



## Characterization and properties of barium bismuth titanate

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### Abstract

*BaBi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> (BBiT) was prepared from stoichiometric amounts of BaTiO<sub>3</sub> (BT) and Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> (BIT) obtained via mechanochemical synthesis. Mechanochemical synthesis was performed in air atmosphere in a planetary ball mill. BBiT ceramics were sintered at 1100°C, 1110°C and 1120°C for 1 h without pre-calcination step. The formation of phase and crystal structure of BT, BIT and BBiT were verified using X-ray analysis. The morphology of obtained powders and microstructure were examined using scanning electron microscopy. The electrical properties of sintered samples were carried out and BBiT shows behaviour typical for relaxor ferroelectrics and dielectric constant at room temperature is approximately 93.*

**Keywords:** mechanochemical synthesis, Aurivillius phase, BaBi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub>

### I. Introduction

The lattice structure of the Aurivillius family of compounds is composed of  $n$  number of perovskite-like  $(A_{n-1}B_nO_{3n+3})^{2-}$  unit cells sandwiched between  $(Bi_2O_2)^{2+}$  slabs along pseudo tetragonal  $c$ -axis. The 12 coordinate perovskite-like A-site is typically occupied by a large cation such as Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Pb<sup>2+</sup>, Bi<sup>3+</sup> or Ln<sup>3+</sup> and the 6-coordinate perovskite-like B-site by smaller cations such as Fe<sup>3+</sup>, Cr<sup>3+</sup>, Ti<sup>4+</sup>, Nb<sup>5+</sup> or W<sup>6+</sup>. BaBi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> (BBiT), as the  $n = 4$  member of the Aurivillius family has Ba and Bi ions at the A sites and Ti ions at the B sites of the perovskite block  $[(Bi_2O_2)^{2+} \cdot ((BaBi_2)Ti_4O_{13})^{2-}]$  [1]. BBiT remain unexplored, whereas being promising candidate for high-temperature piezoelectric application, memory application and ferroelectric non-volatile memories (Fe-RAM) [2,3]

Synthesis of BBiT ceramics is mainly based on chemical and solid-state reaction methods. Mostly used chemical methods are the polymeric precursors-Pechini process, sol-gel, co-precipitation and hydrothermal method [4,5]. BBiT can be also produced by conventional solid-state reaction starting from BaCO<sub>3</sub>, TiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub> [6]. Generally, the conventional ceramic route for the synthesis of bismuth based materials leads to non-stoichiometric composition of the resultant powder, in

consequence of the undesirable loss in bismuth content through volatilization of Bi<sub>2</sub>O<sub>3</sub> at elevated temperature [7]. Recently, high energy mechanochemical milling process has been shown that ferroelectric materials can be synthesized directly from their oxide precursors in the form of nano-sized powders (mechanochemical synthesis), without the need for the calcination at intermediate temperatures, thus making the process very simple and cost-effective. A large number of simple ferroelectric materials, including BaTiO<sub>3</sub> (BT) and Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> (BIT) have been synthesized using the high-energy milling process [8]. The aim of the present work is to prepare BBiT ceramics from mechanochemically synthesised BT and BIT without calcination step. The phase composition, morphology and particle size, microstructure and electrical properties were discussed.

### II. Experimental

In present work BBiT was prepared from stoichiometric quantities of BT and BIT obtained via mechanochemical synthesis. BT has been synthesized from mixture of BaO (BaO, Alfa Aesar, p.a. 99 %) and TiO<sub>2</sub> in anatase crystal form (TiO<sub>2</sub>, Alfa Aesar, p.a. 99,9 %) and BIT was prepared starting from Bi<sub>2</sub>O<sub>3</sub> (Bi<sub>2</sub>O<sub>3</sub>, Alfa Aesar, p.a. 99,8 %) and TiO<sub>2</sub>, the same type such as for BT. Mechanochemical synthesis was performed in air atmosphere in a planetary ball mill (Fritsch Pulverisette 5). BT powder was formed after 1 h and BIT powder after

