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# Study of Barium Bismuth Titanate Prepared by Mechanochemical Synthesis

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*Abstract:*

> *Barium-bismuth titanate, BaBi$_4$Ti$_4$O$_{15}$ (BBT), a member of Aurivillius bismuth-based layer-structure perovskites, was prepared from stoichiometric amounts of barium titanate and bismuth titanate obtained via mechanochemical synthesis. Mechanochemical synthesis was performed in air atmosphere in a planetary ball mill. The reaction mechanism of BaBi$_4$Ti$_4$O$_{15}$ 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 BaBi$_4$Ti$_4$O$_{15}$ ceramic forms at 1100 °C for 4 h without a pre-calcination step. The microstructure of BaBi$_4$Ti$_4$O$_{15}$ exhibits plate-like grains typical for the Bi-layered structured material and spherical and polygonal grains. The Ba$^{2+}$ addition leads to changes in the microstructure development, particularly in the change of the average grain size.*
> *Keywords: Ceramics, BaBi$_4$Ti$_4$O$_{15}$, XRD, Raman spectroscopy, SEM.*

## 1. Introduction

Bi-based Aurivillius family of compounds have received considerable attention as materials for ferroelectric random access memory (FRAM) because of their low operating voltage, field, superior polarization fatigue resistant characteristics and high Curie temperature [1-8]. A large remnant polarization, low coercive field and high Curie temperature are required for better performance of FRAM devices.

Bi-based Aurivillius family of compounds is generalized as Bi$_2$A$_{n-1}$B$_n$O$_{3n+3}$ [9]. The crystal structure consist of `n` number of $(A_{n-1}B_nO_{3n+3})^{2-}$ slabs sandwiched between $(Bi_2O_2)^{2+}$ layers, where `A` represents monovalent, divalent or trivalent elements and `B` represents trivalent, pentavalent or hexavalent metallic cations which are in 12-fold and 6-fold co-ordination, respectively [10-12]. Our present work deals with the compound BBT with `n`=4 and structural formula as $(Bi_2O_2)^{2+}((BaBi_2)Ti_4O_{13})^{2-}$, where the Ba- and Bi-ions occupies the A-site and Ti-ions resides in the B-site, respectively.

Synthesis of BBT ceramics is mainly based on chemical and solid-state reaction methods. Mostly used chemical methods are the polymeric precursors-Pechini process and sol-gel, co-precipitation and hydrothermal method [6, 13]. BBT can be also produced by conventional solid-state reaction starting from BaCO$_3$, TiO$_2$, Bi$_2$O$_3$ [2]. The solid-state reactions initiated by intensive milling in high-energy ball mills could be a good choice for

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ceramic powder preparation. An important criterion for intensive milling is the formation of highly dispersed phased materials typical for metal powders or oxide based materials (mechanical activation) or the formation of a new product because of a solid-state reaction (mechanochemical synthesis). Intensive milling increases the area of contact between the reactant powder particles due to reduction in particle size and allows fresh surfaces to come into contact. This allows the reduction to proceed without the necessity for diffusion through the product layer. As a consequence, solid-state reactions that normally require high temperatures will occur at lower temperature during mechanochemical synthesis without any externally applied heat.

Mechanically activated processes have been recently employed by Benjamin and Gilman to prepare nanosized oxides and compounds [14]. The intrinsic characteristic of this technique is that the solid-state reaction is activated via mechanical energy instead of heat energy (high temperature). Several advantages can be listed for this mechanical synthesis process. Firstly, it uses low-cost and widely available oxides as the starting materials and skips the calcinations step at an intermediate temperature, leading to a simplified process [15, 16]. Secondly, it takes place at a temperature close to room temperature in a sealed container. Furthermore, the mechanically derived powders possess a higher sinterability than those powders synthesized by a conventional solid-state reaction and most wet-chemical processes. Mechanical activation is a very effective method for obtaining nanostructure powders, which are of the main interest of miniaturization and integration of electronic components. Having this in mind, the synthesis of more resistive bismuth based materials would be a preferable advance in obtaining well-dense ceramic with small grains randomly oriented to limit the conductivity along the $(Bi_2O_2)^{2+}$ layers. The conventional ceramic route for the synthesis leads to non-stoichiometry in the composition of the resultant BIT powder, in consequence of the undesirable loss in bismuth content through volatilization of $Bi_2O_3$ at elevated temperature [17, 18]. Mechanical activation has not been studied much for the bismuth-based layer structure perovskites such as $BaBi_4Ti_4O_{15}$ ceramics. Taking this in account, the objective of this work is to study the feasibility of formation of BBT by mechanochemical synthesis. BBT ceramic is formed from a mixture of barium titanate $BaTiO_3$ (BT) and bismuth titanate $Bi_4Ti_3O_{12}$ (BIT). BT species were prepared by milling from BaO and $TiO_2$ and BIT was obtained from $TiO_2$ and $Bi_2O_3$. After that the mixture of amorphous BT and BIT was homogenized and sintered. The structure and properties of BBT powder and BBT ceramic were determined.

