

Study of ferroelectric BaBi₄Ti₄O₁₅ obtained via mechanochemical synthesis

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Bi-layered structure ferroelectric material-bismuth titanate, Bi₄Ti₃O₁₂ (BIT) and barium-bismuth titanate, BaBi₄Ti₄O₁₅ (BBT) ceramic powders were prepared by mechanical synthesis process. BaBi₄Ti₄O₁₅ was prepared from stoichiometric quantities of barium titanate and bismuth titanate obtained via mechanochemical synthesis. Barium titanate, BaTiO₃ has been synthesized from mixture of BaO and TiO₂ and bismuth titanate, Bi₄Ti₃O₁₂ was prepared starting from Bi₂O₃ and TiO₂, commercially available. The reaction mechanism of BaBi₄Ti₄O₁₅ and the preparation and characteristics of BBT ceramic powders were studied using XRD, Raman spectroscopy, particle analysis and SEM. The Bi-layered perovskite structure of BaBi₄Ti₄O₁₅ ceramic forms at 1100 °C for 4 h. Microstructure of Bi₄Ti₃O₁₂ is in accordance with the view that Bi₄Ti₃O₁₂ exhibits plate-like grains with the average grain size increasing with the sintering temperature. It is evident that Ba²⁺ addition lead to the change in the microstructure development, particularly in the change of the average grain size.

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1. Introduction

Barium-bismuth titanate, BaBi₄Ti₄O₁₅ has been extensively studied for its ferroelectric and other excellent properties. BaBi₄Ti₄O₁₅ is a candidate material for high temperature piezoelectric applications, memory storage, and optical displays because of its high Curie temperature and electro-optical properties. The properties and way of synthesis of BaBi₄Ti₄O₁₅ have been reported in a number of papers, cited among others in references [1, 2]. But, mechanically assisted synthesis of BaBi₄Ti₄O₁₅ ceramic powders shows much better characteristics than same ceramic powders synthesized by conventional solid-state reaction. However BBT ceramic powder synthesis has very limited reports using milling technique and mechanical activation processes.

This family of bismuth oxides, discovered more than 60 years ago by Aurivillius [3]. The structure of the Aurivillius family of compounds consist of (Bi₂O₂)²⁺ layers interleaved with perovskite-like (A_{n-1}B_nO_{3n+3})²⁻ layers. Their intrinsic electric properties are anisotropic, with the maximum value of conductivity and the major component of spontaneous polarization parallel to the (Bi₂O₂)²⁺ layers. As a result, properties of the polycrystalline materials are strongly affected by their microstructure, especially by the orientation of the plate-like grains and by the length-to-thickness ratio of the grains.

Crystallographic studies have demonstrated the key role of the A-site cation in the ferroelectric behavior of these materials and at the first approximation, a direct relation between the average ionic radii of the A-site cation and the temperature of the ferroelectric-paraelectric transition (*T_c*) can be established [4]. Apart from polar

displacements, the ferroelectric phases are also characterized by cooperative tilting of the BO₆ octahedral.

BaBi₄Ti₄O₁₅ as the *n* = 4 member of the Aurivillius family has Ba ions at the A sites and Ti ions at the B sites of the perovskite (A_{n-1}B_nO_{3n+3})²⁻ block ((Bi₂O₂)²⁺ · ((BaBi₂)Ti₄O₁₃)²⁻) (Fig. 1). It has a high Curie temperature of 417 °C [5]. The crystal structure of BaBi₄Ti₄O₁₅ can be described by an orthorhombic or a pseudo tetragonal unit cell.

A number of these phases have been investigated from the point of view of both structural and electrical properties, either as bulk materials or thin films [6]. BaBi₄Ti₄O₁₅ has been prepared by techniques such as sol-gel [2] and citrate gel [7] methods. Also, bulk BaBi₄Ti₄O₁₅ ceramic powder synthesis has very limited reports using non-conventional techniques other than conventional solid-state method.

BaBi₄Ti₄O₁₅ is traditionally synthesized by the solid-state reaction among mixed oxides by calcinations at an elevated temperature of ~ 500°C. The conventional ceramic route often leads to non-stoichiometry in composition of the resultant BaBi₄Ti₄O₁₅ powder, as a result of the undesirable loss in bismuth content through volatilization of Bi₂O₃ at elevated temperatures. In addition, crystallite coarsening and particle aggregation are unavoidable because of the interfacial diffusions and reactions that occur at the calcinations temperature. Accordingly, the sintering and microstructural development of BaBi₄Ti₄O₁₅ are adversely affected by the presence of hard aggregates, where differential sintering among aggregates of differing green density can occur at the sintering temperature and therefore adversely affect the ferroelectric properties.

