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Crystal structure and ferroelectric properties of mixed bismuth layer-structured $Bi_7Ti_{4+x/2}Nb_{1-x}W_{x/2}O_{21}$ ceramics

Atsushi Yokoi *, Hirotaka Ogawa

Faculty of Science and Technology, Meijo University, 1-501 Shiogamaguchi, Tempaku-ku, Nagoya 468-8502, Japan

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Abstract

The effects of Ti and W substitutions for Nb on the ferroelectric properties and the crystal structure of $Bi_7Ti_{4+x/2}Nb_{1-x}W_{x/2}O_{21}$ ceramics were investigated in this study. From the XRPD patterns, no impurity phase was observed in the composition range from 0 to 1. The solid solutions have orthorhombic symmetry, with *I2cm* space group. The curve representing the relationship between composition x and remanent polarization (P_r) passes through a maximum at approximately $x = 0.75$; therefore, the maximum P_r value of 12.4 μC/cm^2 was obtained for this composition. The variation in the structural distortion of oxygen octahedra in the pseudo-perovskite block showed the same tendency as that of the P_r values. On the other hand, the coercive field (E_c) of the samples at the composition range from 0 to 1 remained the approximately constant value of 90 kV/cm. Moreover, the Curie temperature (T_c) of the samples was decreased from 840 to 715 °C by the increase of the structural distortion of the pseudo-perovskite block, which was caused by the Ti and W substitutions for Nb.

Keywords: Layer structures; Titanium oxide; Tungsten oxide; Electron microscopy

1. Introduction

The Aurivillius family of layered bismuth oxides is one of the important classes of ferroelectric materials, which have been recently investigated in particular for their potential uses in commercial applications such as the ferroelectric random access memory devices (FeRAM) [1–4]. The Aurivillius phases, which are a family of the bismuth layer-structured ferroelectrics (BLSFs) are represented as $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$, where A is a mono-, di-, or trivalent ion; therefore, B is a tetra-, penta-, or hexavalent ion. Moreover, m is the number of BO_6 octahedra in the perovskitelike blocks ($m = 1$–5) [5]. The pseudo-perovskite blocks $(A_{m-1}B_mO_{3m+1})^{2-}$ are sandwiched between $(Bi_2O_2)^{2+}$ layers along the c-axis. This one acts as an insulating paraelectric layer and considerably affect the electronic response such as the electrical conductivity, band gap, etc., while the ferroelectricity results mainly in the pseudo-perovskite block [6]. However, the bismuth layer-structured ferroelectrics suffer from two defects: a relatively low remanent polarization and a high processing temperature [7]. Thereby, the improvement of these drawbacks is necessary for their use in commercial applications.

The $Bi_7Ti_4NbO_{21}$ compound is one of these complex layered bismuth compounds, where the crystal structure is presented by $Bi_4A_{2m-1}B_{2m+1}O_{6m+9}$ with $m = 1$–3. The crystal structure of this compound is a regular intergrowth of Bi_3TiNbO_9 ($m = 2$) and $Bi_4Ti_3O_{12}$ ($m = 3$) layers along c-axis [8]. Also, the ferroelectric properties of $Bi_7Ti_4NbO_{21}$ ceramic were reported to have a remanent polarization (P_r) of 6 μC/cm^2 and a coercive field (E_c) of 70 kV/cm [9]; therefore, the P_r value of $Bi_7Ti_4NbO_{21}$ ceramic is lower than that of $SrBi_2Ta_2O_9$ ceramic which is widely investigated for use in the nonvolatile memory applications. Thus, in order to improve the ferroelectric properties, the influences of Ti and W substitutions for Nb on the ferroelectric properties and the crystal structure of $Bi_7Ti_{4+x/2}Nb_{1-x}W_{x/2}O_{21}$ ceramics have been investigated in this study.

