

Rational design of dielectric oxide materials
through first-principles calculations and
machine-learning technique

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Chapter 1: General Introduction

1.1 Dielectric materials and capacitors

1.1.1 Dielectric materials

Dielectric materials exhibit dielectric polarization when an external electric field is applied. Dielectric materials also generally have a large energy gap between the valence and conduction bands. Therefore, dielectric materials are used widely as electric insulators in components like memory chips, filters, sensors, and ceramic capacitors.

Dielectric polarization is governed by four basic mechanisms: (a) interfacial polarization, (b) orientation polarization, (c) ionic polarization, and (d) electronic polarization. These four polarization mechanisms are illustrated schematically in Fig. 1.1.1.¹⁾ Interfacial polarization occurs when charges accumulate at the interface between two materials. Interfacial polarization is usually observed in polycrystalline solids. Interfacial polarization originates with the motion of ions within a material. Interfacial polarization often arises in ionic conductors and oxides with lattice defects. Orientational polarization arises when the material hosts a permanent dipole moments. Materials like H₂O have a permanent net dipole moment because of the polarity of the charge distribution in the molecular structure. In H₂O molecules, the H atoms have positive charge and O atoms have negative charge, causing the molecule to be dipolar. The dipolar nature of the molecule causes a dipole moment in the material at the molecular level. However, in the absence of an electric field, this dipole moment is canceled out by thermal agitation, so bulk water has no net dipole moment. When an electric field is applied, the molecules will align with the field. Ionic polarization typically occurs in ionic crystals like NaCl. The interiors of these materials have no net polarization in the absence of an external electric field because the dipole moments of the negative ions are balanced by the positive ions. An external field will displace the ions, polarizing the material. Ionic polarization contributes greatly to materials' dielectric behavior. Electric polarization is caused by small relative shifts in the distributions of positive and negative charges within

dielectric materials. The negatively charged electronic clouds around positive nuclei are distorted by the applied external electric field. These small charge separations sum up to bulk polarization.

Each of these polarizations depends differently on the frequency of the applied field. The frequency dependence of the dielectric constant is shown in Fig. 1.1.2.²⁾ These plots differ because of the different response speeds of each polarization mechanism when an external electric field is applied. In interfacial polarization, charged particles move from one side of an interface to the other, such as from one site in a crystal structure to a nearest-neighbor site. Since the charged particle moves a relatively long distance, the response speed of this mechanism to an electric field is slow. With electric polarization, on the other hand, electrons move only slightly when an external electric field is applied. Since charged particles move only a short distance, the response speed is fast.

Certain materials that go through spontaneous electric polarization with no external electric field are called ferroelectric materials. Ferroelectricity was discovered in Rochelle salt ($\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$) in 1921.³⁾ A single crystal of Rochelle salt has high dielectric constant (~ 4000), but its ferroelectric property disappears over 297 K.⁴⁾ Therefore, Rochelle salt's dielectric constant is not high at room temperature. In 1935, the next major ferroelectric material, KH_2PO_4 , was discovered.⁵⁾ KH_2PO_4 is only ferroelectric at very cold temperatures 123 K⁴⁾, however, so it is not useful in industry.

One of the most important dielectric materials used in industry, barium titanate (BaTiO_3), was discovered in 1942.⁶⁻⁸⁾ The crystal structure of BaTiO_3 at room temperature is illustrated in Fig. 1.1.3. BaTiO_3 has tetragonal crystal structure (space group: $P4mm$) at room temperature. The lattice constants of BaTiO_3 are $a = 3.99 \text{ \AA}$ and $c = 4.04 \text{ \AA}$.⁹⁾ The positions of Ti and O are shifted in the c -direction, causing ionic polarization. The temperature dependence of the dielectric constant of BaTiO_3 is plotted in Fig. 1.1.4.¹⁰⁾ The dielectric constant of BaTiO_3 at room temperature is about 5000, and it increases to about 10000 at 120 °C. At this higher temperature, the crystal structure of BaTiO_3 changes from tetragonal (ferroelectric phase) to cubic (paraelectric phase), which is the so-called Curie temperature.

After the discovery of BaTiO_3 , several more dielectric materials were discovered.¹¹⁻¹⁴⁾ BaTiO_3 is excellent for use in electronics because of its chemical stability and low-cost;

most ceramic materials are still made of BaTiO₃ after over 70 years of development in the industry. However, BaTiO₃ has several weaknesses; among them is the decrease of its dielectric constant at high temperature and frequency. Its dielectric constant also decreases under high DC voltage according to thickness. In addition, the required characteristics of capacitors have increased. For instance, high dielectric constants at high frequencies have been required in order to use capacitors in the electronic circuits of Information and Communication Technology (ICT) devices, and high dielectric constants under high DC voltage per thickness have been required in order to meet the demand for capacitor miniaturization. As such, new high-performance dielectric materials are in strong demand. Further development in capacitor components could be spurred by the discovery of alternative dielectric materials with specialized properties.

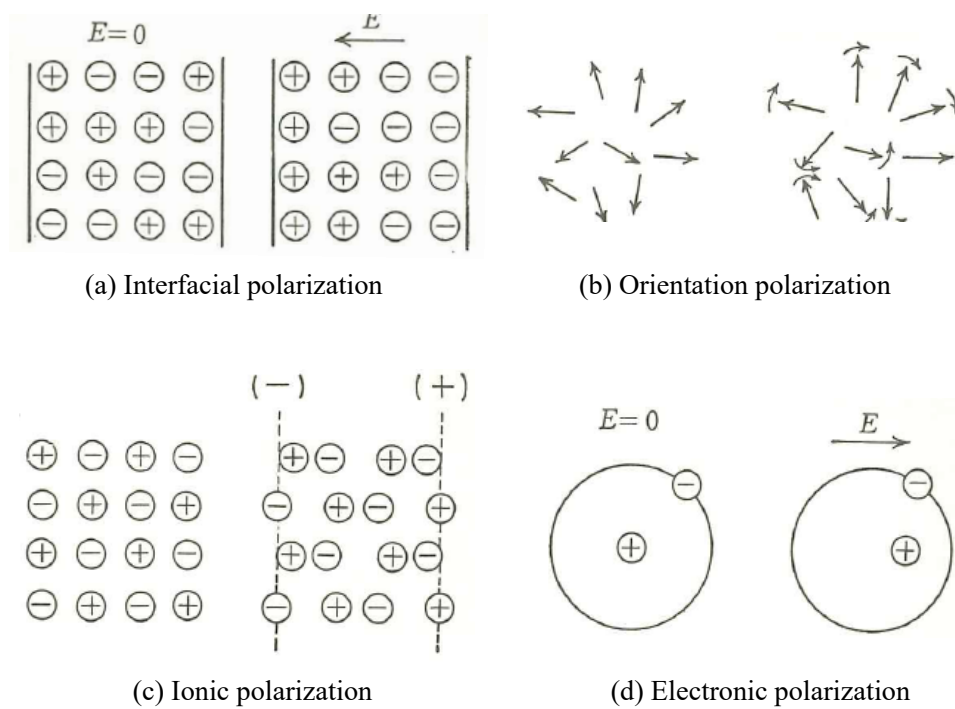


Fig. 1.1.1. Four mechanisms of dielectric polarization.¹⁾

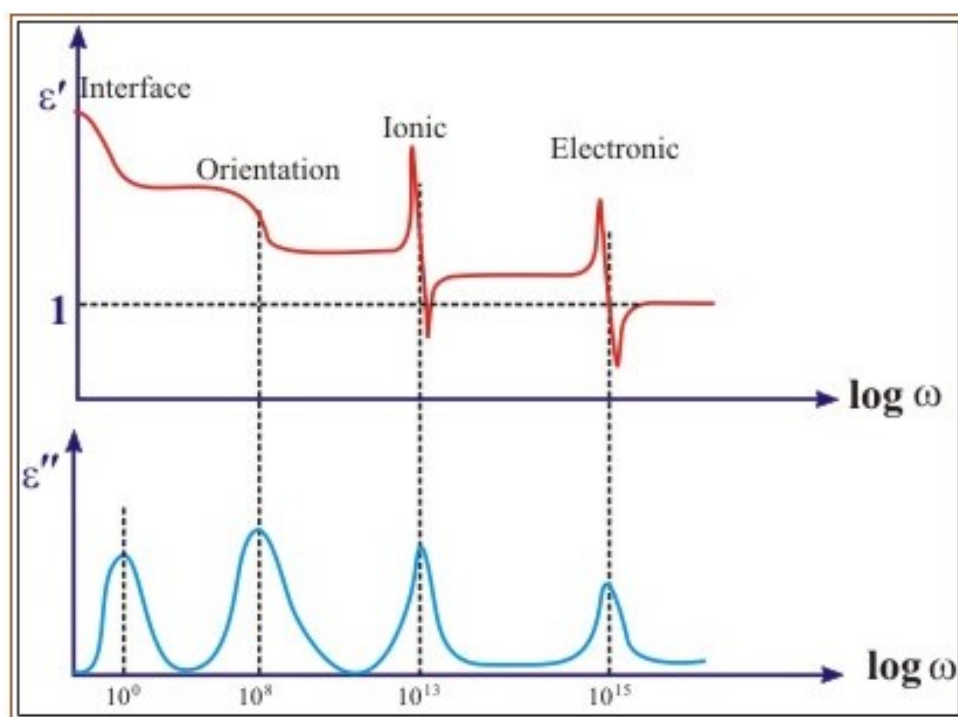


Fig. 1.1.2. Example of the frequency dependence of dielectric constant and its derivatives.²⁾

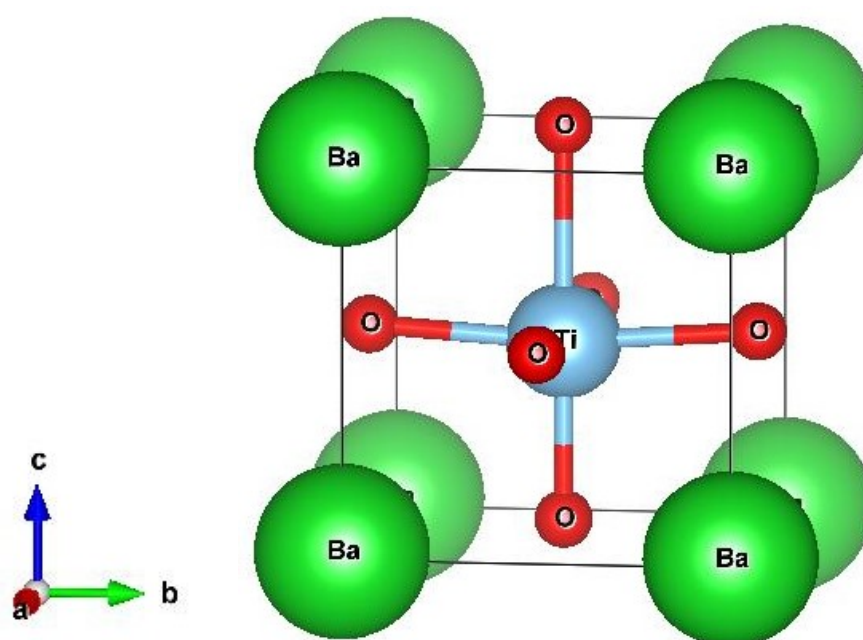


Fig. 1.1.3. Crystal structure of BaTiO₃. This structure was drawn with the VESTA visualization software.¹⁵⁾

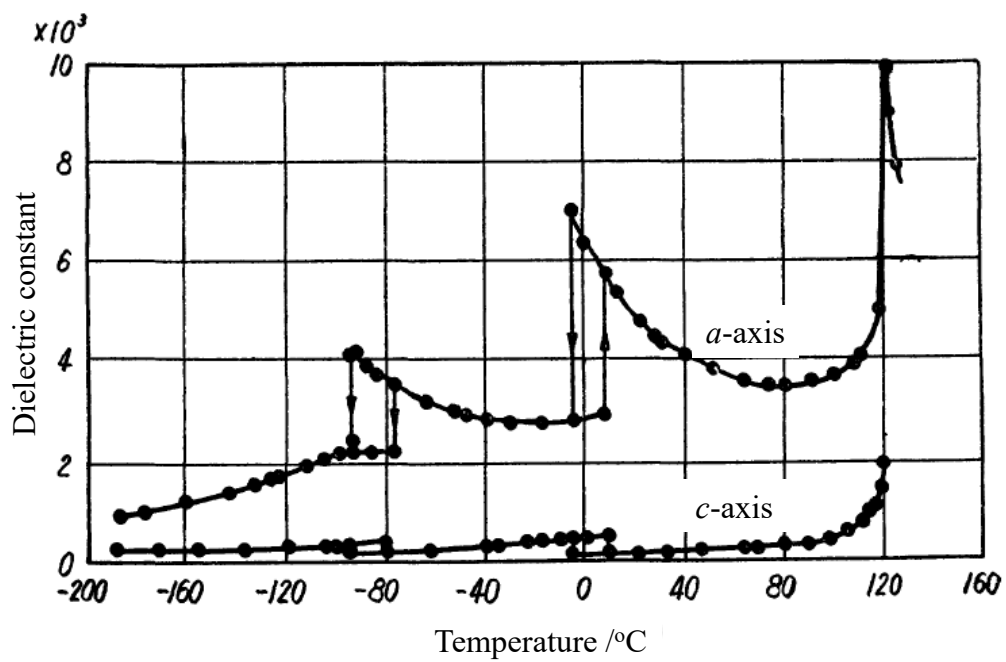


Fig. 1.1.4. Dielectric constant of BaTiO₃ at a wide range of temperatures.¹⁰⁾

1.1.2 Capacitors

Capacitors are passive electronic components that store charge. Usually, capacitors are formed from internal electrodes and a dielectric layer. The dielectric layer is sandwiched between two internal electrodes. Capacitance, which describes the amount of charge the device can store per unit potential, is calculated by following formula.

$$C = n\epsilon_0\epsilon_r \frac{S}{d} \quad (1.1)$$

where n is the number of dielectric layers, ϵ_0 is the relative dielectric constant of a vacuum, ϵ_r is the relative dielectric constant of the dielectric layer, S is the area of the counter electrode, and d is the thickness of the dielectric layer. A typical capacitor is illustrated in Fig. 1.1.5. When the capacitor is connected in a circuit, the external AC or DC electric field moves charged particles in the dielectric layer so that polarization occurs.

Capacitors are used in many ICT devices, industrial equipment, automobiles, and other applications. Capacitors come in many forms, but they basically can be classified into four types: aluminum electrolytic capacitors, tantalum electrolytic capacitors, film capacitors, and ceramic capacitors. These types of capacitors differ mainly in the dielectric materials they use. An oxide film on an Al or Ta electrode surface is used as the dielectric layer in aluminum and tantalum electrolytic capacitors. Plastic is used in film capacitors. BaTiO₃ and other dielectric oxides are used in ceramic capacitors.

These four types of capacitors have different features, which are summarized in Fig. 1.1.6.¹⁶⁾ Film capacitors have higher rated voltage than other capacitors because the plastic dielectric layers in film capacitors are chemically and structurally stable and can withstand high voltages. In addition, their capacitance is not strongly affected by temperature. This class of capacitors is limited in application, however, because film capacitors are expensive and cannot be downsized. Film capacitors are mainly used for audio circuits because of their high rated voltage. Aluminum and tantalum electrolytic capacitors offer higher capacitance than other capacitors because the dielectric layer is very thin. However, the capacitance varies greatly with frequency and the breakdown

voltage is extremely small. In addition, electrolytic capacitors are polarized, so leak current will flow when they are used with a reversed bias. Electrolytic capacitors are typically used for noise removal and power supply smoothing in 50/60 Hz power supply circuits. Ceramic capacitors have lower capacitance and rated voltage than other capacitors, but these properties are relatively constant at all frequencies. In addition, ceramic capacitors are usually smaller and cheaper than other capacitors. Therefore, ceramic capacitors are used in electronic circuits installed around integrated circuit (IC) boards for noise removal.

A market forecast for capacitors is shown in Fig. 1.1.7.¹⁷⁾ and the market share of each type of capacitor in 2016 is shown in Fig. 1.1.8.¹⁸⁾ Even though capacitors are commodity products, the market for them is growing yearly as industrial products become more sophisticated. Most capacitors on the market are ceramic, because of their low-cost and small size. A great deal of ceramic capacitors are used in smartphones, wearable electronics, automobiles, robots, and other 21st century electronics.

Multi-layer ceramic capacitors (MLCCs) are relatively novel. A cross-sectional schematic of a MLCC is shown in Fig. 1.1.9.¹⁹⁾ Typically, BaTiO_3 , CaTiO_3 , and TiO_2 are used as ceramic dielectrics, Ni and Cu are used as internal electrodes, and Cu, Ni, and Sn are used as external electrodes. The size of MLCCs over time is shown in Fig. 1.1.10.²⁰⁾ The horizontal axis gives the year and the vertical axis gives the size of MLCCs in indexed codes that are standard in the industry. For example, “3216” means that the length of MLCCs is 3.2 mm, and the width and height of MLCCs is 1.6 mm. Size 2012 MLCCs dominated the market for MLCCs 20 years ago, but the 0603 size has taken over in recent years as its cost has decreased and electronic devices have become more miniaturized. Miniaturization and higher capacitances are the main trends for the development of MLCCs.

The capacitance of a MLCC is calculated by Eq. 1.1. To achieve higher electrostatic capacitance, the thickness of the dielectric and inner electrode layers can be decreased. In addition, the number of dielectric layers can be increased. The thicknesses of the dielectric and inner electrode layers are plotted over time in Fig. 1.1.11. The horizontal axis gives the year and the vertical axis gives the thickness of dielectric and internal electrode layers. However, reducing the thicknesses of these layers involves several challenges. The

reliability of MLCCs is one such difficulty, because defects become more likely with thinner layers. If only one layer of a MLCC has a defect, the whole MLCC counts as defective. Therefore, advanced manufacturing technology is required to improve manufacturing yields.

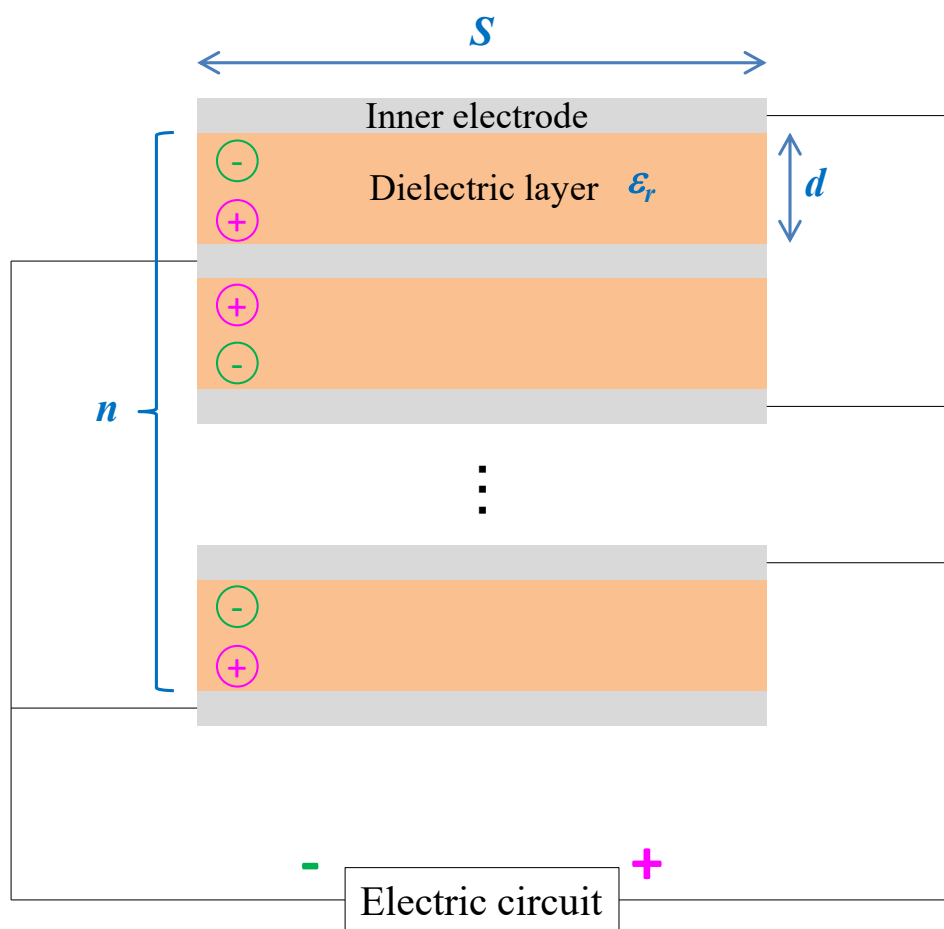


Fig. 1.1.5. Schematic of a capacitor.

