 1(a) shows a TEM micrograph of BT-0.006MgO-0.008Ho<sub>2</sub>O<sub>3</sub>-BaSiO<sub>3</sub> sample sintered at 1320°C. The formation of the core-shell structure was confirmed. A typical ferroelectric domain pattern appeared in the core phase of the grain. Figure 1(b) shows an EDX spectrum of the shell phase. It was found that shell phase was composed of Mg, Ho and BT.

XRD profiles of the sample sintered at various temperatures are shown in Fig. 2(a). It can be seen that the Ho<sub>2</sub>O<sub>3</sub> phase still exists at 1250°C. From EPMA observation of the surface of the sintered sample, it was confirmed that Ho diffusion was slight at temperatures below 1250°C. Figure 2(b) shows XRD profiles focusing on the 200 diffraction peak. A remarkable change in the peak profile occurred at temperatures between 1150 and 1200°C, which indicates that the crystal structure of the sintered sample changed from tetragonal to pseudocubic at 1200°C. It is considered that shell phase has been formed at this stage. Furthermore, it was observed that the peak shifted randomly with increasing sintering temperature: the peak shifted to a smaller angle at temperatures up to 1250°C; however, it shifted to a larger

angle in the range of 1250 to 1300°C and slightly back to a smaller angle above 1300°C. It seems that these peak shifts resulted from the difference in reaction temperature between Mg and Ho with BT.

Figure 3 shows the DSC profiles of BT-MgO-Ho<sub>2</sub>O<sub>3</sub>-BaSiO<sub>3</sub> samples with different Mg/Ho ratios (the total amounts of Mg and Ho were adjusted to same value: 2.2 at.%) sintered at 1350 and 1400°C. These DSC peaks were due to the Curie temperature of the core phase. The peak of Mg-rich sample was sharp compared with that of Ho-rich sample even after sintering at 1400°C. It is considered that the diffusivity of Mg ions into the core phase is much lower than that of Ho ions.

We examined the reaction of Mg and Ho with BT. Figure 4 shows the XRD profiles of Mg-doped and Ho-doped BT sintered at 1100°C. The peak profile of Mg-doped BT was broad even at 1100°C. It appears that Mg reacted with BT at low temperatures compared with Ho. Figures 5(a) and 5(b) show respectively SEM micrographs of Mg-doped and Ho-doped BT sintered at 1350°C. Grain growth occurred in the Ho-doped sample, but not in the Mg-doped sample. It also appears that Mg ions act as inhibitors of grain growth in BT.

From these results, it is found that Mg ions play an important role in the formation of the core-shell structure in the BT-MgO-Ho<sub>2</sub>O<sub>3</sub>-based system. It seems that Mg controls the diffusivity of Ho into the grain core. Chazono and Fujimoto reported that Nb suppresses the diffusion of Co into grains in the BT-Nb<sub>2</sub>O<sub>5</sub>-Co<sub>3</sub>O<sub>4</sub> ternary

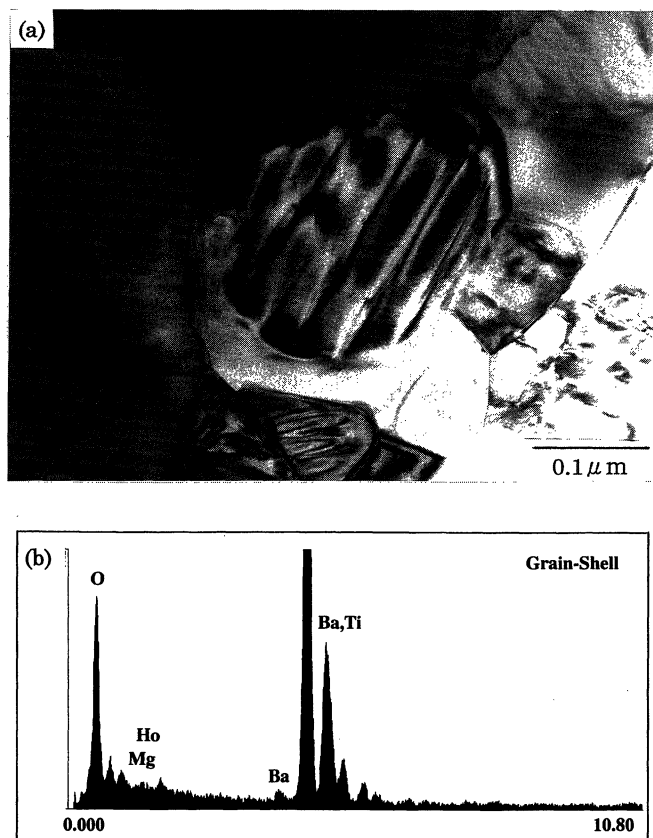


Fig. 1. (a) TEM micrograph of grain and (b) EDX spectrum of grain shell of BT-MgO-Ho<sub>2</sub>O<sub>3</sub>-based ceramics sintered at 1320°C.