2. Experimental method

High-purity (>99.9%) Bi_2O_3, TiO_2, Nb_2O_5 and WO_3 powders weighed on the basis of the their stoichiometric composition and the mixed and calcined at 800 °C for 20 h in air. These powders were milled and mixed with a polyvinyl alcohol, and then pressed into a pellet of 12 mm diameter and 3 mm

* Corresponding author. Tel.: +81 52 832 1151; fax: +81 52 832 1253.
E-mail address: m0553503@ccmailg.meijo-u.ac.jp (A. Yokoi).

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thickness (100 MPa). Subsequently, these pellets were sintered in the temperature range of 1100 °C–1150 °C for 2 h in air. The bulk densities were determined by Archimedes-method on the sintered samples. The crystalline phases of crushed samples were identified by the X-ray powder diffraction (XRPD) and the crystal structures of samples were refined according to the Rietveld analysis (RIETAN) [10,11]. Moreover, the morphological changes in the samples were investigated by using a field emission scanning electron microscopy (FE-SEM). In order to perform the dielectric measurements, platinum electrodes were deposited on both surfaces of the pellets, using a platinum paste fired at 1050 °C for 30 min. The temperature dependence of the dielectric constant was measured at 1 MHz by a LCR-meter from room temperature to 800 °C. The *P–E* hysteresis loop at room temperature was measured using an aixACCT TF2000FE-HV ferroelectric test unit at 50 Hz in a silicon oil bath.

3. Results and discussion

Fig. 1 shows the XRPD patterns of $Bi_7Ti_{4+x/2}Nb_{1-x}W_{x/2}O_{21}$ ceramics sintered at the various temperatures for 2 h in air. From the XRPD results of Ti- and W-substituted $Bi_7Ti_{4+x/2}Nb_{1-x}W_{x/2}O_{21}$ ceramics, no secondary phase was detected over the composition range. The ceramics are identified to be an orthorhombic crystal structure with *I2cm* space group as reported by Mercurio et al. [12]; therefore, the crystal structure of $Bi_7Ti_4NbO_{21}$ ceramic consists of the structural units of two parent phases such as Bi_3TiNbO_9 ($m = 2$) and $Bi_4Ti_3O_{12}$ ($m = 3$) compounds by sharing the 'Bi_2O_2' sheets along the *c*-axis as shown in Fig. 2. The niobium atoms are located in the mixed Ti(2)/Nb(2) sites; therefore, the site occupancies of Ti and Nb cations are known to be 0.5 and 0.5, respectively. In this study, we focused on the Ti and W substitution for Nb in the mixed Ti(2)/Nb(2) sites, because the octahedral sites occupied by Ti^{4+} ions in the $Bi_4Ti_3O_{12}$ ($m = 3$) block cannot be modified by such a substitution as shown in Fig. 2. Thus, in order to clarify the influence of the difference in the ionic radii which change according to $Nb^{5+} = 0.5$ ($Ti^{4+} + W^{6+}$) on the Ti(2)/Nb(2) site, the lattice parameters and unit cell volume of the samples are determined by the Rietveld method, and the results are shown in Fig. 3 and Table 1. All the lattice parameters of $Bi_7Ti_{4+x/2}Nb_{1-x}W_{x/2}O_{21}$ ceramics decreased linearly with increasing the composition *x*. These decreases are primary due to the difference in the ionic radii of Nb^{5+} (0.64 Å), Ti^{4+} (0.605 Å) and W^{6+} (0.60 Å), when the coordination number is sixth [13]. Also, as the lattice parameters varied linearly throughout the entire composition range, $Bi_7Ti_{4+x/2}Nb_{1-x}W_{x/2}O_{21}$ ceramics satisfy Vegard's Law which confirms the formation of solid solutions. Moreover, we focused on the oxygen octahedra in the pseudo-perovskite block, in which the ferroelectricity predominantly arises [6]. Therefore,