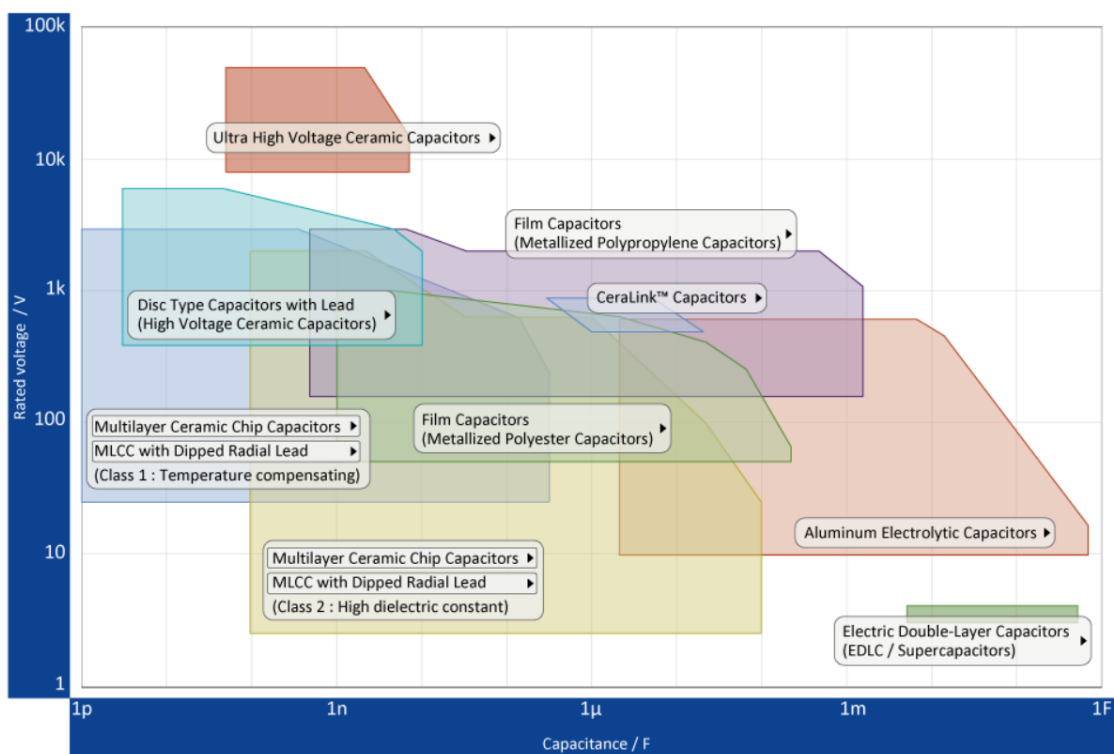


Fig. 1.1.6 Features of several capacitors with a range of rated voltages and capacitances.¹⁶⁾

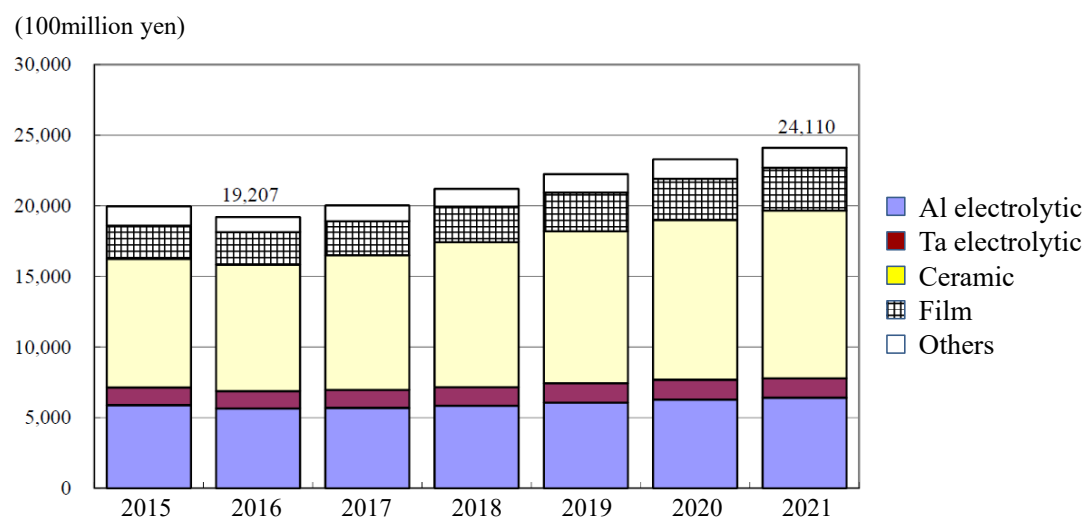


Fig. 1.1.7. Production forecasts for capacitors made from several materials.¹⁷⁾

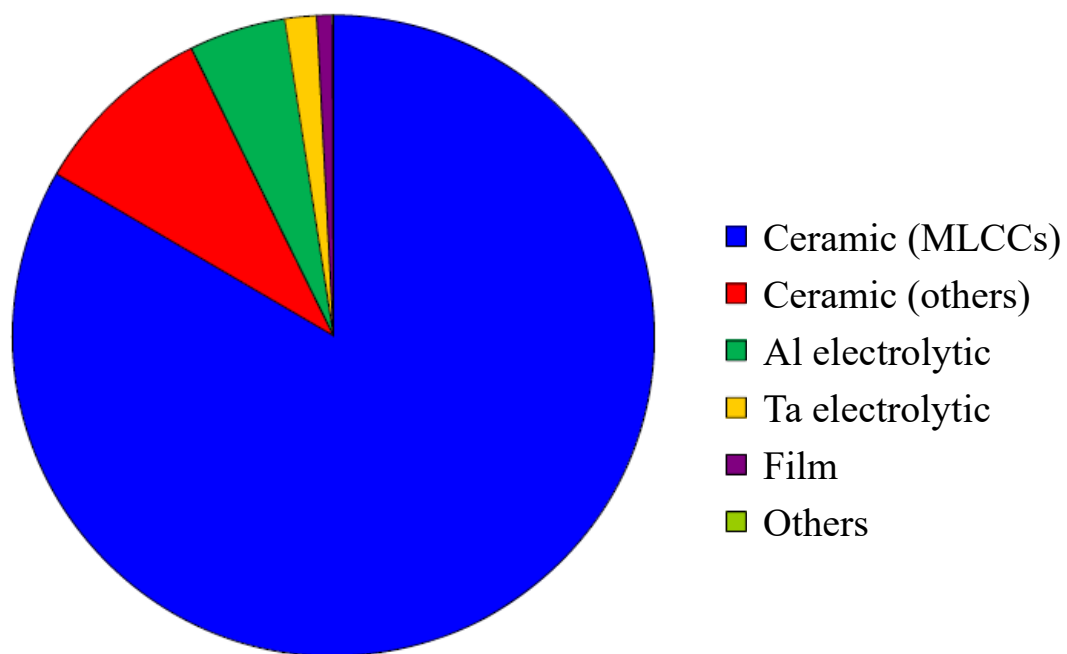


Fig. 1.1.8. Market shares of capacitors made of different materials in 2016. ¹⁸⁾

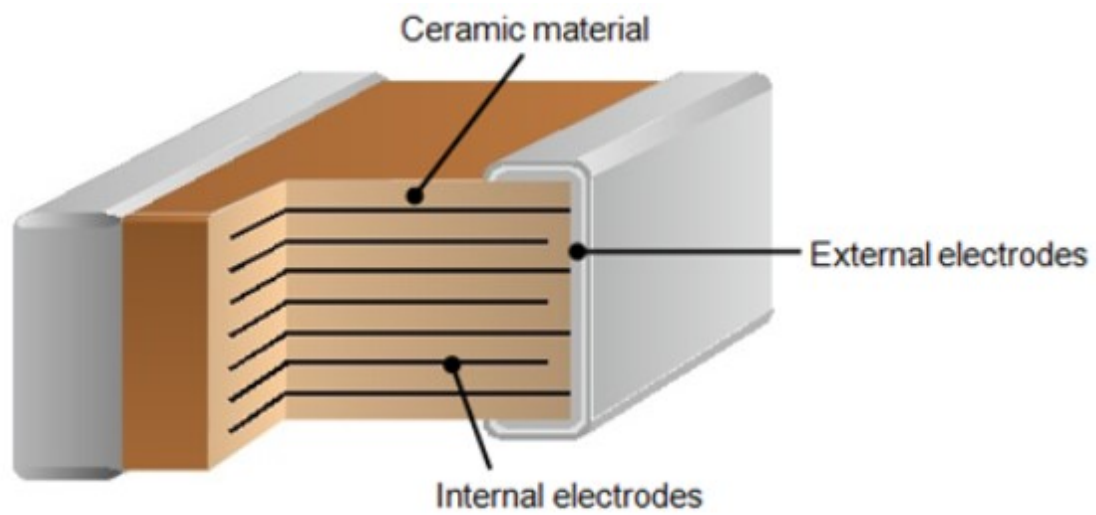


Fig. 1.1.9. Cross-sectional schematic of MLCCs.¹⁹⁾

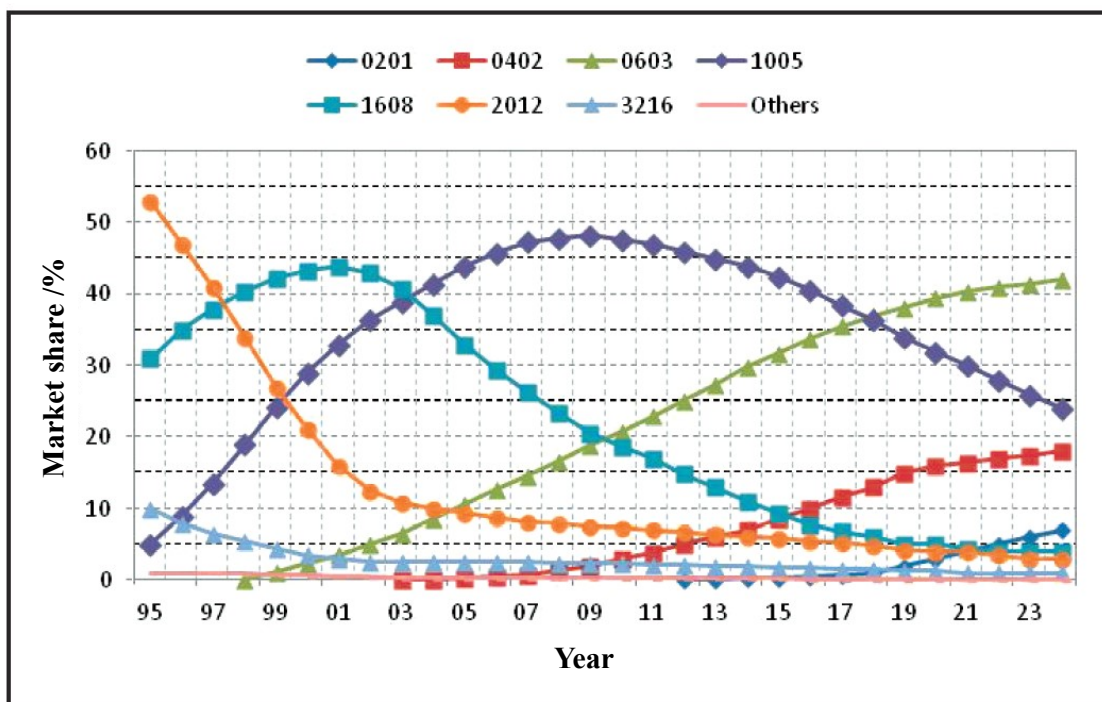


Fig. 1.1.10. Forecast market share of MLCCs.²⁰⁾

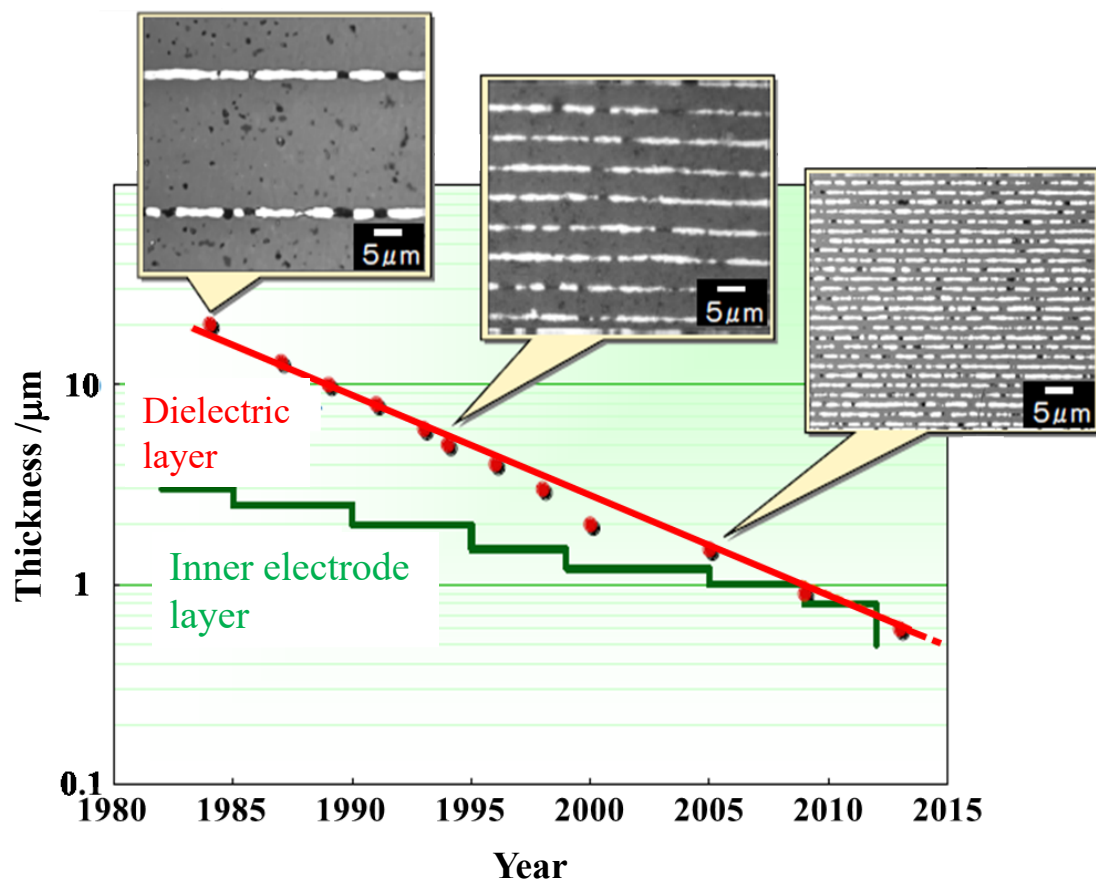


Fig. 1.1.11. Thickness of dielectric and inner electrode layers from 1980-2015.

1.2 Issues in the development of MLCCs

MLCCs are mainly used for noise removal, power supply assistance, and separating direct current and alternating current. The production volume of MLCCs is increasing year by year, and is expected to reach 400 billion capacitors a year in 2020.²¹⁾ About 1,000 MLCCs are mounted in a single high-end smartphone, and about 6,000 MLCCs are mounted in an electric vehicle.²²⁾ Miniature and high-capacitance MLCCs are needed in IoT devices like smartphones. On the other hand, the strict safety standards involved in automotive applications require MLCCs that are extremely reliable when subjected to high voltage, temperature, or frequency. These somewhat opposed requirements of ICT devices and automobiles mean that materials scientists must improve MLCCs' reliability per thickness under a certain voltage while increasing the devices' electrostatic capacitance. To achieve these goals, researchers are working toward the development of highly reliable dielectric materials with high dielectric constants. Research on the mechanisms behind dielectric reliability and high dielectric constants is continuing in parallel.

1.3 Objectives of this thesis

This thesis research aims to use rational design strategies to discover novel reliable and high-performance dielectric materials using first-principles calculations.

The rest of this thesis discusses the calculations and models that I used to approach this goal of optimized dielectric materials. In chapter 2, the formation and migration energy of oxygen vacancies in BaTiO_3 and $\text{BaM}_x\text{Ti}_{1-x}\text{O}_3$ ($M = \text{Zr, Ge}$) are calculated quantitatively by first-principles calculations and experiments. The migration of oxygen vacancies within dielectric materials likely explains how the resistance of MLCCs decreases over time. First-principles calculations reveal how dopants in BaTiO_3 MLCCs affect reliability. Chapter 3 describes a search for novel paraelectric materials in which the dielectric constants of 3,382 compounds were calculated exhaustively from first-principles. The crystal structures of 3,382 compounds were taken from a database for these calculations. The calculated dielectric constants of some compounds are higher than that of TiO_2 , which is a typical paraelectric material. Chapter 4 discusses a prediction model for dielectric constants that uses first-principles calculations and machine-learning technique in conjunction. Systematic error between the calculated and experimentally observed dielectric constants is apparent. To mitigate this error, machine-learning was used to predict dielectric constants from the first-principles calculations and 275 feature variables using elemental descriptors. Chapter 5, finally, summarizes the thesis research.

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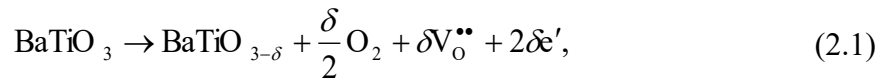
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Chapter 2: Oxygen vacancies in Ba(Ti,M)O₃ (M = Zr, Ge)

2.1 Introduction

BaTiO₃ is one of the most important ferroelectric materials used in MLCCs. During the development of MLCCs, Ag or Pd was used as the internal electrode at first for its chemical stability. However, in recent years, Ni metal has become more common for commercial reasons. In the production of metallic internal electrodes for MLCCs, the metals are usually sintered under a reducing atmosphere. The Ellingham diagrams for several metal oxides are shown in Fig. 2.1.1.¹⁾ MLCCs are usually sintered at about 1200 °C. These diagrams show that if the partial pressure of oxygen gas (p_{O_2}) is greater than about 10^{-9} MPa, Ni inner electrodes will oxidize and will no longer be conductive. In industrial applications, when MLCCs are sintered, the partial pressure of oxygen gas is usually under 10^{-10} MPa.²⁾ Under such conditions, BaTiO₃ is easily reduced, and oxygen vacancies with n -type carriers are generated through the following reaction,³⁾



where $V_{\text{O}}^{\bullet\bullet}$ denotes an oxygen vacancy in the BaTiO₃ lattice that carries an effective charge of +2, using Kröger-Vink notation.

In the early history of the development of MLCCs, Ni-electrode MLCCs were unreliable and their electrical resistance was compromised if DC voltage was applied for a long duration. This decrease in resistance was a critical problem in the development of high-performance and compact Ni-electrode MLCCs. Chazono and Kishi proposed a mechanism that explains this decrease in electric resistance with the migration of oxygen vacancies in MLCCs toward the interface between dielectric grains and the Ni electrode.⁴⁾

These oxygen vacancies generate Schottky emissions at the interface. An illustration of the formation and migration of oxygen vacancies in MLCCs is shown in Fig. 2.1.2. Chazono and Kishi discussed two methods for improving the reliability of Ni-electrode MLCCs: suppressing the formation of oxygen vacancies or inhibiting their migration. Sakabe *et al.*⁵⁾, Saito *et al.*⁶⁾, and Nakano *et al.*⁷⁾ reported that doping with rare-earth (RE) elements can effectively improve the reliability of dielectric materials. The mechanism behind this improvement remains unclear, but RE dopants may effectively suppress both the formation and migration of oxygen vacancies because of their preference for specific sites in BaTiO₃.⁸⁾ Levi found with experimental observations that Zr-doped BaTiO₃ (BaZr_xTi_{1-x}O₃) has a lower concentration of oxygen vacancies than BaTiO₃.⁹⁾ In addition, we used first-principles calculations to determine that the formation energy for oxygen vacancies is higher in BaZr_xTi_{1-x}O₃ than in pure BaTiO₃.¹⁰⁾ These two reports give evidence that RE dopants are useful for improving the reliability of dielectrics for use in MLCCs.

The present study is focused on a quantitative investigation of the formation and migration of oxygen vacancies in BaTiO₃ and BaM_xTi_{1-x}O₃ (M=Zr, Ge). Specifically, the analysis compares the effects of Zr and Ge as dopants, which are both tetravalent in BaM_xTi_{1-x}O₃ but have different valence electrons. First-principles calculations are used to reveal how doping affects the reliability of MLCCs.

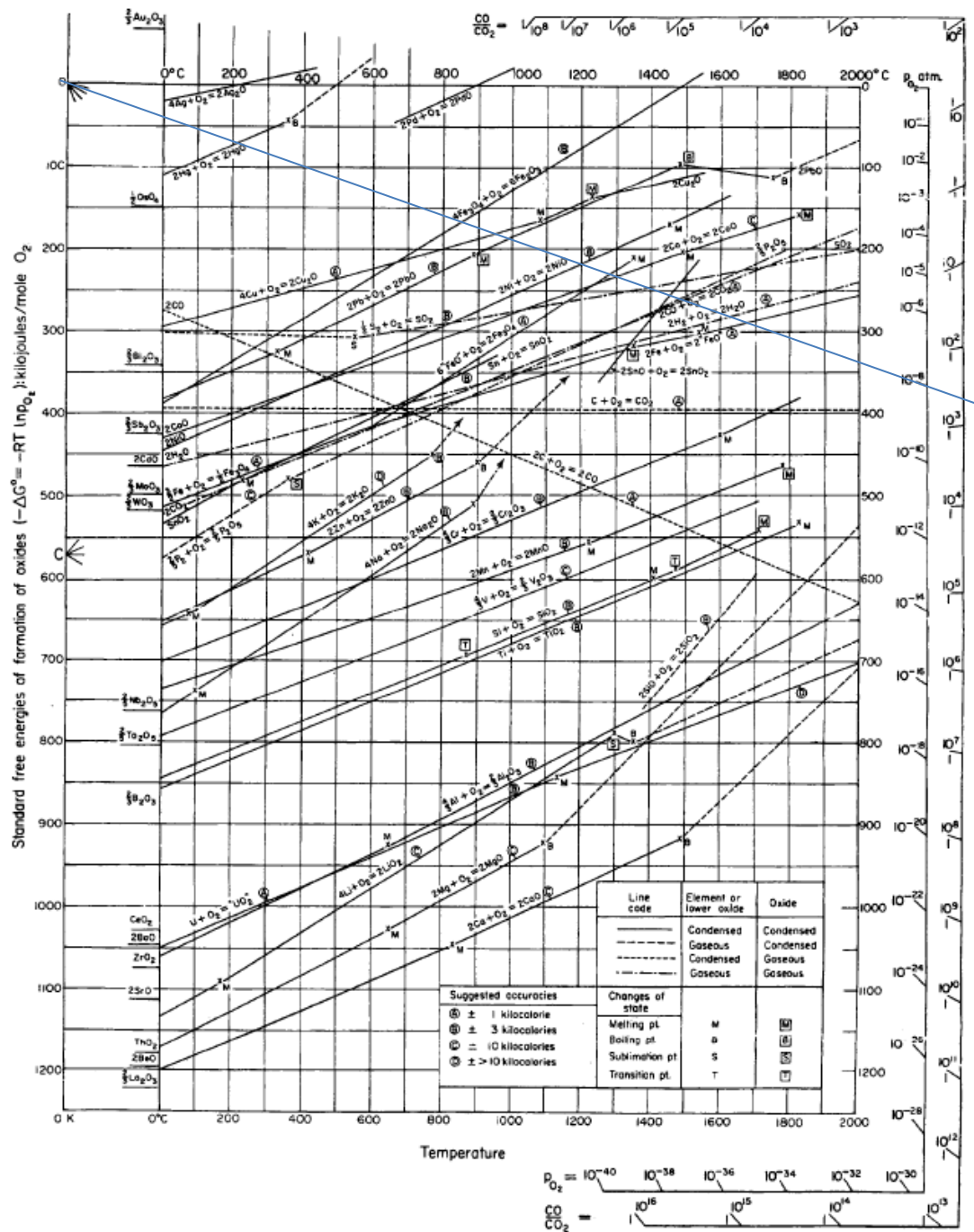


Fig. 2.1.1. Ellingham diagrams for several metal oxides.¹⁾

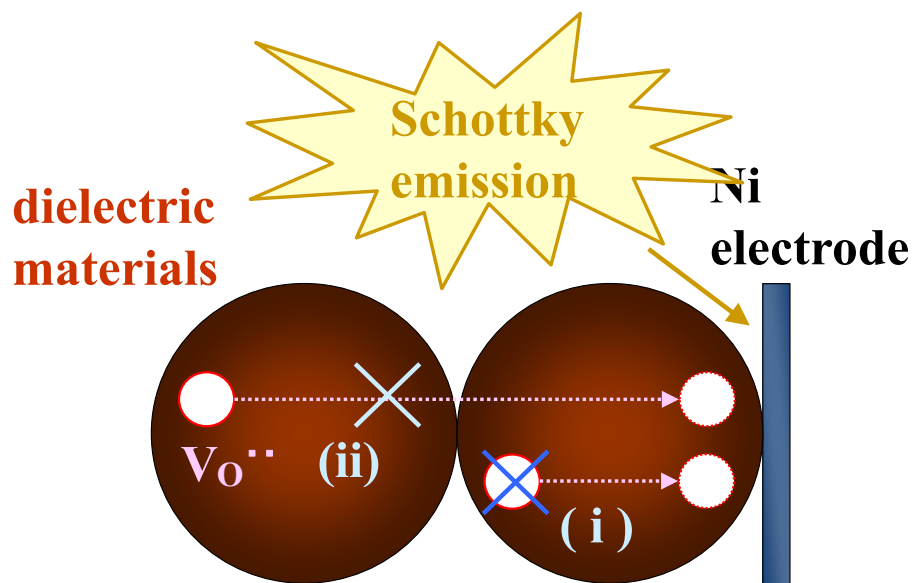


Fig. 2.1.2. Schematic illustrations of the formation and migration of oxygen vacancies in MLCCs. (i) If the formation of oxygen vacancies is suppressed, Schottky emission is also suppressed. (ii) If the migration of oxygen vacancies is suppressed, Schottky emission is also suppressed.