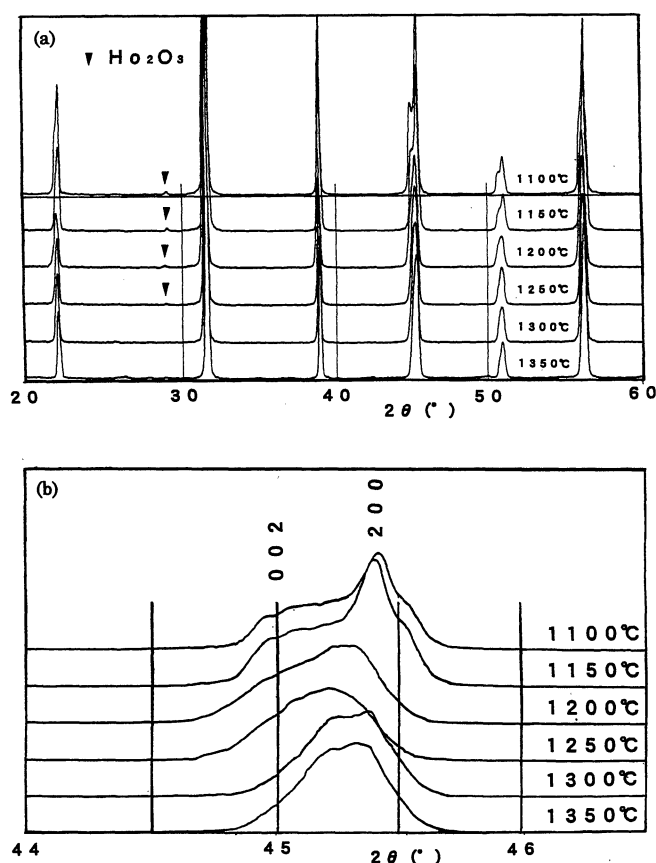


Fig. 2. XRD profiles of BT-MgO-Ho<sub>2</sub>O<sub>3</sub>-based ceramics sintered at various temperatures.

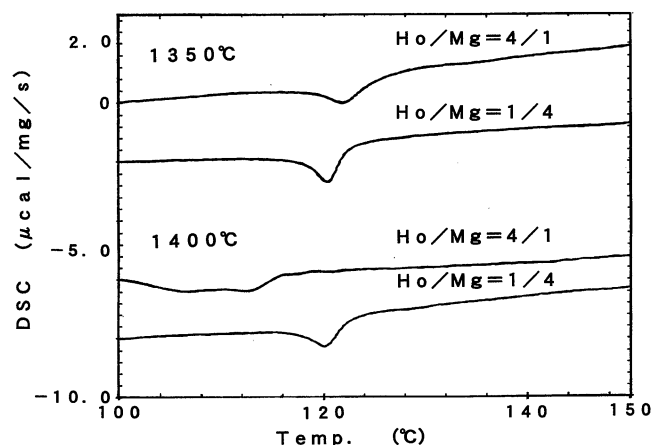


Fig. 3. DSC profiles of BT-MgO-Ho<sub>2</sub>O<sub>3</sub>-based ceramics with different Mg/Ho ratios sintered at 1350 and 1400°C.

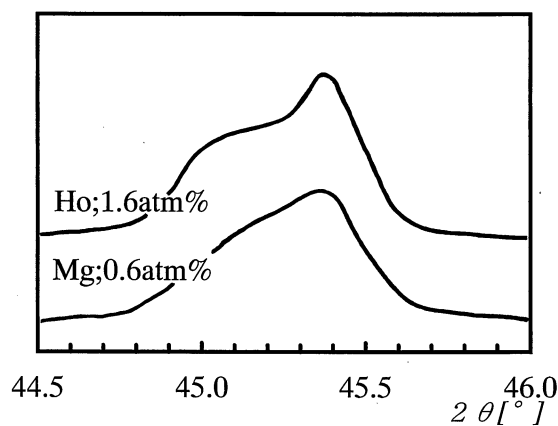


Fig. 4. XRD profiles of Mg-doped and Ho-doped BT sintered at 1100°C.