## 2. Experimental procedure

In the present work BBT was prepared from stoichiometric quantities of BT and BIT obtained via mechanochemical synthesis. BT was synthesized from mixture of BaO (BaO, Alfa Aesar, p.a. 99%) and $TiO_2$ in anatase crystal form ($TiO_2$, Alfa Aesar, p.a. 99.9%) and BIT was prepared starting from $Bi_2O_3$ ($Bi_2O_3$, Alfa Aesar, p.a. 99.8%) and $TiO_2$ [18], 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 6 h of milling. Milling conditions were: zirconium oxide jars and zirconium oxide balls ($d$ = 10 mm), ball-to-powder weight ration 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 BT and BIT was homogenized for 30 min (speed 142 min−1) and then pressed into pellets using a cold isostatic press (8 mm in diameter and  3 mm thick). Their powder mixture was sintered at 1100∘C for 4 h (Lenton-UK oven) without the pre-calcinations step. The heating rate was 10 °C min$^{-1}$, with natural cooling in air atmosphere. Separately, BIT was sintered at 1000 °C for 12 h and BT was sintered at 1300 °C for 2 h. Formation of the phase and crystal structure

of BT, BIT and BBT was followed using a X-ray diffractometer (XRD, Model D5000, Siemens) with Cu kα radiation ($\lambda_{k\alpha1}$ = 1.5405 Å , $\lambda_{k\alpha2}$ = 1.5443 Å, $I_{k\alpha1}/I_{k\alpha2}$ = 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 morphology and microstructure of obtained powders were examined using scanning electron microscope (SEM, Model JEOL-JSM5300 and SEM, Model Topcon SM-300). Powders were prepared for SEM examination by dissolving in ethanol in an ultrasonic bath. Disc shaped sintered samples were prepared for microstructure examination and electrical properties by polishing to a thickness of 1 mm with silicon carbide and alumina powder and cleaning in an ultrasonic bath in ethanol. For SEM analysis the samples were thermally etched at 950 °C for 20 min.

Raman measurement of BBT was performed at room temperature in the spectral range from 100 to 1000 cm$^{-1}$, in back scattering geometry. Raman spectra 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$^{-2}$.


## 3. Results and discussions

Formation mechanisms of nanopowders by mechanically assisted synthesis (mechanochemical synthesis) are complex and not yet clear. During the ferroelectric materials formation, the process passes through several steps. Generally, it starts with the decrease in particle and grain size of starting materials following by nucleation and crystallization of the target compound. As the result of mechanically assisted synthesis, nanocrystalline powders can be obtained directly from their oxide mixtures after milling. Fig. 1 shows the SEM photograph of the powder mixture of $Bi_4Ti_3O_{12}$ and $BaTiO_3$. The morphology of the mixture powders after mechanical activation consists of particles and its agglomerates. In order to determine the individual particle size, the smallest agglomerate was chosen. Meanwhile, it was rather difficult to evaluate the correct value. By rough estimation and using Scherrer`s formula:

$$\tau = \frac{0.9\lambda}{\beta_\tau \cos\vartheta}$$

where $\tau$ is the crystallite size, 0.9 (*K*) is shape factor, $\beta_\tau$ is the line broadening due to the effect of small crystallites and $\theta$ the diffraction angle [19]. Here $\beta_\tau = (B - b)$, *B* being the breadth of the observed diffraction line at its half-intensity maximum, and *b* the instrumental broadening. It was found that the individual particle size of powders was approximately 50 nm.
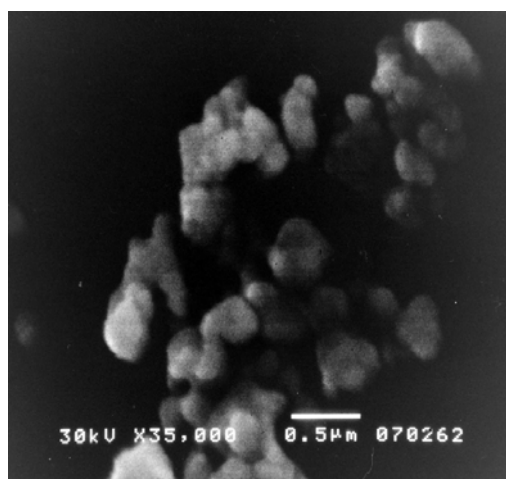


