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Effect of processing route on the phase formation and properties of $Bi_4Ti_3O_{12}$ ceramics

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Abstract

Our efforts were directed to the preparation of bismuth titanate—$Bi_4Ti_3O_{12}$ (BIT) by two procedures: mechanically assisted synthesis and polymeric precursor method to display a variety of their advantages. To follow the nucleation and phase formation of BIT, XRD and Rietveld refinement analysis were used and it was shown that $Bi_4Ti_3O_{12}$ ceramic can been successfully prepared from nano-sized powders obtained by both methods. The ferroelectric properties were determined and the loops from BIT obtained by polymeric precursor method were not fully saturated with a remnant polarization of 20 $\mu C/cm^2$ and coercitive field of 1500 kV/cm. BIT obtained from powders prepared by mechanically assisted synthesis shows a remnant polarization of 0.65 $\mu C/cm^2$ and coercitive field of 1050 kV/cm. The grain morphology may be the factor causing the observed differences.

Keywords: A. Milling; A. Powders: chemical preparation; B. X-ray methods; B. Electron microscopy; C. Ferroelectric properties; D. Titanates

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1. Introduction

Bismuth titanate—$Bi_4Ti_3O_{12}$ (BIT) is a ferroelectric material with wide applications in the electronic industry, as capacitors, memory devices and sensors [1–3]. Its ferroelectric-to-paraelectric phase transition temperature is near 675 °C [3], which gives it a potential applicability as a suitable candidate for high temperature piezoelectric device. In addition, BIT is an interesting material that is lead-free and environmental friendly.

Bismuth titanate is the simplest compound in the Aurivillius family that can be presented by the general formula $(Bi_2O_2)\,[A_{m-1}(B)_mO_{3m+1}]$, which consists of $(Bi_2O_2)^{2+}$ sheets alternating with $(Bi_2Ti_3O_{10})^{2-}$ perovskite-like-layers [4]. BIT possesses an electrical conductivity that is highly anisotropic with the maximum value in the same plane as the polarization that makes BIT very difficult to pole [5].

$Bi_4Ti_3O_{12}$ ceramics were conventionally prepared by solid-state reaction process, where oxide mixture of Bi_2O_3 and TiO_2 was ball milled, calcined at an intermediate temperature and finally sintered at high temperature [6,7]. The conventional method requires a high calcination temperature, usually leading to inevitable particle coarsening and aggregation of the $Bi_4Ti_3O_{12}$ powders. The presence of hard particle agglomerates will also result in poor microstructure and properties of the $Bi_4Ti_3O_{12}$ ceramics. Many efforts have been made to avoid this problem by lowering the calcination temperature [8]. The methods reported in the literature to prepare $Bi_4Ti_3O_{12}$ ceramics include chemistry-based preparations [10], such as precipitation [11], sol–gel [12], hydrothermal [13], and molten salt route [14] and recently mechanically assisted synthesis.

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The wet-chemistry involve chemicals that are sensitive to moisture or light, which makes them difficult to deal with, especially for bismuth salts. In addition, those processes are time consuming and most of the chemistry-based processing routes require post-precursor calcination at elevated temperature to obtain the precursor-to-ceramic conversion. It is known that sol–gel process utilizes expensive precursors and that the drying process is a critical operation. The co-precipitation process is limited to cation solutions with similar solubility constants. However, polymeric precursor method, which employs complexing of cations in an organic media, makes use of low cost precursors resulting in a homogeneous ion distribution at molecular level [15]. Because of the formation of a polyester resin during the synthesis, there is no segregation of cations during the thermal decomposition of organic matter.

Mechanically activated processes have been recently employed by Benjamin and Gilman to prepare nano-sized oxides and compounds [16]. In many cases, the mechanical technique is superior to both the conventional solid-state reaction and the wet-chemistry-based processing routes for the ceramic powder preparation for several reasons. It uses low-cost and widely available oxides as starting materials and skips the calcination step at an intermediate temperature, conducting to simplified process [17]. Although mechanical activation has been successful with Pb-based electroceramics of perovskite structure, it has not been much studied for the layered structured compounds, such as $Bi_3Ti_4O_{12}$ ceramics.

