Multi layer ceramic capacitors materials research using first-principles calculations

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In this paper the multi-layer ceramic capacitors (MLCCs) materials research using first-principles calculations are explained. For example, doping with 3d transition metals, particularly Mn, is thought to play an important role in determining the reliability of dielectrics used in MLCCs. However, a detailed examination of the electronic structure, solution energies and compensation mechanisms of these systems is lacking. The quantitative analysis of the substitution of Mn in perovskite-type BaTiO3 using first-principles calculations in combination with chemical thermodynamics is reported. The solution energies of dopants with vacancy and n-type and p-type charge compensations have been systematically calculated. Substitution onto the two crystallographically different cation sites in cubic BaTiO3 under four different thermodynamic conditions with different chemical potentials is also examined. Mn is found to be stable on Ti sites under all conditions examined, although its charge state varies. In the oxidizing limit, Mn substitutes for Ti as a Mn$^{4+}$ ion, but in the reducing limit, Mn substitutes for Ti as a Mn$^{2+}$ ion compensated by the formation of an O vacancy. Depending on the Fermi level of the system, the valence state of Mn varies from Mn$^{4+}$ under p-type conditions, to Mn$^{2+}$ under n-type conditions. Mn$^{2+}$ is not found to be stable. These results agree well with the experimentally determined site preferences and valence states of Mn and help to further elucidate the features of Mn-doped BaTiO3 at the atomic level.

Key-words : First-principles calculations, BaTiO3, Perovskite structure, Solution energy, Mn-doping, MLCC

1. Introduction

Among ferroelectric compounds, Perovskite-type barium titanate, BaTiO3 is one of the most technologically important ceramic materials, being used in capacitors and piezoelectric devices. BaTiO3 shows a ferroelectric phase transition at 406 K, transforming from the high-temperature paraelectric cubic phase (P$\text{m}3\text{m}$) to the low-temperature ferroelectric tetragonal phase (P$\text{4}$$\text{mm}$). Substantial experimental$^{1}$–$^{9}$ and theoretical$^{9}$–$^{22}$ work has focused on the properties of this compound. BaTiO3-based materials are also important in modern technology because they show extremely high electrical permittivity around room temperature. This behavior is exploited in multilayer ceramic capacitors (MLCCs), which have large (up to 100 μF) capacitances. In order to tailor the material’s properties, e.g., temperature dependence of permittivity, long-term stability, and so forth, BaTiO3 is often doped with alkaline-earth elements, rare-earth elements and 3d transition metal elements. Ni metal has replaced Pd and Pd alloys as the internal electrodes in MLCCs for commercial (cost) reasons. However, to produce a metallic internal electrode, processing must be carried out under reducing conditions, which requires modification of the processes developed for forming Pd electrodes, as well as dielectric materials that are stable under reducing atmospheres. To prevent oxidation, sintering of Ni-internal-electrode MLCCs (Ni-MLCCs) is usually performed in an atmosphere with less than the equilibrium oxygen partial pressure ($P_2O$) of the oxidation reaction $\ce{Ni + (1/2)O2 \rightarrow NiO}$ (e.g., $P_2O < 10^{-10}$ MPa at 1400 K). The formation of oxygen vacancies in BaTiO3, with the concomitant generation of n-type carriers, under reducing atmospheres can critically affect the dielectric performance of MLCCs. An oxygen vacancy in BaTiO3 generates n-type carriers via the reaction