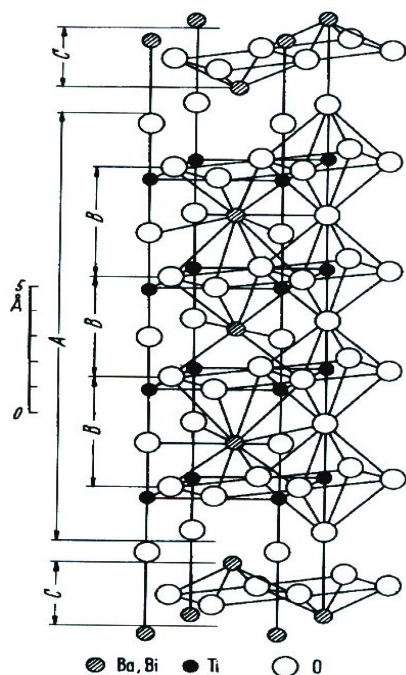


Fig. 1. The lattice structure of BBT ceramics.

2. Experimental procedures

Barium bismuth titanate, BaBi₄Ti₄O₁₅ (BBT) was prepared from stoichiometric quantities of barium titanate, BaTiO₃ (BT) and bismuth titanate, Bi₄Ti₃O₁₂ (BIT) obtained via mechanochemical synthesis. BaTiO₃ has been synthesized from mixture of BaO (BaO, Alfa Aesar, p.a. 99 %) and TiO₂ in anatase crystal form (TiO₂, Alfa Aesar, p.a. 99.9 %) and Bi₄Ti₃O₁₂ was prepared starting from Bi₂O₃ (Bi₂O₃, Alfa Aesar, p.a. 99.8 %) and TiO₂, the same type such as for BaTiO₃. Mechanochemical synthesis was performed in air atmosphere in a planetary ball mill (Fritsch Pulverisette 5). BaTiO₃ powder was formed after 1 h and Bi₄Ti₃O₁₂ powder after 6 h of milling. Milling conditions were: zirconium oxide jars and zirconium oxide balls (d=10 mm), ball-to-powder weight ratio 20:1 and determined at basic disc rotation speed 320 min⁻¹ and rotation speed of discs with jars ~ 400 rpm. The powder mixture of BaTiO₃ and Bi₄Ti₃O₁₂ was homogenized for 30 min (speed 142 min⁻¹) and then pressed into pallets using a cold isostatic press (8 mm in diameter and ~ 3 mm thick).

Characterization of the obtained samples was carried out by:

- the X-ray diffraction data for milled powders and sintered ceramics were collected using a Rigaku[®] RINT2000 diffractometer (42kV × 120mA) with Cu K_α radiation ($\lambda_{K\alpha 1} = 1.5405 \text{ \AA}$, $\lambda_{K\alpha 2} = 1.5443 \text{ \AA}$, $I_{K\alpha 1}/I_{K\alpha 2} = 0.5$), 2θ range between 15° and 110°, step size of 0.02° (2θ), divergence slit = 0.5 mm, receiving slit = 0.3 mm. The Rietveld analysis [8] was performed with the Rietveld refinement program package General Structure Analysis System (GSAS) of Larson and Von Dreele. The peak profile function was modeled using a convolution of the pseudo-Voigt with the asymmetry function described by

Finger et al., which accounts for the asymmetry due to axial diverge. Rietveld refinements were performed to identify the symmetry of the BaBi₄Ti₄O₁₅ phase.

- room temperature Raman spectra in spectral range from 100 to 1000 cm⁻¹, in back scattering geometry, were obtained by Micro Raman Chromex 2000 using 514 nm of a frequency doubled Nd:YAG laser. The spectral resolution was 1 cm⁻¹. The average power density on the sample was about 250 mW mm⁻².

- scanning electron microscopy (SEM, Model JOEL-5300) was used to study particle size and powder morphology of activated powders and sintered samples. The powder mixture was sintered at 1100 °C for 4 h (Lenton-UK oven) without pre-calcinations step. Heating rate was 10 °C min⁻¹, with nature cooling in air atmosphere.

- the ferroelectric properties of BaBi₄Ti₄O₁₅ ceramic samples were confirmed on the basis of following characteristic parameter: coercive field, spontaneous and remnant polarization. Silver paste electrodes for electrical measurements were applied to the polished surfaces of 1 mm thick samples by the screen printing method. The silver paste was then polymerized at 600 °C for 30 min. The spontaneous (P_s) and remnant (P_r) polarization, as well as the coercive field (E_c), were determined by evaluating ferroelectric hysteresis loops obtained by means of a modified Sawyer-Tower circuit [9].

