Oxygen Diffusion and Defect Chemistry in Rare-Earth-Doped BaTiO₃

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希土類添加 BaTiO₃ の酸素拡散と欠陥化学

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The oxygen diffusion coefficients of nondoped, Ho-doped and La-doped BaTiO₃ polycrystals were evaluated by secondary ion mass spectrometry (SIMS). The La-doped and Ho-doped systems have a greatly reduced oxygen diffusion coefficient compared to nondoped BaTiO₃. The oxygen diffusion coefficient of La-doped BaTiO₃ was dependent on the amount of La dopant, while the amount of Ho did not influence oxygen diffusion. According to the change of the cooling rate during the fabrication process, the oxygen diffusion of the La-doped BaTiO₃ was influenced but that of Ho-doped BaTiO₃ changed little.

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1. Introduction

Dielectric compounds having a perovskite structure as exemplified by barium titanate (BaTiO₃) have long been known. Their physical properties have been exploited in a wide range of practical functional ceramics applications including capacitors, filters, nonvolatile memory, thermistors, and other devices. A typical case illustrating the great utility of BaTiO₃ is the application of this material to multilayer ceramic capacitors (MLCCs), a class of device that has seen significant progress in recent years.

The basic requirements of MLCCs are high capacity, low dielectric loss, temperature independence, and long life, and integration technology is adopted to satisfy all these requirements. For example, the bonding technology between the electrode and the dielectric is essential for the improvement of capacity and low-loss characteristics, and the optimal control of the core-shell structure in the dielectric material is necessary for the improvement of the thermal stability and lifetime of MLCCs. In an earlier study, we reported Ni diffusion behavior at the interface between the Ni electrode and the dielectric as research on “ceramics integration,”¹⁾ and here we report our recent work and findings regarding the dielectric material.

Recently the effectiveness of doping with rare-earth elements to extend the lifetime of MLCCs with Ni internal electrodes was recognized, and the rare-earth-doped BaTiO₃ having a core-shell structure is now being employed in practical fabrications.^{2)–6)}

In addition, doping with mid-to-heavy rare-earth elements such as Y, Dy, and Ho is highly effective for extending the lifetime of ceramic components. These elements have relatively small-diameter ions compared to other rare-earth elements, and occupy either A- or B-sites in BaTiO₃.^{7)–10)} It should be possible to enhance the electrical characteristics of devices through the self-compensating effect of A-site occupying donors and B-site occupying acceptors canceling each other out.

Waser et al. advanced the theory that the diminished lifetime of the components can be attributed to the degradation of insulation resistance.¹¹⁾ One factor diminishing the resistance is the electromigration of oxygen defects in the diele-

ctric. Nomura et al. analyzed emissions from cathode luminescence, and experimentally demonstrated that the electromigration of oxygen defects degraded the resistance.¹²⁾

In this study we focused on the relationship between rare-earth doping and oxygen defects, and quantitatively evaluated the oxygen diffusion coefficient closely associated with oxygen defects using secondary ion mass spectrometry (SIMS).¹³⁾ Our approach is to analyze BaTiO₃ doped with Ho and La, and consider the role of the rare-earth element in dielectrics from the perspective of defect chemistry.

2. Experimental

2.1 Synthesizing ceramics

BaTiO₃ ceramics were fabricated with the compositions (BaLa_x)(Ti_{1+x})O_{3+δ} and (BaHo_x)(Ti_{1+x})O_{3+δ} where $x = 0$ to 0.04 by solid-state reaction. Hydrothermally synthesized BaTiO₃ powder (BT-05, Sakai Chemical Industry Co.) was used as a raw material. La₂O₃ (Wako Pure Chemical Industries) and Ho₂O₃ (Nippon Yttrium Co.) were added to the BaTiO₃ as the dopants. BaCO₃ (Sakai Chemical Industry Co.) and TiO₂ (Ishihara Sangyo Kaisha) were used to maintain the A/B (Ba/Ti in BaTiO₃) ratio of 1. Figure 1 shows a flowchart of the fabrication process. The mixtures were prepared by ball-milling, adding 1 mass% polyvinyl alcohol solution (PVA) as a binder, and then pressing (60 MPa) into pellets approximately 10 mmφ (1.4 mm t in size). The pellets were fired at 1360°C for 1 h in air, followed by cooling as shown in Fig. 2. Cooling was carried out by two processes, A-process and B-process. The A-process, a fast cooling process, was performed at the rate of 100°C/h and the B-process, an extremely slow cooling process, was performed at the rate of 2°C/h from 1250 to 700°C. The ceramics fabricated by these processes exhibited >95% of the theoretical density. The primary impurities of the ceramics were SrO <0.02%, SiO₂ <20 ppm and traces of CaO, Na₂O, Al₂O₃, Fe₂O₃ (all <10 ppm).