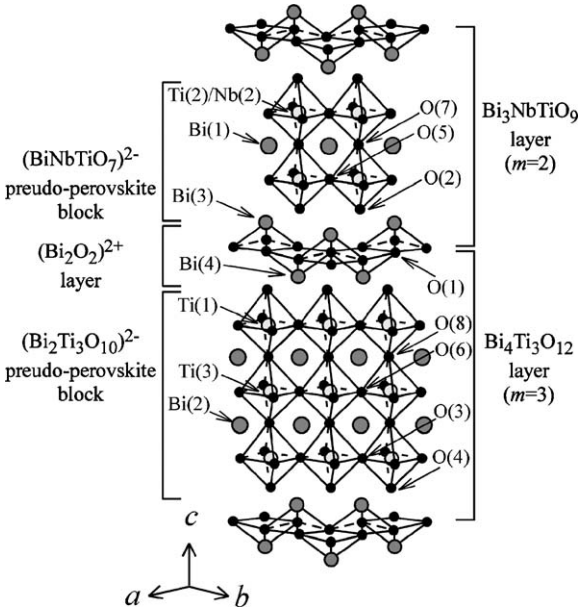

Fig. 2. Schematic representation of crystal structure of $Bi_7Ti_4NbO_{21}$ ceramic.

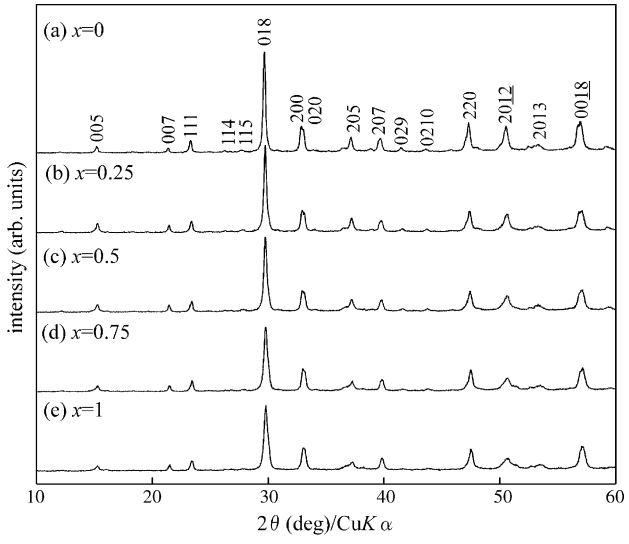

Fig. 1. XRPD patterns of $Bi_7Ti_{4+x/2}Nb_{1-x}W_{x/2}O_{21}$ ceramics sintered at various temperatures for 2 h in air.

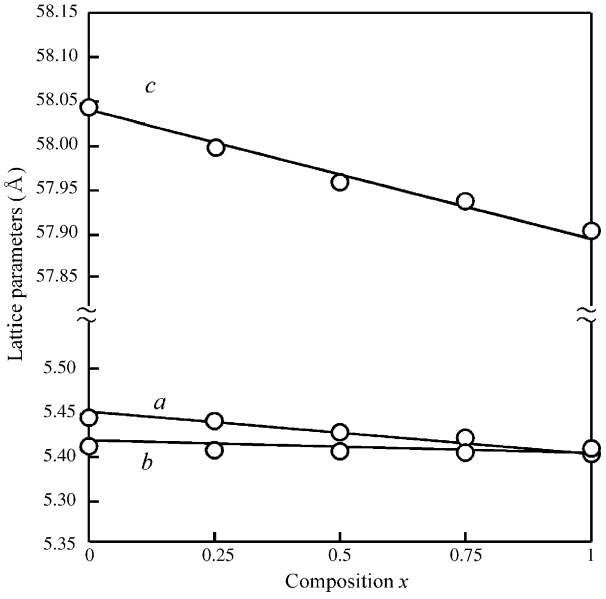

Fig. 3. Variations in lattice parameters of $Bi_7Ti_{4+x/2}Nb_{1-x}W_{x/2}O_{21}$ ceramics.