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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  $320 \text{ min}^{-1}$  and rotation speed of discs with jars  $\sim 400 \text{ rpm}$ . The powder of BT and BIT was mixed for 4 h using ethanol as liquid medium (speed  $142 \text{ min}^{-1}$ ) with aim to homogenize the mixture and to destroy agglomerates. Obtained mixture was pressed into pellets at 98 MPa using a cold isostatic press (8 mm in diameter and  $\sim 3$  mm thick). Shrinkage behaviour of pressed pallet prepared from homogenized mixture of BT and BIT powder is used to determinate appropriate temperature of sintering. Their powder mixture was fired at  $1100^\circ\text{C}$ ,  $1110^\circ\text{C}$  and  $1120^\circ\text{C}$  for 1 h (Lenton-UK oven) without pre-calcination step in closed alumina crucibles to avoid bismuth loss. Heating rate was  $10^\circ\text{C}/\text{min}$ , with natural cooling in air atmosphere. The formation of phase and crystal structure of BT, BIT and BBiT were verified using the X-ray diffractometer (XRD, Model D5000, Siemens) with  $\text{CuK}_\alpha$  radiation ( $\lambda_{ka1} = 1.5405\text{\AA}$ ,  $\lambda_{ka2} = 1.5443\text{\AA}$ ,  $I_{ka1}/I_{ka2} = 0.5$ ),  $2\theta$  range between  $15^\circ$  and  $110^\circ$ , step size of  $0.02^\circ$  ( $2\theta$ ), divergence slit = 0.5 mm, receiving slit = 0.3 mm. For particle size distribution of BT, BIT and powder mixture of BT and BIT was used Microtrac S3500. The morphology and microstructure of obtained powders were examined using scanning electron microscope (SEM, Model JEOL-JSM 5300 and SEM, Model Topcon SM-300). Samples for SEM examination were prepared from powders dissolved in ethanol in an ultrasonic bath to destroy the hard agglomerates. For microstructure examination and electrical properties the sintered samples in the disc shape were polished to thickness of 1 mm with silicon carbide and alumina powder and cleaned in an ultrasonic bath in ethanol. The electrical properties of sintered samples (dielectric constant and dielectric losses) were measured using a HP 3457A.

### III. Results and discussions

The Fig. 1. shows the phase formation and crystal structure of BIT and BT powders that have been obtained by mechanochemical synthesis for 6 h and 1 h, respectively. The observed peaks at  $2\theta$  angles  $30.0$ ,  $32.8$ ,  $23.1$ ,  $56.9$  and  $39.6^\circ$  can be attributed to the formation of BIT (Fig 1a). The formed structure could be tetragonal or orthorhombic (JCPDS 47-0398, 35-0795) as it was discussed in previous paper [9]. The X-ray reflections at  $2\theta=31.6$ ,  $38.9$ ,  $45.3$ ,  $56.1$  are in correlation with JCPDS standards (JCPDS 31-0174) which make evident the formation of cubic phase of BT (Fig 1b). X-ray data for BIT and BT powders indicate that powders are not well crystallized and that the significant amount of amorphous phase is present. Partical size distribution of BT, BIT and oxide mixture of those two powders is presented on Table 1. It could be concluded that the partical size of powders is mostly under  $1 \mu\text{m}$  confirming that the mechanochemical synthesis leads to nanosized powder.

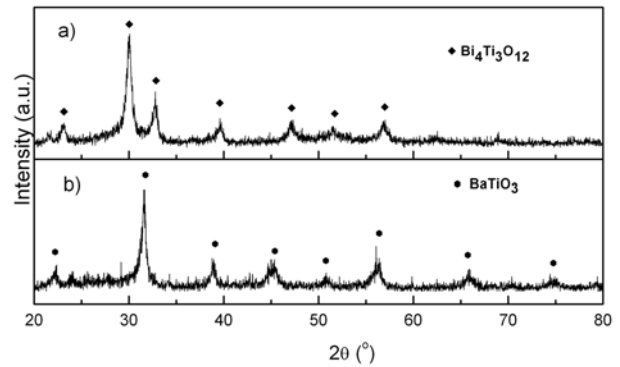


Figure 1. X-ray diffraction patterns of a) BIT and b) BT powders

Table 1. Particle size distribution of BT, BIT and powder mixture of BIT and BT

Powder	$D_{10}$ [ $\mu\text{m}$ ]	$D_{50}$ [ $\mu\text{m}$ ]	$D_{90}$ [ $\mu\text{m}$ ]	< $1 \mu\text{m}$ [%]
BT	0.2100	0.487	2.882	82.50
BIT	0.2060	0.432	1.891	85.82
mixture BT+BIT	0.1800	0.394	1.077	89.80