$$\ce{O0 \rightarrow 1/2O2 + V^{*}_O + 2e^-},$$

where $\ce{O0}$ denotes an oxygen atom on a regular O lattice site, and $V^{*}_O$ denotes an oxygen vacancy with an effective charge of +2 relative to the BaTiO3 lattice. Sakabe and Takagi$^{23}$ mitigated the formation of n-type carriers by doping with Ca, producing an MLCC with an Ni inner electrode that is now sold commercially. A typical composition is $(\ce{Ba_{1-x}Ca_x})\ce{O_{3-m}TiO_2}$, where $m$ is greater than 1. They reported that Ca ions occupy not only Ba sites but also Ti sites in BaTiO3; this may play an important role in stabilizing the material against chemical reduction during the sintering process, since by substituting Ca on Ti sites in BaTiO3, a large amount of O vacancies are introduced into the material before processing of the MLCC. When first developed, Ni-MLCCs showed poor performance, particularly deterioration (increasing conductivity) under long-term DC voltages. The reasons for this deterioration are still not fully understood, although migration of O vacancies under DC voltages is thought to be critical.$^{24}$ In an effort to overcome this problem, doping with Mn, especially co-doping with rare-earth elements, was attempted and found to be effective. A large number of studies on Mn substitution in BaTiO3 have been carried out subsequently to reveal the mechanisms involved. Morita et al.$^{25}$ reported the effects of Mn doping on the long-term reliability under DC voltage of MLCCs. Lee et al.$^{26}$ pointed out the importance of co-doping with rare-earth elements and Mn on long-term reliability.
under DC voltage. Kishi et al.27 described how Mn occupies Ti sites in BaTiO3 and its valence state changes depending on the surrounding oxygen partial pressure in terms of defect chemistry. They showed that under reducing conditions, Mn occupies Ti sites as Mn4+, but under oxidizing conditions its valence state changes from Mn3+ to Mn2+. Valence states of doped Mn in BaTiO3 have also been reported by Hagemann and Hirsch.28 They performed electron paramagnetic resonance (EPR) and magnetic susceptibility measurements in oxidizing and reducing atmospheres. They found that the valence state of Mn changes from Mn4+ in oxidizing atmosphere to Mn2+ (high-spin state) in reducing atmosphere. However, the electronic structure of Mn-doped BaTiO3 has not been studied in detail, although Moretti and Michel-Calendini performed molecular orbital cluster calculations in the late eighties.29 In this study, solution energies of Mn and Rare-earth element in BaTiO3 are evaluated relative to the chemical potentials of constituent elements at a realistic sintering temperature by combining first-principles calculations with thermodynamic theory. The substitution mechanisms involved in this process are also examined in detail.

2. Calculation methods

All calculations for Mn doping were performed within the local density approximation (LDA) of density functional theory (DFT) with the +U extension (LDA+U method)30 using plane-wave basis projector augmented wave (PAW) pseudopotentials as incorporated in the VASP code.31,32 A series of unmodified LDA calculations was also performed for comparison with results from the LDA+U method. In order to minimize interactions between vacancies in neighboring cells, calculations were carried out using a 3 x 3 x 3 supercell composed of 135 atoms, i.e., 27 times more than in the primitive cell of BaTiO3. We took the high-temperature cubic phase of BaTiO3 (space group Pm3m) as the reference structure as this is the phase stable at typical sintering temperatures. In the PAW potentials, 2s and 2p electrons for O, 3s, 3p, 3d and 4s electrons for Ti, 3s, 3p, 3d and 4s electrons for Mn were explicitly treated as valence electrons. The U parameter, which adjusts the electron correlation contribution (on-site coulombic effects), was set at 5.04 eV for Mn-3d electrons.33 A plane-wave cutoff energy of 600 eV was used. The convergence of the vacancy formation energies with respect to the cutoff energy up to 800 eV was better than 0.01 eV. Numerical integration was carried out using 8 k-points in the Brillouin zone. The convergence with respect to the number of k-points was better than that of the cutoff energy. Atomic positions around the solute ion were relaxed to zero force. The relaxation procedure was terminated when all the residual forces for the atoms were smaller than 0.01 eV/Å. We also carried out calculations for a number of reference phases, viz., Ba (bcc), Ti (hcp), TiO2 (pM2/mnm), BaO (Fm3m), Mn3O4 (F4/amd), and gaseous O2. Spin polarization was taken into account in all calculations including Mn and gaseous O2. For consistency, total energies of reference phases were obtained after their structures had been optimized by the same computational method used for BaTiO3.

