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Theoretical and experimental analysis for site preference of rare earth elements in $BaTiO_3$

Y. Umeda [a,*], K. Masuzawa [a], S. Ueda [b], S. Ootsuki [b], A. Kuwabara [c], H. Moriwake [c]

[a] *Materials & Process Development Center, TDK Corporation, Chiba 286-8588, Japan*
[b] *Application & Analysis Center, TDK Corporation, Chiba 286-8588, Japan*
[c] *Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya 456-8587, Japan*

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Abstract

Rare earth (RE) elements such as Y, Ho, and Dy are considered to play an important role in the long-term reliability of multilayer ceramic capacitors (MLCCs). Theoretical calculations of the site preference of RE elements in $BaTiO_3$ are useful tools for understanding this mechanism, especially when the RE elements are co-doped with other additive elements. In this study, the site preference of RE elements doped with and without Mg in $BaTiO_3$ is investigated by performing first-principles calculations and experiments. The calculation results indicate that the site preference of RE elements is strongly related to their ionic radii. In the simulation of Dy, Dy atoms replace both Ba and Ti atoms without Mg co-doping. On the other hand, when Dy is co-doped with Mg, Dy atoms prefer to occupy the Ba site instead of the Ti site in $BaTiO_3$. Experiments were also performed to analyze element concentrations in Dy-doped $BaTiO_3$ with and without Mg co-doping by scanning transmission electron microscopy with energy-dispersive X-ray spectroscopy. The theoretical calculation and experimental measurement agree quite well on the site preference of Dy with and without Mg co-doping. Our theoretical and experimental results reveal the influence of Mg co-doping on the site preference of the RE elements in $BaTiO_3$.

Keywords: B. Microstructure-final; C. Lifetime; D. $BaTiO_3$ and titanates; E. Capacitors

1. Introduction

Barium titanate ($BaTiO_3$) is the one of the most important ferroelectric materials utilized for multilayer ceramic capacitors (MLCCs) because of its high permittivity. Ni metal is used as the internal electrode in MLCCs for commercial reasons. To produce the metallic internal electrode, MLCCs are usually sintered under a reducing atmosphere [1] (e.g., $p_{O_2} < 10^{-10}$ MPa). However, under such reducing conditions, $BaTiO_3$ is easily reduced and oxygen vacancies with *n*-type carriers are generated by the following reaction:

$$BaTiO_3 \rightarrow BaTiO_{3-\delta} + \frac{\delta}{2}O_2 + V_O^{\bullet\bullet} + 2e' \quad (1)$$

where $V_O^{\bullet\bullet}$ denotes an oxygen vacancy with an effective charge of 2+ related to the $BaTiO_3$ lattice according to the Kröger–Vink notation.

In their early development stages, Ni-electrode MLCCs showed poor reliability. Their electrical resistance decreased under long-term DC voltages. This was one of the most serious problems encountered during the development of small-size, high-performance Ni-electrode MLCCs. To overcome this problem, rare earth (RE) element doping was found to be effective [2,3]. Extensive studies on RE element doping in $BaTiO_3$ have been carried out to reveal the mechanisms involved [4]. Earlier X-ray diffraction (XRD) results suggested that Er, Y, Ho, and Dy occupied both Ba and Ti sites in $BaTiO_3$, whereas La occupied only Ba sites [5,6]. On the other hand, it was also reported that the site preference of doped RE elements was strongly affected by the Ba/Ti ratio of host $BaTiO_3$.

Moriwake et al. [7] investigated the site preference of RE elements in $BaTiO_3$ quantitatively by theoretical calculations. Their results seemed reasonable because their results corre-

* Corresponding author. Tel.: +81 476 37 1635; fax: +81 476 37 1648.
E-mail address: yujiume@jp.tdk.com (Y. Umeda).

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spond well not only to former experimental findings but also to considerations of ionic radii. MLCC dielectric materials contain not only RE elements but also other additive elements in $BaTiO_3$. Hence, a quantitative study on the site preference of RE elements coexisting with other additive elements is required.