The objective of this work is to study the feasibility of $Bi_3Ti_4O_{12}$ formation and ceramics properties obtained from powders prepared by polymeric precursor method and by mechanically activating the constituent oxides.

2. Experimental procedure

The procedure of $Bi_4Ti_3O_{12}$ synthesis, based on polymeric precursor method, starts from the fact that certain α-hydroxycarboxylic organic acids can form the polybasic acid chelates with several cations. After adding of a polyhydroxylic alcohol and heating, the chelate transforms into a polymer, with homogeneously distribution of cations. Titanium isopropoxide (Hulls AG) and bismuth nitrate (Aldrich) were used as raw materials. The precursor solutions of bismuth and titanium were prepared by adding the raw materials to ethylene glycol and concentrate aqueous citric acid under heating and stirring. Appropriate quantities of solutions of Bi and Ti were mixed and homogenized by stirring at 90 °C for 3 h. Next, the temperature was increased to 130–140 °C, yielding a high viscous polyester resin. The molar ratio of metal:citric acid:ethylene glycol was 1:4:16. In this work, an excess of 3 wt.% bismuth oxide was added to the solution aiming to minimize the bismuth loss during the thermal treatment. The organic part is subsequently eliminated at temperatures as low as 300 °C, forming reactive oxides with well-controlled stoichiometry. The calcination step was performed at 700 °C for 4 h.

The bismuth titanate prepared by mechanically assisted synthesis started from bismuth oxide (Bi_2O_3, Fluka, p.a. 99.8%) and titanium oxide (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 BIT composition, corresponding amount of Bi_2O_3 and TiO_2 were weighed and loaded into zirconia jars together with zirconia milling balls ~10 mm in diameter. Mechanical activation (mechanochemical synthesis) was performed in air atmosphere in a planetary ball mill (Fritch Pulverisette 5). Milling conditions were the following: ball-to-powder weight ratio was 20:1, basic disc rotation speed was 317 min^{-1}, rotation speed of disc with jars was 396 min^{-1}, milling time was from 0, 60, 120 to 360 min.

The X-ray diffraction data for BIT powders were collected using a Rigaku® RINT2000 diffractometer. For Rietveld analyses X-ray diffraction data were collected under the following experimental conditions: 40 kV, 30 mA, $20^\circ \leq 2\theta \leq 120^\circ$, $\Delta 2\theta = 0.02^\circ$, λCu Kα monochromatized by a graphite crystal, divergence slit = 2 mm, reception slit = 0.6 mm, step time = 10 s. The Rietveld analysis was performed with the Rietveld refinement program DBWS-941 1 [18,19]. The profile function used was the modified Thompson–Cox–Hasting pseudo-Voigt, in which η (the lorentzian fraction of the function) varies with the Gauss and Lorentz components of the full width at half maximum.

Specific surface areas were determined based on isotherms of nitrogen adsorption using the BET method (Micrometrics ASAP 2010). The samples were prepared by pressing at 210 MPa and sintered inside a box furnace with heating rate of 5 °C/min from room temperature up to 1000 °C for 4 h using a closed system containing 3 wt.% of B_2O_3, relative to the pellets' mass, to generate a bismuth atmosphere. The density of the pellets was determined by the water displacement method (Archimedes). A scanning electron microscope (SEM, Topcom SM-300) was used to analyze the microstructure.

The gold electrode for electrical measurements was applied to polished surface of sintered discs by evaporation through a sputtering system. Ferroelectric properties of the BIT sample were measured on a Radiant Technology RT6600A tester equipped with a micrometer probe station in a virtual ground mode.

