



## Local structure of Ca dopant in BaTiO<sub>3</sub> by Ca K-edge X-ray absorption near-edge structure and first-principles calculations

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### ABSTRACT

The local environment of Ca dopants in barium titanate, BaTiO<sub>3</sub>, is investigated by Ca K-edge X-ray absorption near-edge structure (XANES) spectroscopy. In conjunction with experiments, first-principles calculations by two methods are systematically made. The projector-augmented wave (PAW) method is used to optimize the local structure and obtain the formation energy. The augmented plane wave plus local orbitals method is adopted to obtain theoretical XANES spectra. A comparison between experimental and theoretical XANES spectra shows that Ca dopants are located at the Ba<sup>2+</sup> sites forming Ca<sup>2+</sup>. Formation energy calculations of Ca doped BaTiO<sub>3</sub> by the PAW method also give the same results. The Ca atom in BaTiO<sub>3</sub> is off-centering in comparison with the Ba site in BaTiO<sub>3</sub>. The off-centering of Ca atom is newly revealed by the combination of XANES spectroscopy and first-principles DFT calculations.

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### 1. Introduction

X-ray absorption fine structure (XAFS) spectroscopy is a powerful tool for investigating the local environment of probe atoms [1]. A spectrum is composed of X-ray absorption fine structure (XANES), also known as the near-edge X-ray absorption fine structure (NEXAFS), and extended X-ray absorption fine structure (EXAFS). The XANES corresponds to the first 30–50 eV of XAFS from the X-ray absorption edge, with the EXAFS lying at energies higher than that of the XANES. The XANES is sensitive to the chemical environment of a specific element, such as chemical bonding, charge state, and magnetic state. On the other hand, EXAFS can give quantitative information on the local coordination of an atom, such as coordination number and bond length. With the development of third generation synchrotron radiation sources, XANES spectroscopy has become an important branch of X-ray spectroscopy. This is no more one of analytical tools for the characterization, but a unique technique to deeply investigate the local environment of selected elements [1–3]. On the use of such spectroscopic methods, it is critically important to make the correct interpretation of the spectra on the basis of solid theoretical framework. The relationship between the XANES features and the geometric and electronic structures

of materials has been explored with the assistance of theoretical calculations. Recently, first-principles band-structure calculations based on density functional theory (DFT) that using the orthogonalized linear combination of atomic orbital (OLCAO) method [4] and the linearized augmented plane wave plus local orbitals (APW+lo) method [5] have been successful in quantitatively reproducing the fine structures of many kinds of solid state materials [6–9]. It should be noted that XANES is very sensitive to change in local environments of ultra dilute dopants or impurities at a concentration level of atomic ppm [7], though such analysis is very difficult with the EXAFS technique. In addition, it is difficult to obtain reliable EXAFS spectra for light atoms with low concentrations in materials including heavy atoms.

Barium titanate, BaTiO<sub>3</sub>, is a typical ferroelectric material with a perovskite-type structure [10]. BaTiO<sub>3</sub> exhibits a very high dielectric constant near room temperature. Many investigations have been also carried out to study its various properties [11–15]. The use of multi-layer ceramic capacitors (MLCCs) using BaTiO<sub>3</sub> has contributed to miniaturizing and increasing the performance of today's advanced electronic devices [16,17]. In order to improve the properties of BaTiO<sub>3</sub>, doping by various impurity atoms, such as alkaline earth elements, rare earth elements, and 3d transition elements, has been intensively investigated. Doping with alkaline earth elements, such as Mg, Ca, and Sr, has been particularly studied. The solution site of these elements in BaTiO<sub>3</sub> has been investigated by experimental and theoretical methods [18–21]. These results have shown that Ca and Sr solutes substitute into the Ba site, whereas