In this study, we investigate the influence of doping elements on the site preference of RE elements in $BaTiO_3$ using theoretical calculations and experiments. Mg was selected as a typical additive element to be co-doped with RE elements in an MLCC dielectric material. Analysis was carried out by the evaluation of site preference of RE elements doped in $BaTiO_3$ with and without co-doping of Mg. Finally, corresponding dielectric ceramic samples sintered under reducing atmospheres were analyzed by scanning transmission electron microscopy with energy-dispersive X-ray spectroscopy (STEM-EDS) for comparison.

2. Calculation procedures

The Vienna *ab initio* simulation package [8] was employed for all the calculations. The site preference of each element was clarified by total energy calculations combined with thermodynamic theory. Cubic $BaTiO_3$ (space group: $Pm\bar{3}m$) was chosen as a model for calculations because the substitution of dopants usually occurs at high temperatures during sintering. The cut-off energy of the plane wave basis set was set to 400 eV. The supercells consisted of $3 \times 3 \times 3$ unit cells of cubic $BaTiO_3$. Numerical integration was carried out using the Γ point in a Brillouin zone. Structural optimization was carried out until the residual force on all atoms became less than 0.02 eV/Å.

The solution energy of a dopant in a crystal generally depends on the chemical potential of the atom in the system and the charge state of the dopant, q. If a trivalent rare-earth element (RE^{3+}) substitutes for Ba^{2+} site atoms in $BaTiO_3$, the dopant simultaneously introduces an excess positive charge. In this case, it must be compensated by an effective negative charge. There are three possible means for compensating the charge imbalance: carrier electrons, Ba^{2+} vacancy, or Ti^{4+} vacancy. On the other hand, when the RE element substitutes an atom in the Ti^{4+} site, one RE atom introduces an effective negative charge. This charge must be compensated by a corresponding positive charge. Two possible patterns, hole or O^{2-} vacancy, were calculated in this case. To obtain the solution energy for each case, calculations were performed on all the five patterns. Details on the calculations can be found in Refs. [7,9].

The solution energy of RE elements when Mg was co-doped with RE elements was also calculated. For this purpose, it is assumed that Mg replaces the Ti site atoms in $BaTiO_3$ as reported in Ref. [10]. Six patterns of charge compensation could be found based on the above assumptions. For example, when RE atom occupies the Ba sites and Mg occupies the Ti sites, and to compensate charge imbalance half an O vacancy per RE ion is produced, the solution energy can be calculated by

$$\begin{aligned} E_s\left(\mathrm{RE_{Ba}}^{\bullet} + \mathrm{Mg}''_{\mathrm{Ti}}, \frac{1}{2}\mathrm{V_O}^{\bullet\bullet}\right) &= E_t(\mathrm{Ba}_{n-1}\mathrm{RETi}_{n-1}\mathrm{MgO}_{3n}, q=-1) \\ &+ \frac{1}{2}E_t(\mathrm{Ba}_n\mathrm{Ti}_n\mathrm{O}_{3n-1}, q=+2) \\ &- \frac{3}{2}E_t(\mathrm{Ba}_n\mathrm{Ti}_n\mathrm{O}_{3n}, q=0) + \mu_{\mathrm{Ba}} + \mu_{\mathrm{Ti}} - \mu_{\mathrm{RE}} \\ &- \mu_{\mathrm{Mg}} + \frac{1}{2}\mu_{\mathrm{O_2}} + \Delta V_{\mathrm{av}} \end{aligned} \quad (2)$$

where E_t is the total energy of each molecule in charge state q, μ_X is the atomic chemical potential of atom X, n is the number of atoms included in the supercell, and ΔV_{av} is the resulting correction term of valence band top energy caused by the finite size of supercells [11]. In this study, we have taken into account the influence of temperature and partial pressure on the chemical potential of oxygen gas from the thermochemical data shown in Ref. [12]. By assuming O_2 to be an ideal gas, the chemical potential of oxygen at partial pressure p and temperature T can be described as

$$\mu_{\mathrm{O}} = \frac{1}{2}\left[\mu_{\mathrm{O_2}}(T, p^{\circ}) + k_{\mathrm{B}}T\ln\frac{p}{p^{\circ}}\right] \quad (3)$$

where p° is the partial pressure in the standard state, i.e., 1 atm, and $\mu_{O_2}(T, p^{\circ})$ corresponds to the total energy per O_2 molecule at temperature T and partial pressure p°.