3. Results and discussion

The $Bi_4Ti_3O_{12}$ phase evolution was monitored by X-ray analysis. The best condition to obtain a single bismuth titanate prepared by polymeric precursor method was evaluated on the BIT powders calcinated on several temperatures (Fig. 1a–d). The BIT powders calcinated at 700 °C for 4 h showed the main peaks related to the pure BIT

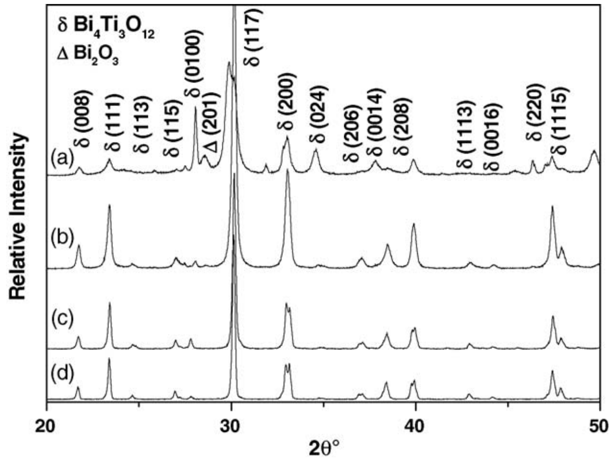


Fig. 1. X-ray data for BIT powders calcinated for 4 h at: (a) 500 °C; (b) 600 °C; (c) 700 °C; and (d) 800 °C.

system indicating that the polymeric precursor method allowed obtaining a single BIT crystalline phase. The mechanically activated powders (Fig. 2) observed by XRD are refereed to the mixture of Bi_2O_3 and TiO_2, milled for various times. It was evident that before mechanical activation, sharp peaks of crystalline Bi_2O_3 and TiO_2 were observed (inset in Fig. 2), since the conventional ball milling used for homogenization did not trigger any reaction among mixed oxides. In the XRD patterns of milled powders the majority of these sharp peaks disappeared and after 60 min of milling broadened peaks at 2θ angles at around 32 and 39° were observed, which was reported previously [23,24]. It indicates that upon grinding the solid-state reaction between initial oxides starts resulting in the mechanochemical synthesis reaction. After 120 min of milling, the broadened peaks were separated in few main peaks indicating the formation orthorhombic perovskite $Bi_4Ti_3O_{12}$ phase. The crystalline phase $Bi_4Ti_3O_{12}$, formed after 120 min of milling time, possesses rather small amount of amorphous phase, which shows a small increase upon 360 min of milling.

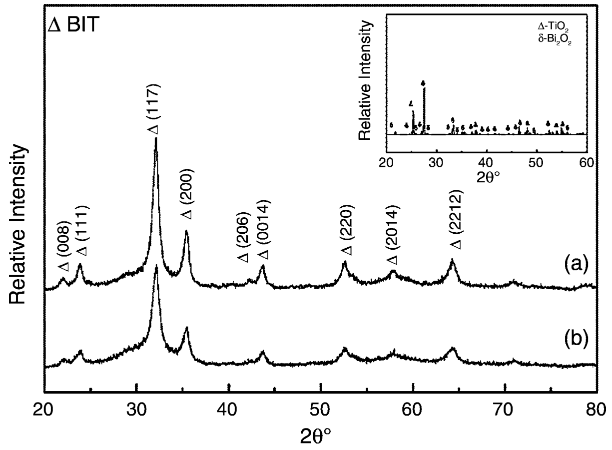


Fig. 2. X-ray data for BIT powders prepared by mechanically assisted synthesis: (a) 120 min of milling and (b) 360 min of milling; and on onset: mixture of Bi_2O_3 and TiO_2 homogenized powders.