The solution energy of a dopant in a compound generally depends on the atomic chemical potentials of the system and the charge state of the dopant, q. The solution energy of Mn incorporated onto a Ba site in BaTiO3, with charge state q, $E^q$[MnBa,q] can be calculated using34,35

$$E^q[\text{MnBa}, q] = E_0[\text{Ba}_{n-1}\text{Mn}_1\text{Ti}_n\text{O}_{3n}, q = 0] - E_0[\text{Ba}_n\text{Ti}_n\text{O}_{3n}, q = 0] + \mu_{\text{Ba}} - \mu_{\text{Mn}} + qE_c,$$

where $E_c$ is the total energy of the supercell with/without the dopant, $\mu_X$ is the atomic chemical potential of atom X, n is the number of formula units included in the supercell, and $E_0$ is the Fermi energy of the system, noting that $\mu_X$ and $E_0$ vary depending on the chemical and electronic environment of the system. Depending on its valence state, the dopant ion may introduce an excess negative or positive charge, which must be compensated by oppositely charged species. In the case of Mn substitution on the Ba2+ site, four scenarios are possible in BaTiO3, to compensate this charge difference. The first scenario is that Mn exists as Mn3+. In this case, $E^q[\text{Mn}^{2+}\text{Ba}, q = 0]$ can be calculated using

$$E^q[\text{Mn}^{2+}\text{Ba}, q = 0] = E_0[\text{Ba}_{n-1}\text{Mn}_1\text{Ti}_n\text{O}_{3n}, q = 0] - E_0[\text{Ba}_n\text{Ti}_n\text{O}_{3n}, q = 0] + \mu_{\text{Ba}} - \mu_{\text{Mn}},$$

(3)

The second scenario is that Mn exists as Mn4+ (as explained below, Mn3+ is found to be unstable). In this case, the energy can be calculated according to

$$E^q[\text{Mn}^{4+}\text{Ba}, q = 0] = E_0[\text{Ba}_{n-1}\text{Mn}_1\text{Ti}_n\text{O}_{3n}, q = 0] - E_0[\text{Ba}_n\text{Ti}_n\text{O}_{3n}, q = 0] + \mu_{\text{Ba}} - \mu_{\text{Mn}} + 2E_c.$$

(4)

The third scenario is that Mn occupies the Ba site as Mn4+. Mn4+ substitution is compensated by formation of one Ba vacancy. In this case, the solution energy of a cluster containing one dopant atom and a Ba vacancy can be calculated, in principle, using a supercell of composition Ba$_{n-2}$Mn$_1$Ti$_n$O$_{3n}$ giving a neutral system. However, in order to approximate an isolated defect cluster, a considerably larger supercell is required than that for individual defects. Because this would require excessive computing resources, the solution energy for this solution mechanism was calculated as the sum of $E^q[\text{Mn}^{4+}\text{Ba}, q = 0]$ and $E^q[V^\text{Ba}_n, q = -2]$ from two separate calculations according to

$$E^q[\text{Mn}^{4+}\text{Ba}, q = 0] = E_0[\text{Ba}_{n-1}\text{Mn}_1\text{Ti}_n\text{O}_{3n}, q = 0] - E_0[\text{Ba}_n\text{Ti}_n\text{O}_{3n}, q = 0] + \mu_{\text{Ba}} - \mu_{\text{Mn}},$$

(5)

where $E^q$ denotes formation energy. In these calculations, the non-zero charge of the supercell was neutralized using a “jellium” background. Equation (5) therefore assumes that the Mn solute and Ba vacancy maintain the same Fermi energy but are infinitely separated.

