Structure study of Bi₄Ti₃O₁₂ produced via mechanochemically assisted synthesis

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Abstract
Nanosized bismuth titanate was prepared via high-energy ball milling process through mechanically assisted synthesis directly from their oxide mixture of Bi₂O₃ and TiO₂. Only Bi₄Ti₃O₁₂ phase was formed after 3 h of milling time. The excess of 3 wt% Bi₂O₃ added in the initial mixture before milling does not improve significantly the formation of Bi₄Ti₃O₁₂ phase comparing to stoichiometric mixture. The formed phase was amorphized independently of the milling time. The Rietveld analysis was adopted to determine the crystal structure symmetry, amount of amorphous phase, crystallite size and microstrains. With increasing the milling time from 3 to 12 h, the particle size of formed Bi₄Ti₃O₁₂ did not reduced significantly. That was confirmed by SEM and TEM analysis. The particle size was less than 20 nm and show strong tendency to agglomeration. The electron diffraction pattern indicates that Bi₄Ti₃O₁₂ crystalline powder is embedded in an amorphous phase of bismuth titanate. Phase composition and atom ratio in BIT ceramics were determined by X-ray diffraction and EDS analysis.

Keywords: A. Ceramics; A. Nanostructures; C. Electron microscopy; C. X-ray diffraction; D. Crystal structure

1. Introduction
Bismuth titanate—Bi₄Ti₃O₁₂ (BIT) belongs to the Aurivillius family with a general formula (Bi₂O₂) [Aₘ₋₁(B)ₘO₃ₘ₊₁], which consists of (Bi₂O₂)²⁺ sheets alternating with (Bi₂Ti₃O₁₀)²⁻ perovskite-like-layers [1]. In general formula m represents the number of octahedra stacked along the direction perpendicular to the sheets, and A and B are the 12- and 6-fold coordination sites of perovskite slab, respectively [2]. This kind of structure promotes plate-like morphology. The platelets are apparently single crystals with c-axis perpendicular to the major face [2] and with the higher component of its spontaneous polarization parallel to a–b plane [3]. At room temperature the symmetry of BIT is monoclinic, while by the X-ray and neutron diffraction patterns can be considered as orthorhombic structure with a = 0.5448, b = 0.411 and c = 3.283 nm [3,4].

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BIT is a ferroelectric material with wide application in the electronic industry as capacitors, memory devices and sensors [4]. It undergoes a ferroelectric to paraelectric phase transition at the Curie temperature at 675 °C [3], which give it a potential applicability as a suitable candidate for high temperature piezoelectric device. Moreover, it is considered to be a promising lead-free, environmentally friendly material alternative to PZT [7].

Recently, efforts have been devoted to Bi_4Ti_3O_12 ceramics and thin films fabricated by various methods. The conventional ceramic route usually causes the non-stoichiometry, in consequence of the undesirable loss in bismuth content through volatilization of Bi_2O_3 at elevated temperature [5–8]. In addition, crystallite coarsening and particle aggregation are unavoidable because of the interfacial diffusions and reactions that occur at the rather high calcinations temperature [9]. Many efforts have been made to avoid this problem by lowering the calcinations temperatures [14] or using wet-chemistry-based methods. Hence, many chemistry-based preparations, such as precipitation, sol–gel, hydrothermal and molten salt route have been investigated as alternatives [5–12]. However, the wet-chemistry involves chemicals that are sensitive to moisture or light, which makes them difficult to deal with, especially for bismuth salts [13]. Most of the chemistry-based processing routes require post-precursor calcinations to realize the precursor-to-ceramic conversion [11–16].

Benjamin [17], along with co-workers, made the important discovery of mechanical alloying, which was devised for synthesizing alloys and intermetallics. Recently, mechanically activated processes have been employed to prepare nanosized oxides and compounds pointing that the mechanical technique can be superior to conventional solid-state reaction and wet-chemistry-based processing routes for several reasons. It uses low-cost and widely available oxides as starting materials, in certain cases make possible the solid-state reaction during milling (mechanically assisted synthesis) skipping the calcinations step and simplifying the process.

The mechanical activation based on milling process has been employed with success for Pb-based materials [18]. Meanwhile, it has not been much mentioned for layered structured materials as Bi_4Ti_3O_12 ceramics. Several articles including our previous results were published in regard to preparation of BIT using milling technique [18–21]. In this paper, we present advanced results due to mechanically assisted synthesis of BIT with aim to explain the influence of milling into formation of crystalline and amorphous form of bismuth titanate powders considering Bi_4Ti_3O_12 crystal symmetry, crystallite size, microstrains and powder morphology. Orthorhombic crystal structure of BIT ceramics was approved.