2.2 Methods

2.2.1 Computational methods

Cubic lattices (space group: $Pm\bar{3}m$) were chosen as models for first-principles calculations with $BaTiO_3$ and $BaM_xTi_{1-x}O_3$. This lattice structure was chosen because reliability tests are usually performed at about 200 °C, which is higher than the Curie temperature of $BaTiO_3$. $BaGeO_3$ usually has orthorhombic structure (space group: $P2_12_12_1$), but I will assume that it has the same structure as $BaTiO_3$ with only small amounts of Ge in $BaGe_xTi_{1-x}O_3$. Supercells for the analysis consisted of $3 \times 3 \times 3$ unit cells, each containing 135 atoms in total. One of the Ti atoms in each supercell is replaced by the dopant atom M (M = Zr or Ge), resulting in the structure $Ba_nMTi_{n-1}O_{3n}$ ($n=27$).

During first-principles analysis, the lattice volumes of $(BaTiO_3)_n$ and $Ba_nMTi_{n-1}O_{3n}$ and the internal atomic locations are optimized and the total energy is calculated. After that, the total energy of $Ba_nTi_nO_{3n-1}$ and $Ba_nMTi_{n-1}O_{3n-1}$ which has one oxygen atom removed from $(BaTiO_3)_n$ and $Ba_nMTi_{n-1}O_{3n}$ are calculated with only optimization step applied for internal atomic positions. In this case, when the distance between M and oxygen vacancies is changed, the total energy of $Ba_nMTi_{n-1}O_{3n-1}$ changes. Therefore, four models with different distances between M atoms and oxygen vacancies were analyzed with first-principles calculations. All crystal structures were visualized using VESTA.¹¹⁾ The formation energy for oxygen vacancies in $(BaTiO_3)_n$ is,

$$E_f(V_O^x) = E_t(Ba_nTi_nO_{3n-1}, q=0) - E_t(Ba_nTi_nO_{3n}, q=0) + \frac{1}{2}\mu_{O_2} + \Delta V_{av}, \quad (2.2)$$

where E_t is the total energy of each molecule in charge state q , μ_{O_2} is the chemical potential of oxygen gas, n is the number of atoms in the supercell, and ΔV_{av} is a correction term that accounts for changes in valence band energy caused by the finite size of the supercell.¹²⁾ The formation energy for oxygen vacancies in $Ba_nMTi_{n-1}O_{3n}$ is,

$$E_f(V_O^X) = E_t(\text{Ba}_n\text{MTi}_{n-1}\text{O}_{3n-1}, q=0) - E_t(\text{Ba}_n\text{MTi}_{n-1}\text{O}_{3n}, q=0) + \frac{1}{2}\mu_{\text{O}_2} + \Delta V_{av} \quad (2.3)$$

where $E_t(\text{Ba}_n\text{MTi}_{n-1}\text{O}_{3n-1}, q=0)$ has the lowest total energy among the above four models. The chemical potential of oxygen, μ_{O} , is calculated under the assumption of an equilibrium state.¹³⁾ In reality, in a Ba-Ti-O system, many compositions other than BaTiO₃ are known to be present, such as Ba₄Ti₁₃O₃₀,¹⁴⁾ Ba₂TiO₄,¹⁵⁾ and others. However, BaTiO₃ is considered to be the most commercially important and is the most well-known composition of Ba-Ti-O systems. Therefore, the simple equilibrium state is assumed to hold in the present analysis, as illustrated in Fig. 2.2.2. For example, if BaTiO₃, BaO, and O₂ are assumed to be in equilibrium, the chemical potentials of Ba, Ti, and O simply satisfy the equation

$$\begin{aligned} \mu_{\text{BaTiO}_3} &= \mu_{\text{Ba}} + \mu_{\text{Ti}} + \mu_{\text{O}} \\ \mu_{\text{BaO}} &= \mu_{\text{Ba}} + \mu_{\text{O}} \\ \mu_{\text{O}_2} &= 2\mu_{\text{O}} \end{aligned} \quad (2.4)$$

where μ_X is the chemical potential of atom X. On the other hand, μ_{BaTiO_3} , μ_{BaO} and μ_{O_2} are the also chemical potential of BaTiO₃, BaO and O₂ gas and these chemical potentials can be calculated directly with first-principles calculations. The chemical potential of oxygen gas in the ground state μ_{O} is calculated from eq. (2.4). In addition, the influence of temperature and partial pressure on the atomic chemical potential of oxygen gas is inferred from the thermochemical data reported in Ref. 16. If we assume that O₂ is an ideal gas, the atomic chemical potential of oxygen at partial pressure p and temperature T can be described as

$$\mu_O(T, p) = \frac{1}{2} \left[\mu_{O_2}(T, p^0) + k_B T \ln \frac{p}{p^0} \right] \quad (2.5)$$

where p^0 is the partial pressure in the standard state, i.e., 1 atm, and $\mu_{O_2}(T, p^0)$ corresponds to the total energy per molecule of O_2 gas at temperature T and partial pressure p^0 . The chemical potential of O_2 gas μ_{O_2} is calculated as double the atomic chemical potential obtained from eq. (2.5). The formation energy of oxygen vacancies is calculated by substituting the chemical potential of O_2 gas, calculated by eq. (2.4) and (2.5), into eq. (2.2) and (2.3). In this study, BaO (space group: $Fm\bar{3}m$), TiO_2 (space group: $P4_2/mnm$), Ti (space group: $P6_3/mmc$), and O_2 (space group: Pl) were used for calculating chemical potentials μ_{Ba} , μ_{Ti} , μ_{Zr} , μ_{Ge} , and μ_O . The lattice volumes of BaO, TiO_2 , and Ti and the internal atomic positions are optimized when calculating the total energy. On the other hand, only the internal atomic positions are optimized when calculating total energy of O_2 . The lattice constant of O_2 is fixed at 10 Å.

When an oxygen vacancy with an effective charge of +2 is formed in $BaTiO_3$, two positive charges are introduced. These excess charges must be compensated by corresponding negative charges. Three routes are possible for compensating for the charge imbalance: formation of a Ba^{2+} vacancy, formation of a Ti^{4+} (Zr^{4+}) vacancy, or a carrier-electron (no vacancy, as when changing the valence of a cation). In each of these cases, the formation energy of oxygen vacancies in $BaTiO_3$ is calculated as follows:

$$\begin{aligned} E_f(V_O^{\bullet\bullet}) = & E_t(Ba_n Ti_n O_{3n-1}, q=2) + E_t(Ba_{n-1} Ti_n O_{3n}, q=-2) \\ & - 2E_t(Ba_n Ti_n O_{3n}, q=0) + \frac{1}{2}\mu_{O_2} + \mu_{Ba} + \Delta V_{av} \end{aligned} \quad (2.6)$$

$$E_f(V_O^{\bullet\bullet}) = E_t(Ba_n Ti_n O_{3n-1}, q=2) + \frac{1}{2} E_t(Ba_n Ti_{n-1} O_{3n}, q=-4) - \frac{3}{2} E_t(Ba_n Ti_n O_{3n}, q=0) + \frac{1}{2} \mu_{O_2} + \frac{1}{2} \mu_{Ti} + \Delta V_{av} \quad (2.7)$$

$$E_f(V_O^{\bullet\bullet}) = E_t(Ba_n Ti_n O_{3n-1}, q=2) + E_t(Ba_n Ti_n O_{3n}, q=-2) - 2E_t(Ba_n Ti_n O_{3n}, q=0) + \frac{1}{2} \mu_{O_2} + \Delta V_{av} \quad (2.8)$$

When the charge imbalance is compensated for by a Ba^{2+} vacancy, the formation energy for the oxygen vacancy is calculated by eq. (2.6). When the charge imbalance is compensated by a Ti^{4+} vacancy, the formation energy for the oxygen vacancy is calculated by eq. (2.7). When the charge imbalance is compensated by carrier-electrons, the formation energy for the oxygen vacancy is calculated by eq. (2.8).

On the other hand, the activation energy for oxygen vacancy migration in $Ba_n Ti_n O_{3n-1}$ and $Ba_n MTi_{n-1} O_{3n-1}$ is calculated by the nudged elastic band (NEB) method.¹⁷⁾ As a model for calculation, the migration paths of oxygen vacancies in $Ba_n Ti_n O_{3n-1}$ and $Ba_n MTi_{n-1} O_{3n-1}$ are shown in Fig. 2.2.3. In $Ba_n MTi_{n-1} O_{3n-1}$, the migration energy of an oxygen vacancy may be different if the distance between M and the oxygen vacancy changes. Therefore, the migration energy when the oxygen vacancy migrates from the first nearest-neighbor of M to the fourth nearest-neighbor of M is calculated in this $3 \times 3 \times 3$ unit cell.

All first-principles calculations used the projector-augmented wave (PAW) method in conjunction with the generated gradient approximation (GGA-PBE) algorithm as implemented in the VASP software package.¹⁸⁻²⁰⁾ The cutoff energy was set to 600 eV, because the difference in the calculated total energy between when the cutoff energy is 600eV and that is 700eV is just a few meV. Numerical integration was carried out at a Γ point in the Brillouin zone to save calculation resources. In the PAW potential, ($5s^2, 5p^6, 6s^2$) are treated as the valence electrons for Ba, ($3p^6, 3d^2, 4s^2$) for Ti, ($2s^2, 2p^4$) for O, ($4p^6, 4d^2, 5s^2$) for Zr, and ($3d^{10}, 4s^2, 4p^2$) for Ge. The self-consistent calculation loop is broken if the total change in free energy between two steps is smaller than 1×10^{-5} eV and the Hellmann-Feynman forces are smaller than 20 meV/Å.

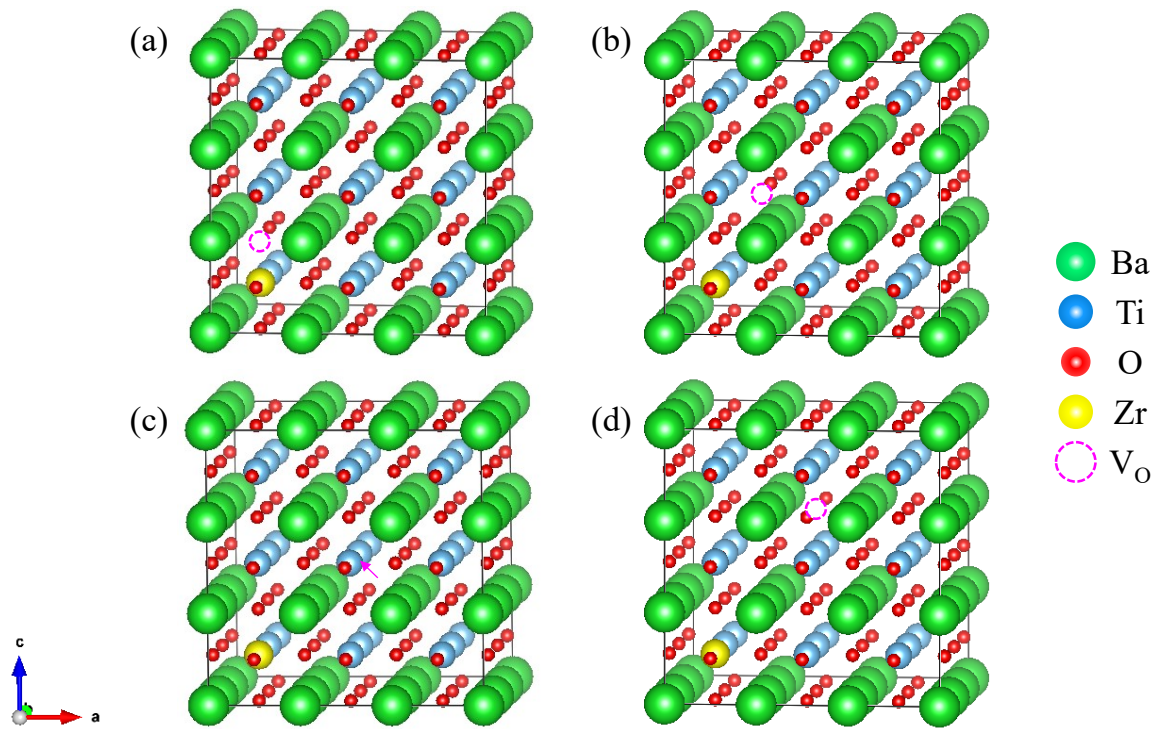


Fig. 2.2.1. Calculation model of $\text{Ba}_n\text{MTi}_{n-1}\text{O}_{3n-1}$. (a) Oxygen vacancy is on the first nearest-neighbor of M. (b) On second nearest-neighbor. (c) On third nearest-neighbor. (d) On fourth nearest-neighbor.

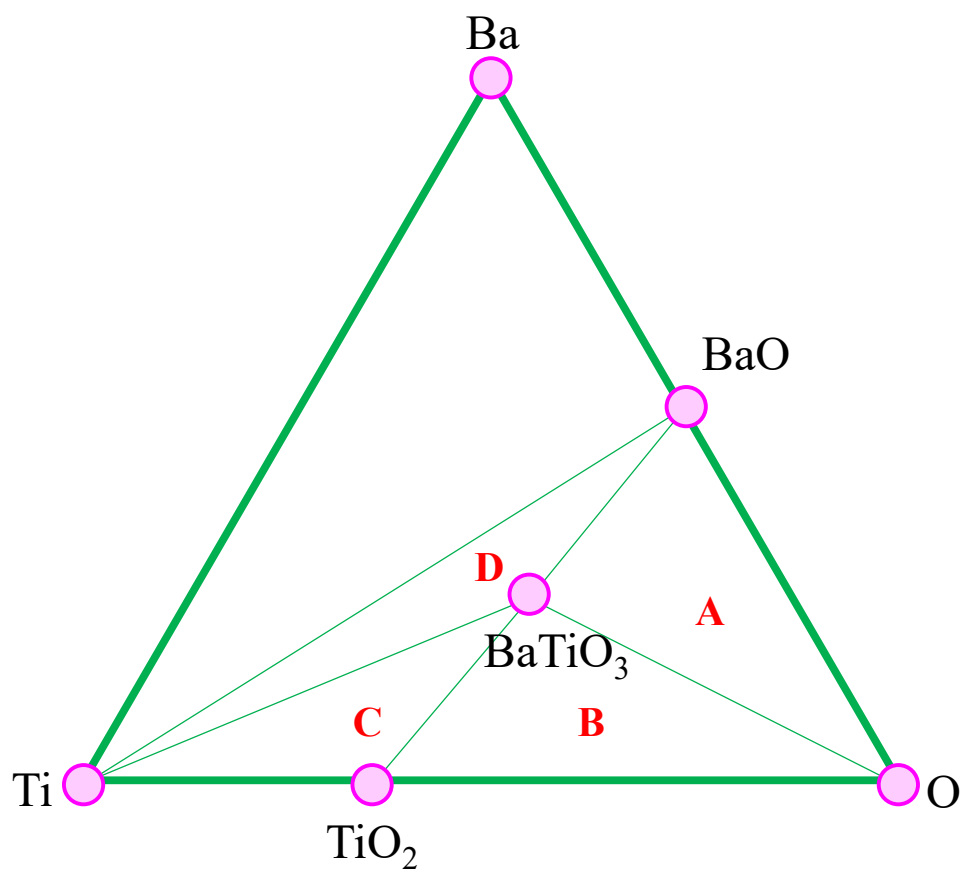


Fig. 2.2.2. Simplified ternary phase diagram of Ba-Ti-O. A–D denote thermodynamic equilibrium phases in which BaTiO_3 coexists in equilibrium with two phases.¹⁸⁾

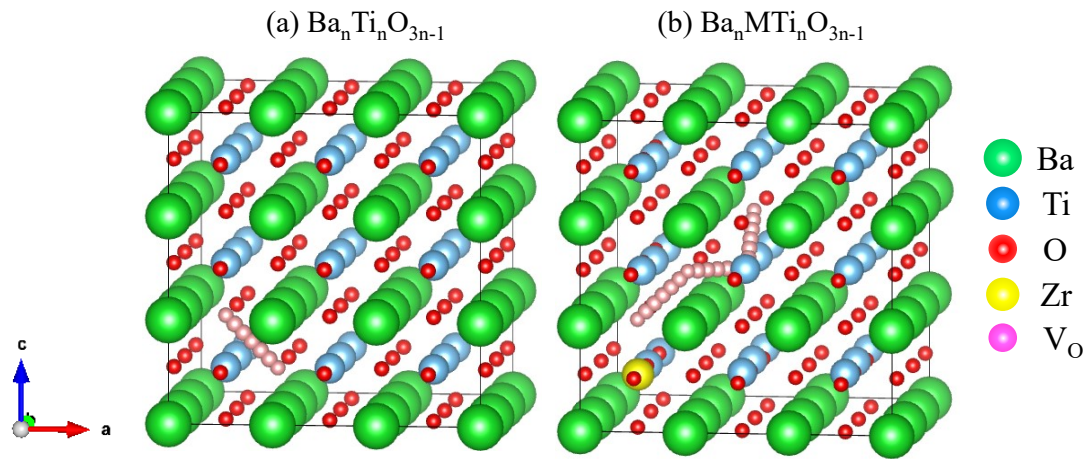


Fig. 2.2.3. Migration paths of oxygen vacancy. (a) in $\text{Ba}_n\text{Ti}_n\text{O}_{3n-1}$, (b) in $\text{Ba}_n\text{MTi}_n\text{O}_{3n-1}$.

2.2.2 Experimental procedure

Simple experiments were used to confirm the calculated results. Ceramic specimens of BaTiO_3 and $\text{BaM}_x\text{Ti}_{1-x}\text{O}_3$ ($M = \text{Zr, Ge}$) are prepared by the traditional sintering method. To obtain specimens having the desired composition, three precursor powders of BaCO_3 , TiO_2 and MO_2 were mixed according to the appropriate stoichiometric ratio. They were sintered in air at temperatures between 1523 and 1623 K. After that, the specimen lifetime, defined as the time until the insulation resistance is reduced by one order of magnitude under an applied DC voltage, was measured at several temperatures.

The activation energy is calculated from the lifetime results as follows

$$k = A \exp\left(-\frac{E_a}{k_B T}\right) \quad (2.9)$$

where, k is the reaction speed, A is a temperature-independent constant, E_a is the activation energy, k_B is the Boltzmann constant, and T is the temperature. Equation (2.9) is called the Arrhenius equation. In this case, k is the mean lifetime, which is related to the reaction speed of Schottky effect. T is the temperature at which the lifetime was measured. From Eq. (2.9), $\ln(k)$ and $1/T$ can be measured and plotted on a graph, and E_a can be calculated from the slope of this graph. This plot is called the Arrhenius plot.

2.3 Results

2.3.1 Calculated results of lattice constants

The calculated lattice constants of BaTiO_3 , $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$, and $\text{BaGe}_x\text{Ti}_{1-x}\text{O}_3$ are shown in Table 2.3.1. These results were calculated by dividing the first-principles calculated lattice constants of $(\text{BaTiO}_3)_n$, $\text{Ba}_n\text{ZrTi}_{n-1}\text{O}_{3n}$, and $\text{Ba}_n\text{GaTi}_{n-1}\text{O}_{3n}$ ($n=27$) by 3. For BaTiO_3 , the calculations agree well with experimental values within the errors of density functional theory (DFT).²¹⁾ The lattice constant of $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ is found to expand when the material is doped with the larger atom of Zr^{4+} , whereas that of $\text{BaGe}_x\text{Ti}_{1-x}\text{O}_3$ is found to contract when doped with the smaller Ge^{4+} .²²⁾

Table 2.3.1. Calculated lattice constants of BaTiO₃, BaZr_xTi_{1-x}O₃, and BaGe_xTi_{1-x}O₃.