3. Results and discussion

The effect of mechanochemical activation can be detected after carrying out thermal treatments on the sample. The spectrum of the sample sintered at 1100 °C for 4 h, without pre-calcinations step, shows clear peaks crystalline BBT and demonstrates complete Bi-layered perovskite structure phase formation. The observed pattern was in excellent agreement with that reported for tetragonal BaBi₄Ti₄O₁₅ in JCPDS #35-0757.

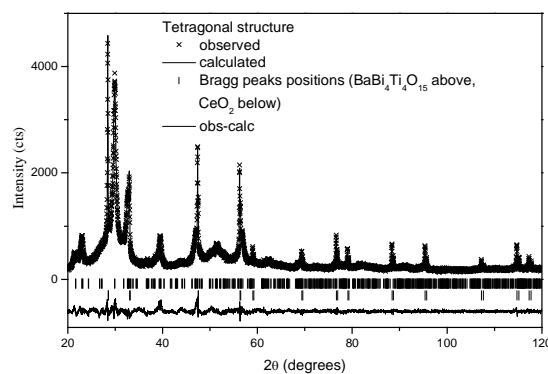


Fig. 2. Rietveld refinement plot showing the observed (x), calculated (solid line) diffraction profiles for BaBi₄Ti₄O₁₅ at room temperature.

It is notable that materials with small crystallite size, as it was in the investigated case, belong to higher crystal structure symmetry. The tetragonal structure was also mentioned by Bobic and co-authors for BBT obtained at low calcinations temperature confirming the influence of small crystallite size on crystal symmetry. Thus, in further calculation the barium bismuth titanate shall be mentioned as material with tetragonal crystal symmetry of an Aurivillius phase Bi-layered oxide. The bismuth layer of $(\text{Bi}_2\text{O}_2)^{2+}$ interleaved with the perovskitelike $(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ layers. It has been shown that the ferroelectric properties of the Aurivillius bismuth-layer compounds are strongly dependent on the number of layers and the chemical elements in the *A* and *B* sites. The $\text{MBi}_4\text{Ti}_4\text{O}_{15}$ compounds with layer number $m = 4$ ($M = \text{Ca}, \text{Ba}, \text{Sr}$) are a subgroup of this bismuth-layer structure compounds (Fig. 4).

XRD pattern of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ was analyzed by the Rietveld method (Fig. 2). $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ is tetragonal and the structure was refined in $I4/mmm$, $a = 3.89360(5)$ Å, $c = 42.2914(7)$ Å, $R_p = 2.75$, $R_{wp} = 4.36$ and $\chi = 4.96$.

The Raman spectra of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ have three modes at around 160, 280 and 880 cm^{-1} at room temperature (Fig. 3). The low-frequency modes are considerably damped, whereas the basic modes are wider in comparison to Raman modes originated from a pure $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Such damped frequencies provide indications for this compound to take a disordered structure, i.e. Ba-ions are likely to be randomly configured on Bi-ion sites in the $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ crystal lattice. The noticed mode at 160 cm^{-1} is ascribed to the vibration of rigid-layer modes that are typical in these layered structures where a layer makes vibrations as a whole. The mode at 280 cm^{-1} arises from TiO_6 octahedral vibrations and represents a combination made of bending-stretching vibrations. Also, the mode at 880 cm^{-1} , whose frequency amounts 851 cm^{-1} in the case of a pure $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ compound, depends on the sort of ions which are embedded in the lattice instead of Bi. The most probably, these vibrations are closely related to the vibrations of the Ba-O bond.

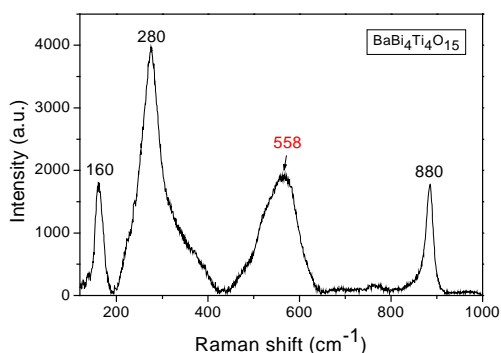


Fig. 3. Raman spectra at room temperature of the $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ ceramic sintered at 1100 °C for 4 h.

Fig. 4 shows the microstructure of the $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ ceramic prepared from BBT powders obtained by mechanical activation after 30 min and sintered at 1100 °C

for 4 h. The heat treatment leads to an exhaust of some volatile species (e.g. bismuth oxide) and formation BBT phase as final component (here the perovskite-like phase). The brown powder is composed of 50-100 μm long amorphous aggregates. The removal of some volatile species after 4 h at 1100 °C broke the aggregates into smaller fragment which were subsequently used for nucleation and growth of crystalline phases. As shown in Fig. 4, the morphologies of resulting crystallites are 5 μm wide plate like-shaped and 1 μm spherical-shaped. The density of the sintered BBT ceramics was found to be 93 % of their theoretical density.