2. Experimental procedure

The bismuth titanate was prepared starting from bismuth oxide (Bi_2O_3, Fluka, p.a.99.8%) and titanium oxide (TiO_2), in an anatase crystal form, TiO_2 anatase, Carlo Erba p.a. 99% commercially available. These oxide powders exhibited a particle size distribution in the range 2–4 μm for TiO_2 and 1–5 μm for Bi_2O_3. To make a batch required for stoichiometric BIT composition and BIT with 3 wt% excess of Bi_2O_3, corresponding amount of Bi_2O_3 and TiO_2 were weighed and loaded into zirconium jars together with zirconium milling balls ~10 mm in diameter. Mechanically assisted synthesis was performed in air atmosphere in a planetary ball mill (Fritch Pulverisette 5). Milling conditions were the following: zirconium oxide jars and zirconium oxide balls, ball-to-powder weight ratio 20:1, air atmosphere, basic disc rotation speed was 317 min\(^{-1}\), rotation speed of disc with jars 396 min\(^{-1}\), and milling time 0, 1, 3, 6 and 12 h. Sintering of BIT was performed in chamber furnace in close system at 1000 °C for 2 h with heating rate 10 °C min\(^{-1}\).

The X-ray diffraction data for milled powders and sintered ceramics were collected using a Rigaku\textsuperscript{\textregistered} RINT2000 diffractometer (42 kV X 120 mA) with Cu kα radiation (λ\(_{kα1}\) = 1.5405 Å, λ\(_{kα2}\) = 1.5443 Å, I\(_{kα1}/I_{kα2}\) = 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 [22] was performed with the Rietveld refinement program package General Structure Analysis System (GSAS) of Larson and Von Dreede [23]. The peak profile function was modeled using a convolution of the pseudo-Voigt [24] with the asymmetry function described by Finger et al. [25], which accounts for the asymmetry due to axial divergence. To account the percent of crystalline and amorphous phase in BIT powders, well crystalline cerium oxide was used as the internal standard in X-ray diffraction analysis. The powder mixture consisted of approximately 93 wt% of BIT and 7 wt% of CeO_2 (Table 1). Rietveld refinements were performed to identify the amount of crystalline and amorphous phase and the symmetry of the Bi_4Ti_3O_12 phase (tetragonal or orthorhombic).

Scanning electron microscopy (SEM, Model JOEL-5300) was used to carry out the agglomerate size and particle size; however, the particle size was performed only as a rough estimation. EDS–PGT digital Spectrometer observation
was made to identify chemical phase composition of sintered BIT sample and estimated ratio of Bi/O, Ti/O and Bi/Ti. Transmission electron microscopy (TEM, Model Philips CM200) was carried out to particle size and powder morphology analysis. The electron diffraction pattern of TEM was used to study the coexistence of the crystalline/amorphous phase in synthesized BIT powder. BET analysis was performed to consider the specific surface area change affected by milling time.

3. Results and discussion

Formation mechanisms of nanosized powders via mechanochemical process are complex and not yet clear. It is recognized that during the ferroelectric materials formation, the process passes through few steps. Generally, it starts with the decrease in particle and grain size of starting materials following by the nucleation and crystallization of target compound. As the result of mechanically assisted synthesis, nanocrystalline powders can be obtained directly from their oxide mixtures after milling.

The Bi₄Ti₃O₁₂ phase evolution prepared as stoichiometric composition or with 3 wt% excess of Bi₂O₃ was monitored by X-ray analysis (Figs. 1 and 2). The XRD analysis of BIT powder, treated for different milling time, showed a rapid increase of the Bi₄Ti₃O₁₂ phase formation after 60 min of milling time. Longer time of milling (3, 6 and 12 h, respectively) triggered strong solid state reaction among amorphised initial species. Upon 3 h of milling, the observed peaks at 2θ angles 21.5°, 22.9°, 29.8°, 32.7°, 39.6°, 47.1°, 51.4° and 56.8° can be attributed to the formation of bismuth titanate—Bi₄Ti₃O₁₂. The formed structure can be tetragonal or orthorhombic. However, in this case it is rather difficult to distinguish between these two crystal structures based only on the observations of XRD data due to the intense superposition of the broadened peaks. Then, the crystal structure of stoichiometric bismuth titanate obtained for 12 h of milling time was analyzed by Rietveld method, considering both cases: tetragonal and