		BaTiO ₃			BaZr _x Ti _{1-x} O ₃	BaGe _x Ti _{1-x} O ₃
	Ref. ²¹⁾	Exp. ²¹⁾	Theory	Error /%	Theory	Theory
$a / \text{\AA}$	4.047	4.012	4.037	0.614	4.045	4.034
$b / \text{\AA}$	4.047	4.012	4.037	0.614	4.045	4.034
$c / \text{\AA}$	4.047	4.012	4.037	0.614	4.045	4.034

2.3.2 Calculated results for formation of oxygen vacancies

The calculated relationship between the relative total energy and the distance between the sites of oxygen vacancy and dopant atoms in $\text{Ba}_n\text{MTi}_{n-1}\text{O}_{3n-1}$ ($\text{M} = \text{Zr}, \text{Ge}$) ($n = 27$) is shown in Fig. 2.3.1. The horizontal axis gives the distance of the oxygen vacancy from the doped cation, M. In this analysis, the positions of oxygen vacancies are assumed to be juxtaposed against the sites of the removed oxygen atoms. The vertical axis gives the calculated total energy of model cells, which changes depending on the distance of the oxygen vacancy relative to the dopant atoms in $\text{Ba}_n\text{MTi}_{n-1}\text{O}_{3n-1}$. These total energies are relative to the minimum energy, which is set to zero. For Zr-doped $\text{Ba}_n\text{ZrTi}_{n-1}\text{O}_{3n-1}$, the relative total energy is lowest for the second nearest-neighbor oxygen sites of the dopant Zr, whereas for Ge-doped $\text{Ba}_n\text{GeTi}_{n-1}\text{O}_{3n-1}$ the lowest energy is found to be the first-nearest-neighbor oxygen sites of the dopant Ge. This difference is explained once we notice that the valence states of Zr and Ge differ when oxygen vacancies form, as will be discussed later.

Equations (2.2) to (2.5) were used to calculate the formation energies of oxygen vacancies in $(\text{BaTiO}_3)_n$, $\text{Ba}_n\text{ZrTi}_{n-1}\text{O}_{3n}$, $\text{Ba}_n\text{GeTi}_{n-1}\text{O}_{3n}$, and $(\text{BaZrO}_3)_n$ at 1500 K under an oxygen partial pressure of 10^{-13} MPa, which are common sintering conditions for MLCCs, and the results are plotted in Fig. 2.3.2. Calculated ΔV_{av} values range from -0.1 to -0.04 eV. These calculations used equilibrium condition A in Fig 2.2.2 because MLCCs are usually synthesized from the composition $\text{Ba}_{1+\delta}\text{TiO}_3$ ($\delta > 0$). The vertical axis gives the calculated formation energy of oxygen vacancies. Negative formation energy means that an oxygen vacancy is formed in $(\text{BaTiO}_3)_n$ and $\text{Ba}_n\text{GeTi}_{n-1}\text{O}_{3n}$. On the other hand, positive formation energy means that oxygen vacancies hardly form in $\text{Ba}_n\text{ZrTi}_{n-1}\text{O}_{3n}$ and $(\text{BaZrO}_3)_n$. The formation energies for oxygen vacancies in $\text{Ba}_n\text{ZrTi}_{n-1}\text{O}_{3n}$ and $(\text{BaZrO}_3)_n$ are larger than that in $(\text{BaTiO}_3)_n$. On the other hand, the formation energy for oxygen vacancies in $\text{Ba}_n\text{GeTi}_{n-1}\text{O}_{3n}$ is much smaller than that in $(\text{BaTiO}_3)_n$ because of the difference in the valences of Ti, Zr, and Ge in $\text{Ba}_n\text{Ti}_n\text{O}_{3n-1}$ and $\text{Ba}_n\text{MTi}_{n-1}\text{O}_{3n-1}$. Therefore, the formation of oxygen vacancies is suppressed when Zr is doped in BaTiO_3 . On the other hand, the formation of oxygen vacancies is accelerated when BaTiO_3 is doped with Ge.

Equations (2.6) to (2.8) were used to calculate the formation energy of oxygen

vacancies at $T = 1500$ K for $(\text{BaTiO}_3)_n$ and $(\text{BaZrO}_3)_n$ using each of the three methods to compensate for the charge imbalance; the results are shown in Fig. 2.3.3. The horizontal axis gives the oxygen partial pressure during the sintering process and the vertical axis gives the formation energy for oxygen vacancies $E_f(\text{V}_\text{O})$. The slope of $E_f(\text{V}_\text{O})$ with carrier-electron compensation is determined by μ_{O_2} , which is related to $\log_{10}(p_{\text{O}_2})$. The lowest $E_f(\text{V}_\text{O})$ values appear with carrier-electron compensation in both $(\text{BaTiO}_3)_n$ and $(\text{BaZrO}_3)_n$ under a reducing atmosphere ($< 10^{-10}$ MPa). However, the value of $E_f(\text{V}_\text{O})$ differs greatly between $(\text{BaTiO}_3)_n$ and $(\text{BaZrO}_3)_n$. Therefore, oxygen vacancies are less likely to form in BaZrO_3 than they are in BaTiO_3 . In addition, the difference between the lowest and the second-lowest $E_f(\text{V}_\text{O})$ is smaller in $(\text{BaZrO}_3)_n$ than in $(\text{BaTiO}_3)_n$. For example, $E_f(\text{V}_\text{O}) = 2.37$ eV for $(\text{BaTiO}_3)_n$ and $E_f(\text{V}_\text{O}) = 0.65$ eV for $(\text{BaZrO}_3)_n$ under $p_{\text{O}_2} = 10^{-13}$ MPa. This difference is explained by the difference in the fourth ionization energy of Ti and Zr. The valence of Ti changes easily and the dissociation reaction of oxygen uses the resulting compensating electron, as described by the following equation.



The local partial densities of states (LPDOS) of Zr in $\text{Ba}_n\text{ZrTi}_{n-1}\text{O}_{3n}$, Ge in $\text{Ba}_n\text{GeTi}_{n-1}\text{O}_{3n}$, Zr in $\text{Ba}_n\text{ZrTi}_{n-1}\text{O}_{3n-1}$, and Ge in $\text{Ba}_n\text{GeTi}_{n-1}\text{O}_{3n-1}$ were calculated with the oxygen vacancy occupying a lattice point, and are plotted in Fig. 2.3.4. The horizontal axis of the subplots give the energy of each band obtained by setting the Fermi level to zero, and the vertical axis gives the density of states (DOS). The valence of Zr changes from Zr^{4+} to $\text{Zr}^{(4-\delta)+}$ when an oxygen vacancy forms. $\text{Zr}^{(4-\delta)+}$ may less of a stable valence state than $\text{Ti}^{(4-\delta)+}$ because of the different magnitudes of the elements' fourth ionization energies.³¹⁻³² In other words, the valence of Ti^{4+} changes more easily than that of Zr^{4+} . Therefore, the formation of oxygen vacancies in $\text{Ba}_n\text{ZrTi}_{n-1}\text{O}_{3n}$ is less likely than it is in $(\text{BaTiO}_3)_n$. On the other hand, the valence of Ge transitions from Ge^{4+} to Ge^{2+} when an oxygen vacancy forms. The formation of oxygen vacancies is encouraged in $\text{Ba}_n\text{GeTi}_{n-1}\text{O}_{3n}$ by the stability of the valence state of Ge^{2+} .

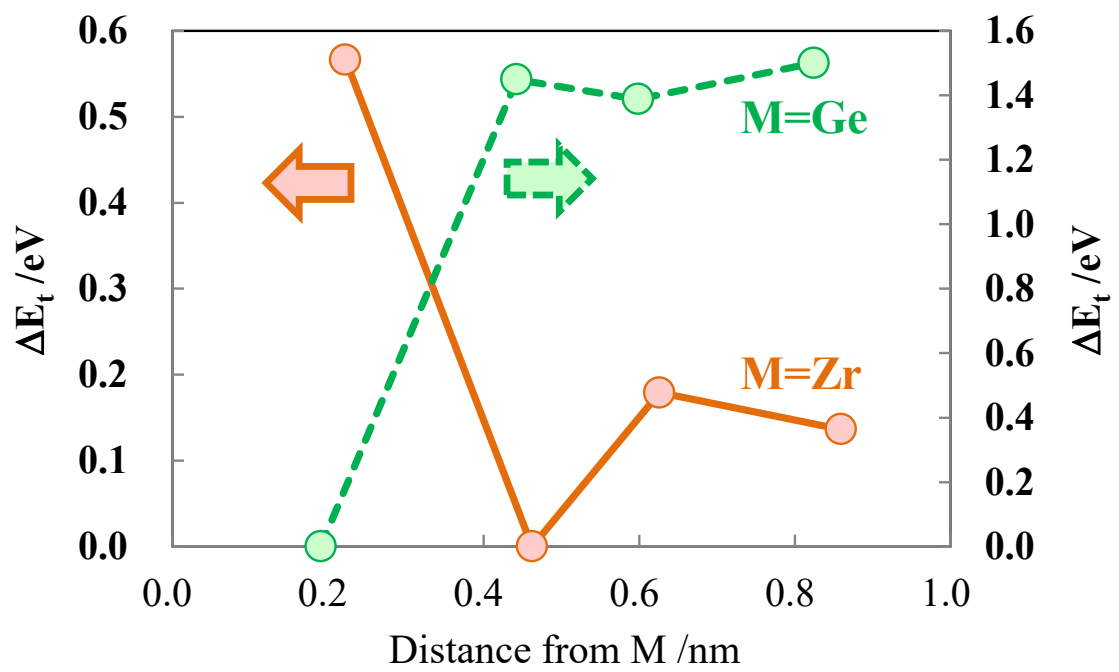


Fig. 2.3.1. Calculated relationship between the relative total energy and the distance between sites of oxygen vacancies and dopant atoms M in $\text{Ba}_n\text{MTi}_{n-1}\text{O}_{3n-1}$ (M = Zr, Ge) (n = 27).

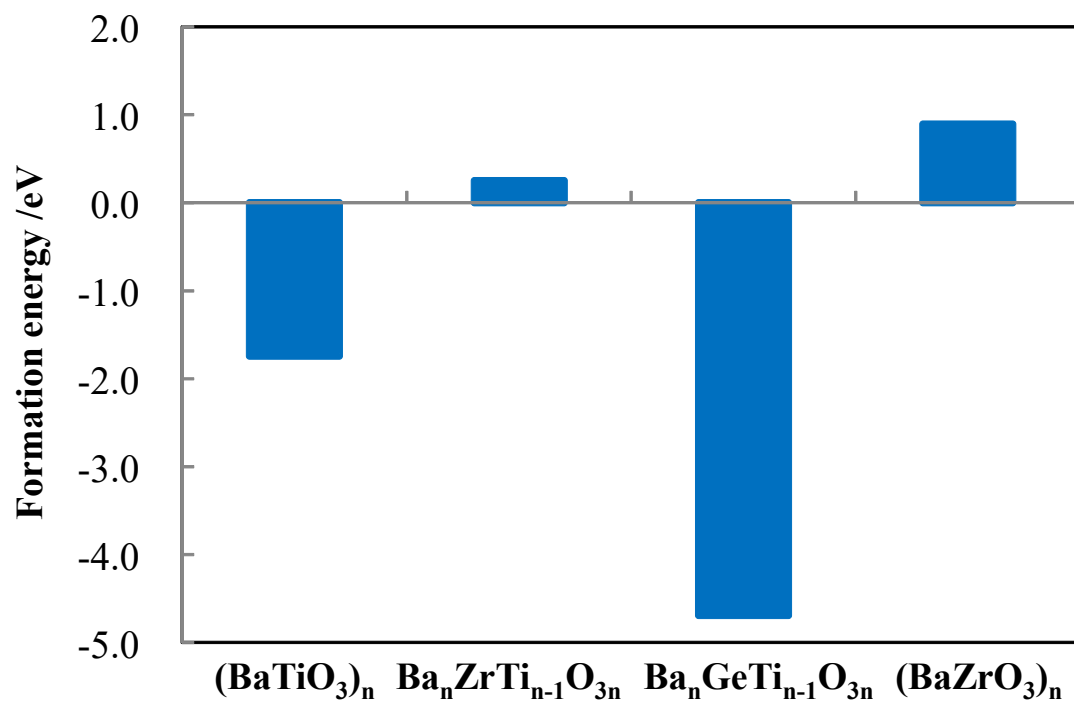


Fig. 2.3.2. Calculated formation energies of oxygen vacancies in $\text{Ba}_n\text{ZrTi}_{n-1}\text{O}_{3n}$, $\text{Ba}_n\text{GeTi}_{n-1}\text{O}_{3n}$, and $(\text{BaZrO}_3)_n$ at 1500 K under oxygen partial pressure of 10^{-13} MPa.

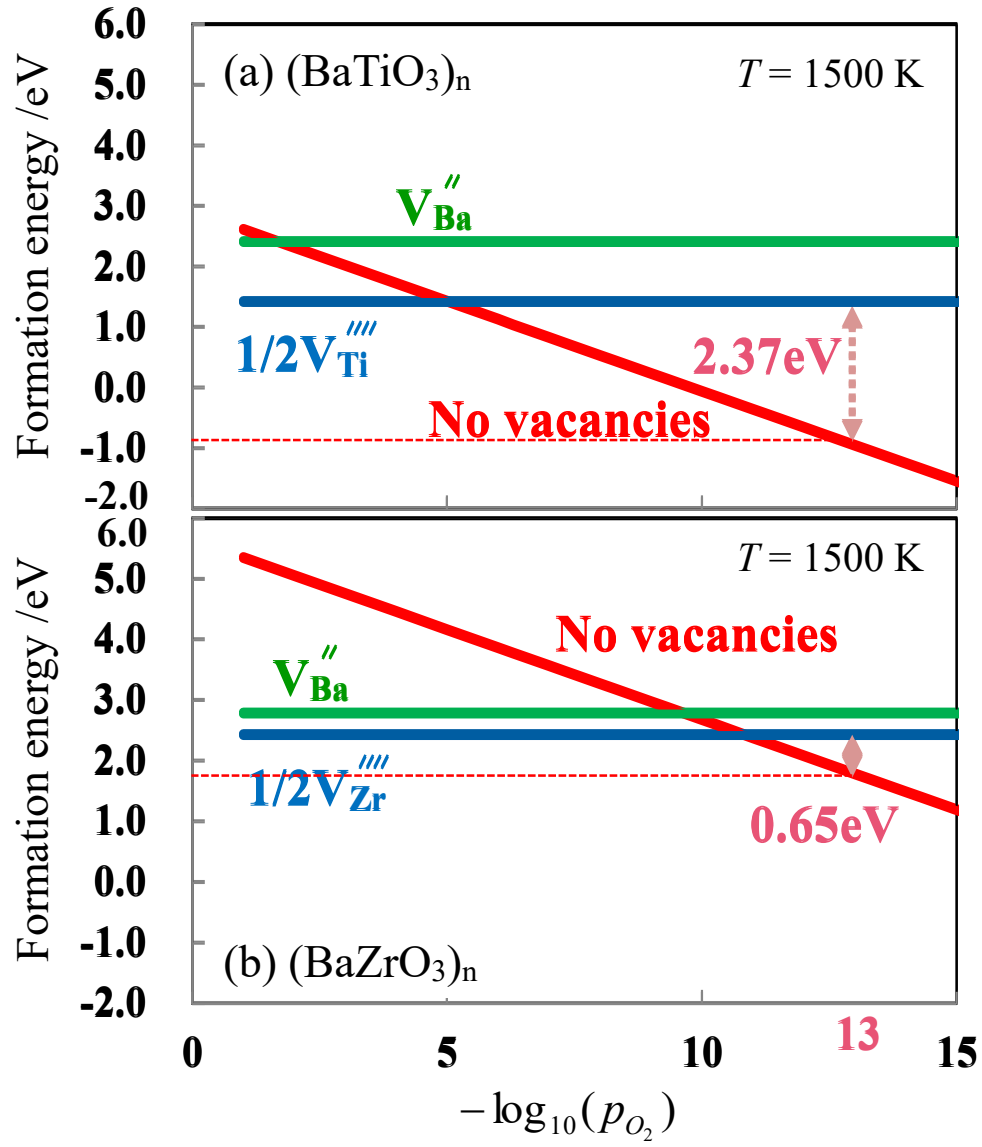


Fig. 2.3.3. Calculated formation energy of oxygen vacancies at $T = 1500$ K for $(BaTiO_3)_n$ and $(BaZrO_3)_n$.

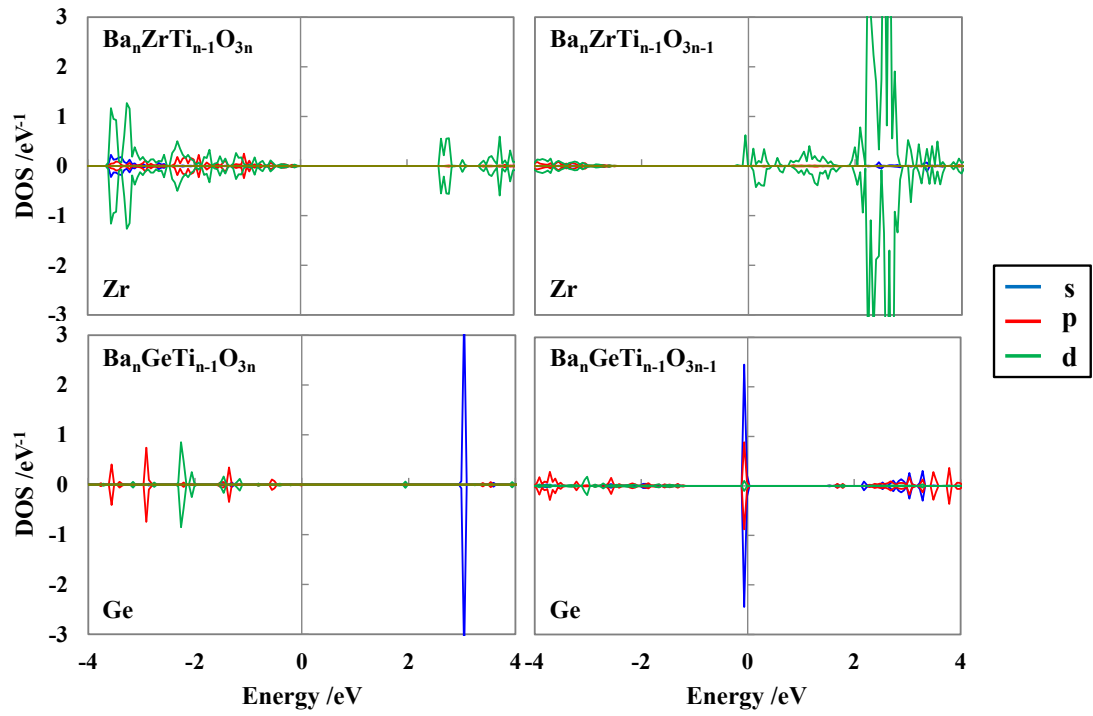


Fig. 2.3.4. Local partial densities of states (LPDOS) of Zr in Ba_nZrTi_{n-1}O_{3n}, Ge in Ba_nGeTi_{n-1}O_{3n}, Zr in Ba_nZrTi_{n-1}O_{3n-1}, and Ge in Ba_nGeTi_{n-1}O_{3n-1} calculated with an oxygen vacancy occupying a lattice point.

2.3.3 Calculated results for migration of oxygen vacancies

The calculated total energies when an oxygen vacancy is on the migration path is plotted in Fig. 2.3.5, 2.3.6, and 2.3.7. The vertical axis of each graph gives the calculated total energy. The horizontal axis of Fig 2.3.5 gives the relative position of the oxygen vacancy, and those of Fig. 2.3.6 and 2.3.7 give the distance from the dopant atom to the oxygen vacancy. The oxygen vacancy is assumed to not be shifted by the nudged elastic band (NEB) calculation of the distance between Zr or Ge and the oxygen vacancy. In addition, the calculated activation energies of oxygen vacancy migration in $(\text{BaTiO}_3)_n$, $\text{Ba}_n\text{ZrTi}_{n-1}\text{O}_{3n}$, and $\text{Ba}_n\text{GeTi}_{n-1}\text{O}_{3n}$ are shown in Fig. 2.3.8. The activation energy is calculated for the migration of oxygen vacancy from the most stable oxygen site to the next neighboring site. In $\text{Ba}_n\text{ZrTi}_{n-1}\text{O}_{3n}$, the oxygen vacancy migrates from the second-nearest-neighbor site of the doped Zr to the first- or third-nearest-neighbor site. In $\text{Ba}_n\text{GeTi}_{n-1}\text{O}_{3n}$, the oxygen vacancy migrates from the first-nearest-neighbor site of the doped Ge to the second-nearest-neighbor site. The NEB calculations confirm that the activation energies of oxygen vacancy migration in $\text{Ba}_n\text{ZrTi}_{n-1}\text{O}_{3n}$ and $\text{Ba}_n\text{GeTi}_{n-1}\text{O}_{3n}$ are the largest. The activation energies of oxygen vacancy migration in $\text{Ba}_n\text{ZrTi}_{n-1}\text{O}_{3n}$ and $\text{Ba}_n\text{GeTi}_{n-1}\text{O}_{3n}$ are both larger than that in $(\text{BaTiO}_3)_n$. The migration energy in $\text{Ba}_n\text{GeTi}_{n-1}\text{O}_{3n}$ is five times larger. This result indicates that the migration of oxygen vacancy is prevented if both Zr and Ge are doped in BaTiO_3 , and that the suppression of oxygen vacancy migration is most effective in $\text{Ba}_n\text{GeTi}_{n-1}\text{O}_{3n}$. In addition, the reliability of MLCCs with $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ as the dominant material could be improved because of the smaller concentration of oxygen vacancies and their slower diffusion.

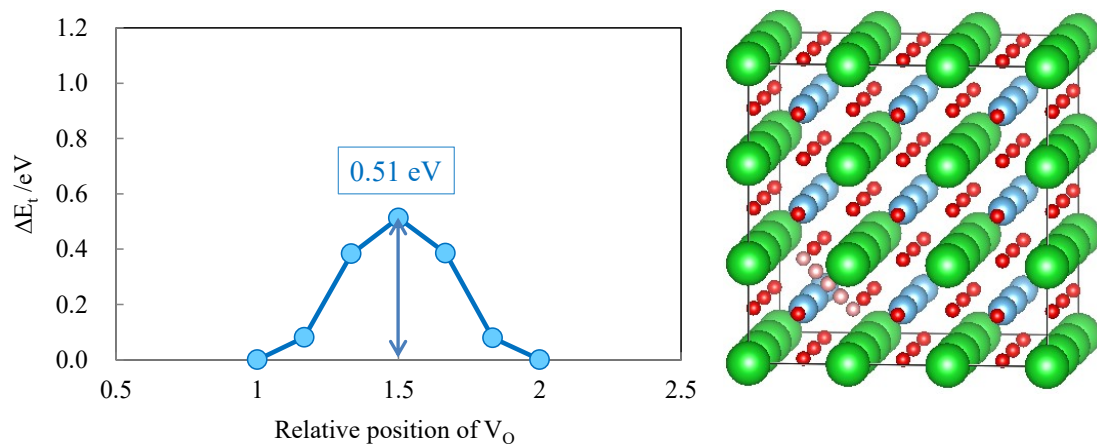


Fig. 2.3.5. Calculated total energy of $\text{Ba}_n\text{Ti}_n\text{O}_{3n-1}$ when the oxygen vacancy is on the migration path shown to the right.