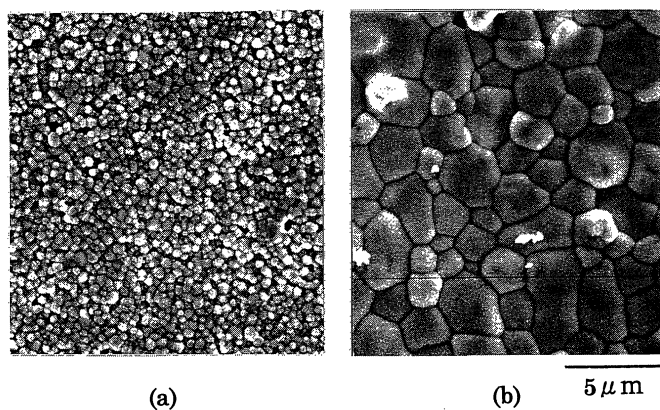


Fig. 5. SEM micrographs of (a) Mg-doped and (b) Ho-doped BT sintered at 1350°C.

system, and that an appropriate amount of Nb is necessary for the formation of the core-shell structure.<sup>4)</sup> The role of Mg ions in the present system is similar to that of Nb ions in the BT-Nb<sub>2</sub>O<sub>5</sub>-based system.

Thus, the formation behavior of the core-shell structure in the BT-MgO-Ho<sub>2</sub>O<sub>3</sub> system is considered as follows: 1) Mg reacts with BT at low temperatures to form the shell phase, and 2) Ho reacts with the shell phase

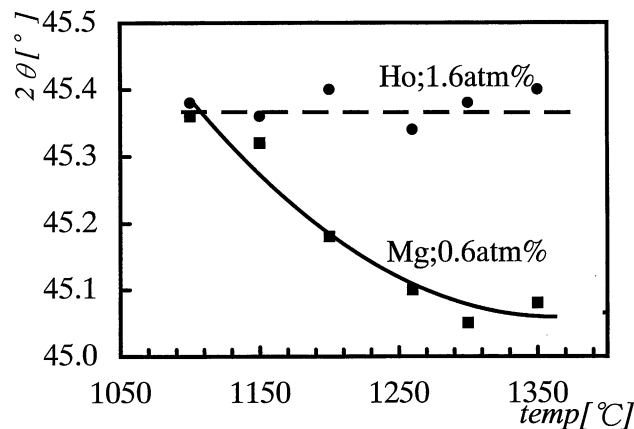


Fig. 6. Change in 200 diffraction peak of Mg-doped and Ho-doped BT as a function of sintering temperature.

at high temperatures and its diffusion into the core is suppressed by Mg.

### 3.2 Solubility modes of Mg and Ho

The conductivity behavior of BT is strongly influenced by the solubility mode of the dopant which is dependent on the valence state and the ionic radius. The ionic radius of Ti with 6 coordinates is 0.605 Å and that of Ba with 12 coordinates is 1.61 Å. The ionic radius of Mg with 6 coordinates is 0.720 Å, which is close to that of Ti ion. On the other hand, the ionic radius of Ho ion with 6 coordinates is 0.901 Å and that with 12 coordinates is 1.234 Å, based on the relationship between coordination number and effective ionic radii given in Shannon's table.<sup>8)</sup> The ionic radius of Ho is between those of Ba and Ti.

Figure 6 shows the change in the 200 diffraction peak of Mg-doped and Ho-doped samples sintered at various temperatures. In the case of Mg-doped sample, the spacing of lattice planes increased with increasing temperature. On the other hand, Ho-doped sample showed little change. The increase in lattice parameter of Mg-doped sample is consistent with previous reports that Mg acts as an acceptor dopant that is incorporated to a Ti site.<sup>9,10)</sup> Takada *et al.* showed that rare-earth ions of intermediate size in BT occupy both Ba and Ti sites.<sup>11)</sup> The change in XRD profiles shown in Fig. 2 suggests that site occupancy change occurs in this system. Therefore, we synthesized the samples according to the following compositions: Ba(Ti<sub>1-x</sub>Mg<sub>x</sub>)O<sub>3-x</sub> and (Ba<sub>1-x</sub>Ho<sub>x</sub>)(Ti<sub>1-x</sub>Ho<sub>x</sub>)O<sub>3</sub> ( $x = 0.001$  to 0.10).