In the fourth scenario, Mn3+ substitution is compensated by formation of one-half of a Ti vacancy ($V^\text{Ti}_n$). For the same reason as in the third scenario, the solution energy per pair of charged solute ions was calculated as the sum of $E^q[\text{MnBa}, q = -2]$ and $E^q[V^\text{Ti}_n, q = -1]$ from two separate calculations using

$$E^q[\text{Mn}^{3+}\text{Ba}, q = -2] = E_0[\text{Ba}_{n-1}\text{Mn}_1\text{Ti}_n\text{O}_{3n}, q = -2] - 2E_0[\text{Ba}_n\text{Ti}_n\text{O}_{3n}, q = 0] + \mu_{\text{Ba}} - \mu_{\text{Mn}} + 1/2E_c.$$

(6)

For substitution of Mn on the Ti4+ site, three possible scenarios were considered. In the first and second scenarios, Mn occupies the Ti site as Mn4+ or Mn3+ without any vacancy formation. In these cases, the solution energy can be obtained in a similar manner to Mn substituted on a Ba site. The third scenario involves formation of one oxygen vacancy ($V^\text{O}_n$) per dopant ion. In this case, the solution energy was calculated per pair of charged solute ions as the sum of $E^q[\text{Mn}^{2+}\text{Ba}, q = -2]$ and $E^q[V^\text{O}_n, q = +2]$ from two separate calculations according to

$$E^q[\text{Mn}^{3+}\text{Ba}, q = -2] = E_0[\text{Ba}_{n-1}\text{Mn}_1\text{Ti}_n\text{O}_{3n}, q = -2] - 2E_0[\text{Ba}_n\text{Ti}_n\text{O}_{3n}, q = 0] + \mu_{\text{Ba}} - \mu_{\text{Mn}} + 1/2E_c.$$
Assuming O2 to be an ideal gas, the chemical potential of oxygen also taken into account when calculating the solution energies. In the present study, the temperature dependences of H exist. However, in practice, BaTiO3 is the most widely used and the majority phase BaTiO3 coexists in equilibrium with various combinations of Ti, O, BaO and TiO2 as minority phases. The labels A, B, C and D in Fig. 1 correspond to conditions in which only compound; other compounds (such as Ba4Ti13O37, Ba6Ti17O40,38) BaTi4O9,38) and Ba2TiO439) are also known to exist. In both cases, the total system has 3 \mu_2 magnetic moments per Mn ion, corresponding to Mn^{4+} (3d^3). However, the electronic structures of the Mn ion are different. In the case of LDA, the conduction band bottom (CBB) mainly consists of the minority spin Mn 3d bands and the majority spin Mn 3d bands have much higher energy. If an electron were added, this energy band would lead to a low-spin electron configuration. In contrast, in the case of LDA+U, the CBB mainly consists of the majority spin Mn 3d bands, and the minority spin Mn 3d bands are much higher in energy. If an electron were added, this energy band would lead to a high-spin electron configuration.

3. Results and discussion

3.1 Mn doping

Figure 1 shows a schematic phase diagram of the Ba–Ti–O ternary system. In the Ba–Ti–O system, BaTiO3 is not the only compound; other compounds (such as Ba4Ti13O37, Ba6Ti17O40,38) BaTi4O9,38) and Ba2TiO439) are also known to exist. However, in practice, BaTiO3 is the most widely used and commercially important of these compounds. For simplicity, we assume the three chemical potentials of the constituent elements satisfy the equation

\[
\mu_{Ba} + \mu_{Ti} + 3\mu_{O} = \mu_{BaTiO3 \text{ (bulk)}}.
\]