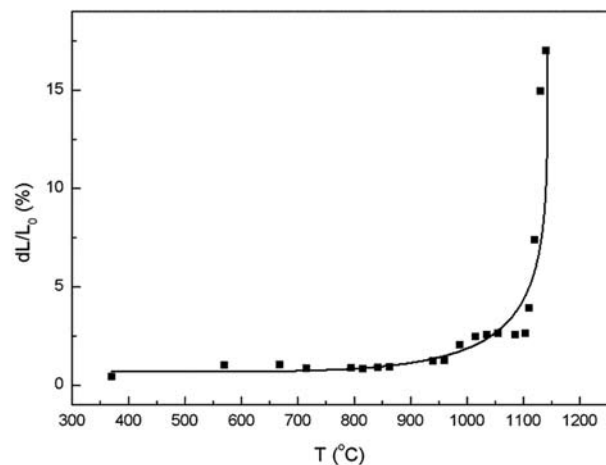


Figure 2. Relative shrinkage ( $\Delta L/L_0$ ) of powder mixture of BT and BIT

Shrinkage behaviour of the pressed pellet prepared from homogenized mixture of BT and BIT powder is presented in Fig. 2 with aim to determinate appropriate temperature of sintering. The shrinkage process that starts at  $720^\circ\text{C}$  can be attributed to solid state reaction between BT and BIT and the shrinkage rate reaches a maximum at  $1120^\circ\text{C}$ . The temperature range of sintering is narrow, from  $1100^\circ\text{C}$  to  $1140^\circ\text{C}$  and whole process can be described as solid state sintering process. According to that BBiT ceramics were sintered at  $1100^\circ\text{C}$ ,  $1110^\circ\text{C}$  and  $1120^\circ\text{C}$  for 1 h without pre-calcination step. The density of sample is about 74.5%, 87.5% and 94%, respectively, indicating the influence of sintering temperature. X-ray analysis of sin-

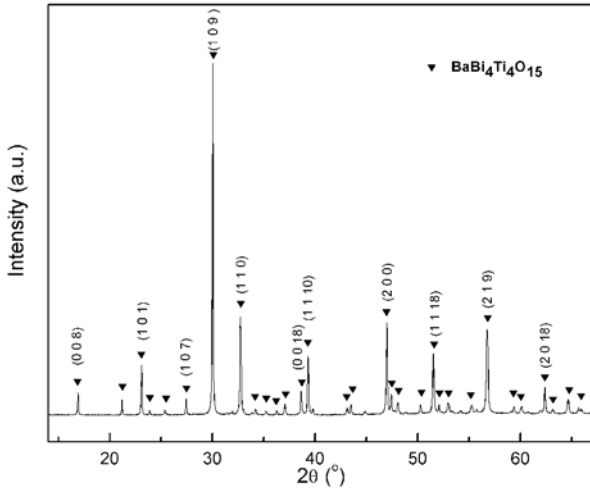


Figure 3. X-ray diffraction pattern of BBiT ceramic sintered at 1120°C for 1 h

tered sample BBiT sintered at 1120°C for 1 h is given in Fig. 3. The observed pattern was in quite good agreement with that reported for tetragonal BBiT (JCPDS 35-0757). BBiT phase was well crystallized and XRD data did not indicate presence of secondary phases.