**Fig.1.** SEM micrograph of homogenized powder mixture of $Bi_4Ti_3O_{12}$ and $BaTiO_3$.

The effect of mechanical treatment on the crystallite size is quite evident: the agglomerates and particles depend on the synthesis method. The particles have a spherical and polygonal shape. The mixture consists of agglomerates of various size and morphology with an approximate size of about 250 nm.
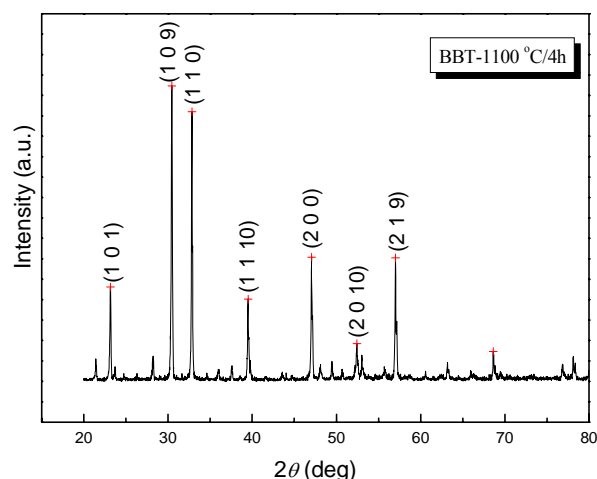


**Fig. 2.** X-ray diffraction pattern of $BaBi_4Ti_4O_{15}$ ceramic sintered at 1100 °C for 4 h.

Fig. 2 shows the X-ray diffraction spectra of $BaBi_4Ti_4O_{15}$ ceramics. The effect of mechanochemical activation can be detected after carrying out thermal treatment on the sample. The spectrum of the sample sintered at 1100 °C for 4 h, without a pre-calcinations step, shows clear peaks of crystalline BBT and demonstrates complete Bi-layered perovskite structure phase formation. BBT phase is well crystallized and secondary phases were not observed. The observed pattern was in excellent agreement with that reported for tetragonal $BaBi_4Ti_4O_{15}$ in JCPDS #35-0757.

It is notable that materials with a small crystallite size, as in the investigated case, belong to a higher crystal structure symmetry. The tetragonal structure was also mentioned by Bobic and co-authors for BBT obtained at low calcination temperatures confirming the influence of small crystallite size on crystal symmetry [20]. Thus, in further calculations barium bismuth titanate shall be mentioned as a material with a tetragonal crystal symmetry of an Aurivillius phase Bi-layered oxide. The bismuth layer of $(Bi_2O_2)^{2+}$ interleaved with the perovskite like $(A_{m-1}B_mO_{3m+1})^{2-}$ layers. It has been shown that the ferroelectric properties of the Aurivilius bismuth-layer compounds are strongly dependent on the number of layers and the chemical elements in the *A* and *B* sites [21]. The $MBi_4Ti_4O_{15}$ compounds with layer number $m = 4$ ($M$ = Ca, Ba, Sr) are a subgroup of this bismuth-layer structure compounds (Fig. 3).

The Raman spectra of $BaBi_4Ti_4O_{15}$ have three modes at around 160, 280 and 880 cm$^{-1}$ at room temperature (Fig. 4). The low-frequency modes are considerably damped, whereas the basic modes are wider in comparison to Raman modes originating from pure $Bi_4Ti_3O_{12}$. Such damped frequencies provide indications that this compound has a disordered structure, i.e. Ba-ions are likely to be randomly configured on Bi-ion sites in the $BaBi_4Ti_4O_{15}$ 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. The two modes of $Bi_4Ti_3O_{12}$ around 537 cm$^{-1}$ and 615 cm$^{-1}$ change into a band in $ABi_4Ti_4O_{15}$ ($A$= Ba) around 558 cm$^{-1}$. This fact can be due to the line-broadening of the two modes caused by the structural disorder in $BaBi_4Ti_4O_{15}$ [22]. Hence this

