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# Effect of site occupancies of rare earth ions on electrical properties in Ni-MLCC based on $BaTiO_3$

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## Abstract

The site occupancies of rare earth ions for Ba-site to Ti-site were quantitatively estimated in $(Ba_{1-x},R_x)(Ti_{1-x},R_x)O_3$ (R = Eu, Ho), $(Ba_{1-3x}Eu_{2x})TiO_3$, and $Ba(Ti_{1-2x}Eu_{2x})O_{3-x}$ systems by applying the Rietveld refinement to the data obtained from the synchrotron radiation powder diffraction measurement. The occupational ratio of Ba-site to Ti-site for the larger rare earth ion (Eu) was 49/51 ($x = 0.10$), whereas for the smaller ion (Ho) was 9/91 ($x = 0.01$) in $(Ba_{1-x},R_x)(Ti_{1-x},R_x)O_3$ system. Furthermore, the occupational ratio was greatly dependent on the Ba/Ti ratio, in $(Ba_{1-3x}Eu_{2x})TiO_3$ system it was 92/8 ($x = 0.03$), whereas that in $Ba(Ti_{1-2x}Eu_{2x})O_{3-x}$ system was 20/80 ($x = 0.01$). The Curie point shifted to lower temperature effectively with increasing in the occupational ratio of rare earth ion into Ba-site.

*Keywords:* X-ray methods; Capacitors; $BaTiO_3$ and titanates; Electrical properties; Lifetime

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## 1. Introduction

Currently, the capacitance density in multi-layer ceramic capacitors with Ni internal electrodes (Ni-MLCCs) has been increasing at the rate of about two orders per decade, which is almost in accordance with Moore's Law. It is well known that the lifetime of Ni-MLCCs fabricated on $BaTiO_3$ (BT) can be drastically improved by the addition of rare earth ions. Furthermore, the incorporation of rare earth ions into the BT lattice depends on their ionic radii. In particular, the rare earth ions with intermediate values of ionic radii can be simultaneously substituted at both the Ba and Ti sites; they can act as both donor and acceptor ions. Table 1 lists the ionic radii of several rare earth ions, which are categorized into three groups.[1,2] Many researchers have reported that the lifetime of Ni-MLCCs can be optimized by the incorporation of Dy or Ho ions in the group with intermediate values of ionic radii.[1,3] Furthermore, it is well known that the donor/acceptor ratio and the grain boundary characteristics have a decisive role on lifetime.[1,4] On the other hand, the incorporation of rare earth ions into the BT lattice has a drastic influence on its electrical properties.[5,6] Controlling the Curie temperature ($T_c$) is one of the most important techniques to improve the temperature characteristics of the capacitance (TCC) of Ni-MLCCs. Although studies propose that the site occupancy of rare earth ions in a BT lattice is considerably essential for both the lifetime and electrical properties of Ni-MLCCs, only a few studies have been conducted including the quantitative analysis regarding the site occupancy ratio of the rare earth ions. In this study, the quantitative analysis of the rare earth ions in a BT lattice was carried out and the relationship between the site occupancies of rare earth ions and $T_c$ was investigated. Eu and Ho were selected as the rare earth ions, which belong to the group with intermediate values of ionic radii; the ionic radius of Eu is slightly greater than that of Ho, as shown in Table 1.

## 2. Experimental procedure

Samples with the chemical formula of $(Ba_{1-x}R_x)(Ti_{1-x}R_x)O_3$, where R = Eu and Ho ($x = 0$–$0.10$), were prepared by using the conventional ceramic sintering method. Further, the samples with the chemical formulae of $(Ba_{1-3x}Eu_{2x})TiO_3$ and $Ba(Ti_{1-2x}Eu_{2x})O_{3-x}$ were prepared to clarify the influence of the Ba/Ti ratio on the site occupancies of rare earth ions in the BT lattice. Hereafter, $(Ba_{1-x}R_x)(Ti_{1-x}R_x)O_3$ (R = Eu, Ho), $(Ba_{1-3x}Eu_{2x})TiO_3$, and $Ba(Ti_{1-2x}Eu_{2x})O_{3-x}$ systems are