The crystalline phases were identified by a diffractometer (model RINT2200, Rigaku) using Cu K α radiation, 40 kV–20 mA, and a scanning speed of 2°/min. The ceramics were ground to measure X-ray diffraction (XRD).

Fig. 1. Flowchart for preparation of (BaLa_x)(Ti_{1+x})O_{3+δ} and (BaHo_x)(Ti_{1+x})O_{3+δ} ceramics.

Fig. 2. Sintering patterns of the two cooling processes: A-process and B-process.

2.2 Oxygen diffusion analysis

The oxygen diffusion was evaluated by the gas(¹⁸O)-solid(¹⁶O) exchange method employing the stable isotope of oxygen ¹⁸O as the tracer.¹⁴⁾ The samples for diffusion analysis were polished with a diamond paste and cut into pieces of 3 mm $\times$ 3 mm $\times$ 1.2 mm t size. The samples placed in a Pt crucible were closed in a quartz glass vessel. After evacuation to 1.33×10^{-4} Pa, enriched ¹⁸O₂ was introduced into the vessel up to a pressure of 1.20×10^{-2} MPa. For isotope exchange, the Pt crucible containing the samples was heated at 700 to 1320°C for 10 to 20 min by a radio-frequency furnace.

The diffusion of ¹⁸O was examined by secondary ion mass spectrometry (SIMS, model IMS-4F, CAMECA, France) with ¹³³Cs⁺ as the primary ions and an accelerating voltage of 10 kV.¹⁵⁾ An area of $100 \times 100 \mu\text{m}^2$ was scanned by the primary beam. The intensities of ¹⁶O and ¹⁸O were recorded within the central 40% of the area of the sputtered crater. In order to maintain a stable electric field on the surface of the sample, an Au thin film of 0.02 μm was deposited, and electron beam flooding was carried out on the surface of the sample in order to prevent the charge up. After the SIMS analysis, the depth of the crater was measured using a

tracer-type surface roughness gauge (model Dektak 3030, Veeco, CA). Thus, an ¹⁸O-concentration depth profile is obtained.

The SIMS-based diffusion depth profile for the depth direction is derived from the relative concentration of ¹⁸O ions, C , given by

$$C = I(^{18}\text{O}^-) / [I(^{16}\text{O}^-) + I(^{18}\text{O}^-)] \quad (1)$$

where $I(^{18}\text{O})$ and $I(^{16}\text{O})$ are secondary ion intensities of ¹⁸O and ¹⁶O, respectively.

The volume diffusion coefficient, D_V , is calculated by fitting the diffusion profile according to Eq. (2):

$$\frac{C - C_{\text{bg}}}{C_s - C_{\text{bg}}} = \text{erfc} \left(\frac{x}{\sqrt{4D_V t}} \right) \quad (2)$$

where C is ¹⁸O ion concentration at depth x from the surface of the sample, C_{bg} is the background intensity, C_s is the surface concentration of ¹⁸O, and t is the diffusion annealing time.¹⁶⁾

The temperature dependence on D_V is given by the Arrhenius equation

$$D_V = D_0 \exp(-\Delta H/RT) \quad (3)$$

3. Results

3.1 X-ray diffraction patterns of La- and Ho-doped BaTiO₃ ceramics

Figure 3 shows the XRD patterns of the (BaLa_x)(Ti_{1+x})O_{3+δ}, La-doped BTO and the (BaHo_x)(Ti_{1+x})O_{3+δ}, Ho-doped BTO. These exhibited different characteristics according to the dopant amounts x of La and Ho.

The peak of a secondary phase was not observed for all La-doped BTO samples over the range of x amounts studied.

Fig. 3. XRD patterns of rare-earth-doped BaTiO₃: (a) (BaLa_x)(Ti_{1+x})O_{3+δ} and (b) (BaHo_x)(Ti_{1+x})O_{3+δ}.

In contrast, the Ho-doped BTO clearly exhibited a secondary peak around 30° related to the pyrochlore $\text{Ho}_2\text{Ti}_2\text{O}_7$ phase at $x > 0.02$.^{17,18)} Furthermore, the (002) peak appearing near 45° shifted to the (200) peak at higher angles with increasing x , and finally the (002) peak disappeared and only the (200) peak remained at $x = 0.04$ for the La-doped BTO. However, in the case of the Ho-doped BTO, the two peaks were detected in all samples. It was considered that the difference in XRD patterns between La- and Ho-doped BTO was reflected in the solid solubility of La and Ho into BaTiO_3 .