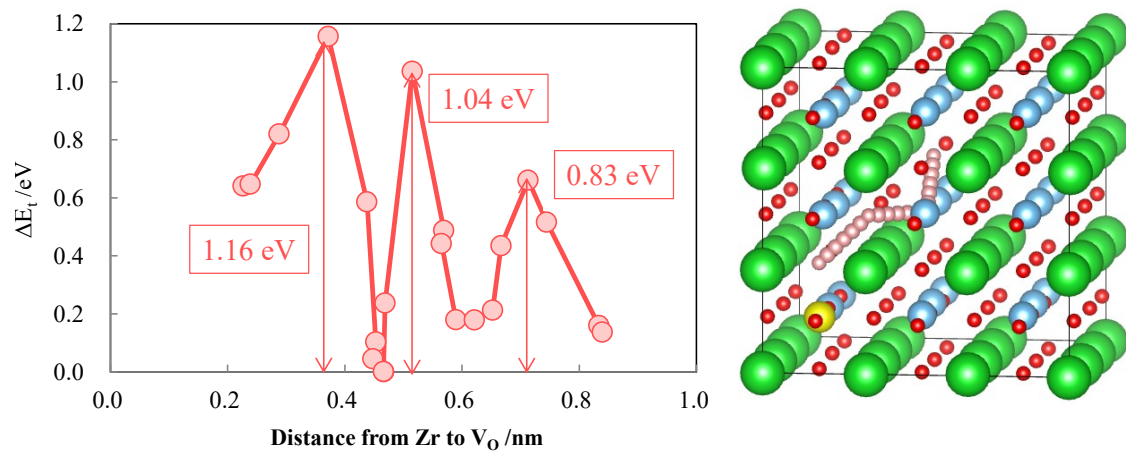


Fig. 2.3.6. Calculated total energy of $Ba_nZrTi_nO_{3n-1}$ when the oxygen vacancy is on the migration path shown to the right.

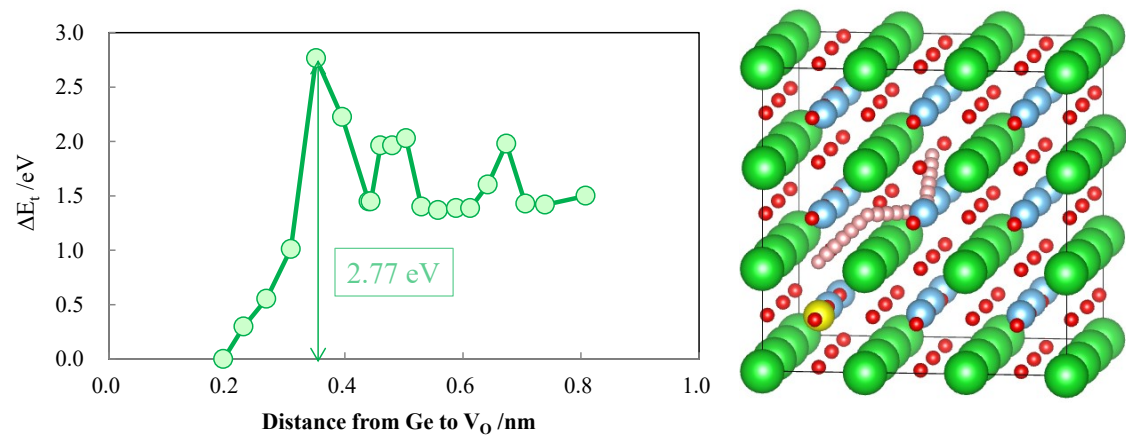


Fig. 2.3.7. Calculated total energy of $\text{Ba}_n\text{GeTi}_n\text{O}_{3n-1}$ when the oxygen vacancy is on the migration path shown to the right.

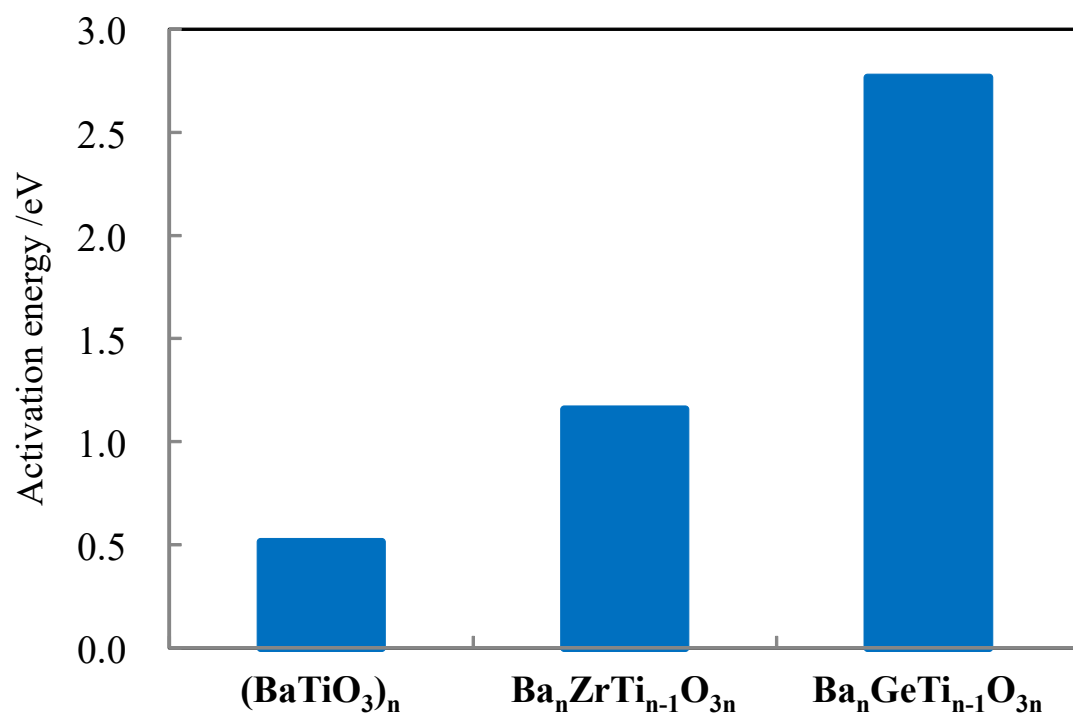


Fig. 2.3.8. Calculated activation energies of oxygen vacancy migration in $(\text{BaTiO}_3)_n$, $\text{Ba}_n\text{ZrTi}_{n-1}\text{O}_{3n}$, and $\text{Ba}_n\text{GeTi}_{n-1}\text{O}_{3n}$.

2.3.4 Experimental results

To confirm the calculated results, ceramic specimens of BaTiO_3 , $\text{BaZr}_{0.1}\text{Ti}_{0.9}\text{O}_3$, and $\text{BaGe}_{0.1}\text{Ti}_{0.9}\text{O}_3$ were prepared by traditional sintering. An indium and gallium alloy was attached to the surface of a specimen as an electrode. Afterwards, its lifetimes were measured in an oven at 130 °C–200 °C while applying a DC voltage of 3 V/ μm (μm is unit for the thickness of specimen). Arrhenius plots of carrier lifetimes are shown in Fig. 2.3.9, and these give estimates of the activation energies of $\text{BaZr}_{0.1}\text{Ti}_{0.9}\text{O}_3$ and BaTiO_3 . The activation energy of $\text{BaZr}_{0.1}\text{Ti}_{0.9}\text{O}_3$ is 1.3 eV, and that of BaTiO_3 is 0.9 eV, respectively. These results agree qualitatively with the theoretical results above.

The insulation resistances of BaTiO_3 and $\text{BaGe}_{0.1}\text{Ti}_{0.9}\text{O}_3$ measured at room temperature while applying a brief DC voltage are shown in Fig. 2.3.10. 10 samples were measured and are plotted with gray filled circles in Fig. 2.3.10. The black filled circles in Fig. 2.3.10 show the average of electrical resistance of these 10 samples. The electrical resistance of $\text{BaGe}_{0.1}\text{Ti}_{0.9}\text{O}_3$ is much lower than that of BaTiO_3 . For BaTiO_3 and $\text{Ba}_n\text{MTi}_{n-1}\text{O}_{3n-1}$ ($M = \text{Zr}, \text{Ge}$), electron carriers are generated by the formation of oxygen vacancies, as described in Eq. (2.1). Therefore, the experimental results corroborate our theoretical calculations of the formation energies of oxygen vacancies in these materials.

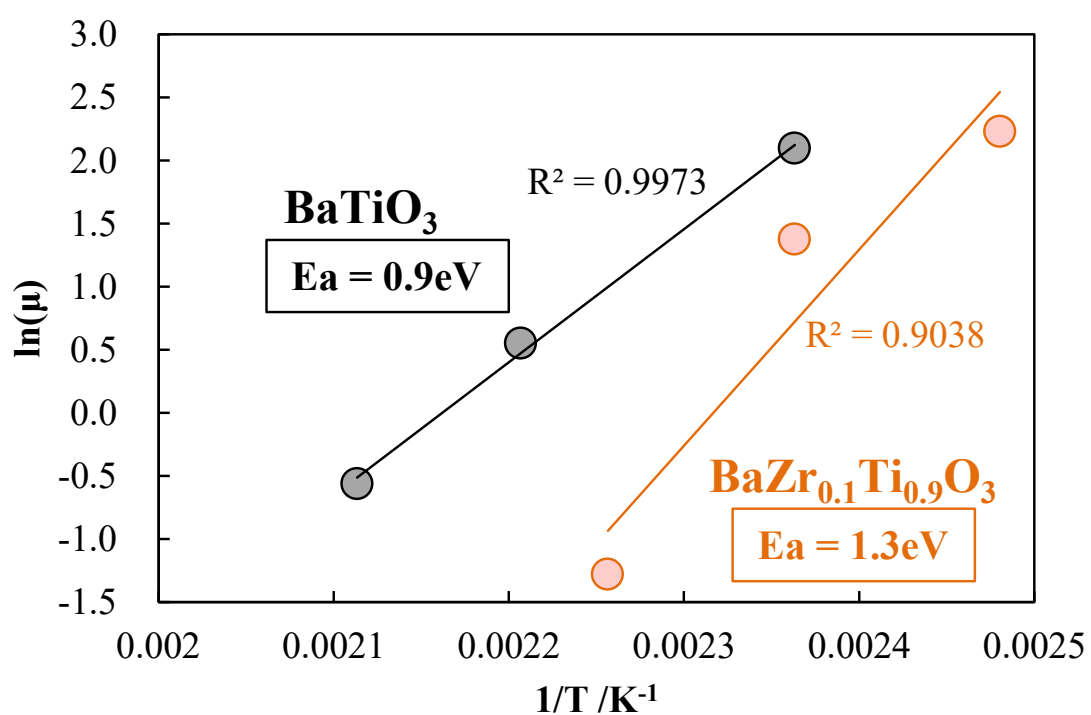


Fig. 2.3.9 Arrhenius plot of carrier lifetimes in BaZr_{0.1}Ti_{0.9}O₃, and BaTiO₃.

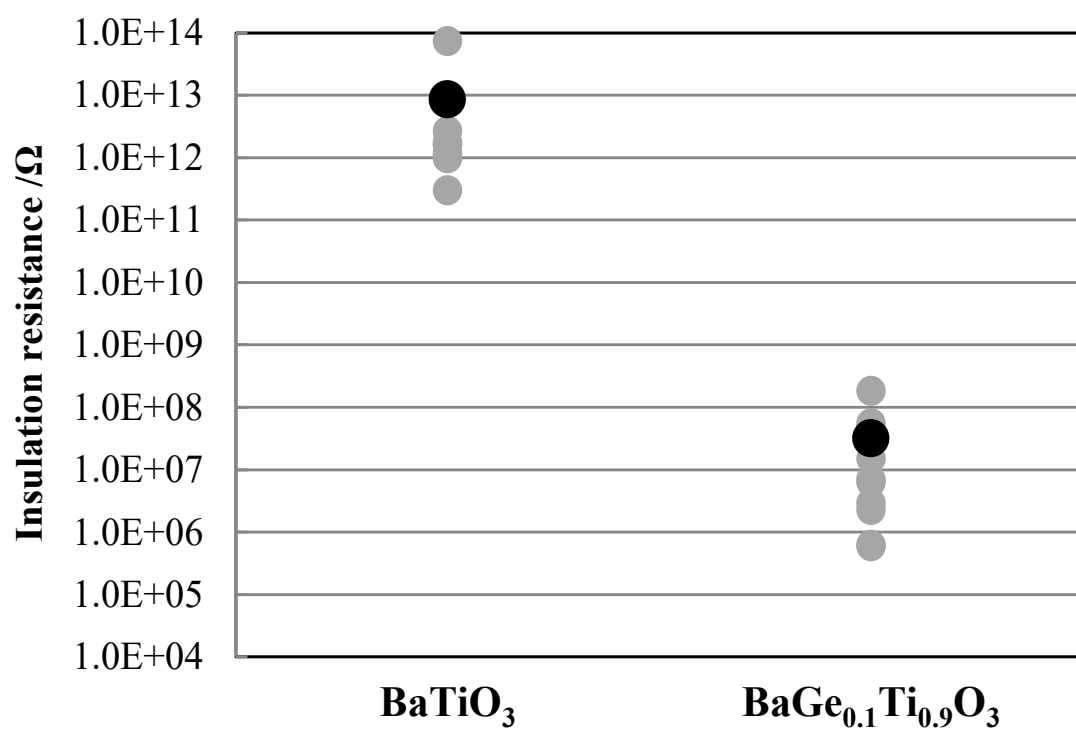


Fig. 2.3.10 Measured results electrical resistances of BaTiO₃ and BaGe_{0.1}Ti_{0.9}O₃ while applying a short-term DC voltage at room temperature.

2.4 Summary

The formation and migration of oxygen vacancies in BaTiO_3 and $\text{Ba}_n\text{MTi}_{n-1}\text{O}_{3n}$ ($M = \text{Zr}, \text{Ge}$) were studied by theoretical calculations and experiments with model systems to understand how cation doping affects the reliability of MLCCs. The formation of oxygen vacancies was evaluated by calculating the formation energy of oxygen vacancies, and the migration of oxygen vacancies was evaluated by calculating the activation energy of oxygen vacancies. Both calculations took only first-principles as inputs.

The calculations show that doping with Zr suppresses both the formation and migration of oxygen vacancies. This result is one possible reason behind the improved reliability of Zr-doped MLCC materials. Doping with Ge, on the other hand, only suppresses oxygen vacancy migration, while encouraging the formation of oxygen vacancies. These theoretical results are confirmed by experimental observations.

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Chapter 3: Searching for new dielectric materials based on first-principles calculations

3.1 Introduction

Barium titanate (BaTiO_3) is among the most important ferroelectric materials for use in ceramic capacitors because of its high dielectric constant at room temperature and its chemical stability. BaTiO_3 is an excellent material, but it has served as the main material in ceramic capacitors over the 70 years since its discovery. Therefore, in order to meet increasing technological demands, new high-performance and low-cost dielectric materials are strongly desired.

The number of ceramic capacitors used in the electronic control units (ECUs) of automobiles has increased as automobiles include more and more electronic components. Ceramic capacitors that can maintain performance at high temperatures are required because ECUs are frequently installed close to the engine. The rated operating temperatures of ceramic capacitors have increased along with the improving performance of automobiles. As the density of electronic components near the engine has increased, more ECUs are subjected to higher temperatures. Several dielectric materials have been suggested for ceramic capacitors used at high temperatures.¹⁻¹²⁾ BaTiO_3 faces problems when used as a dielectric that must maintain high-performance at high temperatures. Since the Curie temperature of BaTiO_3 is about 400 K, the dielectric constant of BaTiO_3 is relatively low at temperatures over 420 K. The dielectric constant of BaTiO_3 below its Curie temperature is about 2,000, but it decreases to about 100 once the Curie temperature is exceeded.¹³⁾

Finding novel materials is usually difficult because a great deal of experimental trial and error is required. Many excellent materials have been discovered because of repeated trial and error. In the 21st century, computer simulations based on first-principles calculations that can predict functional properties from basic physics have proven very helpful in materials science. In addition, following recent developments in computing hardware and computational techniques, databases of first-principles calculations of the physical properties of a number of compounds can be compiled, and these can be used

for high-throughput screening. This approach is known as Materials Informatics. Since US president Obama advocated for the Materials Genome Initiative (MGI) in 2011¹⁴⁾, materials informatics has been promoted with huge budgets all over the world. Several national projects are underway in Japan. The Materials Informatics and Integration (Mi²i) project, for example, is focused on battery materials, magnetic materials, materials with controllable heat transfer, and thermoelectric materials.¹⁵⁾

Recently, several searches for novel compounds, structures, and materials have used using high-throughput screening with data collected from first-principles calculations.¹⁶⁻²¹⁾ In addition, many effort are being made to build open-access databases, like the Materials Project Database (MPD)²²⁾, AFLOW²³⁾, OQM²⁴⁾, and AtomWork²⁵⁾. This chapter will discuss a search for novel dielectric materials that can be used use in ceramic capacitors operating at high temperatures.

Yim *et al.* published the dielectric constants of more than 1,800 oxides (not including 3d-transition metal oxides) as predicted with first-principles calculations.²⁶⁾ They searched for compounds with high dielectric constants that are outliers from the simple inverse correlation between the material's band gap and dielectric constant. Petousis *et al.* reported first-principles calculated dielectric tensors for 1,056 inorganic compounds.²⁷⁾ These results are included in the MPD.²²⁾

The present study is a search for novel paraelectric materials that have high effective dielectric constants. First-principles calculations are performed to calculate dielectric constants for compounds selected using novel criteria including structural, thermodynamic, and electronic information published in the MPD.²²⁾

3.2 Procedure

Exhaustive first-principles calculations were performed to find new compounds with high dielectric constants. Crystal data of the candidate compounds for first-principles calculations were obtained from the MPD.²²⁾ Compounds with no technetium, promethium, rare-gas elements, or actinoids that also meet the following criteria were selected: the compound must a) be an oxide, b) be binary or ternary, c) have unit or primitive cells contain fewer than 40 atoms, d) have formation energy above the convex hull less than 0.05 eV as listed in the MPD, and e) have electronic band gap energy larger than 0.5 eV as listed in the MPD. Conditions b) and c) ensure that the calculations can be finished in a practical amount of time. Conditions a), d), and e) ensure that the compounds are suitable for use in ceramic capacitors. 3,382 compounds fulfill these conditions. The structural information of a compound was first obtained from the MPD,²²⁾ and is then optimized to our computational conditions. The dielectric constants of 2,504 compounds with no imaginary phonons were exhaustively calculated using density functional perturbation theory (DFPT). Compounds with high dielectric constants are considered as good paraelectric materials. A flowchart of this investigation is shown in Fig. 3.2.1.

All first-principles calculations used the projector-augmented wave (PAW) method as implemented in the VASP software package.²⁸⁻³⁰⁾ The generalized gradient approximation (GGA-PBEsol)³¹⁾ was employed. Strong on-site Coulomb interaction of *d* orbitals were corrected using the simple $+U$ method with the *U* values listed in Ref. 32. When an element with an open *d* shell is included in a compound, spin polarization with ferromagnetic structure is assumed. On the other hand, *f*-orbital electrons are treated as inner-core electrons. Therefore, when an element with an open *f*-shell is included in a compound, spin polarization with ferromagnetic structure is not assumed.

The plane-wave cutoff energy, the *k*-space integration mesh over the Brillouin zone, and the PAW potential for oxygen were chosen for preliminary validation of the calculated dielectric constants of MgO³³⁾, Al₂O₃³⁴⁾, and ZrO₂³⁵⁾, which have been reported in the literature. If the calculated values are close to the reported values under a set of calculation conditions, those conditions are then adopted for the exhaustive first-principles calculations. With the cutoff energy and PAW potential of oxygen varied, the calculation

results are shown in Fig. 3.2.2. The horizontal axis gives the cutoff energy, the vertical axis gives the calculated dielectric constant, and the dashed line plots the dielectric constant as reported in the literature.³³⁻³⁵⁾ The following calculation conditions were adopted because of these preliminary calculations: the cutoff energy was set to 500 eV, which generates a gamma-centered k -point mesh with grid size of $0.2 \text{ \AA}^{-1}$ for Brillouin zone sampling, and the standard PAW potential for oxygen was used. The self-consistent calculation loop is broken if the change in the total free energy between two steps is less than $1 \times 10^{-7} \text{ eV}$ and the Hellmann-Feynman forces are weaker than $0.5 \text{ meV/\AA}$. The other conditions match those used to calculate the values in the MPD.

The calculations were focused on evaluating the polycrystalline dielectric constants. Single-crystal dielectric tensors of ionic and electron contributions were calculated by DFPT method. The polycrystalline dielectric constant is determined as a simple average of the eigenvalues of the single-crystal dielectric tensor, as in the following equations from (3.1) to (3.3).

$$\epsilon_0 = \begin{pmatrix} \epsilon_0^{11} & \epsilon_0^{12} & \epsilon_0^{13} \\ \epsilon_0^{21} & \epsilon_0^{22} & \epsilon_0^{23} \\ \epsilon_0^{31} & \epsilon_0^{32} & \epsilon_0^{33} \end{pmatrix} \quad (3.1)$$

$$\epsilon_\infty = \begin{pmatrix} \epsilon_\infty^{11} & \epsilon_\infty^{12} & \epsilon_\infty^{13} \\ \epsilon_\infty^{21} & \epsilon_\infty^{22} & \epsilon_\infty^{23} \\ \epsilon_\infty^{31} & \epsilon_\infty^{32} & \epsilon_\infty^{33} \end{pmatrix} \quad (3.2)$$

$$\epsilon = \frac{(\epsilon_0^{11} + \epsilon_0^{22} + \epsilon_0^{33})}{3} + \frac{(\epsilon_\infty^{11} + \epsilon_\infty^{22} + \epsilon_\infty^{33})}{3} \quad (3.3)$$

where ϵ_0 is the dielectric constant of ionic contribution, ϵ_∞ is of electron contribution, and ϵ is the polycrystalline dielectric constant.