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Table 1
Ionic radii of rare earth ions

| | Coordination number | |
|---|---|---|
| | 6 | 12 |
| Light rare earth ions (large ionic radius) | | |
| $La^{3+}$ | 1.032 | 1.360 |
| $Ce^{3+}$ | 1.01 | 1.340 |
| $Nd^{3+}$ | 0.983 | 1.270 |
| Middle weight rare earth ion (intermediate ionic radius) | | |
| $Sm^{3+}$ | 0.958 | 1.240 |
| $Eu^{3+}$ | 0.947 | 1.266 |
| $Gd^{3+}$ | 0.938 | 1.253 |
| $Dy^{3+}$ | 0.912 | 1.229 |
| $Ho^{3+}$ | 0.901 | 1.218 |
| $Er^{3+}$ | 0.89 | 1.208 |
| Heavy rare earth ions (small ionic radius) | | |
| $Yb^{3+}$ | 0.868 | 1.188 |
| $Lu^{3+}$ | 0.861 | 1.178 |
| $Ba^{2+}$ | | 1.61 |
| $Ti^{4+}$ | 0.605 | |

The ionic radii of Eu, Gd, Dy, Ho, Er, Yb, and Lu ion in 12 coordinate are based on the relationship between coordination number and effective ionic radius base on Shannon's table.

abbreviated as AB-R(Eu, Ho), A-R(Eu), and B-R(Eu), respectively. The raw materials – $BaCO_3$, $R_2O_3$, and $TiO_2$ – were mixed and then calcined at 1100 °C for 2 h in air, and they were granulated and formed into a pellet shape; then, these pellets were fired at 1250 – 1400 °C for 2 h. We have previously confirmed that the firing condition, such as temperature and atmosphere, had little effect on the lattice parameter in $(Ba,La)(Ti,Mg)O_3$ and $(Ba,Ho)(Ti,Mg)O_3$ system. Therefore, in this study, firing temperature was decided as the temperature showing the sufficient relative density for the fired samples.[7] The samples were crushed and pulverized into powders, and they were analyzed by X-ray powder diffraction (XRD) in order to identify the crystalline phases. The lattice constants were precisely refined using the whole-powder-pattern decomposition (WPPD) program.[8] In this study, the XRD measurement was carried out using an internal standard sample at 300 °C, which is greater than the Curie point of BT in order to avoid the influence of phase transitions occurring due to the doping of the rare earth ions. Furthermore, the Rietveld analysis was applied to the data obtained from the synchrotron radiation powder diffraction measurement, and the site occupancy of the rare earth ions was quantitatively evaluated using the RIETAN-2000 program.[9] The synchrotron experiments were performed at BL-B2 in the Photon Factory of the High Energy Accelerator Research Organization (PF-KEK), Tsukuba, Japan; the powder diffractions were obtained by a $2\theta$ multiple-detector system (MDS).

In order to evaluate the electrical properties, a silver electrode was grown on both the sides of the pellet samples. The Curie point of the samples was determined by measuring the dielectric constant using an impedance analyzer (Agilent, HP-4294A) in the temperature range from 25 °C to 225 °C.

## 3. Results and discussion

### 3.1. Site occupancies of rare earth ions in BT solid solutions

The precipitated phases of the samples are summarized in Table 2. It was found that a single phase of the BT solid solution was obtained in the AB-R system in a wide range of samples substituted by the larger rare earth ion (Eu) as compared to that by a smaller rare earth ion (Ho). Secondary phases were not observed in the range up to $x = 0.10$ for the AB-R(Eu) system. On the other hand, the single phase of the BT solid solution was obtained in an extremely narrow range up to $x = 0.005$ in the case of the AB-R(Ho) system. Secondary phases such as the pyrochlore phase of $R_2Ti_2O_7$ and $R_2O_3$ were observed. In both the A-R(Eu) and B-R(Eu) systems, the single phase of the BT solid solution was obtained in a narrow range of samples as compared to that in the AB-R(Eu) system. These results suggest that the solubility of Eu ions in the BT lattice is considerably greater than that of Ho ions.