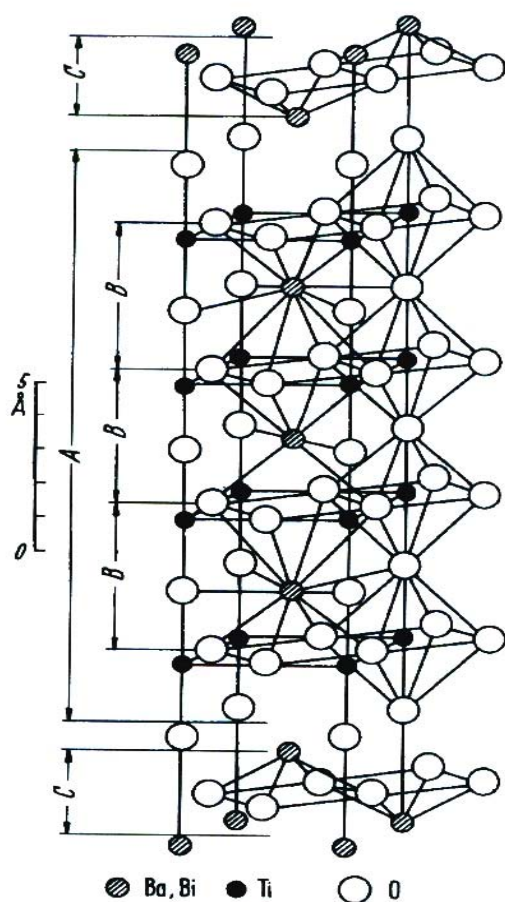mode corresponds to the vibration in a pseudo-perovskite layer.



**Fig. 3.** The lattice structure of BBT ceramics.

Also, the mode at 880 cm$^{-1}$, whose frequency amounts 851 cm$^{-1}$ in the case of a pure Bi$_4$Ti$_3$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 vibrations of the Ba-O bond.
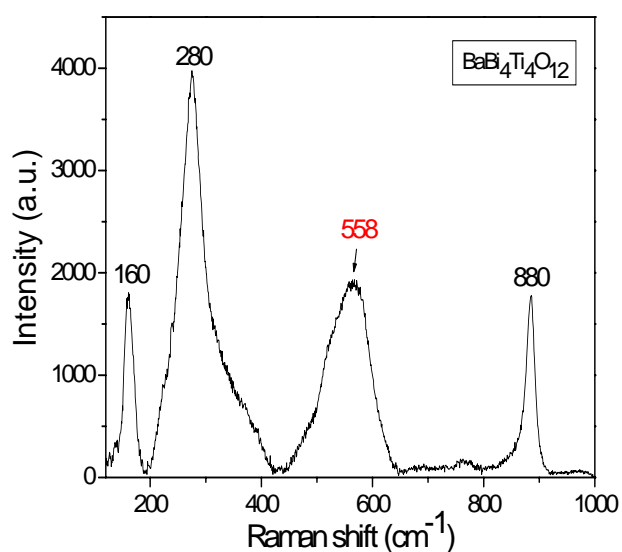


**Fig. 4.** Raman spectra at room temperature of the BaBi$_4$Ti$_4$O$_{15}$ ceramic sintered at 1100 °C for 4 h.

Fig. 5 shows the microstructure of the $BaBi_4Ti_4O_{15}$ ceramic prepared from BBT powders obtained by mechanical activation after 30 min and sintered at 1100 °C for 4 h. It can be observed that in sintered sample of BBT beside plate-like grains also spherical and polygonal grains exist. Having in mind that the microstructure has a strong influence on properties, a detailed investigation of the sintering process and microstructure of BBT is in progress.
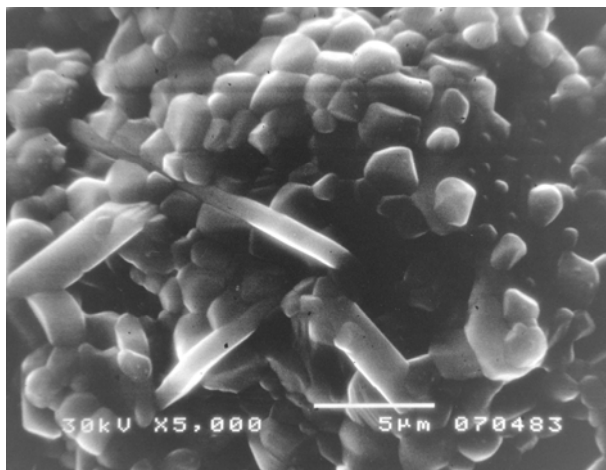


**Fig. 5.** SEM micrograph pattern of $BaBi_4Ti_4O_{15}$ ceramic sintered at 1100 °C for 4 h.

The removal of the same 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. 5, 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 the theoretical density.