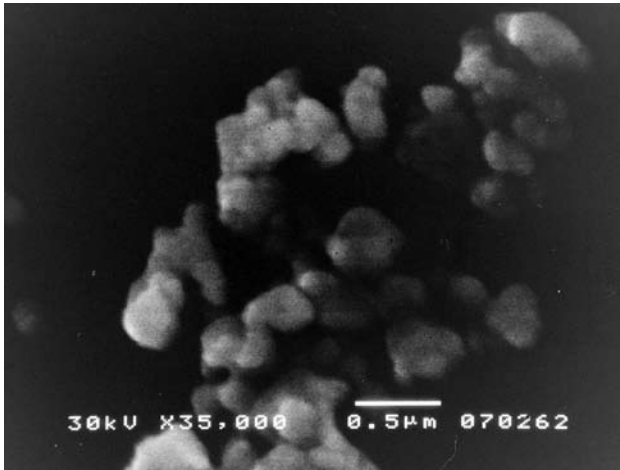


Figure 4. SEM micrograph of homogenized powder mixture of BIT and BT

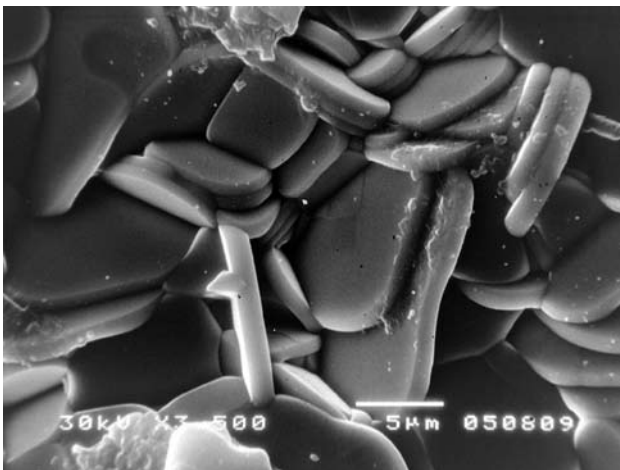


Figure 5. SEM micrograph pattern of BBiT ceramics sintered at 1120°C for 1 h

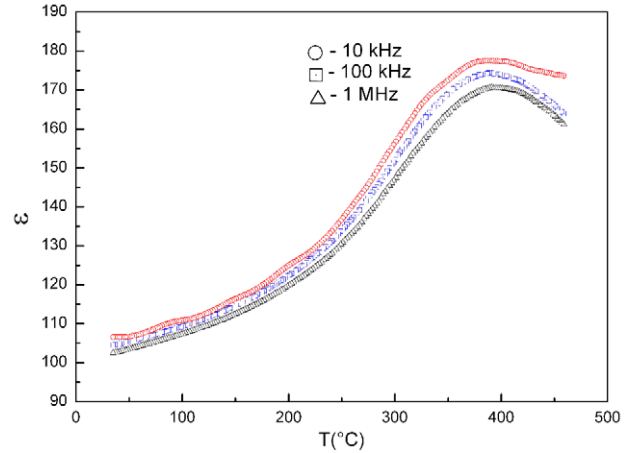


Figure 6. Temperature dependence of dielectric permittivity of BBiT ceramics at 10 kHz and 1 MHz

SEM micrographs of BIT and BT powder mixture are presented in Fig. 4. The mixture consists of agglomerates various size and morphology with approximately size about 250 nm. Meanwhile, it was rather difficult to distinguish separate particles. SEM micrograph of sintered sample of BBiT is shown in Fig. 5. The microstructure of BBiT is dominated by the presence of rounded edges platelet-like grains up to 15 µm size and 1 µm thickness. Similar grain shape has already been observed for many bismuth layered materials, connected with strong anisotropy of crystal structure [10]. The rounded edges of grains could be attributed to liquid phase sintering.

Fig. 6 displays temperature dependence of dielectric permittivity of BBiT ceramics sintered at 1120°C for 1h measured in frequency interval from 10 kHz to 1 MHz. The results give an evidence of a diffuse phase transition accompanied by a relaxation of the permittivity. The temperature  $T_m$  of the maximum permittivity ( $\epsilon_m$ ) is shifted from 380°C to 390°C as the frequency increases from 10 kHz to 1 MHz. This behavior is typical for relaxor ferroelectric. Such a phenomenon has already been observed in several Ba-bearing Aurivillius compounds. The dielectric constant of BBiT ceramic was measured at room temperature in frequency interval from 10 Hz to 1 MHz is 92–94. The dielectric losses measured at room temperature in same frequency range are very small, about 0.008–0.013 (Table 2).

Table 2. Dielectric constant and dielectric losses of BBiT ceramic sintered at 1120°C for 1h, as a function of frequency at room temperature

	1kHz	10 kHz	100 kHz	1 MHz
Capacity, C [pF]	8.2	8.28	8.19	8.06
Dielectric constant, $\epsilon$	93	94	93	92
Dielectric losses, $tg\delta$	/	0.013	0.009	0.008

#### IV. Conclusions

BBiT ceramics were prepared from stoichiometric amount of BT and BIT powders obtained via mechanochemical synthesis by high-energy milling. Powder mixture of BT and BIT consists of agglomerates various size and morphology, which approximately size is 250 nm.

BBiT ceramic sintered at 1120°C for 1 h reveals tetragonal crystal structure possessing microstructure with rounded edges platelet-like grains.

The temperature  $T_m$  of the maximum permittivity ( $\epsilon_m$ ) for BBiT is shifted from 380°C to 390°C with increase of frequency from 10 kHz to 1 MHz. This behavior is typical for relaxor ferroelectric. The dielectric constant of BBiT ceramic performed at room temperature in frequency interval from 1 kHz to 1 MHz is constant with value approximately 93. The dielectric losses measured in the same frequency range are very small, approximately 0.011.

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