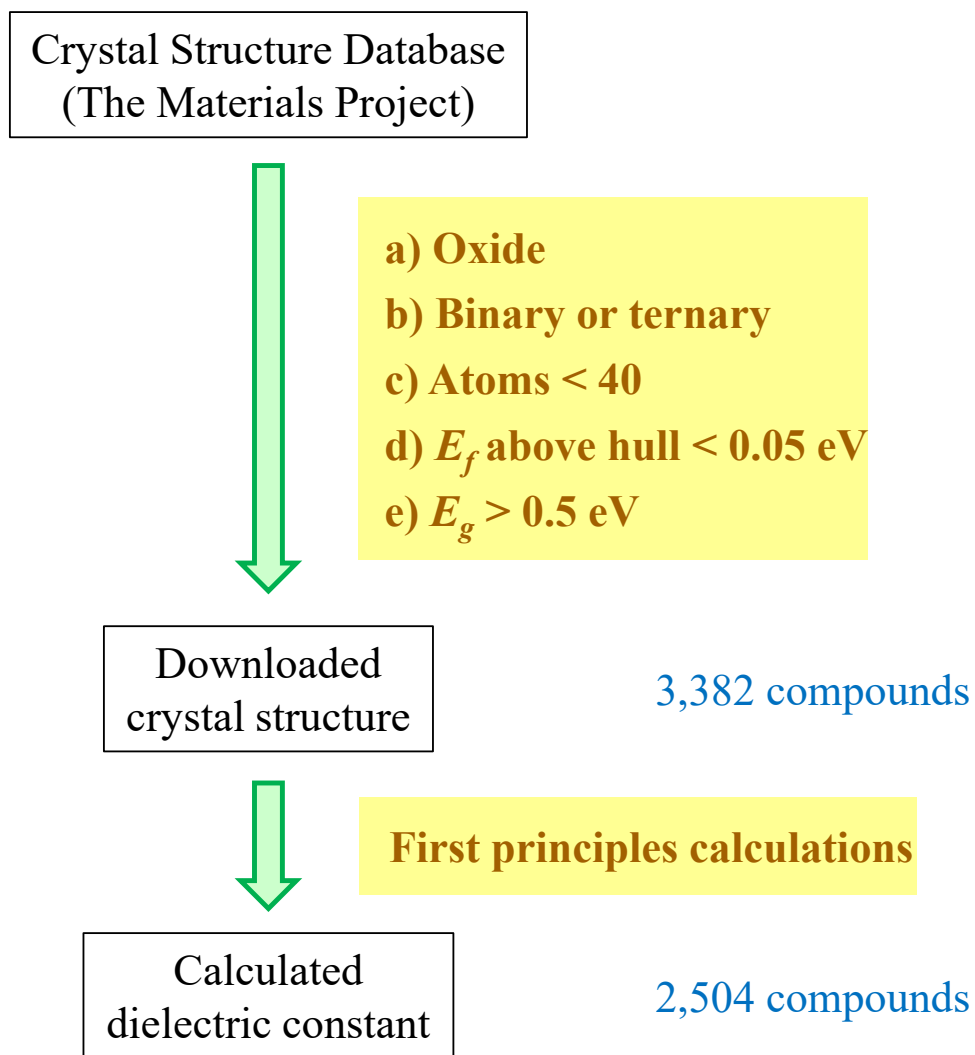


Fig. 3.2.1. The flowchart of calculation for dielectric constant using MPD.²²⁾

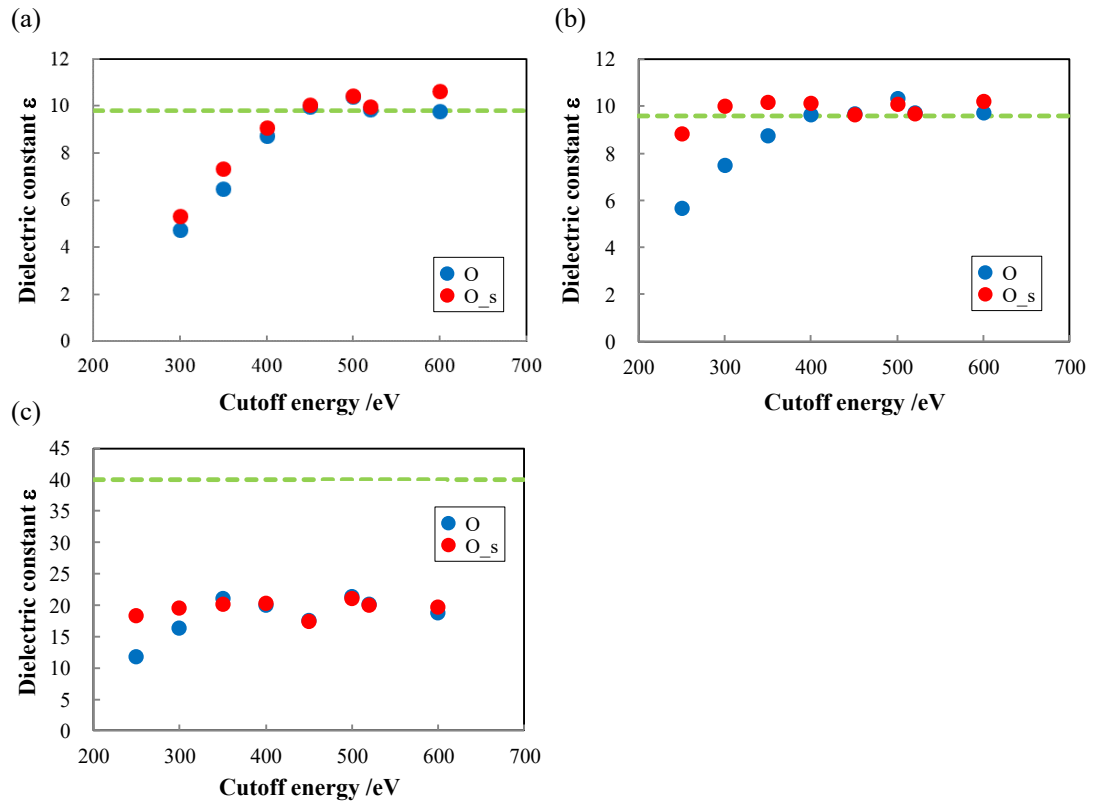


Fig. 3.2.2. Calculated dielectric constants of (a) MgO, (b) Al₂O₃, (c) ZrO₂, when the cutoff energy and PAW potential for oxygen are varied. The dashed line is the dielectric constant reported in the literature.³³⁻³⁵⁾

3.3 Results

3.3.1 Exhaustive calculations

The dielectric constants of 3,382 compounds were exhaustively calculated. The sums of the contributions of ionic polarization and electronic polarization, ϵ_0 and ϵ_∞ respectively, for 2,504 compounds with no imaginary phonon mode are plotted in Fig. 3.3.1. The vertical axis gives the calculated polycrystalline dielectric constant. The horizontal axis gives the index of each compound. The room-temperature dielectric constant of rutile TiO_2 , which is a typical paraelectric material, is reported at 86–170.³⁶⁾ The dielectric constants of some of the compounds exceed 100. The compounds with dielectric constants greater than 100 are listed in Table 3.3.1. Some compounds that are currently used as dielectric and/or piezoelectric materials, such as SrHfO_3 , KTaO_3 , and AgTaO_3 , are included in Table 3.3.1. However, many of the identified compounds are not commonly used as dielectric and/or piezoelectric materials. If materials with very high dielectric constants, like FeAgO_2 could be used in MLCCs it would be possible to reduce the size of MLCCs to 1/10 or less than MLCCs made of rutile TiO_2 . The crystal structure of FeAgO_2 , which has a high dielectric constant, is shown in Fig. 3.3.2. The space group of FeAgO_2 is $R\bar{3}m$. The lattice constants of FeAgO_2 as determined by first-principles calculations are 2.917 Å along the a -axis and 18.178 Å along the c -axis. The calculated dielectric tensor values of FeAgO_2 are as follows: $\epsilon_0^{11} = 2006$, $\epsilon_0^{22} = 2006$, $\epsilon_0^{33} = 362$,

$\epsilon_\infty^{11} = 1.90$, $\epsilon_\infty^{22} = 3.50$, and $\epsilon_\infty^{33} = 0.63$. I do not have a clear explanation for why FeAgO_2 has such a high dielectric constant. However, ionic polarization may be relatively intense in this material because of the large distortion of the Fe-O octahedron in FeAgO_2 .

The compounds listed in Table 3.3.1 are commonly known and are included in the MPD.²²⁾ However, they are not commonly used as dielectric materials. Therefore, they are important candidates for novel dielectric materials.

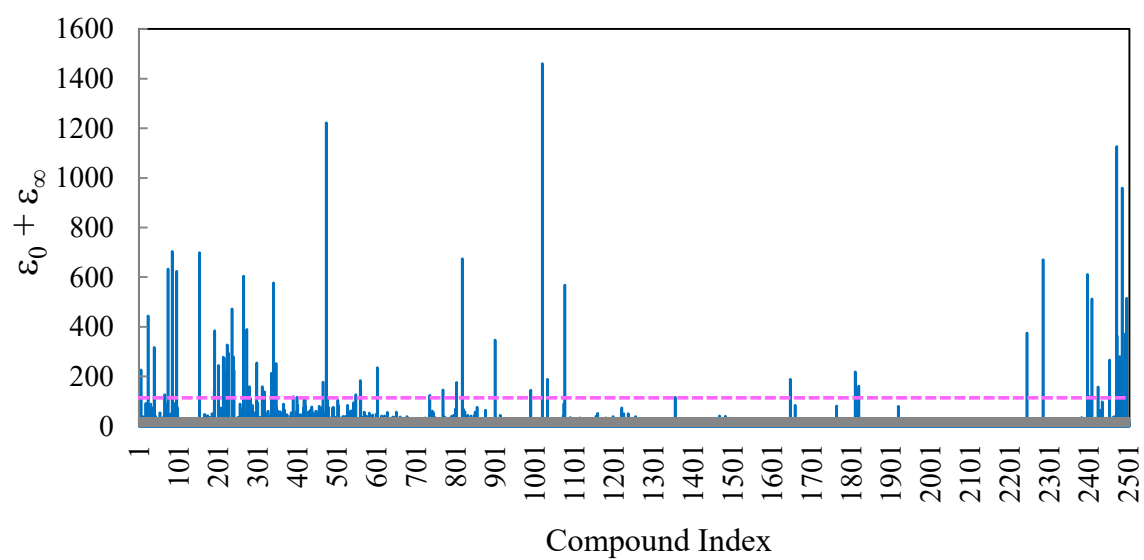


Fig. 3.3.1. Calculated dielectric constants of 2,504 compounds. The dashed line marks the dielectric constant of 100.

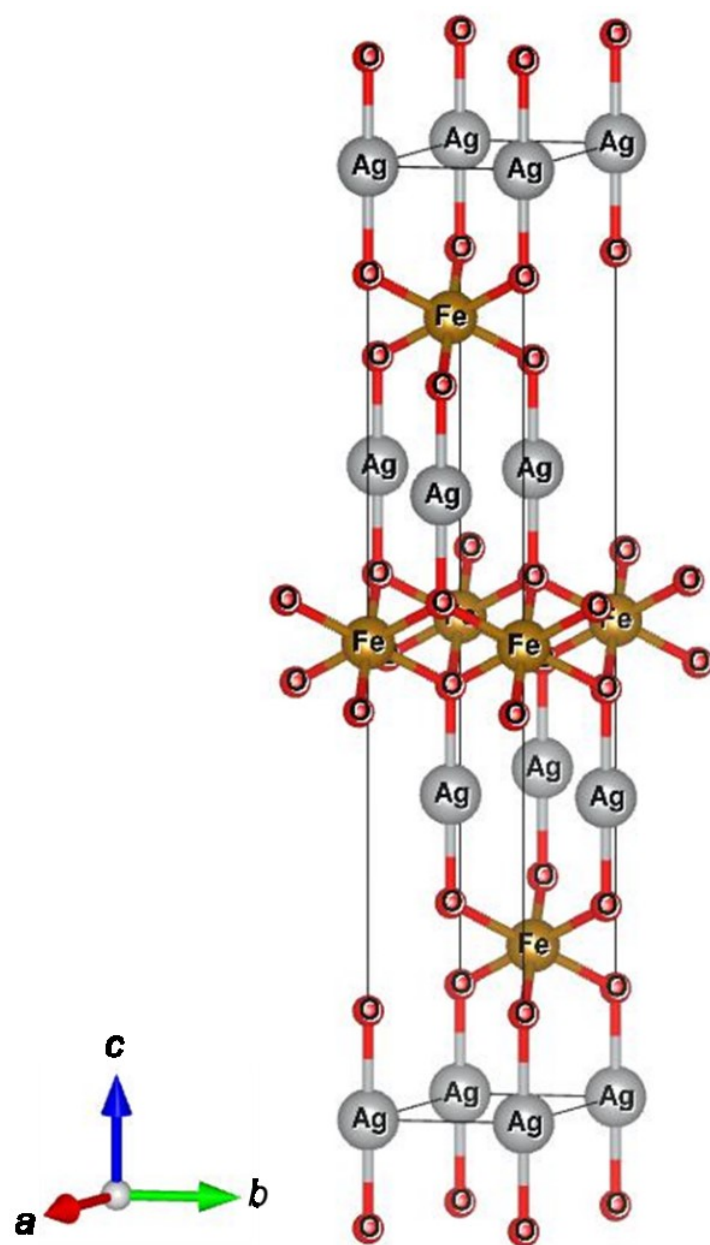


Fig. 3.3.2. Crystal structure of FeAgO₂ as drawn in VESTA.³⁷⁾

Table 3.3.1. Compounds with high dielectric constants calculated from first-principles

compound	calculated ε	compound	calculated ε
FeAgO ₂	1460	ErCrO ₃	244
NaVO ₂	704	KTaO ₃	241
Li ₅ NbO ₅	675	AgTaO ₃	236
V ₂ WO ₆	633	NdTa ₃ O ₉	226
CdTiO ₃	604	GdVO ₄	220
FeCuO ₂	473	NbVO ₅	177
PrCrO ₃	444	NaNbO ₃	158
MnWO ₄	389	NbAgO ₃	153
SrHfO ₃	328	Sr ₃ Fe ₂ O ₆	145
VBO ₃	317	NaTaO ₃	138
Ti ₄ Bi ₂ O ₁₁	279	Sr ₃ Ti ₂ O ₇	119
Sr ₄ Ti ₃ O ₁₀	252	YbGeO ₃	105

3.3.2 Experiments

Experimental observations were used to confirm the validity of the first-principles calculations. I understand that many compounds in Table 3.3.1 include transition metals that may form valence charge distributions depending on processing conditions like the sintering or annealing temperature and oxygen partial pressure. The formation of oxide-ion vacancies and other defects may be harm the material's usefulness in capacitor applications because these defects will cause high leakage current.

As the first step in our experimental trials, I focused on V_2WO_6 and its isostructural compound of Cr_2WO_6 . V_2WO_6 is interesting in the current study because of its high predicted dielectric constant. Both compounds are thermodynamically stable since they have formation energy on the convex hull between V_2O_3/Cr_2O_3 and WO_3 , as listed in the MPD. They also exhibit a trirutile structure (space group $P4_2/mnm$), as shown in Fig. 3.3.3. The lattice constants from first-principles calculations of V_2WO_6 are 4.633 Å along the a -axis and 9.111 Å along the c -axis. Those of Cr_2WO_6 are 4.597 Å along the a -axis and 9.011 Å along the c -axis. The calculated dielectric tensor values of V_2WO_6 are as follows: $\epsilon_0^{11} = 904$, $\epsilon_0^{22} = 904$, $\epsilon_0^{33} = 46.8$, $\epsilon_\infty^{11} = 13.5$, $\epsilon_\infty^{22} = 13.5$, and $\epsilon_\infty^{33} = 18.5$. Those of Cr_2WO_6 are as follows: $\epsilon_0^{11} = 7.07$, $\epsilon_0^{22} = 7.07$, $\epsilon_0^{33} = 19.8$, $\epsilon_\infty^{11} = 8.44$, $\epsilon_\infty^{22} = 8.44$, and $\epsilon_\infty^{33} = 6.42$. The mechanism behind the high dielectric constant of V_2WO_6 is also unclear. Perhaps the cations at the center of the M-O octahedrons are relatively easy to displace because of the characteristic crystal structure.

In the literature, V_2WO_6 has been synthesized by vacuum annealing of a stoichiometric mixture of V_2O_3 and WO_3 powders.³⁸⁾ Solid-state reactions have been used to synthesize Cr_2WO_6 .³⁹⁾ I attempted to synthesize both Cr_2WO_6 and V_2WO_6 by standard solid-state reaction methods. Precursor powders of Cr/V_2O_3 and WO_3 were combined in a stoichiometric ratio and were mixed using ZrO_2 balls in water for 16 hours. After drying in an oven and passing through a sieve, the mixture was pressed into pellets with polyvinyl alcohol used as a solvent. The pellets were 12 mm in diameter and 1 mm thick. Subsequently, Cr_2O_3 and WO_3 mixture was sintered at 1250-1350 K in air for 2 hrs. The V_2O_3 and WO_3 mixtures were sintered 1173 K in a reducing atmosphere for 2 hrs.

X-ray diffraction (XRD) patterns the crushed sintered samples are shown in Figs. 3.3.4 and 3.3.5. These results show that Cr_2WO_6 was successfully synthesized, as shown in Fig. 3.3.4, which compares the observed XRD pattern with a reference pattern.⁴⁰⁾ The synthesis of V_2WO_6 was not successful, however, as shown by the comparison with a reference pattern in Fig. 3.3.5.⁴¹⁾ I also attempted to synthesize V_2WO_6 by spark plasma sintering, but this attempt was also unsuccessful, and the development of a method for fabricating a sintered sample of V_2WO_6 is underway.

The sintered body of Cr_2WO_6 had a single $P4_2/mnm$ phase, and the synthesis of a material with the desired crystal structure was successful. The sintered sample of Cr_2WO_6 is brown in color, as shown in Fig. 3.3.6. Its electric resistance was measured after attaching electrodes of indium and gallium alloy to the surface. Unfortunately, the electric resistance of the present Cr_2WO_6 sample was too low to measure its dielectric constant using the ordinary capacitor technique. Cr is a typical transition element that easily takes a valence charge.⁴²⁾ Oxide-ion vacancies may be formed by the valence change of Cr, and these vacancies will decrease the sample's electrical resistivity. Attempts to mitigate this dip in electrical resistivity are also underway.

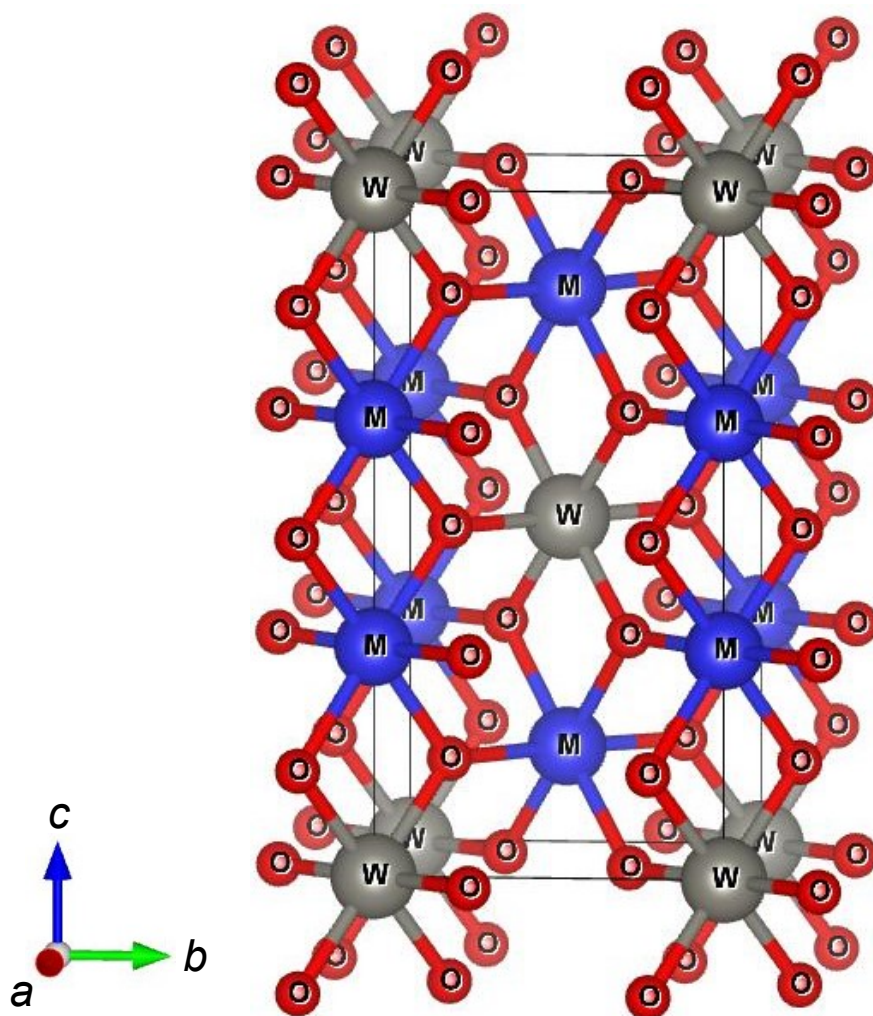


Fig. 3.3.3. Crystal structure of trirutile M_2WO_6 ($M = Cr, V$) visualized with VESTA.³⁷⁾

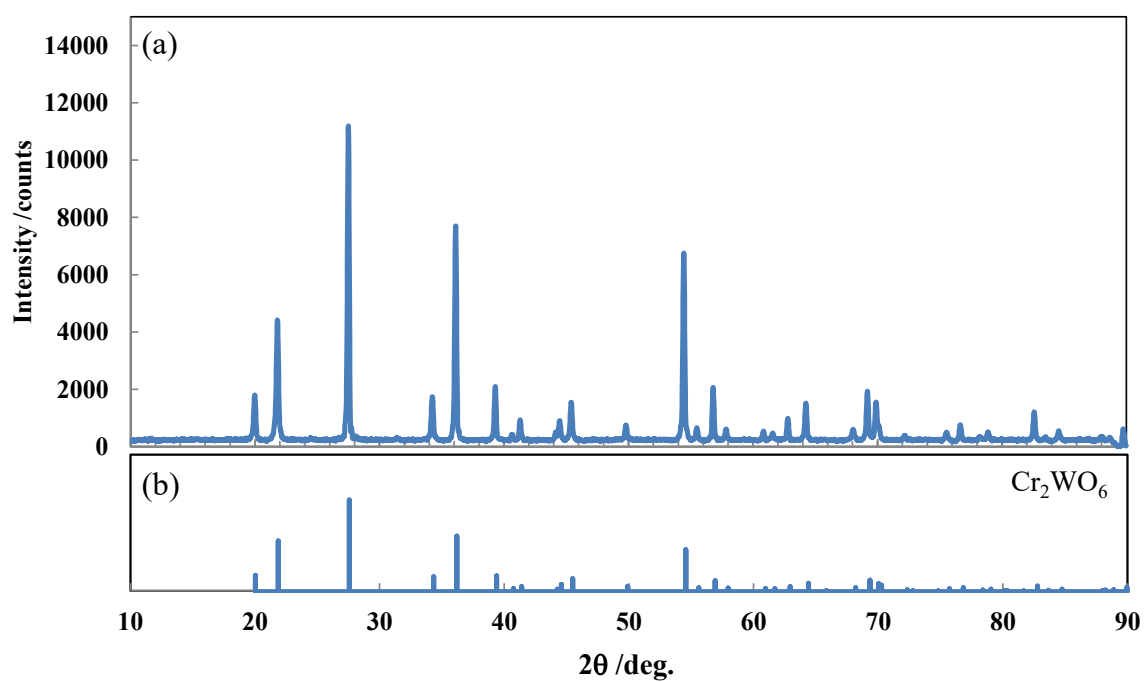


Fig. 3.3.4. (a) X-ray diffraction pattern of a sample of sintered Cr_2WO_6 . (b) Reference X-ray diffraction pattern of Cr_2WO_6 .

