実験番号：2024P2003

Investigation of temperature and concentration effect on the structure of Ca-doped $BaTiO_3$ by X-ray absorption spectroscopy

IESARI Fabio，大曽根 遼，笠井 修一，安川 勝正
京セラ株式会社

キーワード：**XAFS，MLCC，BaTiO3，Ca doping，RMC**

1. 測定実施日

2024 年 8 月 21 日　BL11S2　（2 シフト）
2024 年 8 月 22 日　BL11S2　（1 シフト）
2024 年 8 月 22 日　BL6N1　（1 シフト）
2024 年 10 月 9 日　BL6N1　（2 シフト）

2. 概要

This study investigates the structural properties of calcium-doped barium titanate (BTO). Doping BTO with calcium (Ca) can enhance its temperature stability and increase the Curie temperature, making it suitable for various applications. Using X-ray absorption spectroscopy, we analyzed the effects of Ca doping on BTO, focusing on samples prepared by hydrothermal method with different concentrations. Measurements were conducted at the Aichi Synchrotron Radiation Center, examining Ti K-edge, Ba L-edges, and Ca K-edge to assess structural changes. Results showed no significant changes in Ti and Ba environments up to 5% mol Ca doping, suggesting that such low levels do not alter the BTO structure. Ca K-edge spectra confirm substitution of the Ca dopant at the A site for all concentrations. The study underscores the potential of using synchrotron radiation in refining manufacturing processes for advanced ceramic materials.

3. 背景と研究目的

BTO, due to its excellent ferroelectric properties, has been the material of choice for applications such as multilayer ceramic capacitors (MLCC). Because of the increasing demand for more green technology, it has become the preferred alternative to lead zirconate titanate (PZT), since Pb is toxic to human health. BTO electrical properties can be optimized for different applications through doping. For example, aliovalent transition elements are often used as traps for oxygen vacancies, which are the cause of current leakage in capacitors, extending their usage lifetime. Ca doping is instead used for improving temperature stability and, in low percentage, it also increases the Curie temperature. Because in BTO the electrical properties are closely related to the structure, in particular to the off-centering of the Ti atom, we used X-ray absorption spectroscopy to investigate structural properties of Ca-doped BTO in different doping concentrations and at different temperatures.

4. 実験内容

We measured Ti K-edge and Ba L3, L2, and L1-edges at BL11S2 of Aichi Synchrotron, while measurements of Ca K-edge were carried out at BL6N1. Our samples consisted of BTO nanoparticles prepared by hydrothermal method (average size of 350 nm), undoped and with 2% and 5% molar concentration Ca doping.

For measurements at BL11S2 (Ti K and Ba L-edges), powders of the samples were mixed with BN in appropriate ratio and pressed into a pellet of 7 mm diameter to carry out measurements in transmission mode. The so-prepared pellets were attached to a sample plate with kapton tape and then inserted into the cryostat available at the beamline for measurements at low temperature (Fig. 1). After leaving the samples to cool for a night, the temperature on the sample plate, measured through a thermocouple, was found to be 25 K. We measured the various samples at this temperature, after which we increased the temperature to 200K and measured the samples again. We then left the samples return at room temperature during the night and measured them again the next day.

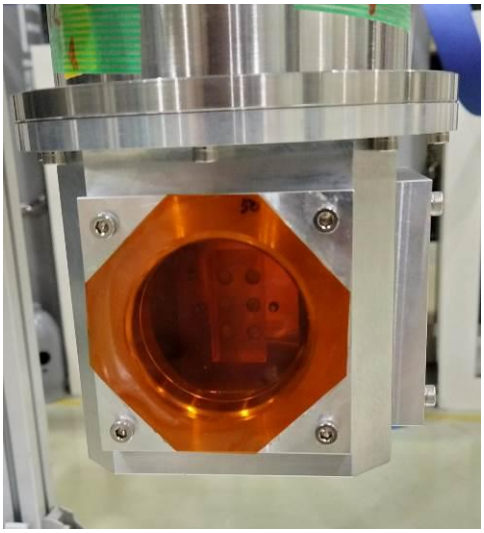

Fig. 1 Photo of the cryostat with the sample plate mounted inside.

For measurements at BL6N1 (Ca K-edge), powders of the various samples were directly deposited on a piece of carbon tape attached to the sample plate. For EXAFS measurements instead we attached a pellet made from powders of the sample, in order to have a stronger fluorescence signal. In our case, because of the low concentration of the dopant, self-absorption effects are negligible. Photo of the sample plate with the samples is shown in Fig. 2.