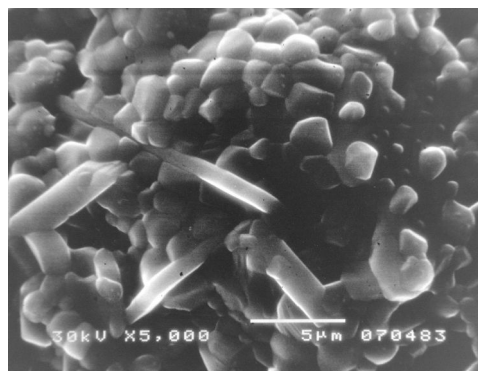


Fig. 4. The microstructure of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ ceramic sintered at 1100 °C for 4 h.

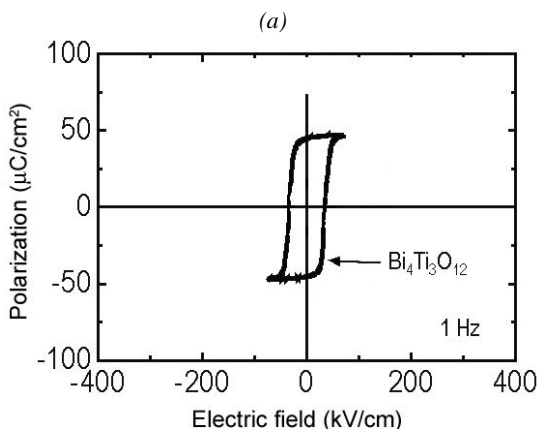
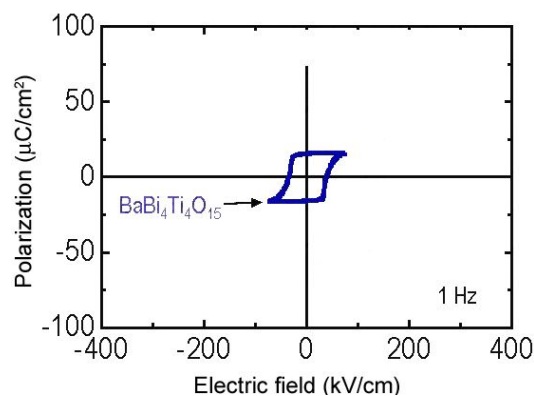


Fig. 5. Hysteresis loops (a) $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ and (b) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramic sintered at 1100 °C for 4 h.

The ferroelectric hysteresis loop parameters measurements of the pallet BaBi₄Ti₄O₁₅ and Bi₄Ti₃O₁₂ sintered at 1100 °C showed the values of remnant polarization (P_r) of $\approx 20 \mu\text{C cm}^{-2}$ and $\approx 50 \mu\text{C cm}^{-2}$, respectively and coercitive field (E_c) of 39 kV cm^{-1} , under an electric field (E) of 60 kV cm^{-1} (Fig. 5). It was found that the polarization properties of the BBT crystals depend strongly on the composition. Ferroelectricity was not observed along the c axis.

4. Conclusions

Bi-layered structure ferroelectric material-bismuth titanate, Bi₄Ti₃O₁₂ (BIT) and barium-bismuth titanate, BaBi₄Ti₄O₁₅ (BBT) ceramic powders were prepared by mechanical synthesis process. XRD shown that synthesized BBT has tetragonal structure of an Aurivillius phase Bi-layered oxide. Only 4 Raman bands are clearly observed. It is evident that Ba²⁺ addition leads to the change in microstructure development, particularly in the change of the average grain size and homogeneity of the grains of BaBi₄Ti₄O₁₅. BBT with good crystalline was formed after sintering without pre-calcinations step with the plate-like structure typical for layered structure materials was obtained. With respect to the ferroelectricity, the saturated remnant polarization was $\approx 20 \mu\text{C cm}^{-2}$ and the saturated coercitive field was $\approx 50 \mu\text{C cm}^{-2}$, along the $a(b)$ axis under an electric field of 60 kV cm^{-1} , and ferroelectricity was not observed along the c axis. The hysteresis loops and values of coercive field, spontaneous and remnant polarization, indicates the ferroelectric behavior of the obtained ceramic material.

The obtained result indicated that nanosized BaBi₄Ti₄O₁₅ ceramic powder synthesized by high-energy ball milling process possesses better sinterability than those prepared by others methods, showing the advantage of the mechanochemical process over conventional solid-state reaction and chemical process.

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