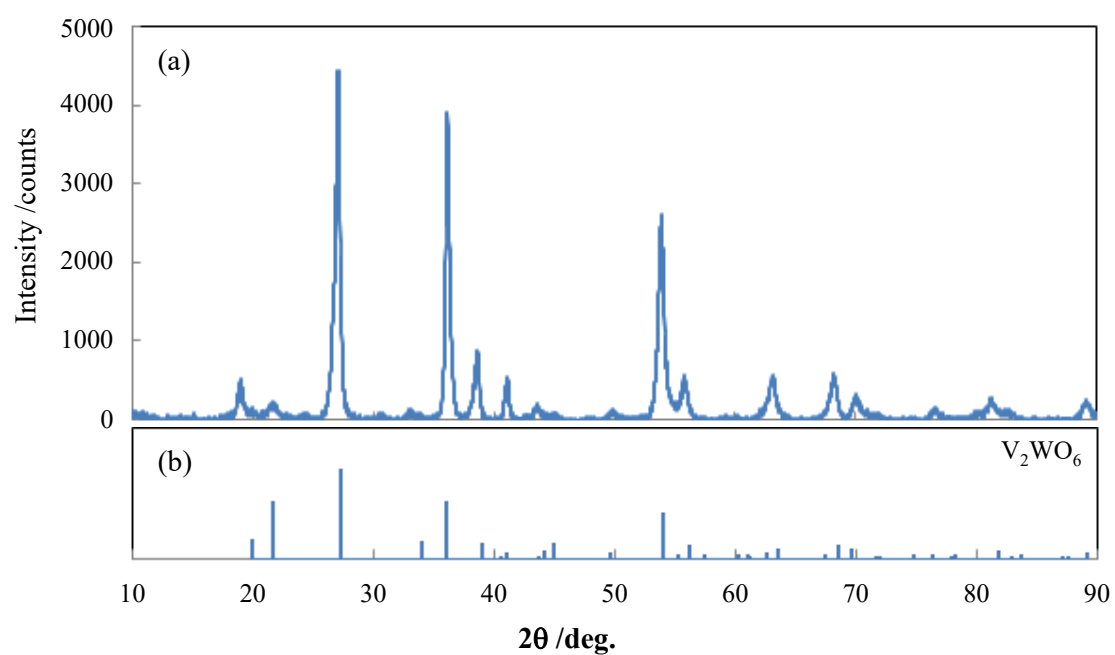


Fig. 3.3.5. (a) X-ray diffraction pattern of V_2O_3 and WO_3 compounds sintered at 1173 K in $p_{O_2} = 10^{-14}$ MPa. (b) Reference X-ray diffraction pattern of V_2WO_6 .

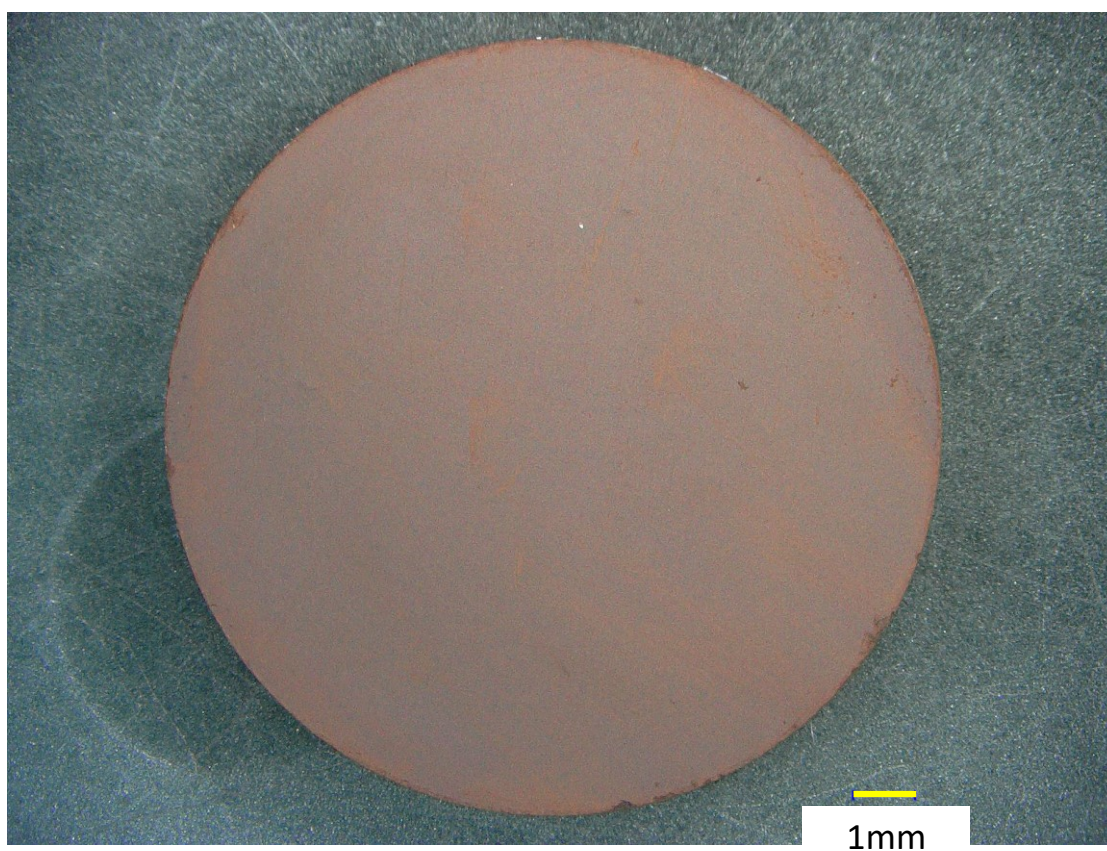


Fig. 3.3.6. Photograph of Cr_2WO_6 sample after sintering at 1250 K.

3.4 Summary

New compounds for dielectric materials were sought using first-principles calculations. We initially used reasonable criteria to choose 3,382 compounds from the MPD. Among these, 2,504 compounds had no imaginary phonon mode and these were analyzed with DFPT to compute their dielectric constants. Among these, 24 compounds have a dielectric constant higher than 100, which is the dielectric constant of rutile TiO_2 , which is a standard paraelectric material. Most of these compounds are not commonly known as dielectric materials, suggesting that important new dielectric materials may be part of the group.

Efforts to experimentally verify these predicted high dielectric constants are under way. In preliminary experimental trials, I focused on V_2WO_6 and the isostructural compound of Cr_2WO_6 . Single-phase Cr_2WO_6 was successfully synthesized by a standard solid-state reaction method, but synthesizing V_2WO_6 proved more difficult. The electric resistance of the Cr_2WO_6 sample was too low for use in capacitors and its dielectric constant could not be measured. Our lab is currently working to reduce the material's electric conductivity by controlling defects during the fabrication process.

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Chapter 4: Prediction model of dielectric constants by combination of first-principles calculations and machine-learning technique

4.1 Introduction

Barium titanate (BaTiO_3) is renowned as a ferroelectric material because of its high dielectric constant at room temperature and its chemical stability. It is used in ceramic capacitors, which are essential for modern technology. Since the discovery of BaTiO_3 as a ferroelectric material, it has served as the main component of ceramic capacitors for more than 70 years. Recently, the demand for ceramic capacitors has increased rapidly because of their use in high-performance advanced industrial products like ICT devices, industrial machinery, and automobiles. Therefore, novel dielectric materials are urgently needed. Several dielectric materials have been suggested as temperature-resistant ceramic capacitors.^{2–13)} However, the search for new materials is still in progress.

Because of recent rapid progress in computer hardware and software, high-throughput screening using first principle calculations to predict physical properties has become a central tool in materials science. Several researchers have tried to find new materials using databases of computed properties and machine-learning techniques.^{14–19)}

Yim *et al.*²⁰⁾ and Petousis *et al.*²¹⁾ reported dielectric constants calculated from first-principles. The results calculated by Petousis *et al.* are registered in the Materials Project database (MPD).²²⁾ Our lab has reported first-principles calculated dielectric constants of 2,393 compounds.²³⁾ Although these databases can be used for high-throughput screening, systematic errors of these calculations from the experimentally reported values have been highlighted. Petousis *et al.*²¹⁾ reported that errors of the database values were less than $\pm 25\%$ of the experimental values. This finding has motivated the use of machine-learning to build a model for correcting first-principles calculated dielectric constants. The following chapter discusses the construction of a machine-learning model using the assumptions that these errors originate from error in the description of chemical elements, so that descriptors of the individual elements can be employed for correcting these errors.

The first-principles approach discussed in the preceding chapters was combined with machine-learning models to deepen this thesis' search for new paraelectric materials with high effective dielectric constant. A machine-learning model was also constructed to predict a dielectric constant more accurately than by using only first-principles calculations.

4.2 Procedure

To begin, first-principles calculations were used to construct a database of the dielectric constants of 2,504 compounds. The dielectric constants were calculated using density function perturbation theory (DFPT).^{24–25)} Before the DFPT calculations, harmonic phonon calculations were used to select only compounds that have no imaginary phonon modes. The first-principles calculations used the projector-augmented wave (PAW) method as implemented in the VASP software package.^{26–28)} The generalized gradient approximation (GGA-PBEsol) was employed.²⁹⁾ Strong on-site Coulomb interactions of the *d* orbitals were corrected using the $+U$ method with the U values listed in Ref. 30. The details of the first-principles calculations are given in Chapter 3.

Experimentally observed dielectric constants for 105 selected compounds were taken from Springer Materials.^{31, 32)} When the dielectric constant of a compound was reported to depend greatly on temperature, the minimum value over the whole temperature range was adopted as long as the crystal structure was stable. An example of an experimental dielectric constant is shown in Fig. 4.2.1. The experimentally observed dielectric constant of AgTaO_3 , for instance, is 100.³¹⁾

Machine-learning was used to predict dielectric constants of candidate materials. The model was trained with 276 feature variables. Of these feature variables, one was a dielectric constant obtained by first-principles calculations; the other 275 were prepared using 22 elemental descriptors. The following elemental descriptors were used: atomic mass, atomic number, atomic radius, period in periodic table, group in periodic table, boiling point, density of solid, melting point, molar volume, thermal conductivity, Van der Waals radius, first ionization energy, second ionization energy, electron affinity, Allen electronegativity, Pauling electronegativity, covalent radius, heat of fusion, specific heat, pseudopotential radius of the *s* orbital, and pseudopotential radius of the *p* orbital. These elemental descriptors include properties of atoms, such as atomic number, first ionization energy, and electronegativity. They also include the physical quantities of pure-element molecules, such as melting and boiling temperature. The average, variance, and covariance of these elemental descriptors were calculated from the chemical composition of each compound. Considering Al_2O_3 , the atomic mass of Al is 26.98, the atomic mass

of O is 16, and the average weighed mass of the molecule is 20.39. This molecular weight was used as one of the feature variables for Al_2O_3 . The procedure is the same as in Ref. 33. A total of 276 feature variables were used to predict the dielectric constant. An illustration of the feature and target variables is shown in Fig. 4.2.2. To improve the regression accuracy, the common logarithms of the experimental and calculated dielectric constants were adopted as target and feature variables.

Linear ridge regression,³⁴⁾ Gaussian process regression,³⁵⁾ and random forest regression³⁶⁾ were used to predict dielectric constant, all as implemented in the scikit-learn python library.³⁷⁾ Hyper parameters for the models were determined by grid-search methods. The regression was repeated 10 times with different data each time. The root mean-square-error (RMSE) and the coefficient of determination (R^2) were also calculated in each iteration.

A flowchart of this investigation is shown in Fig. 4.2.3.

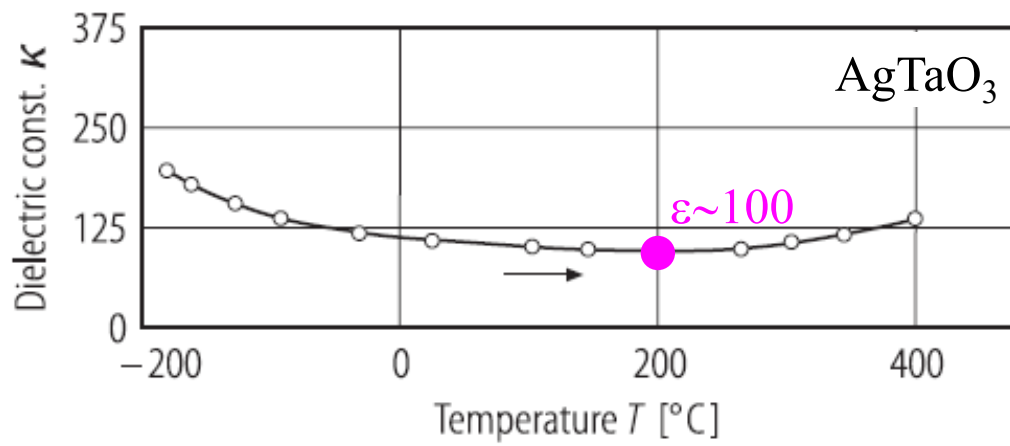


Fig. 4.2.1. Experimental dielectric constant of AgTaO_3 .³¹⁾ In this study, the dielectric constant of AgTaO_3 was observed to be 100.

target variable		feature variables				
molecule	$\log_{10}$ (ϵ exp)	$\log_{10}$ (ϵ calc)	Ave. atomic mass	...	Var. atomic mass	...
AgTaO ₃	2.176	2.373	67.36		4491	
Al ₂ O ₃	1.013	1.009	20.39		28.95	
⋮	⋮	⋮	⋮	⋮	⋮	⋮

105

276

Fig. 4.2.2. Examples of feature and target variables for regression models.

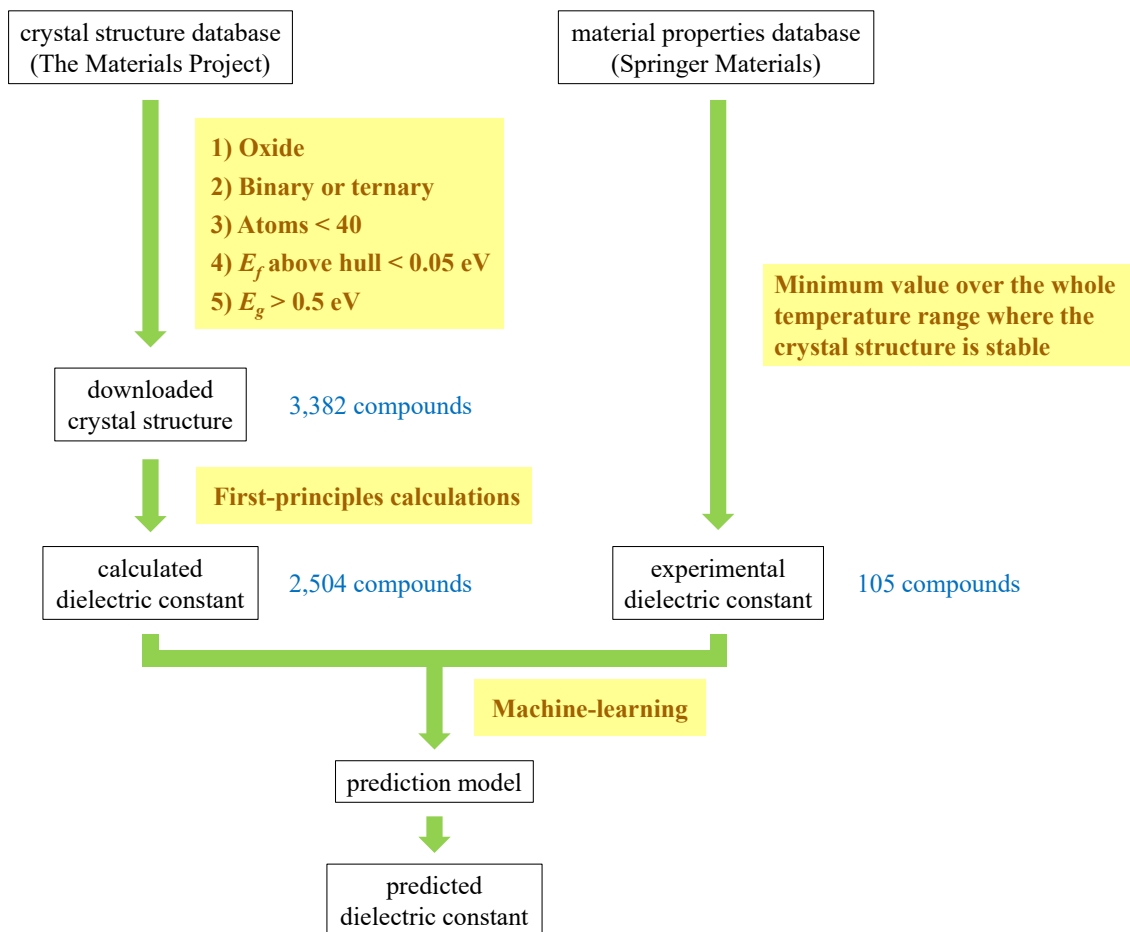


Fig. 4.2.3. The flowchart of prediction for dielectric constant

4.3 Results

4.3.1 Comparison of experimental and calculated dielectric constants

The dielectric constants of 2,504 compounds with no imaginary phonon mode were calculated exhaustively. The dielectric constant is the sum of ionic polarization ϵ_0 and the electronic polarization ϵ_∞ , as described in subsection 3.3.1. This sum yields the polycrystalline dielectric constant, as it corresponds to the simple average of the eigenvalues of the calculated single-crystal dielectric tensor.

The experimental dielectric constants of 105 selected compounds were obtained from Springer Materials. Fig. 4.3.1 compares the experimental dielectric constants and the calculated dielectric constants of these compounds, and the unit-slope dashed line is included for reference. The horizontal axis gives the experimental dielectric constants. The vertical axis gives the calculated dielectric constants discussed in subsection 3.3.1. Large deviations between the experimental and calculated values appear for approximately 20% of the compounds. If the compounds contained rare-earth elements, like YbAsO_4 and $\text{Er}_2\text{Ti}_2\text{O}_7$ do, the calculated dielectric constants would be overestimated. In contrast, the dielectric constants were underestimated for compounds that contain niobium, tantalum, or alkali-metal elements, such as $\text{Sr}_2\text{Ta}_2\text{O}_7$ and SbNbO_4 . The difference between the experimental and the calculated dielectric constants seems to depend on the chemical elements included in the compounds. Machine-learning models trained with descriptors of the chemical elements were therefore used to correct the first-principles calculations.

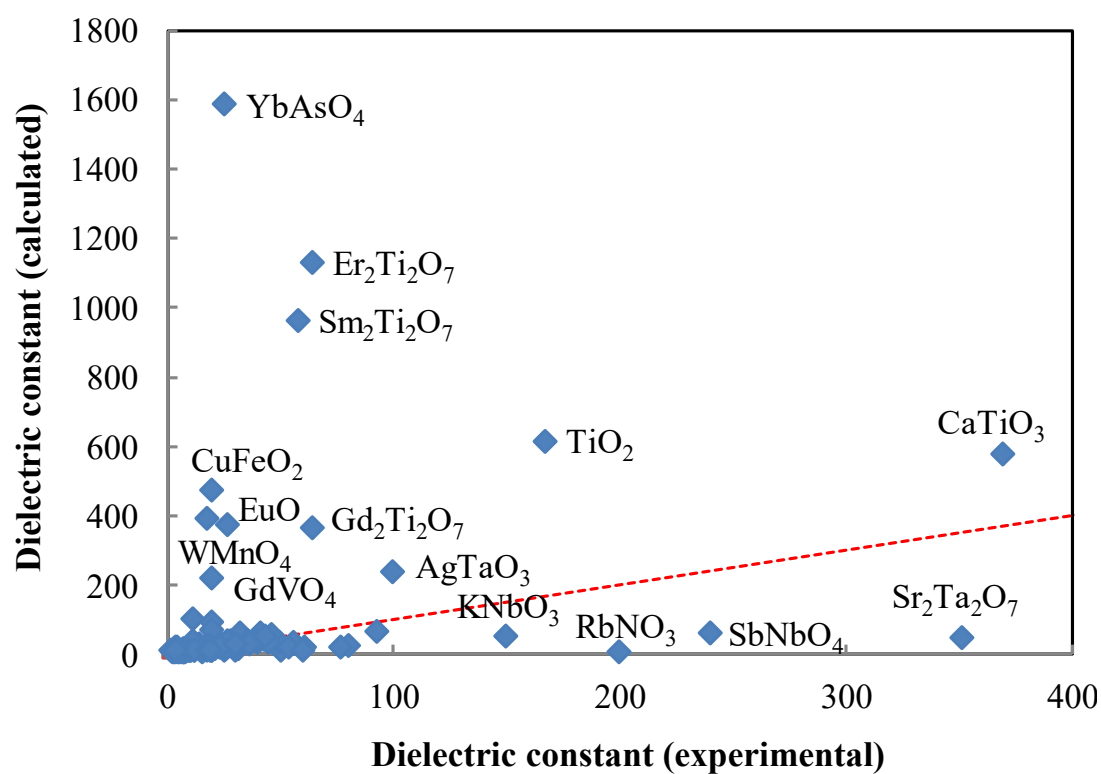


Fig. 4.3.1. Experimental and calculated dielectric constants of 105 selected compounds. The dashed line passing through the origin has unit-slope.