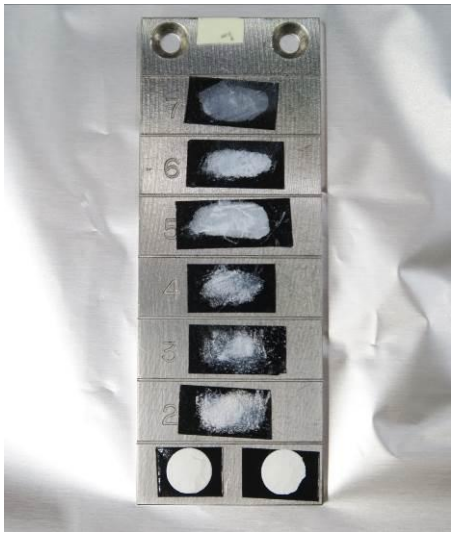

Fig. 2 Photo of the sample plate for measurements at BL6N1.

5. 結果および考察

Fig. 3 and 4 show the Ti K-edge XANES and the extracted EXAFS signals of the various edges for each sample, compared also with a bulk BTO reference sample available at the beamline. The area of the Ti pre-edge peak is known to be directly proportional to the Ti off-centering position in the TiO_6 octahedra [1]. We can see that there are no visible changes in spectra, regardless of the Ca concentration. This shows that low percentage (<10% mol) doping is not sufficient to induce any significant difference in the structure, and on average the surrounding of Ti and Ba atoms remains unchanged with respect to bulk BTO. Fig. 5 and 6 show the same data for the undoped BTO as a function of temperature. In this case, only a reduction in the amplitude of the EXAFS signals due to the increasing thermal disorder (Debye-Waller factor) is visible, but no shifts or change in the oscillations pattern. Same results were also found for the 2% and 5% doped samples. BTO, even when doped with Ca, is known to undergo two phase transitions at low temperature: from tetragonal to orthorhombic at around 278 K and from orthorhombic to rhombohedral at 183 K [1,2]. The main difference between these different phases is the orientation of the Ti distortion, and hence the polarization direction. The fact that the XAFS spectra instead remain unchanged support the idea of the order-disorder model for BTO, first proposed in 1968 [3].

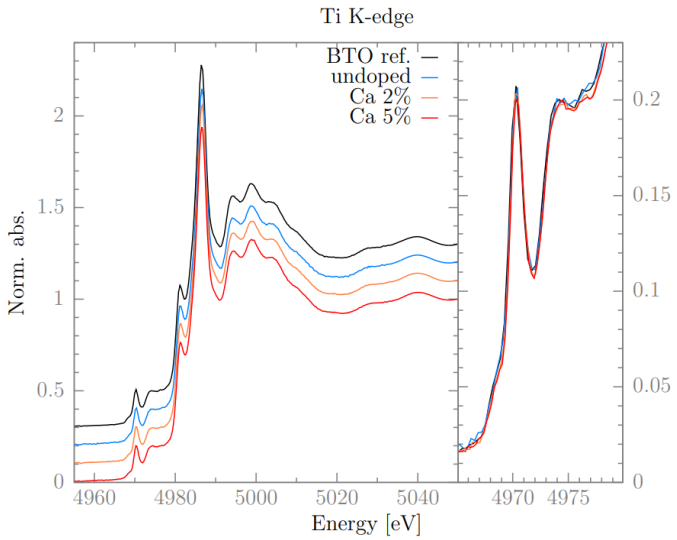

Fig. 3 Ti K-edge XANES data of the various samples.

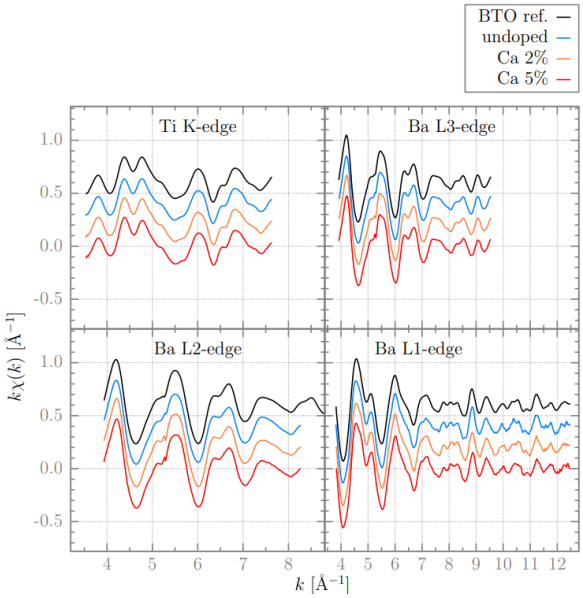

Fig. 4 Extracted EXAFS signals of the Ti K, Ba L3, Ba L2 and Ba L1 edges for the various samples.