3. Results and discussion

3.1. Theoretical site preference of RE elements

The solution energies of La, Sm, Y, Ho, Dy, Tm, and Lu in $BaTiO_3$ at 1500 K under oxygen partial pressure of 10^{-11} MPa are shown in Fig. 1(a). The ionic radii (VI coordination) of RE elements are given in Ref. [13]. For the larger ions La and Sm, the lowest solution energies are obtained by Ba site substitution. In contrast, smaller ions Lu and Tm occupy Ti sites. The calculation results for intermediate size ions Y, Ho, and Dy indicate that these elements prefer Ba site substitution. However, the difference in solution energies between Ba substitution and Ti substitution is small (<1 eV). These theoretical results correspond well with experimental findings that Y, Ho, and Dy occupy not only Ba sites but also Ti sites [2]. The site preference of RE elements in $BaTiO_3$ depends on their ionic radii.

3.2. Theoretical site preference of RE elements co-doped with Mg

First, the distance from an RE atom to Mg was calculated. In the case of Dy, $Dy_{Ba}^{\bullet}$ is at the first nearest Ba^{2+} site and Dy'_{Ti} is at the fourth nearest Ti^{4+} site from Mg''_{Ti} in $3 \times 3 \times 3$ supercells. Next, the calculation results for the solution energies for La, Dy, Ho, Y, and Tm doped with Mg in $BaTiO_3$

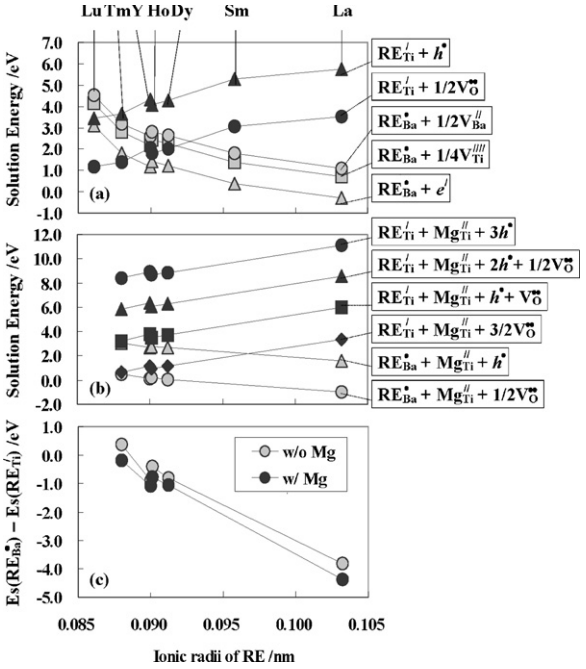

Fig. 1. (a) Theoretical solution energy of RE elements at 1500 K under oxygen partial pressure of 10^{-11} MPa. (b) Theoretical solution energy of RE elements doped with Mg at 1500 K under oxygen partial pressure of 10^{-11} MPa. (c) The difference of theoretical solution energy between Ba site solution and Ti site solution (gray marks: RE elements doped alone without Mg; black marks: RE elements co-doped with Mg).

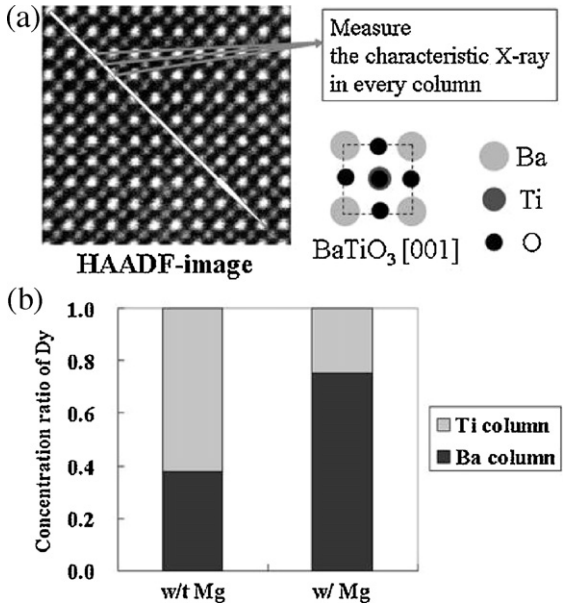

Fig. 2. (a) Site preference measurement by STEM-EDS and HAADF-STEM image analysis. (b) The ratio of integrated intensity of characteristic X-ray spectrum of Dy generated from Ba column to that of Ti + O column by STEM-EDS and HAADF-STEM image analysis.