3.2 Oxygen diffusion coefficient of La- and Ho-doped BTO fabricated by the A-process

Figure 4 shows the diffusion profiles of nondoped BTO ($x = 0$, annealing at 825°C) and La-doped BTO ($x = 0.001$, 0.005 and 0.02 , annealing at 850°C) fabricated by the A-process. The diffusion profile varied with increasing La dopant amount x . The volume diffusion coefficient of oxygen D_V is plotted in Fig. 5 as a function of reciprocal temperature.

Fig. 4. Diffusion profile of ^{18}O obtained from $(\text{BaLa}_x)(\text{Ti}_{1+x})\text{O}_{3+\delta}$ annealed at $825\text{--}850^\circ\text{C}$ for 20 min.

Fig. 5. Arrhenius plot of ^{18}O diffusion coefficients (D_V) obtained from $(\text{BaLa}_x)(\text{Ti}_{1+x})\text{O}_{3+\delta}$.

The Arrhenius plots for the La-doped BTO were divided into two regions over the temperature range studied: a low-temperature region having lower activation energy and a high-temperature region having higher activation energy. The boundaries of the two regions for all compositions were $1/T = 8 \times 10^{-4} (1/\text{K})$, where T was about 970°C . The D_V was dramatically reduced with increasing x especially in the low-temperature region. Table 1 shows the activation energies ΔH and frequency factors D_0 for a low-temperature and a high-temperature region for various x amounts. The activation energy increased with increasing x in the high-temperature region.

Figure 6 shows the diffusion profiles of nondoped BTO ($x = 0$, annealing at 825°C) and Ho-doped BTO ($x = 0.005$ and 0.02 , annealing at 825°C) fabricated by the A-process. The oxygen diffusion in Ho-doped BTO samples was suppressed in comparison with that in nondoped BTO. However, the diffusion profiles of Ho-doped BTO changed little with increasing x , in contrast to those of La-doped BTO. Figure 7 shows the Arrhenius plots of D_V for the Ho-doped BTO. The two temperature regions observed in the Arrhenius plots of La-doped BTO (Fig. 5) were not apparent in those of Ho-doped BTO. The latter was in good agreement with the Arrhenius equation within the limitations of the experimental conditions. The activation energies ΔH and frequency factors D_0 for x are listed in Table 2. The activation energy of Ho-doped BTO was higher than that of La-doped BTO at low temperatures.

Figure 8 shows the dependence of D_V on the amount of x for the La- and Ho-doped BTO fabricated by the A-process

Table 1. Pre-Exponential Factor (D_0) and Activation Energies (ΔH) for Oxygen Diffusion Coefficients (D_V) in $(\text{BaLa}_x)(\text{Ti}_{1+x})\text{O}_{3+\delta}$. $D_V [\text{cm}^2/\text{s}] = D_0 \exp(-\Delta H/RT)$

La conc. x	Low-Temperature Region		High-Temperature Region	
	D_0 ($\text{cm}^2 \cdot \text{s}^{-1}$)	ΔH ($\text{kJ} \cdot \text{mol}^{-1}$)	D_0 ($\text{cm}^2 \cdot \text{s}^{-1}$)	ΔH ($\text{kJ} \cdot \text{mol}^{-1}$)
0	7.567×10^{-4}	158.4		
0.001	4.348×10^{-7}	117.1	2.432×10^{-2}	224.1
0.005	1.247×10^{-5}	166.2	4.875×10^{-1}	278.2
0.020	2.082×10^{-6}	176.1	3.776×10^{-4}	414.9

Fig. 6. Diffusion profile of ^{18}O obtained from $(\text{BaHo}_x)(\text{Ti}_{1+x})\text{O}_{3+\delta}$ annealed at 825°C for 20 min.

Fig. 7. Arrhenius plot of ¹⁸O diffusion coefficients (D_V) for $(\text{BaHo}_x)(\text{Ti}_{1+x})\text{O}_{3+\delta}$.

