

Thesis Summary

Film growth by aerosol deposition method and powder synthesis by mechanochemical solid-state reaction for ferroelectric lead-containing perovskites evaluated using synchrotron-radiation X-ray diffraction

(放射光 X 線回折により評価した鉛を含むペロブスカイト型強誘電体のエアロゾルデポジション法による膜成長とメカノケミカル固相反応による粉末合成)

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Ferroelectric perovskite materials are nowadays one of essential components for functioning of many electronic parts involved with the electrical products. Since lead-containing ferroelectrics such as $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT) exhibit excellent piezoelectric properties, although there are concerns about their negative impact on the environment, they are widely used as a film or ceramic form in industries. Various methods have been proposed for fabricating lead-containing perovskite ceramics and their films, such as sol-gel reaction, spray drying, conventional solid-state reaction, chemical vapor deposition and hydrothermal method, etc. In this study, the film growth and powder synthesis for ferroelectric lead-containing perovskites fabricated using mechanical energy are evaluated using synchrotron-radiation X-ray diffraction (SXRD). The mechanism of film growth and the validity of powder synthesis have been revealed by the state-of-the-art SXRD method.

Firstly, many studies of PbTiO_3 (PT) films, which is the end members of PZT, have been conducted to understand the properties of non-solid-solutions. However, the mechanism of the film growth has not been sufficiently understood. In this work, PT film was fabricated by the aerosol deposition (AD) method on a glass plate to evaluate the film growth. The AD method enables us to coat metal or glass materials with thick and dense ceramics at room temperature (RT). In the process, fine powder mixed with gas, which form an aerosol, are sprayed through a nozzle to form the polycrystalline film. The preferred orientation along c -axis of PT AD film was detected by SXRD experiments at RT in the as-deposited state. According to the electron charge density distribution study, the tetragonal PT powder has a layered structure consisting of two-dimensional (2D) covalent bonding network, stacked along the c -axis at RT. We consider that the preferred orientation of the PT AD film is attributed to the layered characteristics. The weak bonds of PT between layers easily give rise to cleavage or deformation between layer-to-layer. The highest probability of recombination occurs when the particles of PT film recombine and grow with the unique 2D interfaces in the AD process, resulting in PT film exhibiting a c -axis oriented at RT without any post-annealing. Once the PT film was heated up to 1000 K in the paraelectric phase with the cubic structure, the c -axis orientation observed at the as-deposited state disappears at 1000 K and at RT after heating owing to the degree of freedom of the crystal axis on the phase transition. Therefore, we provide direct experimental evidence that the film growth is due to the layered structure of PT at RT. To validate the aforementioned analysis of the film growth, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BiT) film deposited by the AD method has been studied. SXRD experiments demonstrate that the BiT film with the

preferred orientation along the c -axis is formed not only at the as-deposited state but also at 1100 K and RT after heating. The electron density distribution study of the BiT powder is conducted, revealing that the crystal structure of BiT powder is layered structure consisting of 2D covalent bonding network, stacked along c -axis at RT (the ferroelectric phase) and 1100 K (the paraelectric phase). Thus, we concluded that the particles of PT film preferentially recombine and grow with the 2D interface (the ab plane) at RT due to the layered structure of PT stacking along the c -axis.

In another hand, fine ferroelectric perovskite ceramic powder, lead zirconate titanate PZT, was synthesized by mechanochemical solid-state reaction. Mechanochemical solid-state reaction is activated by mechanical energy rather than thermal energy required in the conventional process, thus, has attracted extensive research interest as an environmentally friendly method of synthesis at RT without any post-annealing. SXRD experiments were conducted to examine the validity of PZT synthesis from a mixture of PbZrO_3 (PZ) and PT powders by the mechanochemical solid-state reaction using dry ball milling at RT. The starting powder is consisting of a mixture of PZ and PT powders with a molar ratio of 1 : 1. Based on the observation of scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX), the red (PT powder) and green (PZ powder) were transformed into yellow area in the ball-milled samples. To confirm the yellow area was composed of PZT phase or a mixture of fine PZ and PT particles, the crystal structure of the ball-milled samples have been successfully investigated by analyzing the SXRD data using the Rietveld method, revealing that the yellow in SEM-EDX is composed of PZT phase. The powder synthesis by mechanochemical solid-state reaction was mostly completed in a considerably short time of 4 h. In the 8 h sample, only a single phase of PZT with a composition of $\text{Pb}(\text{Zr}_{0.485(1)}\text{Ti}_{0.515(1)})\text{O}_3$, can be detected. Considering that there is almost no composition deviation in the ball milling process, we hypothesize that PZT with any Zr/Ti composition we want can be synthesized by changing the molar ratio of PZ and PT powders.

In addition, the spontaneous lattice strain of PT film deposited by the AD method at RT is smaller than that of the starting powder. However, the phase transition temperature (T_C) is 100 K higher than that of the powder in the first heating process from the as-deposited state. It has been found that the PT film fabricated using mechanical energy stabilizes the ferroelectricity up to higher temperature, although the spontaneous polarization is suppressed. Similarly, the spontaneous lattice strain of PZT ceramic powder fabricated using mechanical energy is significantly smaller than that of PZT ceramic fabricated using thermal energy, and resembles a cubic structure even at RT. Additionally, the T_C is 100 K higher than that of PZT ceramic fabricated using thermal energy in the first heating process from the as-synthesized state. Therefore, we consider that ferroelectric materials fabricated using mechanical energy mainly may have common properties of low ferroelectricity but higher T_C .