Labels A, B, C and D in Fig. 1 correspond to conditions in which the majority phase BaTiO3 coexists in equilibrium with various combinations of Ti, O, BaO and TiO2 as minority phases. The favorable phase compositions were determined using the theoretical formation energies. Some other metallic phases are known to exist, such as the binary Ba–Ti alloy system, but we do not consider equilibrium with these compounds as their heats of formation do not significantly change the formation energies of the material of interest. Depending on the chemical environment, manganese oxide can exist as MnO, Mn2O3, Mn3O4 or MnO2. Of these, the Mn3O4 phase exists over the widest oxygen partial pressure range at typical sintering temperatures of MLCCs. The chemical potential of Mn was thus determined assuming equilibrium with Mn3O4. Figures 2 and 3 show the calculated density of states (DOS) of Mn placed on a Ti site in BaTiO3 determined by conventional LDA and LDA+U methods, respectively. In both cases, the total system has 3 \mu_2 magnetic moments per Mn ion, corresponding to Mn^{4+} (3d^3). However, the electronic structures of the Mn ion are different. In the case of LDA, the conduction band bottom (CBB) mainly consists of the minority spin Mn 3d bands and the majority spin Mn 3d bands have much higher energy. If an electron were added, this energy band would lead to a low-spin electron configuration. In contrast, in the case of LDA+U, the CBB mainly consists of the majority spin Mn 3d bands, and the minority spin Mn 3d bands are much higher in energy.
energy. If an electron were added, this energy band would lead to a high-spin electron configuration. The valence band top (VBT) mainly consists of O-2p bands, with occupied Mn-3d bands lower in energy. To clarify these electronic states, electron/hole doping calculations were carried out. The results are shown in Fig. 4, where the horizontal axis indicates the total charge of the system; the absolute value corresponds to the number of doped electrons/holes in the system. The vertical axis indicates the total magnetic moment of the system. In the case of LDA, the total magnetic moment of the system decreases upon electron doping, indicating that doped electrons occupy minority spin Mn-3d bands. Upon hole doping, the total magnetic moment of the system decreases, indicating the doped hole occupies the majority spin Mn-3d bands. On the other hand, in the case of LDA+U, the total magnetic moment of the system remains unchanged, indicating the hole does not sit in the Mn-3d bands but the O-2p bands. The electronic structures of Mn-doped BaTiO3 as determined by conventional LDA and LDA+U methods are summarized schematically in Fig. 5. Experimentally, Mn is found to occupy the Ti site with a high-spin configuration. These results suggest that inclusion of the U parameter is essential for reproducing the experimentally observed electronic structure of Mn-doped BaTiO3.

Figure 6 shows the calculated Fermi level dependence of the valence state of Mn on a Ti site in BaTiO3 for thermodynamic state A (coexisting BaTiO3, BaO, Mn3O4, and gaseous O2) at 1400 K. Under p-type conditions (Fermi level located near the valence band top, VBT), Mn4+ has the lowest energy, much lower than those for Mn3+ or Mn2+. Hence, Mn4+ is the most stable valence state of Mn under these conditions. However, as the Fermi level increases, Mn2+ becomes more stable, under n-type conditions, Mn2+ is the most stable valence state. Mn3+ is found to be unstable for all conditions. This is in excellent agreement with experimental findings reported by Schwartz and Wechsler, who determined the valence state of Mn in BaTiO3 by EPR spectroscopy. They observed a smooth transition from Mn4+ to Mn2+, with no Mn3+ detected. They also found that Mn4+ and Mn2+ co-exist in the intermediate oxygen partial pressure region. Mn is generally thought to occupy the Ti site of BaTiO3, and has a significant effect on the long-term reliability of MLCC dielectrics. Figure 7 shows the solution energies for Mn to BaTiO3 under each thermodynamic conditions shown in Fig. 1 at 1400 K.
BaTiO₃, BaO, Mn₂O₄, and gaseous O₂), which corresponds to excess Ba in an oxidizing atmosphere, Mn substitution on the Ti site has the lowest solution energy when its valence state is +4. In this case, no n-type/p-type charge carriers (electrons/holes) are generated. Similarly, for state B (coexisting BaTiO₃, TiO₂, Mn₂O₄, and gaseous O₂), which corresponds to excess Ti in an oxidizing atmosphere, Mn substitution on the Ti site with a charge state of +4 also gives the lowest energy, so that no charge carriers are generated either. In contrast, for state C (coexisting BaTiO₃, BaO, Mn₂O₄, and Ti), which corresponds to excess Ba under reducing atmosphere and state D (coexisting BaTiO₃, TiO₂, Mn₂O₄, and Ti), corresponding to excess Ti under reducing atmosphere, the lowest energy is found when Mn substitutes on the Ti site with a charge of +2 compensated by formation of an oxygen vacancy. These results suggest that, depending on the atmosphere (i.e., oxygen partial pressure), the valence state of Mn changes from +4 under oxidizing conditions to +2 under reducing conditions, that latter compensated by O vacancy formation. In both cases, Mn substitution in BaTiO₃ results in an insulating material. These trends are in excellent agreement with the preferred site of Mn and the dependence of its valence state on the chemical environment determined experimentally.