Table 2. Pre-Exponential Factor (D_0) and Activation Energies (ΔH) for Oxygen Diffusion Coefficients (D_V) in $(\text{BaHo}_x)(\text{Ti}_{1+x})\text{O}_{3+\delta}$. $D_V[\text{cm}^2/\text{s}] = D_0 \exp(-\Delta H/RT)$

Ho conc. x	D_0 ($\text{cm}^2 \cdot \text{s}^{-1}$)	ΔH ($\text{kJ} \cdot \text{mol}^{-1}$)
0	7.567×10^{-4}	158.4
0.001	3.000×10^{-3}	229.7
0.005	9.319×10^{-3}	242.9
0.020	3.278×10^{-3}	229.5

Fig. 8. Dependence of the oxygen diffusion coefficients (D_V) at 850°C on rare-earth doping amount (x) for La- and Ho-doped BaTiO₃ fabricated by A-process.

at 850°C. The result of Shirasaki et al. for the La-doped BTO with $x=0.1$ ¹⁹⁾ is also plotted in Fig. 8. In the case of the La-doped BTO, D_V decreased with increasing x and there

Fig. 9. Arrhenius plot of ¹⁸O diffusion coefficients (D_V) for La- and Ho-doped BaTiO₃ ($x=0.001$) fabricated by A-process and B-process.

was a good linear relationship between $\log D_V$ and $\log x$. On the other hand, the D_V of the Ho-doped BTO changed little even as x was increased, namely, D_V was independent of dopant amount in this case.

3.3 Effects of the cooling rate on the oxygen diffusion coefficient

The cooling rate influences the formation of lattice defects in the fabrication process of the ceramic. Therefore, the oxygen diffusions were compared in the samples ($x=0.001$) fabricated using the two different cooling processes. The D_V values for the La- and Ho-doped BTO obtained with the B-process are plotted in Fig. 9 with the results for the A-process. In the case of the La-doped BTO, the D_V for the low-temperature region was markedly reduced from the value for the A-process, while that for the high-temperature region agreed with the value for the A-process. The cooling rate had a pronounced effect on the oxygen diffusion coefficients of La-doped BTO. In the Ho-doped BTO, the diffusion coefficient for the B-process was nearly the same as that for the A-process. Thus, the cooling rate had little effect on the oxygen diffusion coefficients for the Ho-doped BTO in comparison with that for the La-doped BTO.

4. Discussion

4.1 Crystal structure of La- and Ho-doped BTO

From the results in Fig. 3(a), La-doped BTO was transformed from a tetragonal phase to a cubic phase with the increase in the La concentrations. This phase transformation is based on Ba-site replacement with La^{3+} smaller than Ba^{2+} in the ionic radius. The ionic radii of Ba^{2+} and La^{3+} in the 12-coordinate system are 0.161 nm and 0.136 nm, respectively.²⁰⁾ Thus, the lattice of La-doped BTO was shrunk in the c -axis direction and changed to pseudo-cubic. It is deduced that La^{3+} cations easily to dissolve into BaTiO₃ lattices since a single phase of BaTiO₃ is obtained up to $x=0.04$. On the other hand, in Ho-doped BTO, as shown in Fig. 3(b), the pyrochlore ($\text{Ho}_2\text{Ti}_2\text{O}_7$) as a second phase was formed at $x=0.02$ and above. The tetragonal phase remained even up to $x=0.04$ when the phase transformation of the La-doped BTO occurred. It is evident that the dissolution behavior of La into BaTiO₃ lattice is different from that of Ho. In other words, the solid solubility of Ho into BaTiO₃ is less than that of La, so that Ho is precipitated as a secondary phase at grain boundaries, in the sample with high dop-

ing concentration.

4.2 Solubility effect of rare-earth elements in BaTiO₃

The analysis of the oxygen diffusion by the SIMS clearly revealed that: (1) the volume diffusion coefficients of oxygen for BaTiO₃ systems doped with rare earth elements, such as La and Ho, are significantly reduced, and (2) the volume diffusion coefficients of oxygen for La-doped BTO were dependent on the La dopant concentrations, but those for Ho-doped BTO were independent of the Ho dopant concentrations.

The volume diffusion coefficient of oxygen, D_V , is proportional to the concentration of oxygen defects in the lattice, namely,

$$D_V \propto [V_{O}^{\bullet\bullet}] \quad (4)$$

The D_V for La- or Ho-doped BTO systems was markedly reduced as compared to that for the nondoped BTO. It is apparent that the rare-earth elements act to reduce the oxygen defects in BaTiO₃. The mechanism for the suppression of the oxygen defect formation can be represented by the following reaction formula:

where R represents a rare-earth element. The oxygen defects included in the original BaTiO₃ are consumed by incorporating the rare-earth ions R^{3+} into Ba^{2+} sites. The mechanism works for both La and Ho, and is indeed applicable to all rare-earth elements. It is thought that doping with rare-earth elements contributes to the suppression of oxygen defect formation, and that it is effective for extending the life of MLCCs by the described mechanism.