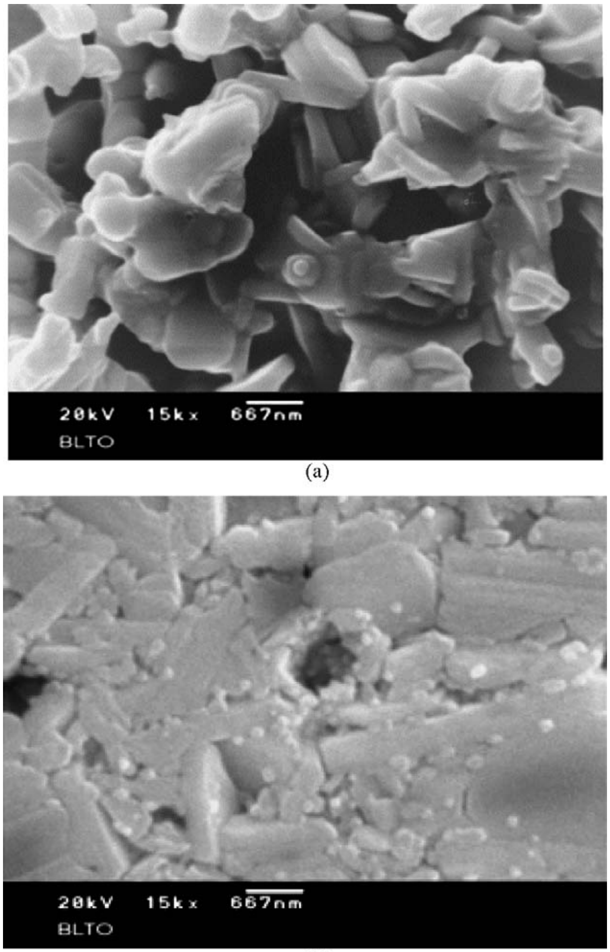
Table 1
Rietveld calculation of lattice parameters (Å) for the BIT powder samples prepared by polymeric precursor method and mechanically assisted synthesis (milled 120 and 360 min)

Parameter	BIT	BT120	BT360
Refinement index			
R_{WP} (%)	11.12	12.57	11.78
R_{EXP}	7.06	8.00	6.60
S	1.57	1.39	1.62
Lattice parameter			
a (Å)	5.4175	5.4651	5.4782
b (Å)	5.4403	5.4452	5.4432
c (Å)	32.7862	32.5781	32.5671
V (Å^3)	966.30	971.86	973.83
D (g/cm^3)	8.02	8.01	8.00
Perovskite (mol%)	97.5 ± 0.5	98.1 ± 0.4	98.1 ± 0.3
Stoichiometry	$Bi_4Ti_3O_{12}$	$Bi_4Ti_3O_{12}$	$Bi_4Ti_3O_{12}$
Refinament	$Bi_4Ti_3O_{11.6}$	$Bi_4Ti_3O_{11.8}$	$Bi_4Ti_3O_{11.7}$

The BIT system has been investigated from a fundamental point of view, regarding the crystal structures of BIT [20]. We adopted the Rietveld refinement technique to investigate the BIT crystal structure. The data collected from BIT calcinated powders (700 °C for 4 h) and that from BIT obtained by mechanical activation (2 and 6 h) were used. Table 1 illustrates the lattice parameters (a, b and c), unit cell volume (V) and refinement data. The space group obtained from the Rietveld analyses was FMMM with the atomic positions belonging to the ICSD card (number 24735). The quantitative phase analysis of powders was calculated according to the reference of Young and Desai [20]. It was shown that synthesized BIT has orthorhombic structure of an Aurivillius phase Bi-layered oxide, denoted by the formula $(Bi_2O_2)^{2+}$ $(Bi_2Ti_3O_{10})^{2-}$, in which perovskite units of Ti–O octahedra are sandwiched between Bi_2O_2 layers. The difference in the crystal lattice parameters for chemically and mechanochemically prepared BIT samples is notable. Comparing to the literature data, BIT prepared by polymeric precursor method shows closer values to literature data concerning to orthorhombic structured bismuth titanate obtained by chemical precipitation method [9]. The fact that the values for crystal parameters of BIT prepared by mechanically assisted synthesis are larger than those for polymeric precursor method can be explained by closer packages of atoms in crystal lattice of BIT obtained by chemical method. Less volume of crystal lattice indicates that. Due to strains induced during milling, the distances of atoms in BIT crystal lattice are bigger resulting in a larger volume of crystal lattice [21,22].