According to this model, Ti distortion consistently occurs in the (111) direction, but as temperature increases, the number of accessible sites rises. This results in different polarization directions due to the average positions of potential sites, indicating local order with lattice-level disorder. This model is supported by various experimental and theoretical studies [4].

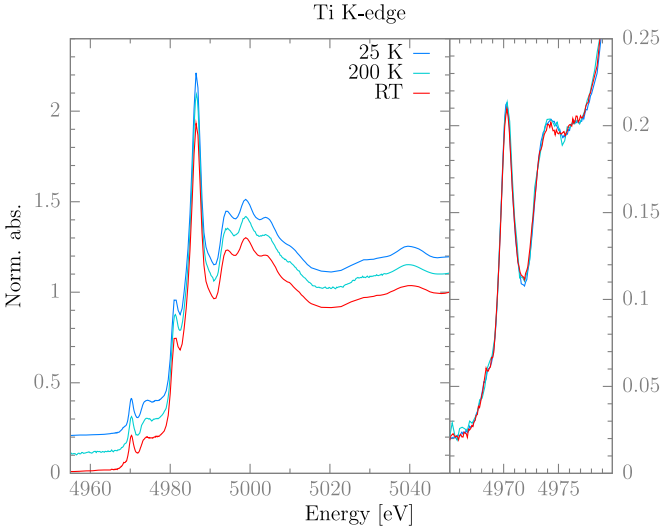

Fig. 5 Ti K-edge XANES for BTO at different temperatures.

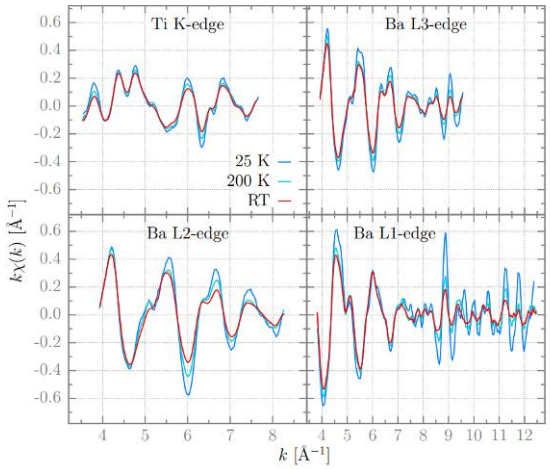

Fig. 6 Extracted EXAFS signals for BTO at different temperatures.

Next, we analyze the Ca K-edge data. The XANES of the doped samples are shown in Fig. 7, compared with the data of $CaTiO_3$. We can see that the spectra are quite similar, and the features resemble quite closely those of calcium titanate, indicating that the Ca dopant sits at the Ba site as intended during preparation. Data are also consistent with previously published XANES calculations for BTO with doped Ca at the A site [5]. For 5% Ca sample, we were also able to obtain data in the EXAFS region with long measurement times. We tried also for 2% Ca sample, but the signal was too weak to be distinguishable from noise. Data of all edges will be analyzed simultaneously using the reverse Monte Carlo method, to obtain a three-dimensional model consistent with the experimental data and get information on the Ti and Ba distortions.

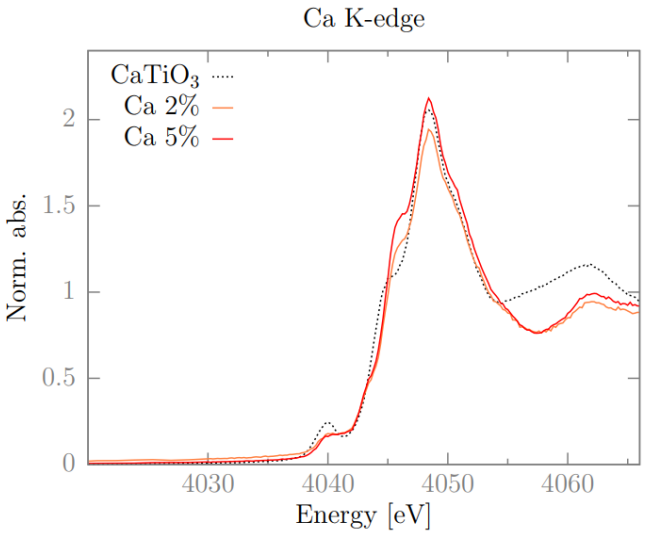

Fig. 7 Ca K-edge XANES of samples prepared with different concentrations compared with CaTiO3.

6. 今後の課題

X-ray diffraction measurements are mostly invisible to small percentages substitution, but thanks to XAFS measurements at different edges we were able to obtain information about the resulting structure of BTO with low percentage Ca doping. This feedback is important to improve the manufacturing process, so we plan to investigate other materials currently under development using synchrotron radiation, such as BTO with different dopants and other ceramic materials.

7. 参考文献

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