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Percentage of BIT and CeO₂ in the mixture used to determine amorphous content in the BIT stoichiometric (s) and with excess (x) of Bi₂O₃, milled for 3 and 12 h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BIT (%)</td>
</tr>
<tr>
<td>3 h</td>
<td></td>
</tr>
<tr>
<td>s</td>
<td>93.07</td>
</tr>
<tr>
<td>x</td>
<td>92.84</td>
</tr>
<tr>
<td>12 h</td>
<td></td>
</tr>
<tr>
<td>s</td>
<td>90.82</td>
</tr>
<tr>
<td>x</td>
<td>94.91</td>
</tr>
</tbody>
</table>

Fig. 1. XRD patterns of stoichiometric Bi₄Ti₃O₁₂ produced by mechanically assisted synthesis by milling for 1, 3, 6 and 12 h.
Fig. 2. XRD patterns of Bi$_4$Ti$_3$O$_{12}$ prepared with 3 wt% excess of Bi$_2$O$_3$ milled for 1, 3, 6 and 12 h.

Fig. 3. Rietveld refinement analysis of Bi$_4$Ti$_3$O$_{12}$ produced by milling for 12 h considering the tetragonal structure symmetry.

Fig. 4. Rietveld refinement analysis of Bi$_4$Ti$_3$O$_{12}$ produced by milling for 12 h considering the orthorhombic structure symmetry.
orthorhombic structure, and comparing with the refinement indexes. The obtained results indicate that the difference is rather small, however with a small advantage to tetragonal crystal structure case (Rwp = 7.26%, $\chi^2 = 1.193$ for tetragonal, and Rwp = 7.59%, $\chi^2 = 2.1614$ for orthorhombic structure). Figs. 3 and 4 present Rietveld plot for tetragonal and orthorhombic symmetry where one can see that there is no visible difference between them.

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 Kan et al. (2002) and Thongtem et al. (2004) for Bi$_4$Ti$_3$O$_{12}$ obtained at low calcinations temperature confirming the influence of small crystallite size on crystal symmetry [14]. Thus, in further calculation the bismuth titanate shall be mentioned as material with tetragonal crystal symmetry of an Aurivillius phase Bi-layered oxide, denoted by the formula (Bi$_2$O$_2$)$_{2+}$ (Bi$_2$Ti$_3$O$_{10}$)$_{2-}$, in which perovskite units of Ti–O octahedra are sandwiched between Bi$_2$O$_2$ layers (Fig. 5). The Rietveld agreement indexes and crystal lattice parameters are shown in Table 2.

![Schematic presentation of crystal structure of an Aurivillius layered Bi$_4$Ti$_3$O$_{12}$ compound.](image-url)
The XRD analysis of Bi$_4$Ti$_3$O$_{12}$ produced by mechanically assisted synthesis through milling show a typical background of an amorphous phase. The wt% of crystalline and amorphous phase calculated using the Rietveld refinements is also presented in Table 2. In species milled for 3 h, it is possible to note a rather small presence of an other phase (denoted as ‘*’ in the Table 2 and Fig. 6), that was not possible to be identified. However, that phase is most probably associated to the Bi$_2$O$_3$, TiO$_2$ rutile and non-stoichiometric Ti$_2$O$_3$, which shall be destroyed during longer milling time without notable influence on the increase of amount of the crystalline phase. All BIT powders prepared with and without excess Bi$_2$O$_3$ showed a minor change in the crystallization/amorphization process. The amorphous phase is in majority and less than 40% of BIT belongs to crystalline phase. Rather small increase of amorphous phase with milling time is observed. The decrease of crystalline phase in compared to amorphous is approximately 4% more in the species prepared with excess of bismuth oxide (60.4% after 3 h in comparison with to 64.1% after 12 h of milling time). Most probably, this is caused by the solid-state reaction of species in the phase denoted as ‘*’, which results in the further formation of amorphous bismuth titanate. The crystal size and microstrains are presented in Table 3. It is obvious that the formed BIT is nanocrystalline with crystallite size 10–17 nm. Small increase of crystallite size is observed with milling time in the BIT species prepared with excess of Bi$_2$O$_3$. The high percentage of amorphous phase and small crystallite size can be possible reason for the tetragonal structure to be formed with small preference. The microstrains $\Delta d/d$ is less than 0.02. The milling time did not affect notable change of microstrains.