The specific surface area of BIT powders prepared by milling process has been changing depending on whether the breaking process of particles or the secondary agglomeration process dominates or mechanically assisted synthesis occurred. When BIT becomes the dominant phase in the milling sample form, mechanically assisted process is dominant to the secondary agglomeration process. This corresponds to the increase of the value of specific surface area, from 5.2 m^2/g at the beginning of milling to 7.2 m^2/g after 120 min. On the contrary, the decrease trend of specific surface area to 6.6 m^2/g can be seen after milling for 360 min as a result of secondary agglomeration processes. The strong powder agglomeration of BIT prepared by mechanically assisted synthesis was confirmed by SEM analysis [24]. The individual crystallite size of approximately 30 nm of BIT powders was observed. Those results were reported previously [24]. The specific surface area of calcinated BIT powders prepared by polymeric precursor method was 7.5 m^2/g. Evidently, this value is higher comparing to BIT powders prepared by high energy ball-milling process.

A rather significant difference in sintered densities of samples obtained by both methods was noted. The density of BIT samples obtained by polymeric precursor method was higher, at least 95% of theoretical density (TD = 8.04 g/cm^3) comparing to ~90% for BIT obtained by mechanochemical process. Compared to green densities values (~60% TD for mechanically assisted synthesis and ~72% TD for polymeric precursor method), the noted difference is assumed to be caused by strong agglomeration of milled powders [24].



(a)

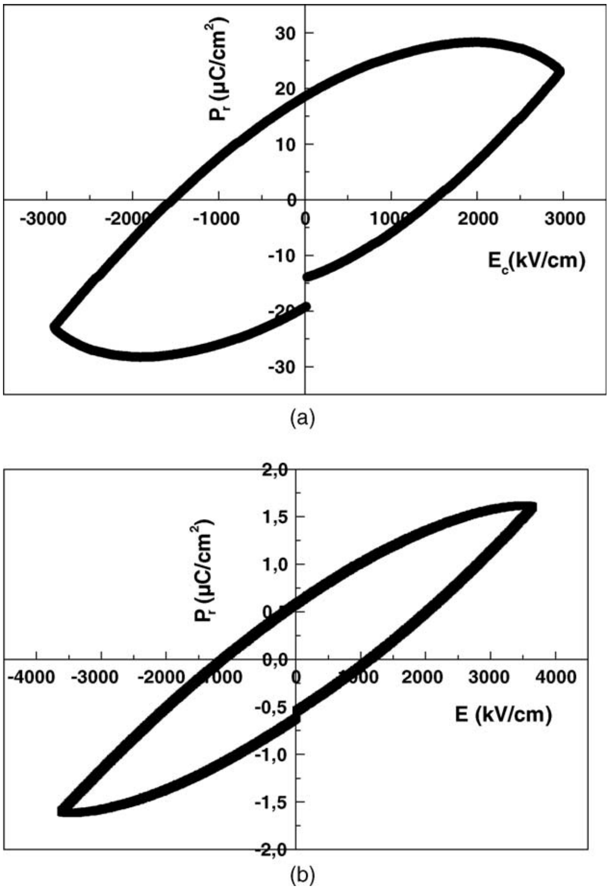
(b)

Fig. 3. SEM micrographies for sintered BIT samples: (a) BIT obtained from mechanochemically synthesized powders milled 120 min and (b) BIT obtained from powders synthesized by polymeric precursor method.

The microstructure of the $Bi_4Ti_3O_{12}$ ceramics prepared from BIT powders obtained by mechanical activation (120 min milling time) and by polymeric precursor method and sintered at 1000 °C for 4 h was presented in Fig. 3a–b. There is a tendency for the plate-like morphology to be more evident in the samples prepared by mechanochemically assisted synthesis. The lower density of BIT samples prepared by this method is believed to be a result of the formation of the plate-like grains as it was reported in literature [23]. BIT obtained from powders prepared by polymeric precursor method presents a mixture of plate-like grains and rod-like grains. This suggests that the powder processing has a significant influence on the structural distortion resulting in different morphology of grains.