## 4. Conclusions

Bi-layered structure ferroelectric material-bismuth titanate, $Bi_4Ti_3O_{12}$ (BIT) and barium-bismuth titanate, $BaBi_4Ti_4O_{15}$ (BBT) ceramic powders were prepared by the mechanical synthesis process. XRD shown that synthesized BBT has a tetragonal structure of an Aurivillius phase Bi-layered oxide. Only 4 Raman bonds were clearly observed. It is evident that $Ba^{2+}$ addition leads to the change in microstructure development. $BaBi_4Ti_4O_{15}$ with good crystalline structure was formed after sintering without a pre-calcination step with a plate-like structure typical for layered structure materials.

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## References

1.  C. A. P. de Araujo, J. D. Cuchiaro, L. D. McMillan, M. Scott, J. F. Scott, Nature, 374

(1995) 627.

2.  B. J. Kennedy, Y. Kubota, B. A. Hunter, Ismunandar, K. Kato, Solid State Commun., 126 (2003) 653.
3.  R. Z. Hou, X. M. Chen, Y. W. Zeng, J. Am. Ceram. Soc., 89 (2006) 2839.
4.  J. Tellier, Ph. Boullay, M. Manier, D. Mercurio, J. Solid State Chem., 177 (2004) 1829.
5.  J. Tellier, Ph. Boullay, D. B. Jennet, D. Mercurio, J. Eur. Ceram. Soc., 27 (2007) 3687.
6.  D. Xie, W. Pan, Mater. Lett., 57 (2003) 2970.
7.  T. Kimura, Y. Yoshida, J. Am. Ceram. Soc., 89 (2006) 869.
8.  A. Chakrabarti, J. Bera, T. P. Sinha, Physica B: Condensed Matter., 404 (2009) 1498
9.  B. Aurivillius, Arkiv. Kemi., 1 (1950) 519.
10. V. Shrivastava, A. K. Jha, R. G. Mendiratta, Solid State Commun., 133 (2005) 125.
11. L. E. Cross, Ferroelectrics, 151 (1994) 437.
12. Ismunandar, T. Kamiyama, A. Hoshikawa, Q. Zhou, B. J. Kennedy, Y. Kubota, K. Kato, J. Solid State Chem., 177 (2004) 4188.
13. A. V. Murugan, S. C. Navale, V. Ravi, Mater. Lett., 60 (2006) 1023.
14. J. S. Benjamin, Sci. Am., 234 (1976) 40.
15. R. M. German, Sintering theory and practice, Wiley, New York, 1996.
16. J. Wang, J. M. Xue, D. M. Wan, B. K. Gan, J. Solid State Chem., 154 (2000) 321.
17. C. Jovalekic, M. Pavlovic, O. Osmokriovic, Lj. Atanasoska, Appl. Phys. Lett., 72 (1998) 1051.
18. B. D. Stojanovic, C. O. Paiva-Santos, C. Jovalekic, A. Z. Simoes, F. M. Filho, Z. Lazarevic, J. A. Varela, Mater. Chem. Phys., 96 (2006) 471.
19. B. E. Warren, X-ray Diffraction, Addison-Wesley, Reading, MA, 1969, p. 253.
20. J. D. Bobic, B. D. Stojanovic, M. M.Vijatovic, T. Rojac, 4th Workshop COST 539 Action - ELENA, 2008, Brussels, Belgium, Programme and Book of Abstracts, 59.
21. V. A. Isupov, Ferroelectrics, 189 (1996) 211.
22. S. Kojima, R. Imaizumi, S. Hamazaki, M. Takashige, Jpn. J. Appl. Phys., 33 (1994) 5559.

**Садржај:** *Баријум бизмут титанат, $BaBi_4Ti_4O_{15}$ (BBT), члан Aurivillius-ове групе перовскитних једињења, је припремљен поступком механохемијске синтезе из одговарајуће количине баријум титаната и бизмут титаната. Механохемијска синтеза је изведена у атмосфери ваздуха у млину са куглама. Реакциони механизам $BaBi_4Ti_4O_{15}$, добијање и карактеристике BBT керамичког праха су биле проучаване користећи методу XRD, Раман спектроскопију, анализу честица и CEM. Bi-слојевита перовскитна структура $BaBi_4Ti_4O_{15}$ керамике је добијена на 1100 °C за 4 h без претходне калцинације. Микроструктура $BaBi_4Ti_4O_{15}$ је у облику плочастих зрна што је типично за Bi-слојевите структурне материјале и сферних и полигоналних зрна. Додатак $Ba^{2+}$ доводи до промене у развоју микроструктуре, нарочито у промени просечне величине зрна.*

**Кључне речи:** *Керамика, $BaBi_4Ti_4O_{15}$, XRD, Раман спектроскопија, CEM.*