Fig. 7(a)–(d) shows the SEM images of BIT powders milled for 1, 3, 6 and 12 h. The powder dissolved in kerosene was de-agglomerate in ultrasonic bath before analysis. The images reveal that beside observed agglomerates, which could not be destroyed in above mentioned process, the material is rather amorphized due to fact that it was not possible to distinguish separate particles. The tendency to be agglomerated increase with milling time. The individual particle size was very difficult to determine due to indistinct image at higher magnification.

### Table 2

<table>
<thead>
<tr>
<th>Bi$_4$Ti$<em>3$O$</em>{12}$</th>
<th></th>
<th></th>
<th></th>
<th>Rwp</th>
<th>$\chi^2$</th>
<th>am %</th>
<th>cr %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 h</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>s</td>
<td>3.8612(5)</td>
<td>32.782(7)</td>
<td>488.7(2)</td>
<td>7.65</td>
<td>2.044</td>
<td>63.4*</td>
<td>36.6</td>
</tr>
<tr>
<td>x</td>
<td>3.8640(5)</td>
<td>32.897(10)</td>
<td>491.2(2)</td>
<td>7.85</td>
<td>2.614</td>
<td>60.4*</td>
<td>39.6</td>
</tr>
<tr>
<td>12 h</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>s</td>
<td>3.8663(6)</td>
<td>32.648(8)</td>
<td>488.0(2)</td>
<td>7.26</td>
<td>1.973</td>
<td>63.1</td>
<td>36.9</td>
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<tr>
<td>x</td>
<td>3.8578(3)</td>
<td>32.604(6)</td>
<td>485.25(8)</td>
<td>7.88</td>
<td>2.193</td>
<td>64.1</td>
<td>35.9</td>
</tr>
</tbody>
</table>

* Including the non-identified phases.

Fig. 6. XRD patterns of Bi$_4$Ti$_3$O$_{12}$ (stoichiometric and with excess of bismuth oxide), including CeO$_2$ internal standard, indicating the non-identified phase.
TEM images of bismuth titanate powder milled for 3 and 12 h are presented in Figs. 8 and 9. The images present in Figs. 8(a) and 9(a) reveal that the specimen consists of nanocrystalline particles and amorphous region with crystallite size less than 20 nm that is in agreement with XRD study. Figs. 8(b) and 9(b) display the electron diffraction pattern of the amorphized powder containing both halo rings and diffraction spots. It can be seen that halo rings are superimposed on the diffraction spots indicating that BIT crystalline powder is embedded in an amorphous phase. However, a pure amorphous material would show only diffuse halo rings without any sign of diffraction spots, which was not observed in the investigated Bi$_4$Ti$_3$O$_{12}$ system. The difference in electron diffraction pattern for BIT powders milled 3 h (Fig. 6(b)) and 12 h (Fig. 7(b)) is not significant, that is in agreement with XRD study. To distinguish the difference in electron pattern more detail study probably shall be necessary. Fig. 10 presents TEM image of

<table>
<thead>
<tr>
<th>Bi$_4$Ti$<em>3$O$</em>{12}$</th>
<th>$t$ (nm)</th>
<th>$(\Delta d/d)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 h</td>
<td></td>
<td></td>
</tr>
<tr>
<td>s</td>
<td>13.8</td>
<td>0.019</td>
</tr>
<tr>
<td>x</td>
<td>10.6</td>
<td>0.014</td>
</tr>
<tr>
<td>12 h</td>
<td></td>
<td></td>
</tr>
<tr>
<td>s</td>
<td>12.9</td>
<td>0.016</td>
</tr>
<tr>
<td>x</td>
<td>17.5</td>
<td>0.016</td>
</tr>
</tbody>
</table>

Table 3
Crystallite size ($t$) and microstrain ($\Delta d/d$) for the Bi$_4$Ti$_3$O$_{12}$ in the BIT stoichiometric (s) and with excess (x) of Bi$_2$O$_3$, milled for 3 and 12 h.

Fig. 7. SEM image of BIT powders milled for (a) 1 h, (b) 3 h, (c) 6 h, and (d) 12 h.
Fig. 8. (a) TEM image of crystalline/amorphous Bi$_4$Ti$_3$O$_{12}$ powder obtained after milling of 3 h and (b) electron diffraction pattern for the same Bi$_4$Ti$_3$O$_{12}$ powder.

Fig. 9. (a) TEM image of crystalline/amorphous Bi$_4$Ti$_3$O$_{12}$ powder obtained after milling of 12 h and (b) electron diffraction pattern for the same Bi$_4$Ti$_3$O$_{12}$ powder.