Due to the special structure of $Bi_4Ti_3O_{12}$, single crystal is strongly anisotropic in all its ferroelectric properties, including saturated polarization (P_s), remnant polarization (P_r) and coercitive field (E_c). The polarization direction of $Bi_4Ti_3O_{12}$ is 4.5° off the base plane of its cell structure, thus giving rise to a much larger in-plane polarization ($P_s = 50\ \mu C/cm^2$) and E_c value for in-plane polarization is 50 kV/cm and E_c value for *c*-orientation is less than 5 kV/cm [23]. For randomly oriented $Bi_4Ti_3O_{12}$ ceramics or thin films, both remnant polarization and coercitive field have values different than those as above presented. Ferroelectricity in the BIT ceramics was performed with a standardized ferroelectric tester and the results are presented in Fig. 4a and b. The hysteresis loops were measured at a frequency of 100 Hz and an applied voltage in the order of 3000 kV/cm. The loops from BIT obtained by polymeric precursor method are not fully saturated with a remnant polarization of 20 $\mu C/cm^2$ and coercitive field of 1500 kV/cm. The lack of saturation of the loops at these low frequencies indicates that the losses are high, suggesting the system is highly conductive. The smaller grain size of the BIT prepared by polymeric precursor method can be the reason for the difficulty in switching the domains, and therefore, the hysteresis is not saturate even at higher applied electric field. One possible explanation for high conductivity can be the presence of oxygen vacancies and dipoles complexes in the system. In order to reduce these defects a co-substitution in both A and B should be employed. Representative *P–E* hysteresis loop of $Bi_4Ti_3O_{12}$ ceramics prepared from powders obtained by mechanochemical synthesis are almost fully saturated with a remnant polarization of 0.65 $\mu C/cm^2$ and coercitive field of 1050 kV/cm. The grain morphology may be the factor causing rather large coercive field. It can be assumed that the difference in the space charge density in comparison to $Bi_4Ti_3O_{12}$ ceramics prepared by polymeric precursor method led to less remnant polarization indicating the decrease in the system conductivity [25].

The difference in the properties of $Bi_4Ti_3O_{12}$ ceramics obtained by both processes can be attributed to the variation



(a)

(b)

Fig. 4. Hysterezis loop for BIT: (a) obtained from powders synthesized by polymeric precursor method and (b) BIT obtained from mechanochemically synthesized powders milled 120 min.

in microstructure and grain size. The increase of grain size reduces the coupling between grain boundaries and the decrease of domain wall can appeared as a result of more difficult reorientation and the domain wall motion. This then translates to an increase in the domain alignment, corresponding to an increase in the values of remnant polarization and in domain wall mobility [23].

4. Conclusions

$Bi_4Ti_3O_{12}$ ceramic has been successfully prepared from nano-sized powders obtained by both methods used: mechanochemical synthesis via a high-energy ball milling process and by chemical synthesis via polymeric precursor method. The differences in the crystal lattice parameters, specific surface area and density data for BIT prepared by both methods are caused by several reasons. The most important ones are the closer packages of atoms in $Bi_4Ti_3O_{12}$ crystal lattice and less powders agglomeration of powders prepared by chemical method than by mechanically assisted synthesis. BIT ceramics obtained from powders prepared by polymeric precursor method presents a mixture of plate-like and rod-like grains comparing to plate-like structure of BIT prepared by milling process. $Bi_4Ti_3O_{12}$ ceramics obtained by both processes possess ferroelectric properties. The mechanochemical process has an advantage over polymeric precursor method because of using low-cost and widely available oxides as starting materials and skips the calcination step at an intermediate temperature, leading to simplified process.

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