For precisely understanding the behavior of the solubility of rare earth ions in the BT lattice, a high-temperature powder XRD analysis was carried out. The lattice constants determined by using the WPPD program are shown in Fig. 1. With regard to the AB-R system, it was found that the solution behavior of the samples substituted with Eu ions was fairly different than that of the samples substituted with Ho ions. In the case of the Eu ions, the

Table 2
Precipitated phases of the $(Ba_{1-x}R_x)(Ti_{1-x}R_x)O_3$ (R = Eu, Ho), $(Ba_{1-3x}Eu_{2x})TiO_3$, and $Ba(Ti_{1-2x}Eu_{2x})O_{3-x}$ solid solution

| Comoposition, $x$ | $(Ba_{1-x}Eu_x)(Ti_{1-x}Eu_x)O_3$ | $(Ba_{1-3x}Eu_{2x})TiO_3$ | $Ba(Ti_{1-2x}Eu_{2x})O_{3-x}$ | $(Ba_{1-x}Ho_x)(Ti_{1-x}Ho_x)O_3$ |
|---|---|---|---|---|
| 0.002 | – | – | – | BT(T) |
| 0.005 | – | – | – | BT(T) |
| 0.01 | BT(T) | BT(T) | BT(T) | BT(T) + R2T2 |
| 0.02 | BT(T) | BT(T) | BT(T) + B2T | BT(T) + R2T2 |
| 0.03 | BT(T) | BT(T) | BT(T) + B2T | BT(T) + R2T2 |
| 0.04 | BT(T) | BT(T) + B4E9T18 | BT(T) + B2T | BT(T) + R2T2 |
| 0.05 | BT(T) | BT(C) + B4E9T18 | BT(C) + B2T + B12E 4T8 | BT(C) + R2T2 + R |
| 0.06 | BT(T) | BT(C) + B4E9T18 | BT(C) + B2T + B12E 4T8 | – |
| 0.08 | BT(C) | BT(C) + B4E9T18 | BT(C) + B2T + B12E4T8 | BT(C) + R2T2 + R |
| 0.10 | BT(C) | BT(C) + B4E9T18 | BT(C) + B2T + B12E4T8 | BT(C) + R2T2 + R |

BT(T): $BaTiO_3$(tetragonal); BT(C): $BaTiO_3$(cubic); B12R 4T8: $Ba_{12}R_{4.67}Ti_8O_{35}$; R 2T2: $R_2Ti_2O_7$; R: $R_2O_3$.

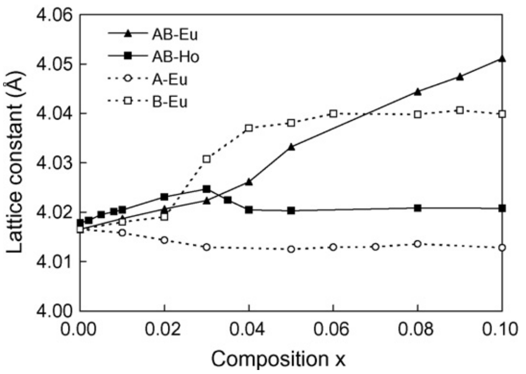

Fig. 1. Lattice constant of $(Ba_{1-x}R_x)(Ti_{1-x}R_x)O_3$ (R = Eu, Ho), $(Ba_{1-3x}Eu_{2x})TiO_3$, and $Ba(Ti_{1-2x}Eu_{2x})O_{3-x}$ solid solution at 300 °C.