Fig. 10. TEM image of stoichiometric Bi$_4$Ti$_3$O$_{12}$ specimen obtained after 6 h of milling time with nanocrystalline particles in an amorphous region and typical order of nanocrystalline planes (inset in Fig. 10).
A stoichiometric Bi$_4$Ti$_3$O$_{12}$ specimen obtained after 6 h of milling time indicating the nanocrystalline particles in an amorphous region and several nanocrystalline planes organized in parallel order (inset in Fig. 10).

The specific surface area of BIT powder changes during milling depending on whether the breaking process of particles or the secondary agglomeration process dominates or mechanically assisted synthesis occurred. At the beginning of milling, the specific surface area decreases compared to specific surface area obtained with prolongation of milling time. When BIT becomes the dominant phase, mechanically assisted synthesis process is dominant to the secondary agglomeration process. This corresponds to the increase of the value of specific surface area, from 5.6 m$^2$ g$^{-1}$ at the beginning of milling to 16.1 m$^2$ g$^{-1}$ after 3 h. The decrease trend of specific surface area from 16.1 to 12.6 m$^2$ g$^{-1}$ can be seen after 12 h of milling as a result of secondary agglomeration processes that was in agreement with SEM results.

Before sintering BIT powders were ultrasonically treated to destroy the agglomerates formed during milling and after that press in pellets. The XRD pattern of BIT sintered at 1000 °C for 2 h as-prepared from powders milled for 12 h is presented in Fig. 11. It can be seen that BIT is well crystallized and that the orthorhombic structure become the dominant phase in compared to tetragonal structure (JCPDS-card 35-0795, orthorhombic and JCPDS-card 47-0398, tetragonal).

![XRD pattern](image)

**Fig. 11.** XRD powder patterns obtained on sample sintered at 1000 °C for 2 h and prepared from mechanically activated powders for 12 h.

![EDS analysis](image)

**Fig. 12.** EDS analysis of BIT.
Table 4
Estimated atom ratio obtained by EDS analysis of BIT

<table>
<thead>
<tr>
<th>Element</th>
<th>Spect. type</th>
<th>Element %</th>
<th>Atom %</th>
<th>Ratio/type</th>
<th>Ratio/theor.</th>
<th>Ratio/exper.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti K</td>
<td>ED</td>
<td>12.46</td>
<td>15.95</td>
<td>Bi/O</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>Bi M</td>
<td>ED</td>
<td>71.06</td>
<td>21.06</td>
<td>Ti/O</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>O</td>
<td></td>
<td>16.48</td>
<td>63.19</td>
<td>Bi/Ti</td>
<td>1.33</td>
<td>1.32</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Qualitative and quantitative EDS analyses of BIT ceramics were performed and the Bi/O, Ti/O and Bi/Ti ratio was calculated. To calculate the ratio, an average of a least five measurements on the sintered sample was taken. As a standard sample was used commercial hot pressed Bi$_4$Ti$_3$O$_{12}$ and the results of quantitative EDS analyses could be considered comparatively. The atomic ratio for standard sample is Bi/O = 0.33, Ti/O = 0.25 and Bi/Ti = 1.33. Investigated BIT ceramics prepared by mechanochemically assisted synthesis shows ratio of Bi/O = 0.33, Ti/O = 0.25 and Bi/Ti = 1.32 (Fig. 12 and Table 4). The obtained results confirm that the single phase of Bi$_4$Ti$_3$O$_{12}$ was obtained.

4. Conclusion

Bismuth titanate has been prepared via a high-energy ball milling process directly from oxide through mechanochemically assisted synthesis. Single Bi$_4$Ti$_3$O$_{12}$ phase was obtained after 3 h of milling time. The 3 wt% excess of Bi$_2$O$_3$ does not show a significant effect on the nucleation and crystallization of BIT. The crystal structure shows small preference for tetragonal symmetry. BIT was formed with small crystallite size of 10–17 nm depending of the milling time. The microstrains do not reveal value higher than 0.02. The formed Bi$_4$Ti$_3$O$_{12}$ is rather amorphous keeping the ratio crystalline/amorphous phase approximately 1:2 independently of milling time. The significant reduction of particle size after 12 h of milling time was not noted; however, the tendency to agglomeration increased. After sintering BIT is well crystallized and the orthorhombic structure become the dominant phase. The estimated ratio Bi/O, Ti/O and Bi/Ti confirms the chemical nature of formed phase indicating the formation of single Bi$_4$Ti$_3$O$_{12}$ phase.

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References