Provided that rare-earth ions R^{3+} occupy B-sites, the following reaction takes place:

In this case, the concentration of oxygen defects increases. However, the volume diffusion coefficient of oxygen in La-doped BTO samples decreased with increasing La dopant concentration. The above assumption is contradicted by this finding.

It was also observed that the diffusion coefficient of oxygen in Ho-doped BTO was independent of the Ho dopant concentrations. From these results, it is believed that the limit of the solid solution of Ho in BaTiO₃ is much less than that of La.

Furthermore, in Fig. 5, the two intersecting regions characterized the Arrhenius plots for the La-doped BTO. It is thought that the low-temperature region is associated with extrinsic defects and that the high-temperature region is related to intrinsic defects. For the La-doped BTO, the high activation energy at an elevated temperature is most likely associated with intrinsic diffusion. As a consequence, the intrinsic oxygen defects were formed at high temperatures, namely above 970°C. The formation of intrinsic oxygen defects may be achieved by the thermal dissociation of the constituent oxygen in the lattice. According to Shirasaki et al., who studied the temperature dependence of the oxygen diffusion coefficient for La-doped BTO, the presence of cation defects (Ba-site vacancies) in La-doped BTO enhances the dissociation of oxygen at elevated temperatures.¹⁹⁾ If a very small portion of a doped quantity of La is consumed for reduction of the number of oxygen defects according to Eq. (5), additional La-doping which does not contribute to the suppression of the oxygen defect formation could act to form Ba-site vacancies, $V_{Ba}^{\prime\prime}$, by the following mechanism:

It is thought that the presence of $V_{Ba}^{\prime\prime}$ is related to the relaxation of the chemical bonding of the host lattice or Ti-O₆ octahedra in the region adjacent to $V_{Ba}^{\prime\prime}$. Shirasaki et al. put forward the argument that the intrinsic region at elevated temperatures was not observed in BTO samples with few $V_{Ba}^{\prime\prime}$, e.g., nondoped BTO, Ba-site excess La-doped BTO. It is assumed that Ho-doped BTO also has few $V_{Ba}^{\prime\prime}$ because the Arrhenius plot for the Ho-doped BTO is linear as shown in Fig. 7.

The solid solubility of La and Ho into BaTiO₃ is assumed to be nearly the same at an x amount of at least 0.001. However, the difference in D_V between La- and Ho-doped BTO is recognized at $x=0.001$ in Fig. 8. This difference is attributed to the thermal dissociation of oxygen in La-doped BTO, so that the D_V for the La-doped BTO is higher than that for the Ho-doped BTO at a small doping concentration. The D_V is affected by the dissociation of oxygen even at low temperatures.

4.3 Effects of nonequilibrium defects on oxygen diffusion

From the results of La-doped BTO in Fig. 9, the low-temperature region observed in the A-process is ascribed to the presence of nonequilibrium defects in the La-doped BTO. This experimental result can be explained as follows. The concentration of intrinsic oxygen defects rapidly increases with the increase of temperature in the La-doped BTO. The La-doped BTO containing the intrinsic oxygen defects which increased at high temperatures is then cooled to room temperature at a gradual rate. However, the high concentration of intrinsic defects cannot be reduced to achieve a low concentration of thermal equilibrium defects at each temperature during cooling. Consequently, the intrinsic defects are frozen into the crystals as nonequilibrium defects, and a higher defect concentration for the La-doped BTO is formed by the A-process than by the B-process at low temperatures. It is believed that this accounts for the presence of the nonequilibrium defects.

On the other hand, the differences in cooling rates between the A- and B-processes had little effect on the oxygen diffusion coefficients in the Ho-doped BTO. The nonequilibrium defects observed in the La-doped BTO are absent or notably reduced in the Ho-doped BTO.

5. Conclusions

Adopting a defect-chemistry approach, the effects of different rare-earth dopants in barium titanate (BaTiO₃) were estimated by analyzing oxygen diffusion behavior using SIMS. The results obtained in this study are summarized as follows:

- (1) The oxygen diffusion coefficient is reduced by doping with Ho and La. Doping rare-earth elements in BaTiO₃ thus had the effect of suppressing oxygen defects in the crystal lattice.
- (2) The oxygen diffusion analysis revealed that La preferentially occupies A-sites of the BaTiO₃ perovskite structure, while Ho clearly exhibited much less solubility in BaTiO₃ than La.
- (3) Arrhenius plots of oxygen diffusion coefficients revealed the presence of nonequilibrium defects in the low-temperature region of La-doped systems, while nonequilibrium defects could not be found in Ho-doped systems.

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