4.3.2 Machine-learning to predict experimental dielectric constants

Regression models were constructed from the elemental descriptors. The models were assessed for quality using the hold-out method. The dataset with 105 selected compounds was randomly partitioned so that 70% was used for training data and 30% was used for test data. The regression analysis was repeated 10 times with different partitions of the data. The root mean-square-errors (RMSE) of the test data over the 10 trials were obtained using the following three regression methods: (a) the linear ridge method, (b) the Gaussian process method, and (c) the random forest method. The regressions are plotted in Fig. 4.3.2. The horizontal axis gives the trial index, and the vertical axis gives the RMSE for each trial. The filled bar associated with each method corresponds to the minimum RMSE. The minimum RMSE was 0.36 for the linear ridge method, 1.2 for the Gaussian process method, and 0.27 for the random forest method, so the analysis proceeded with the random forest method alone.

To simplify the model, the effect of the number of feature variables on the RMSE was examined to find out if fewer feature variables could be used. The regression was initially repeated 10 times and the feature variables having the lowest importance were removed from the trial with the smallest RMSE. By iterating this procedure, the number of feature variables was reduced from 276 to 68. The RMSE of the regression models using only 68 feature variables was found to be within the scatter of RMSEs among the trials that used 276 feature variables, so we concluded that 68 feature variables were sufficient for subsequent regression analysis.

The dielectric constants predicted by the random forest method with 68 feature variables were then compared with experimental dielectric constants, as shown in Fig. 4.4.3. The horizontal axis gives the experimental dielectric constant and the vertical axis gives the predicted dielectric constant. The dashed line has unit-slope, so, if the experimental and predicted dielectric constant match, the data will fall on the dashed line. The RMSE of the test data was 0.26. Dot-dash lines correspond to the upper and the lower bounds of the predicted values with 50% error from the logarithm of the dielectric constant. If the prediction results follow a normal distribution, the RMSE will match the standard deviation σ . In the normal distribution, 95% of the data is in the 2σ range. In this study, $2\sigma = 0.52$, so approximately 90% of the test data were within the 50% error range.

Table 4.3.1 shows this highest-ranking feature variables for the regression model used to find the results in Fig. 4.3.3. The calculated dielectric constant is obviously the most important feature variable in the model, which implies that the difference between the experimental and the calculated dielectric constants is expressed well by the elemental descriptors. Discussion of the physical meaning of the high-ranking feature variables other than the calculated dielectric constant is beyond the scope of this chapter.

Table 4.3.1. High-ranking feature variables for the regression model used in Fig. 4.3.3.

Rank	feature variable 1	feature variable 2	Ave./Var./Covar.	Importance
1	ϵ (calc.)			0.364
2	period	1st ionization energy	covariance	0.064
3	2nd ionization energy		variance	0.044
4	electron affinity	heat of fusion	covariance	0.038
5	boiling point	thermal conduct	covariance	0.028
6	electronegativity (Pauling)	specific heat	covariance	0.024
7	atomic number	atomic radius	covariance	0.021
8	atomic number		variance	0.020
9	atomic number	heat of fusion	covariance	0.020
10	atomic number	2nd ionization energy	covariance	0.020

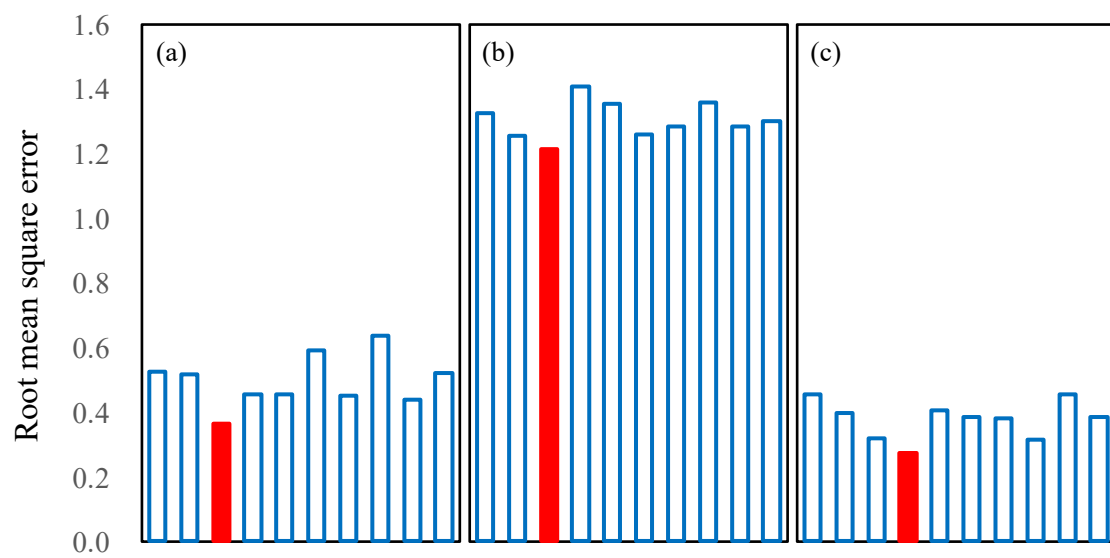


Fig. 4.3.2. RMSE results of the test data for 10 trials for each regression method: (a) linear ridge regression (b) Gaussian process regression (c) random forest regression.

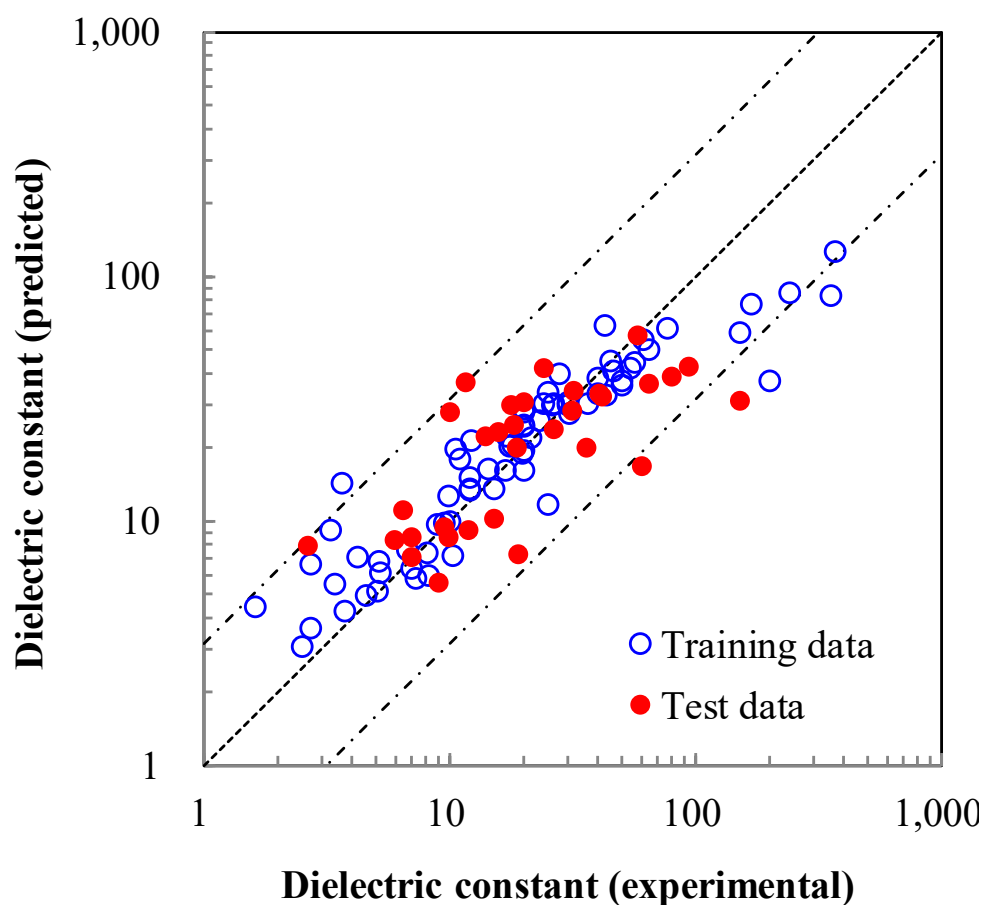


Fig. 4.3.3. Comparison of predicted and experimental dielectric constants. Prediction was performed using the random forest regression model with 68 feature variables; dashed line indicates a unit-slope; dot-dash lines correspond to the upper and the lower bounds of the predicted value with 50% error of the logarithm of the dielectric constant.

4.3.3 Variation of predicted dielectric constants

Next, the dielectric constants of 2,504 compounds were predicted by random forest regression using only 68 feature variables. For this simplified regression, 105 data of experimentally observed dielectric constants were used as supervisor data. The regression results are shown in Figure 4.3.4. The corresponding calculated dielectric constants are displayed on the horizontal axis. The vertical axis gives the predicted dielectric constants. Histograms are also shown for both values. The predicted dielectric constants for most compounds were in the range 3–100. The machine-learning model predicted that some compounds with calculated dielectric constants greater than 100 would have experimentally observed dielectric constants around 100. No novel paraelectric materials with particularly high dielectric constants were found in this analysis. Still, the results indicate that high-throughput screening of dielectric materials can be performed with regression model for dielectric constants trained with elemental descriptors.

The predicted dielectric constants of 12 compounds were greater than 100. These compounds are listed in Table 4.3.2. The highest dielectric constant was predicted for SbNbO_4 , and its crystal structure is illustrated in Fig. 4.3.5. SbNbO_4 has orthorhombic structure with the $Pna2_1$ space group (No. 33). The lattice constants as calculated from first-principles (GGA-PBEsol) are $a = 5.56 \text{ \AA}$, $b = 4.94 \text{ \AA}$, and $c = 11.82 \text{ \AA}$. Nb^{5+} is coordinated octahedrally with six O^{2-} ions. On the other hand, Sb^{3+} is coordinated by five O^{2-} ions. The shape of SbO_5 resembles a half-octahedron, which is typical of lone-pair cations. An example of a ferroelectric compound with lone pair cations is $\text{SrNb}_2\text{Bi}_2\text{O}_9$, in which the lone pair associated with Bi^{3+} forms BiO_5 , which has half-octahedral coordination. This compound is known to behave as a ferroelectric relaxor when doped with Pr^{3+} .³⁹⁾ The high predicted dielectric constant of SbNbO_4 is not yet understood. However, ionic polarization is expected to have a great effect in this material due to the huge distortion of NbO_6 octahedrons in SbNbO_4 .

Table 4.3.2. Predicted dielectric constants.

Compound	Predicted ε	Compound	Predicted ε
NbSbO ₄	240	CdTiO ₃	133
NbNO	181	SrHfO ₃	124
TiO ₂	149	RbNO ₃	120
Sr ₄ Ti ₃ O ₁₀	148	KNbO ₃	109
CaTiO ₃	142	Sr ₃ Ti ₂ O ₇	108
NdTa ₃ O ₉	139	Sr ₃ Fe ₂ O ₆	108

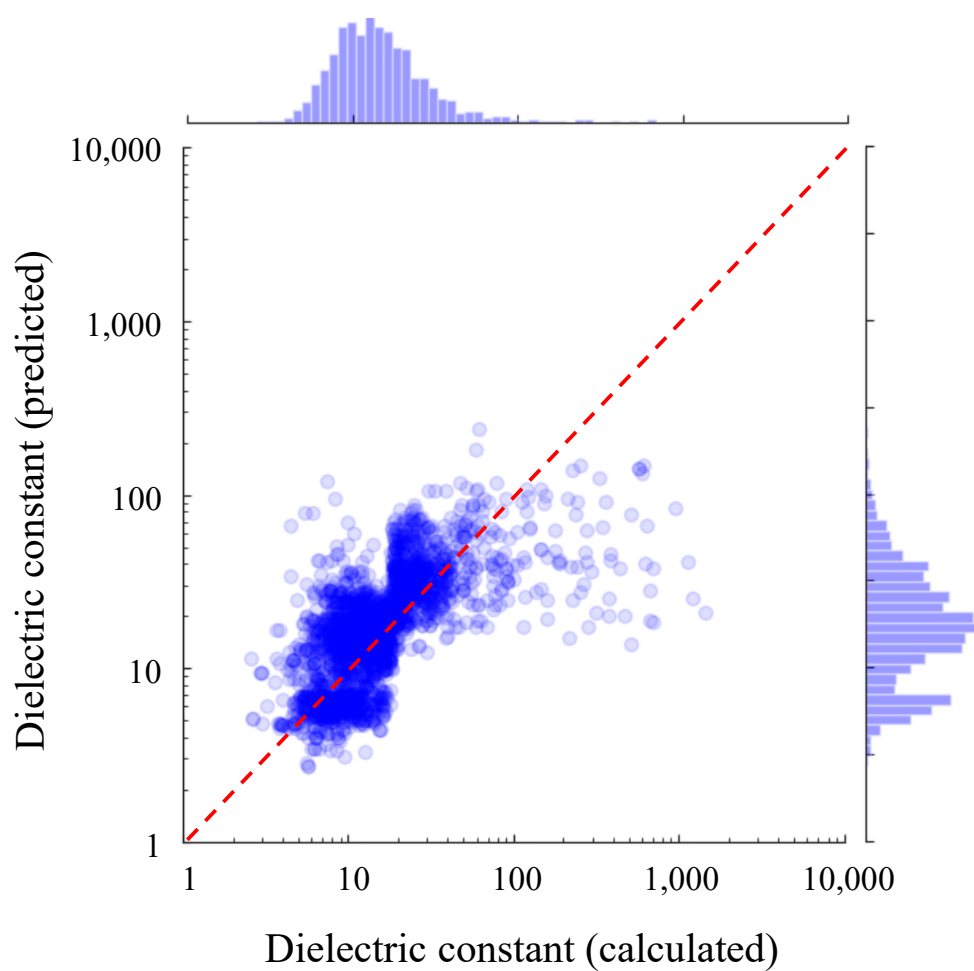


Fig. 4.3.4. Comparison of calculated and predicted dielectric constants of 2,504 compounds. Predictions were made by random forest regression using 68 feature variables. The dashed line indicates unit-slope; histograms for the two axes are also shown.

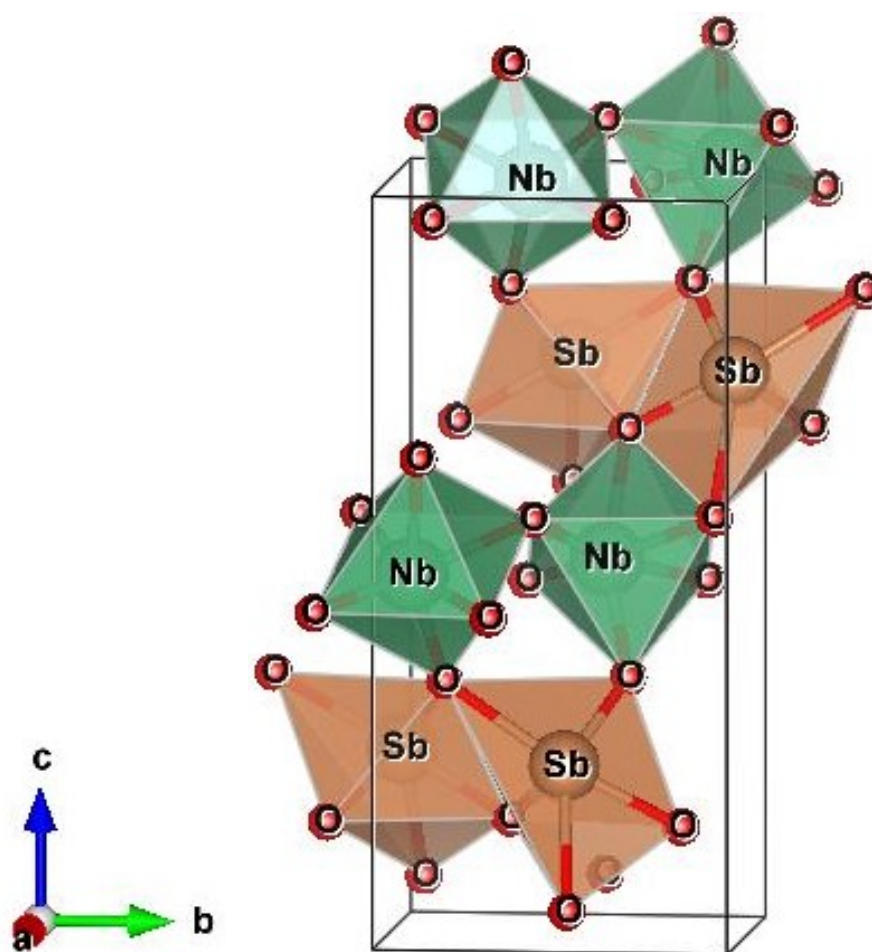


Fig. 4.3.5. Crystal structure of SbNbO_4 drawn with VESTA.³⁸⁾

4.4. Summary

New compounds for dielectric materials were sought by combining a large dataset of first-principles calculations with a machine-learning regression model. Out of the 3,382 candidate compounds selected from the MPD, the dielectric constants of the 2,504 compounds without an imaginary phonon mode were calculated using DFPT. For comparison, the experimental dielectric constants of 105 selected compounds were drawn from the Springer Materials database. Because systematic errors between the calculated and the experimental dielectric constants were apparent, machine-learning was used to correct the calculated dielectric constants, under the assumption that the errors originated from the chemical elements. Linear ridge regression, Gaussian process regression, and random forest regression were used to prepare models of the elemental properties. The quality of the models was assessed using the hold-out method with 70% randomly chosen training data and 30% test data. A random forest model with 68 feature variables predicted the dielectric constants within 50% error range of the logarithm of the dielectric constant. The predicted dielectric constants for most of the compounds were in the range 3–100. The predicted dielectric constants of 12 compounds exceeded 100, including SbNbO_4 , which had the highest predicted dielectric constant of 240.

No new paraelectric materials were identified with very high dielectric constants, however, the results indicate that regression models can be used for high-throughput screening of dielectric materials.

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Chapter 5: Summary of this thesis

BaTiO₃ is one of the most important ferroelectric materials used in MLCCs because of its high dielectric constant at room temperature and its chemical stability. Though BaTiO₃ is excellent for this use, it has served as the main component of ceramic capacitors for more than 70 years. Novel materials could offer even greater performance. To improve the reliability of MLCCs, many compounds and additives based on BaTiO₃ have been proposed. In addition, a mechanism has been proposed to explain how the electric resistance of the material decreases because of the migration of oxygen vacancies. Thanks to recent developments in computing technology, large databases that list the physical quantities of many compounds have been compiled using first-principles calculations. These databases can be used for high-throughput screening. This thesis has discussed several searches for new compounds, structures, and materials using high-throughput screening with data calculated from first-principles.

Chapter 2 discussed an investigation of the formation and migration of oxygen vacancies in BaTiO₃ and BaM_xTi_{1-x}O₃ (M = Zr, Ge), using both first-principles calculations and experimental observations. For first-principles calculations of BaTiO₃ and BaM_xTi_{1-x}O₃ (M = Zr, Ge), a cubic lattice was chosen. The supercells in these calculations consisted of unit cells of $3 \times 3 \times 3$. The predicted formation energy of oxygen vacancies at 1500 K under the oxygen partial pressure of 10^{-13} MPa in BaZr_xTi_{1-x}O₃ is larger than that in BaTiO₃. On the other hand, the formation energy of oxygen vacancies in BaGe_xTi_{1-x}O₃ is much smaller than that in BaTiO₃, because the valence of Ti⁴⁺ is changed more easily than that of Zr⁴⁺. The calculated activation energies of oxygen vacancy migration in BaZr_xTi_{1-x}O₃ and BaGe_xTi_{1-x}O₃ are both larger than that in BaTiO₃. The formation and migration of oxygen vacancies in BaZr_xTi_{1-x}O₃ are both less likely than they are in BaTiO₃. Therefore, MLCCs made from BaZr_xTi_{1-x}O₃ may be more reliable than those made of BaTiO₃. To confirm the calculated results, ceramic specimens of BaTiO₃ and BaZr_{0.1}Ti_{0.9}O₃ were prepared by traditional sintering. The activation energy calculated by Arrhenius plot of BaZr_{0.1}Ti_{0.9}O₃ was observed to be 1.3 eV, and that of BaTiO₃ was observed to be 0.9 eV. These results agree qualitatively with the calculated

predictions.

Chapters 3 and 4 discuss an efficient search for novel paraelectric materials that have high dielectric constants using databases compiled with first-principles calculations. Machine-learning was applied to this database to construct a model for predicting dielectric constants as they would be observed in experiments. The crystalline structures of candidate compounds for the first-principles calculations were drawn from the Materials Project database. Using custom criteria, 3,382 compounds were selected. The dielectric constants of 2,504 compounds with no imaginary phonon modes were exhaustively calculated using density functional perturbation theory (DFPT). Some of these compounds that were predicted to have high dielectric constants are not generally used as dielectric or piezoelectric materials. FeAgO_2 has the calculated dielectric constant of 1460. However, large deviations between the experimental and the calculated values arise for approximately 20% of the compounds we analyzed. Experimentally observed dielectric constants of 105 compounds were drawn from the Springer Materials database. Then machine-learning was used to predict dielectric constants from the first-principles calculations. For these models, 276 feature variables, which is calculated dielectric constant and 275 feature variable calculated using 22 elemental descriptors, were prepared. Hyper parameters for the models were determined using a grid-search. The quality of the models was then assessed using the hold-out method. Dielectric constants were predicted best when using the random forest algorithm. The RMSE of the test data was 0.26, so approximately 90% of the test data were within the 50% error range. After this preliminary validation, the dielectric constants of 2,504 compounds were predicted by random forest regression. The predicted dielectric constants for most compounds were in the range 3–100. No novel paraelectric materials were identified with an unexpectedly high dielectric constant. However, the results indicate that high-throughput screening of dielectric materials can be accomplished by constructing regression models for dielectric constants that adopt elemental descriptors.

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