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Mg solutes occupy the Ti site of  $\text{BaTiO}_3$ . These results also have been widely accepted since they are consistent with the intuition from the view point of ionic radius. In addition, the experimental and theoretical ones show that the Ca solution site could change depending on the equilibrium conditions and temperatures [18,19].  $\text{BaTiO}_3$  shows a structural phase transition at around ( $T_c$ ) 406 K from a paraelectric phase state to a ferroelectric phase state. A large electrostatic capacity cannot be obtained at the higher temperature region, because the dielectric constant of  $\text{BaTiO}_3$  decreases above the  $T_c$ . Ca doping in  $\text{BaTiO}_3$  is one of the methods for increasing  $T_c$  as well as Pb doping and Bi doping. It is important to clarify not only the substitute site of the Ca ions but also the local structures of doped Ca in  $\text{BaTiO}_3$ . However, the local structure and the substitute site of Ca dopant in  $\text{BaTiO}_3$  show still ambiguity. In the present study, we investigate the Ca dopant in  $\text{BaTiO}_3$  by a combination of XANES spectroscopy and first-principles DFT calculations. This method is chosen because it is difficult to obtain reliable EXAFS spectra for the Ca K-edge region in this system. We focus our attention on analyzing the local structure of the Ca dopant in  $\text{BaTiO}_3$ .

## 2. Experimental procedures

Specimens of Ca doped  $\text{BaTiO}_3$  (BTO:Ca) powders were obtained from SAKAI Chemical Industry. The concentrations of Ca to Ba were two and five atomic percentages. Our X-ray diffraction (XRD) measurements for these specimens show only XRD profile from tetragonal structure  $\text{BaTiO}_3$  perovskite ( $P4mm$ ), and the lattice constants of these specimens were slightly smaller than those of pure  $\text{BaTiO}_3$ . The tetragonality ( $c/a$ ) of the BTO:Ca specimens was almost the same as that of pure  $\text{BaTiO}_3$ . Disk samples of 14 mm diameter and 0.8 mm thickness were prepared according to the following procedure for samples of fluorescence yield mode. Powders of BTO:Ca were dried and pre-sintered in air. The samples were then statically pressed at 200 MPa and sintered in air at 1623 K for 2 h, followed by furnace cooling at a rate of 270 K/h. Commercially available high-purity  $\text{CaTiO}_3$  (CTO) powder (SAKAI Chemical) was also used as a reference sample.

XANES spectra measurements of BTO:Ca and CTO at the Ca K-edge were performed using synchrotron radiation from a bending magnet of the 1.4 GeV storage ring at the beamline BL15 of SAGA Light Source in Tosu, Japan [22]. The spectra were measured with a fixed-exit double-crystal monochromator using Si (1 1 1) planes and a rhodium coated bent cylindrical mirror. The XANES spectra of BTO:Ca were obtained in the fluorescence yield mode. An ionization chamber filled with a mixed gas of 70% He gas and 30%  $\text{N}_2$  gas was inserted into the optical path to monitor the photon flux. The emitted X-ray fluorescence from the sample was measured by a Si multi cathode detector. All measurements were done in air at room temperature. The XANES spectrum of the reference sample (CTO) was obtained in the transmission mode.

## 3. Computational procedures

Before making calculations of the XANES spectra, structural optimizations were performed using the projector-augmented wave (PAW) method [23], implemented using the VASP code [24,25]. The effective exchange-correlation function of GGA-type by Perdew and Wang [26] was employed. After careful convergence tests with respect to the number of  $k$ -points and the plane-wave cut off, a Monkhorst–Pack  $k$ -point grid with a spatial resolution of  $0.5 \text{ nm}^{-1}$  and a kinetic energy cut off of 500 eV was used for all calculations.

Fig. 1(a) shows the geometrical structure of the unit cell of  $\text{BaTiO}_3$ . The experimentally reported tetragonal ( $P4mm$ ) perovskite structure was adopted as an initial structure [27]. The unit cell con-