Mg-substituted samples showed that a single phase of BT solid solution was obtained up to  $x = 0.006$ . MgO appeared as secondary phase. The increase in lattice parameter was also confirmed by high-temperature XRD. The lattice parameter became constant above  $x = 0.02$ . Therefore, the limit of solid solutions of Mg was about  $x = 0.02$ . From SEM observation of the sintered samples, it was found that grain growth of the samples was most strongly suppressed at around  $x = 0.01$ .

In the case of Ho-substituted samples, the precipitated phases were as follows: the single phase of BT solid solution was obtained up to  $x = 0.01$ ; as a secondary phase,

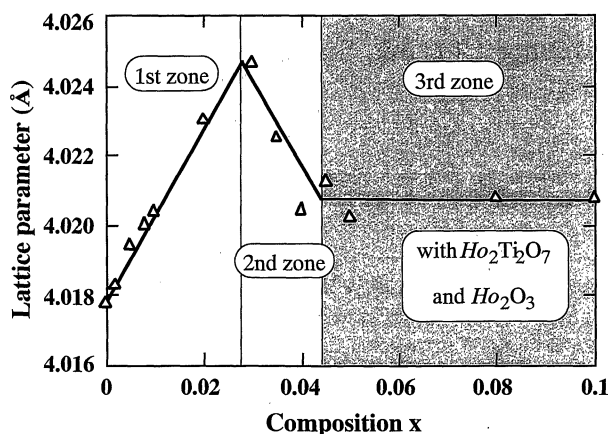


Fig. 7. Lattice parameters of BT- $x$ Ho<sub>2</sub>O<sub>3</sub> solid solutions at 300°C as a function of composition  $x$ .

pyrochlore (Ho<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>) appeared from  $x = 0.02$ ; and as ternary phase, rare-earth oxide (Ho<sub>2</sub>O<sub>3</sub>) appeared from  $x = 0.05$ . Figure 7 shows the lattice parameters of  $a$ -axis of Ho-substituted samples at 300°C, as determined by WPPD. The change in the lattice parameter is divided into three zones. The lattice parameter increased linearly up to  $x = 0.028$  in the first zone and then decreased linearly up to  $x = 0.044$  in the second zone. In the last zone, the lattice parameter showed no change and the composition of the phases was the same. Therefore, the limit of solid solutions of Ho was  $x = 0.044$ . This phenomenon can be attributed to the existence of different modes of Ho substitution at cation sites. The increase in lattice parameter means that Ti ions are replaced by Ho ions, because the ionic radius of Ho with 6 coordinates is larger than that of Ti with 6 coordinates. The decrease in lattice parameter means that Ba ions are replaced by Ho ions, because the ionic radius of Ho with 12 coordinates is smaller than that of Ba with 12 coordinates. Thus, it is considered that the first step of substitution in BT solid solutions mainly depends on the B-site replacement and the second step of substitution mainly depends on the A-site replacement.

Although further investigation is necessary to determine exactly the substitution site of dopant of the shell phase in the BT-MgO-Ho<sub>2</sub>O<sub>3</sub> system, the present results suggest that Mg ions are incorporated at B sites and act as acceptor dopants, and Ho ions are incorporated at both A and B sites and act as both donor and acceptor dopants in the shell phase. This indicates that controlling the solubility modes of rare-earth oxide in the shell phase is very important for improving reliability of MLCs with nickel electrodes.

#### 4. Conclusions

The differences in reaction temperature and diffusivity in BT between Mg and Ho were confirmed. It was found that Mg ions play an important role in the formation of the core-shell structure in the BT-MgO-Ho<sub>2</sub>O<sub>3</sub>-based system. Mg reacted with BT and formed the shell phase at low temperatures. On the other hand, Ho reacted with BT at high temperatures and showed higher diffusivity compared with Mg. Thus, an appropriate amount of Mg was necessary for suppressing the diffusion of Ho into the core.

The solubility modes of Mg and Ho in perovskite were also investigated. Using high-temperature XRD, we confirmed B-site replacement model for Mg ions and both A- and B-site replacement models for Ho ions. The increase in lattice parameter of Mg-substituted sample was confirmed. The limit of solid solution of Mg was about  $x = 0.02$ . The change in lattice parameter of the Ho-substituted sample is divided into three zones. Up to  $x = 0.028$ , Ho mainly dissolved in B sites with increasing lattice parameter, and up to  $x = 0.044$ , Ho mainly dissolved in A sites is based on a decrease in lattice parameter. Limit of solid solutions appeared at  $x = 0.044$ . It is considered that Mg ions act as acceptors and Ho ions act as both donors and acceptors.

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