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PDF analysis on re-crystallized structure from amorphous BiT

Yasuhiro Yoneda [a,*], Shinji Kohara [b], Shin'ichi Hamazaki [c,1], Masaaki Takashige [c], Jun'ichiro Mizuki [a]

[a] *Japan Atomic Energy Research Institute, Synchrotron Radiation Research Center, Kouto 1-1-1, Mikazuki-cho, Sayo-gun, Hyogo 679-5148, Japan*
[b] *Synchrotron Radiation Research Laboratory, Japan Synchrotron Radiation, Research Institute, Kouto 1-1-1, Mikazuki-cho, Sayo-gun, Hyogo 679-5198, Japan*
[c] *Department of Electronics, Iwaki Meisei University, Iino 5-5-1, Chuohdai, Fukushima 970-8551, Japan*

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Abstract

A glass sample of composition $Bi_4Ti_3O_{12}$ was prepared by rapid quenching. The as-quenched sample was confirmed to be amorphous by synchrotron X-ray measurements. The crystallization process of the amorphous sample was also investigated by high-energy X-ray diffraction and by atomic pair distribution function analysis. The perovskite layer in the crystal $Bi_4Ti_3O_{12}$ is transformed to a pyrochlore structure in the amorphous sample. The amorphous sample first crystallized to a metastable phase by acquiring long-range ordering of the pyrochlore structure at T_{cryst1}, and then secondary crystallized into a reverted $Bi_4Ti_3O_{12}$ structure at T_{cryst2}.

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Keywords: High-energy X-ray diffraction; Pair distribution function; Local structure; Amorphous

1. Introduction

The Aurivillius family of layered bismuth oxides is a class of ferroelectrics whose properties have been widely studied. More recently, they have enjoyed renewed interest with the discovery of their fatigue-free behaviour in thin-film nonvolatile memory applications. More importantly, $Bi_4Ti_3O_{12}$ (BiT) thin films can be deposited at 650 °C, which is significantly lower than the synthesis temperature of $SrBi_2Ta_2O_9$ (SBT) ferroelectric thin films [1].

BiT can be obtained in the amorphous state, and the crystallization process has been investigated [2]. We have found that a metastable phase

* Corresponding author. Tel.: +81 791 58 2701; fax: +81 791 58 2740.
E-mail address: yoneda@spring8.or.jp (Y. Yoneda).
[1] Present address: Fukushima National College of Technology, Iwaki, Fukushima 970-8034, Japan.

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was stabilized during the crystallization process from amorphous BiT. Upon heating such amorphous materials, they are transformed into the crystalline state at specific temperatures (crystallization temperature T_{cryst}). Generally, physical properties of ferroelectric materials such as dielectric constant and electrooptic coefficient are strongly affected by the size of crystal grains. Accordingly, amorphous ferroelectric materials have been investigated in order to find useful methods to obtain small polycrystalline particles. However, the grain nucleation was observed around the amorphous-metastable transformation temperature (T_{cryst1}) in the case of the BiT due to the existence of an intermediate structure. We have already investigated the intermediate structure of the metastable phase and reported that the common structure should be a pyrochlore structure [3], but we have not established the structural relationship between the amorphous and the intermediate structure, and between the intermediate structure and the reverted crystal structure which appears beyond T_{cryst2}.

In order to obtain atomic structural information on the amorphous, intermediate and crystal states, we carried out pair distribution function (PDF) analysis [4]. The atomic PDF is a function that gives the number of atoms in a spherical shell of unit thickness at a distance r from a reference atom and thus reflects the structure of materials. By using the PDF approach, the materials that exhibit any given degree of structural coherence, ranging from perfect crystals to nanocrystalline particles and liquids, can be quantitatively studied. In general, neutron diffraction is a more powerful tool for studying the oxygen positions in oxides than X-ray diffraction because of the better scattering contrast of oxygen compared to metal ions. However, neutron diffraction needs a large amount of sample. In this study, we prepared the BiT by a twin-roller quenching system. Since we could not obtain sufficient sample quantity to perform neutron diffraction, we carried out the PDF analysis with synchrotron X-ray diffraction data.

2. Experimental

The details of the sample preparation are given in [2]. To prepare amorphous samples, the twin-roller quenching system was adopted. The $Bi_4Ti_3O_{12}$ powder was melted in a quartz tube at approximately 1100 °C. The melt was sprayed onto the twin roller and rapidly quenched to form an amorphous thick ribbon of 20–40 μm thickness and 1–3 cm length. The amorphous samples were annealed at temperatures of 700 °C and 1000 °C.

Synchrotron X-ray powder diffraction was performed at room temperature with 60 keV on X-rays beamline BL04B2 at SPring-8. Scattered radiation was collected with an intrinsic germanium detector. Structural parameters were refined by the PDF method with the program PDFFIT [5].

3. Results and discussion

From the preliminary experiments, we determined T_{cryst1} and T_{cryst2}, and prepared amorphous (as-quenched), metastable (700°-anneal) and crystallized (1000 °C-anneal) samples for structural analysis. Three samples were investigated by high-energy X-ray powder diffraction. The raw diffraction data were corrected for flux, background, Compton scattering, and sample absorption. The intensities were normalized in absolute electron units, reduced to structure factor $S(Q)$, and Fourier transformed to the corresponding PDFs, $G(r)$. Experimental powder diffraction patterns are shown in Fig. 1(a) and the corresponding PDFs, $G(r)$ in Fig. 2. Sharp Bragg peaks are present in the diffraction patterns of crystal and intermediate structure. The corresponding $G(r)$s of crystal and intermediate structure also feature sharp peaks reflecting the presence of a long-range ordering of these crystalline structures. On the other hand, only the broad diffraction peaks can be seen in the case of the amorphous BiT, characteristic of a glassy structure. It is noticed that there is no crystalline precipitation in the amorphous BiT. It can be also seen that the diffraction pattern of the as-quenched BiT is similar to the diffuse scattering pattern of the 700 °C-annealed sample. (see $S(Q) - 1$ in Fig. 1). The similarity between the as-quenched and the 700 °C-annealed sample is also seen in the radial distribution function of $G(r)$. Accordingly, we tried to fit both as-quenched and 700 °C-annealed BiT to the same model. A