### 3.2 Rare-earth doping

One another example is rare earth element doping in MLCC materials. In an effort to overcome deterioration under DC bias as explained earlier, doping with rare-earth elements was attempted and found to be effective.⁴¹,⁴² A large number of studies on rare-earth element substitution in BaTiO₃ have been carried out subsequently to reveal the mechanisms involved. Tsur et al.⁴³,⁴⁴ described the effects of rare-earth doping in terms of defect chemistry, reporting that Er, Y, Ho and Dy occupy both Ba sites and Ti sites in BaTiO₃, while La occupies only Ba sites. The dopants were found to be compensated by several types of cation vacancies. Using X-ray diffraction (XRD), they also reported the influence of Ba/Ti ratio on the tendency of Ho and Dy to occupy the different sites in the perovskite structure. Mizuno et al.⁴⁵ also investigated the site preference of Ho in BaTiO₃ using XRD, concluding that it occupies both Ba and Ti sites, but again that the Ba/Ti ratio has a strong influence. Makovec et al.⁴⁶ studied occupancies of Ho in BaTiO₃ under reducing atmospheres using XRD and wavelength dispersive spectroscopy (WDS), also finding that the preferred site for Ho is strongly affected by the Ba/Ti ratio. They reported that in Ba excess materials, Ho occupies Ti sites, while in Ti excess materials, Ho occupies Ba sites. Sakabe et al.⁴⁷ investigated the solution behavior of La, Sm, Dy and Yb in BaTiO₃ using XRD, as well as their effect on the long-term performance of MLCCs. They reported that La occupies Ba sites and Dy occupies both Ba and Ti sites. Dy doping significantly improved the reliability of MLCC, while La doping did not. These results have been widely accepted since they are consistent with the trends based on consideration of the relative ionic radii. However, no more detailed studies of the preferred dopant sites have been reported. In order to further improve the properties of MLCCs, quantitative information on substitution sites, mechanisms and solution energies would be highly beneficial.

As explained former section, rare-earth doping, is also effective to improve long term durability of MLCCs. Although, similar chemical properties of the rare-earth elements, effect for the MLCC properties are quite different. Among them, Dy and Ho reported effective dopant for Ni-MLCC materials. On the other hand, La reported not the effective dopant. Therefore, we performed calculation of the solution behavior of these elements. The calculation results of the preferred substitution site, compensation mechanism, and solution energy (E) under reducing conditions at 1400 K (close to the sintering temperature of Ni-MLCC) for each rare-earth element are summarized in Table 1.

| Dopant | Excess Ba | Substitution site | Compensation type | E₁ (eV) | Excess Ti | Substitution site | Compensation type | E₂ (eV) |
|--------|-----------|------------------|------------------|--------|-----------|------------------|------------------|--------|
| La     | Ba        | Electron         | O vacancy        | 0.5    | Ba        | Electron         | O vacancy        | 0.3    |
| Dy     | Ti        | Electron         | O vacancy        | 0.6    | Ti        | Electron         | O vacancy        | 0.6    |
| Ho     | Ti        | Electron         | O vacancy        | 0.4    | Ti        | Electron         | O vacancy        | 0.1    |

### 4. Conclusion

In this paper, the MLCC materials study using first-principles calculations were explained. All works has already published elsewhere.⁴⁷,⁴⁸ As explained in this paper, first-principles calculations powerful tool for materials study especially in the atomistic level. It should be much more powerful when it is using collaboration with precise experiments. Using this scheme, now our group is studying not only ferroelectric materials but also many kinds of materials including Li ion battery, ion conductor, semiconductor, and other materials.⁴⁹-⁵⁵

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