Synthesis and ferroelectric properties of Bi$_4$Ti$_3$O$_{12}$ aurivillius phase

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Abstract

Over the last few decades, the Aurivillius phases have emerged as important candidates for the development of ferroelectric random access memories (FeRAM), piezoelectric devices and ionic conductors. Ferroelectric materials have been intensively investigated due to their remarkable physical properties of practical interest. Bismuth titanate, Bi$_4$Ti$_3$O$_{12}$ is one of the ferroelectric materials with layered structure belonging to the Aurivillius family. Recently, we have carried out computer simulation in atomic scale in order to predict the energies in the Aurivillius structure of Bi$_4$Ti$_3$O$_{12}$. In this work, the stable phase was synthesized using solid state reaction and the product then was characterized using powder X-ray diffraction method. The cell parameters were determined using Rietveld refinement in orthorhombic system with space group of B2cb. Results from the ferroelectric properties measurement of Bi$_4$Ti$_3$O$_{12}$ was also presented.

Keywords: Aurivillius phase; Rietveld refinement; Ferroelectric properties; Bi$_4$Ti$_3$O$_{12}$

Introduction

In recent years, bismuth layer-structured ferroelectrics (BLSF) have been given much attention because some materials, such as Bi$_4$Ti$_3$O$_{12}$, are excellent candidate materials for nonvolatile ferroelectric random access memory (FRAM) applications. BLSF are also better candidates because of their higher Curie points. Ferroelectrics have been investigated widely for potential applications in nonvolatile random-access memories (NVRAM) and dynamic random-access memories (DRAM). It is important in these applications that they have a low coercive field, high remanent polarization, low leakage current, and low polarization fatigue. Bismuth-containing layered perovskites have been found to be ferroelectric by Smolenskii, Isupov, and Agranovskaya.

The oxides of the Aurivillius family, with general formula of [Bi$_2$O$_2$][A$_m$I$_3$BO$_{2m+1}$], can be described as the combination of regular stacking between the [Bi$_2$O$_2$]$^{2+}$ slabs and perovskite-like [A$_m$I$_3$BO$_{2m+1}$]$^{2-}$ blocks. The integer, $m$, describes the number of sheets of corner-sharing BO$_6$ octahedra forming the ABO$_3$-type perovskite blocks. The A could be a mono-, di- or trivalent element (or combination) with cuboctahedral coordination such as Na$^+$, K$^+$, Ca$^{2+}$, Ba$^{2+}$, Pb$^{2+}$ or Ln$^{3+}$ and the 6-coordinate perovskite-like B-site could be filled by smaller cations such as Fe$^{3+}$, Ti$^{4+}$, Nb$^{5+}$ or W$^{6+}$. Whereas the perovskite blocks offer large possibilities in terms of compositional flexibility due to numerous possible combinations of $A$ and $B$ cations, the cation sites in the [Bi$_2$O$_2$]$^{2+}$ layers are almost exclusively occupied by Bi$^{3+}$.

One interesting feature of the Aurivillius phases resides in the compositional flexibility of the perovskite blocks which allows incorporating various cations. It is thus possible to modify the ferroelectric properties according to the chemical composition. Although this phenomenon was observed since many years, its structural origin not yet clearly elucidated. Dopants are added into a wide variety of Aurivillius in order to modify their properties. The goal in some cases is to create or enhance desirable properties, while in other this is to eliminate or reduce undesirable effects.

Subbarao and Newnham showed that it to be a ferroelectric with the highest known Curie point in the bismuth layer-structured ferroelectrics family at that time of 940 °C. However, the information about the effect of doping in this material is still limited.

This paper will present results of synthesis in Bi$_4$Ti$_3$O$_{12}$, with the aim that a better understanding will be gained. Result from the ferroelectric properties measurement of Bi$_4$Ti$_3$O$_{12}$ was also presented.
Materials and Methods

The Aurivillius family of Bi$_4$Ti$_3$O$_{12}$ was prepared by the standard solid-state reaction method. Stoichiometric quantities of high purity powders of Bi$_2$O$_3$ and TiO$_2$ (Aldrich Chem. Co.), all with a purity of 99.99%, were thoroughly mixed and ground, and heated in an alumina crucibles at elevated temperature until phase purity was established. Typical reaction conditions were heated for 24 h at 700 °C, 24 h at 850 °C, 24 h at 1000 °C, and a further 24 h at 1100 °C, with intermediate regrindings between each stage. The sample was slowly cooled to room temperature in air.

The purity of the product was monitored by powder X-ray diffraction using monochromatized Cu K$_{α1}$ radiation $λ = 0.1541$ nm. Unit cell parameters were least squares refined by the RIETICA program. The ferroelectric properties of Bi$_4$Ti$_3$O$_{12}$ were evaluated from the P-E hysteresis curves, using a high-voltage test system (Model RT-66A, Radiant Technologies, Albuquerque, NM).