at 1500 K under oxygen partial pressure of 10^{-11} MPa are shown in Fig. 1(b). The site preference of RE elements co-doped with Mg is very similar to that without Mg doping. Comparison of the calculated solution energies with and without Mg co-doping is shown in Fig. 1(c). $E_s(RE_{Ba}^{\bullet}) - E_s(RE'_{Ti})$ is the difference between the solution energies during Ba site substitution and Ti site substitution. In this figure, the negative value of $E_s(RE_{Ba}^{\bullet}) - E_s(RE'_{Ti})$ indicates that RE ions are more stable at Ba sites than at Ti sites. For all the RE elements, Ba site substitution is more favorable when Mg is co-doped with RE elements. This suggests that substitution sites for RE elements in $BaTiO_3$ are affected by co-doping with Mg. For example, when Dy is co-doped with Mg, $E_s(RE_{Ba}^{\bullet}) - E_s(RE'_{Ti})$ is -1.05 eV, which is 0.25 eV lower than that without Mg co-doping. Our calculation results demonstrated that the site preference of RE elements in $BaTiO_3$ is affected by Mg co-doping.

3.3. Experimental site preference

To confirm our theoretical calculations results, ceramic samples of Dy doped with and without Mg co-doping were prepared by reducing atmosphere sintering ($T = 1630$ K, $p_{O_2} < 10^{-12}$ MPa). The nominal compositions of the samples are 5 mol% Dy_2O_3 and 5 mol% $MgCO_3$ per $BaTiO_3$. The site preference of RE elements was evaluated by means of STEM-EDS measurements within atomistic resolution [14]. The high angle annular dark field (HAADF)-STEM image of a [0 0 1] oriented $BaTiO_3$ particle is shown in Fig. 2(a). In this figure, Ba columns are observed as brighter spots while Ti + O columns are observed as darker spots. The EDS spectra collected from Ba columns and from Ti + O columns are integrated separately. Using STEM-EDS, we could obtain atomic concentrations within atomistic resolution. If the RE elements replace Ba site atoms, the intensity of the characteristic X-ray of RE elements generated from Ba columns will be stronger than that from Ti + O columns. On the other hand, if RE elements occupy both Ba and Ti sites, the difference between Ba columns and Ti+O columns cannot be identified. Fig. 2(b) shows a result of site preference analyzed by using STEM-EDS. The concentration ratio (Dy at Ba column):(Dy at Ti column) = 40:60 is clarified for samples of Dy doped $BaTiO_3$ without Mg. This indicates that Dy occupied both Ba sites and Ti sites of $BaTiO_3$ when it is doped without Mg in $BaTiO_3$. This corresponds well to former experimental findings [2]. On the other hand, when Dy and Mg are co-doped in $BaTiO_3$, the concentration ratio of (Dy at Ba column):(Dy at Ti column) increased to 75:25. This indicates that a majority of the Dy atoms occupy Ba sites. Therefore, the ratio of RE elements occupying Ba sites in $BaTiO_3$ is increased by co-doping with Mg. The experimental results agree well with the theoretical results described in the previous sections.

4. Conclusions

The site preference of RE elements with and without Mg co-doping in $BaTiO_3$ has been studied by theoretical calculations and experimental evaluations using STEM-EDS. The theoretical calculations indicate that RE elements with intermediate ionic radii, such as Y, Ho, and Dy tend to replace both Ba and Ti site atoms, consistent with former experimental findings. Our calculations also suggest that the site preference of doped RE

elements in $BaTiO_3$ is influenced by Mg co-doping. This has been confirmed experimentally for Dy with and without Mg co-doping in $BaTiO_3$ by atomistic resolution analysis using STEM-EDS.

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