lattice constant increased as a function of composition $x$. However, a marginal change is observed in $x$ – between 0.03 and 0.05 – in this range, the lattice constant increased more as compared to its increase in the other ranges of $x$. Therefore, the changes in the lattice constant can be divided into the following three stages: During the first stage ($0 < x < 0.03$), the lattice constant increased gradually; then, it increased drastically during the second stage ($0.03 < x \leq 0.05$). During the third stage ($0.05 < x < 0.10$), the increase in the lattice constant was similar to that during the first stage. On the other hand, the change in the lattice constant in the samples substituted by Ho ions could also be divided into the following three stages: During the first stage ($0 < x < 0.03$), the lattice constant increased linearly with an increase in the value of $x$; then, it decreased during the second stage ($0.03 < x < 0.04$). During the third stage ($0.04 < x < 0.10$), it assumed a constant value. Furthermore, it was found that a change in the lattice constant considerably depended on the Ba/Ti ratio. In the A-R(Eu) system, the lattice constant decreased gradually up to $x = 0.03$; it then assumed a constant value. On the other hand, in the B-R(Eu) system, the lattice constant increased gradually up to $x = 0.02$; it then increased drastically up to $x = 0.04$. These behaviors can be attributed to the different modes in the substitution of the rare earth ions at the cation sites. The increase in the value of the lattice constant is due to the replacement of the Ti ion by a rare earth ion having a size greater than that of the Ti ion. In contrast, the decrease in the lattice constant is due to the replacement of the Ba ion by a rare earth ion having a size smaller than that of the Ba ion. In the AB-R(Eu) system, the change in the lattice constant is considered to progress as follows: Eu is preferentially substituted at the Ti site, and the substitution ratio of the rare earth ions at the Ba and/or Ti sites depends on composition $x$. This implies that the substitution ratio with regard to the Ti site is greater for the second stage than the first and third stages. On the other hand, in the case of the smaller rare earth ions (Ho), it is considered that the decrease in the lattice constants during the second stage is caused by an increase in the Ba-site occupancy ratio of Ho. This explanation can also be applied to the decrease in the lattice constant up to $x = 0.03$ in the A-R(Eu) system. Therefore, the site occupancies of the rare earth ions in the BT lattice were qualitatively evaluated according to the analysis of the lattice constant at 300 °C, as shown in Fig. 1.

The Rietveld refinements were carried out using the synchrotron radiation powder diffraction data, and the site occupancies of the rare earth ions were quantitatively estimated. The occupancy ratio was determined as the ratio showing the minimum value of the reliability factor (S factor). The occupancy ratio of the Ba site to the Ti site for the various compositions is summarized in Table 3. The occupancy ratios for Eu in the AB-R system were 47/53, 43/57, and 49/51 at $x = 0.03$, 0.05, and 0.10, respectively. On the other hand, the occupancy ratios for Ho in the AB-R(Ho) system were 0/100 and 9/91 at $x = 0.005$ and 0.01, respectively. Furthermore, the occupancy ratio for Eu was strongly dependent on the Ba/Ti ratio; its value was 92/8 in the A-R(Eu) system, whereas 20/80 in the B-R(Eu) system. These results quantitatively indicate that the occupancy ratio of the Ba site to the Ti site increases with an increase in the ionic radius in the AB-R system. Furthermore, it appears that the occupancy ratio at $x = 0.10$, which is marginally greater than those at $x = 0.03$ and 0.05, was associated with a change in the slope of the lattice constants at 300 °C as a function of composition $x$ (see Fig. 1). It is evident that the site occupancy of the rare earth ions in the BT lattice can be quantitatively calculated. The difference in the lifetimes between the MLCC samples substituted by Ho or Dy ions and the samples substituted by other intermediate rare earth ions (as reported in previous studies[1,2]) might be attributed to the unbalanced donor/acceptor ratios and the grain boundary characteristics, which originate from the higher solubility of Eu ions into the BT lattice as compared to that of the Ho ions, as reported by Chazono.[4]

### 3.2. *The effect of site occupancy on electrical properties*

The effect of the site occupancy of rare earth ions in the BT lattice on the electrical properties of Ni-MLCCs was investigated by means of $T_c$ measurements as indicated Fig. 2. Fig. 3 shows the Curie points as a function of composition $x$. It was found that the $T_c$ value linearly shifted to a lower temperature with the Eu content, whereas the Ho ions present in AB-R system exhibited a marginal influence on $T_c$. Furthermore, it was clarified that the changing rate of $T_c$ as a function of composition $x$ was strongly