Results and Discussion

The X-ray diffraction pattern of the as-prepared powder showed that structure of Bi$_4$Ti$_3$O$_{12}$ is orthorombic with space group $B2cb$. Preliminary examination of the raw X-ray powder diffraction data for the composition suggested that this powder is single phase compound and also can be indexed with the orthorombic symmetry. The Rietveld refinement with orthorombic and $B2cb$ space group was then carried out and proceed without incident. Typical Rietveld plot are shown in Figure 1. The powder X-ray diffraction patterns of the composition suggest that the sample is isostructure with the parent Bi$_4$Ti$_3$O$_{12}$. The cell parameters of the prepared material are listed in Table 1.

Atomistic simulation techniques have been employed to investigate the Aurivillius oxides phases: Bi$_4$TiNbO$_8$, Bi$_4$Ti$_5$O$_{12}$, BaBi$_4$Ti$_4$O$_{15}$ and Ba$_2$Bi$_4$Ti$_5$O$_{18}$. The simulation suggested that generally show good accord with experimental data.

Table 1 Cell parameters for Bi$_4$Ti$_3$O$_{12}$ was determined using Rietveld refinement applying orthorombic system, in space group $B2cb$.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Aurivillius Oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_4$Ti$<em>3$O$</em>{12}$</td>
<td>Bi$_4$Ti$<em>3$O$</em>{12}$</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>5.4444(1)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>5.4086(1)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>32.8425(6)</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>967.10</td>
</tr>
<tr>
<td>$R_p$</td>
<td>5.809</td>
</tr>
<tr>
<td>$R_{wp}$</td>
<td>9.0</td>
</tr>
<tr>
<td>$R_{Bragg}$</td>
<td>4.31</td>
</tr>
</tbody>
</table>

$^*$Hervoches et al. (1999)
The bismuth titanate, Bi₄Ti₃O₁₂, have the orthorhombic structure as shown in Figure 2. The structure of Bi₄Ti₃O₁₂ is thus built up of [Bi₂O₂]²⁺ layer between which [Bi₂Ti₃O₁₀]²⁻ layers are inserted. In the Bi₂Ti₃O₁₀ units, Bi/Ti ions are enclosed by oxygen octahedra which are linked through corners forming O-Bi/Ti-O octahedra. Thus Bi₂Ti₃O₁₀ units pose a remarkable similarity to the perovskite-type structure. The height of the perovskite-type layer sandwiched between Bi₂O₂ layers in Bi₄Ti₃O₁₂ is equal to six for O-Bi/Ti-O distances or approximately to \( m = 3 \) \( ABO_3 \) perovskites.

![Figure 2](image)

**Figure 2** Structure of Bi₄Ti₃O₁₂ consist of [Bi₂O₂]²⁺ layer interleaved with perovskite-like [Bi₂Ti₃O₁₀]²⁻ blocks.

Aurivillius ceramics are interesting ferroelectrics. The layered structure makes this kind of ferroelectrics have good fatigue endurance. Figure 3 shows the P-E hysteresis loops of the Bi₄Ti₃O₁₂ ceramic, which indicates the ferroelectricity in this compound. The disadvantage of the layer-structure perovskite materials for high-temperature piezoelectric applications is their relatively high ferroelectricity. This ferroelectricity is electronic-type and, therefore, can be suppressed by doping.

![Figure 3](image)

**Figure 3** The P-E hysteresis loops of the Bi₄Ti₃O₁₂ ceramics

The obtained values of remanent polarization \( P_r \) for Bi₄Ti₃O₁₂, \( P_r = 12.97 \, \mu C/cm^2 \) in coercive field \( E_c = 50.45 \, kV/cm \) is in good agreement with the value reported in previous studies. The layer-structure perovskite materials, Bi₄Ti₃O₁₂ ceramic, have found a higher polarization in the randomly oriented. The obtained values of \( P_r \), show that the polarization can be reoriented only in the plane parallel to the Bi₂O₂ layers (the \( ab \)-plane of the orthorhombic structure). The two-dimensional configuration of polarization leads to a very high coercive force along the polar axis for most of the bismuth layer-structured ferroelectrics. Bismuth ions in the (Bi₂O₂)²⁺ layer are coordinated to five oxygens arranged in a pyramid on one side, four in the bismuth oxide layer and one in the pseudo-perovskite block. This asymmetric configuration of ions increases the ionic polarizability in the (Bi₂O₂)²⁺ layer and contributes to the spontaneous polarization in the bismuth layer-structured ferroelectrics, but the polar components are apparently confined within the pseudo-perovskite block. The \( P_r \) and \( E_c \) results in the samples are caused by the random orientation of the grains. Newnham et al. have reported that the perovskite layers in BSLFs compounds ‘zigzag’ along the \( c \)-axis depend on dopant.

**Conclusions**

The combined X-ray diffraction and Rietveld refinement confirm that Bi₄Ti₃O₁₂ adopt orthorhombic system, in space group \( B2cb \). The the P-E hysteresis loop of the ceramic indicates the ferroelectricity in this compound. The remanent polarization, \( P_r \), of value Bi₄Ti₃O₁₂ is 12.97 \( \mu C/cm^2 \) in coercive field \( E_c = 50.45 \, kV/cm \).
References