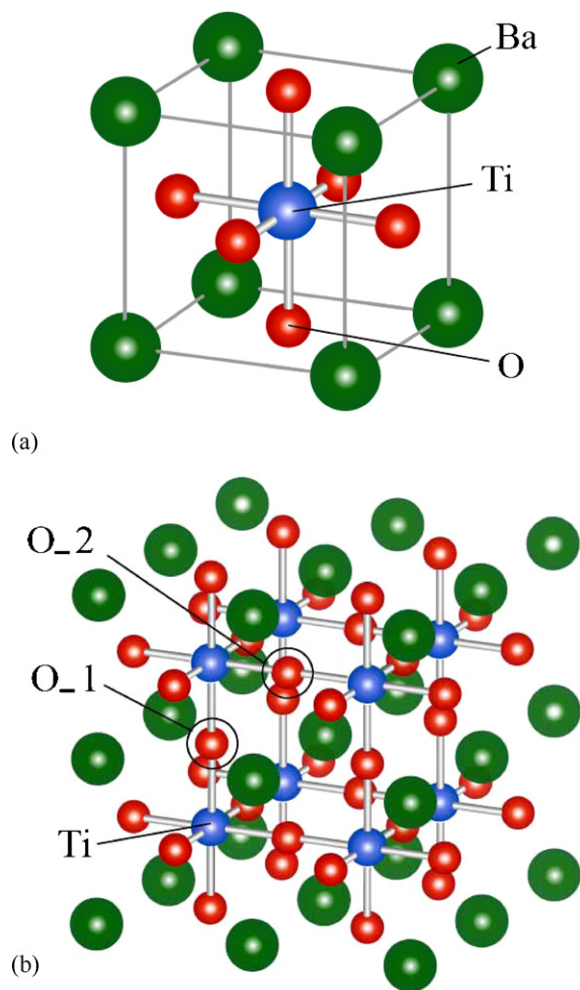


Fig. 1. (a) Unit cell of  $\text{BaTiO}_3$ . (b)  $2 \times 2 \times 2$  supercell of  $\text{BaTiO}_3$ .

tains a Ba ion, a Ti ion, and three O ions. In the figure, these ions are represented by the large green spheres, small blue sphere, and small red spheres, respectively. (For interpretation of the references to color in this text, the reader is referred to the web version of the article.) In the calculations, a supercell consisting of eight unit cells with  $2 \times 2 \times 2$  of the optimized unit cell (40 atoms) was employed as shown in Fig. 1(b). The Ba and Ti are 12-fold and 6-fold coordinated with the O, respectively. The coordination number (CN) of O ions for Ba ions is 12 and of O ions for Ti ions is 6. Three models were examined by changing the positions of the Ca dopants and O vacancy. Model 1 (Ba site model) contains a substitutional  $\text{Ca}^{2+}$  ion at  $\text{Ba}^{2+}$  site. It can be denoted by  $\text{Ca}_{\text{Ba}}^x$  according to Kröger–Vink notation, or simply  $\text{Ca}_{\text{Ba}}(\text{O})$ . The CN of O ion for a Ca ion is 12 for model 1. Models 2 (Ti site model 1) and 3 (Ti site model 2) contain a substitutional  $\text{Ca}^{2+}$  ion at a  $\text{Ti}^{4+}$  site [site Ti in Fig. 1(b)] and one O vacancy,  $\text{V}_\text{O}$ , following the defect equation  $\text{Ca}_{\text{Ti}}(\text{O}) \rightarrow \text{Ca}_{\text{Ti}}(+2) + \text{V}_\text{O}(-2)$ . Here  $\text{V}_\text{O}$  is introduced to compensate the charge imbalance due to the  $\text{Ca}^{2+}$  ion instead of a  $\text{Ti}^{4+}$  ion. In model 2,  $\text{V}_\text{O}$  is located at the first nearest-neighboring (NN) position [site O.1 in Fig. 1(b)] from the Ca ion. The Ca ion is 5-fold coordinated with the O ions. In model 3,  $\text{V}_\text{O}$  is located at the second NN position [site O.2 in Fig. 1(b)] from the Ca ion. The Ca ion is 6-fold coordinated with the O ions. In all the PAW calculations, the internal atomic positions of the ions in the cells were allowed to relax with a fixed size of the supercell, i.e., the shape of the supercell was fixed at a theoretically optimized ones for pure  $\text{BaTiO}_3$ , as we assumed the conditions at the dilute limit.

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