

ヤマモト ユウタ

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学 位 論 文 題 目 LOCAL STRUCTURE ANALYSES OF PEROVSKITE MATERIALS USING
ATOMIC RESOLUTION HOLOGRAPHY
(原子分解能ホログラフィーによるペロブスカイト構造材料の局所
構造研究)

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論文内容の要旨

A small difference in the local structure of a material can change the material's properties. Measuring such difference in the local structures requires specialized technique. Atomic resolution holography is one of the techniques for local structural analysis, and it has the unique advantages of possibility to measure three-dimensional local structures around specific element, especially around a dopant, which is necessary for the development of high-performance materials. We used X-ray fluorescence holography (XFH) and inverse photoelectron holography (IPEH), to reveal the local structure of perovskite-structured materials and to investigate the relationship between the properties and the local structure.

This study used two kinds of materials: an oxynitride ferroelectric material SrTaO_2N and a lead-free piezoelectric material, BCZT. In the study of oxynitride ferroelectrics, the local structure around the anion, which is difficult to measure with conventional measurement methods, was measured using a new atomic resolution holography technique called inverse photoelectron

holography. In the study of lead-free piezoelectric materials, local structures around Ca and Zr were measured using X-ray fluorescence holography, and the structural distortion and atomic fluctuations around each element were measured.

We first measured O $K\alpha$ holograms using SrTiO_3 single crystal as reference material to demonstrate the measurability of the new technique of inverse photoelectron holography for light elements. The measurement environment and data processing environment for the reverse photoelectron holography were constructed, and two holograms with different energies were successfully obtained, demonstrating the possibility of measuring light elements with reverse photoelectron holography. In addition, the possibility of adjusting the measurement depth by adjusting the energy was revealed by comparing the hologram patterns.

Second, we performed hologram measurements on SrTaO_2N thin films using IPEH. In this measurement, the signals from O $K\alpha$ and N $K\alpha$ were separated by fitting the characteristic X-ray spectra obtained in the measurement, and the oxygen and nitrogen holograms were successfully measured simultaneously in a single measurement. In these obtained holograms, it was found that the amplitude of the hologram of oxygen was smaller than that of nitrogen. From this, it was confirmed that the structure around the oxygen was greatly disordered compared to that around the nitrogen. Analysis of the holographic patterns revealed that the structure could be explained by the superposition of trans-type structures in which the nitrogen is linearly arranged.

At last, we measure XFH using the measurement of lead-free piezoelectric materials. We measured the local structure analysis around Ca was performed first. In this measurement, instead of using BCT. A peak shift and peak splitting were observed in the atomic image around Ca in this measurement. The direction and length of the local polarization of Ca and Ba were determined by optimization calculations based on the profiles of the atomic images. The local structure measurements around the B-site-substituted Zr were also performed using single crystals of BCZT and CZT. In both atomic images, it was confirmed that the A-site atoms around Zr were pushed outward due to the difference in ionic radii between Zr and Ti. In addition, only in the case of BCZT, only the Zr atoms in the first proximity were found to be shifted significantly, and this shift is a characteristic of BCZT.

These measurements confirmed that specific structural changes occurred around the dopant elements Ca and Zr. The measurement of the atomic displacements of these cations will be very important for the development of future materials.

論文審査結果の要旨

The aims of the dissertation of Mr. Yuta Yamamoto are the applications of atomic resolution holography to ferroelectric perovskites and clarifications of the relationships between local structures and physical properties in the developments of new ferroelectric materials. Two types of atomic resolution holography called inverse photoelectron holography (IPEH) and X-ray fluorescence holography (XFH) have been used to investigate the local structures around specific elements, which cannot be obtained by conventional methods.

The IPEH is a recently developed atomic resolution holography method. Although it had been expected for the local structure analysis around light elements, such as oxygen and nitrogen, no one had tried it. In the dissertation, IPEH measurements were performed using a standard sample of SrTiO_3 single crystal. Then, clear electron holograms of SrTiO_3 could be measured and atomic images around oxygen were reconstructed successfully using a fitting-based algorithm. This demonstration clearly shows the possibility of local structure analyses around light elements.

SrTaO_2N is the first ferroelectric oxynitride, and it was known that the arrangement of nitrogen and oxygen was significantly related to the ferroelectric property. Therefore, IPEH was applied to determine the arrangement of light element. By comparing experimental hologram and theoretical ones calculated from various possible models, it was found that the ferroelectric trans-type configurations with three crystallographic orientations existed in the SrTaO_2N thin film. This result is promising for the evaluation of local structures in composite anionic materials.

In the latter part of the dissertation, the XFH studies on perovskite materials are described. Here, XFH was applied to samples related to a lead-free piezoelectric material, $(\text{Ba,Ca})(\text{Ti,Zr})\text{O}_3$. The roles of diluted Ca and Zr are an area of interest. In the research of $(\text{Ba,Ca})\text{TiO}_3$ (BCT) to investigate the behavior of Ca, it was found that the Ba around Ca was displaced inward. The directions of the displacement of Ca and Ba were successfully determined by the deep descent method combined with the experimental and calculated holograms. Although the first-principles calculations by other group also predicted a shift of Ca, the XFH results revealed clearly the direction and magnitude of the Ca off-center displacement and the local Ba sub-lattice distortion. This result suggests additive element with a smaller ionic radius can enhance the ferroelectric property, which is a clue of the further development of ferroelectric materials.

In addition, XFH measurements on a single crystal of BCZT, in which the Zr concentration is very low, were carried out in order to investigate the effect of Zr doping. A unique structural modification around Zr was observed in the reconstructed atomic images. In particular, the first neighboring B-site atoms around Zr are attracted in the direction of Zr. While, such a displacement was not observed for the paraelectric sample, $\text{Ca}(\text{Ti,Zr})\text{O}_3$. A new model for the enhancement of the piezoelectric performance was proposed based on these B-site cations' behaviors. The knowledge obtained from this study will be useful for the future development of lead-free piezoelectric materials, including BCZT.

The abovementioned findings are significant in terms of local structure researches, which will help scientists to understand the origin of the ferroelectric properties. These achievements have an impact on the development of higher performance perovskite ferroelectrics. The research findings were published in reputed international journals. Therefore, the dissertation of Mr. Yuta Yamamoto is enough worth for conferring Ph.D.