Table 3
Calculated site occupancies of rare earth ion in the $(Ba_{1-x}R_x)(Ti_{1-x}R_x)O_3$ (R = Eu, Ho), $(Ba_{1-3x}Eu_{2x})TiO_3$, and $Ba(Ti_{1-2x}Eu_{2x})O_{3-x}$ solid solution

| Comoposition, $x$ | $(Ba_{1-x}Eu_x)(Ti_{1-x}Eu_x)O_3$ | $(Ba_{1-3x}Eu_{2x})TiO_3$ | $Ba(Ti_{1-2x}Eu_{2x})O_{3-x}$ | $(Ba_{1-x}Ho_x)(Ti_{1-x}Ho_x)O_3$ |
|---|---|---|---|---|
| 0.005 | | | | 0/100 |
| 0.01 | | | 20/80 | 9/91 |
| 0.03 | 47/53 | 92/8 | | |
| 0.05 | 43/57 | | | |
| 0.10 | 49/51 | | | |

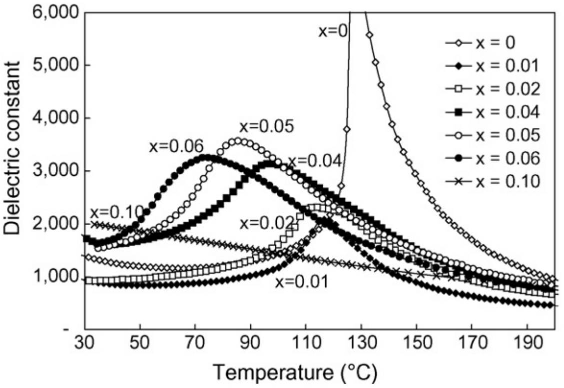

Fig. 2. Temperature characteristics of dielectric constant in the $(Ba_{1-x}Eu_x)(Ti_{1-x}Eu_x)O_3$ system.

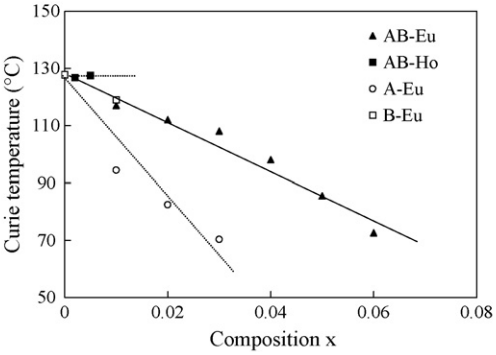

Fig. 3. Curie temperature of $(Ba_{1-x}R_x)(Ti_{1-x}R_x)O_3$ (R = Eu, Ho), $(Ba_{1-3x}Eu_{2x})TiO_3$, and $Ba(Ti_{1-2x}Eu_{2x})O_{3-x}$ as a function of composition $x$.

dependent on the occupancy ratio at the Ba site. It was considered that $T_c$ effectively shifted to a lower temperature with an increase in the occupancy ratio of the rare earth ions at the Ba site.

## 4. Conclusion

Detailed XRD measurements were performed at 300 °C to investigate the precipitated phases and changes in the lattice constants; the results strongly suggest that the solubility of the Eu ions in the BT lattice was greater than that of the Ho ions. The occupancy ratio was quantitatively estimated; in the AB-R system, the value of the ratio of the Ba site to the Ti site is greater for the Eu ions than for the Ho ions. The change in the lattice constant as a function of composition $x$ corresponded to the occupancy ratio of the rare earth ion at the Ba site. The difference in the lifetimes between the MLCC samples substituted by Ho or Dy ions and by other intermediate rare earth ions might be attributed to the unbalanced donor/acceptor ratios and grain boundary characteristics, which originated from the difference in the solubility of the rare earth ions. The value of $T_c$ effectively shifted to a lower temperature with an increase in the occupancy ratio of the rare earth ion at the Ba site.

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