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Characterization of Bismuth Titanate Ceramics Derived by Mechanochemical Synthesis

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Abstract:

Bismuth titanate, $Bi_4Ti_3O_{12}$ (BIT) nanosized powders have been successfully synthesized via high energy mechanochemical activation. The phase formation of BIT, crystal structure, microstructure, crystallite size and specific surface area were followed by XRD, scanning electron microscopy (SEM) and the BET specific surface area measurements. The BIT milled 2 h shows the orthorhombic crystalline structure with small amount of amorphous phase. The microstructure of $Bi_4Ti_3O_{12}$ ceramics sintered at 1000 ^oC for 12h exhibit plate-like grain structure.

Keywords: *Bismuth titanate, Ceramics powders, Mechanochemical synthesis*

Introduction

Bismuth titanate, $Bi_4Ti_3O_{12}$ is the most famous Aurivillius type ferroelectric material with m = 3 [1-4]. It is a good candidate for high-temperature piezoelectric applications, memory storage, and optical displays because of its high Curie temperature (T = 675 ˚C) and good electro-optical switching behavior [5-8].

It is well known that materials performances are closely related to the ways they are processed. Synthesis method of ferroelectric powders has played a significant role in determining the microstructural, electrical and optical properties of ferroelectric ceramics [9]. Ferroelectric powders were conventionally synthesized via a solid-state reaction process, using constituent oxides as starting materials. Due to their relatively rough grains, these powders require relatively high sintering temperature to obtain ferroelectric ceramics with designed compositions and desired performances [9]. To reduce the sintering temperature, it is necessary to use powders of ferroelectric compounds with small grain size and narrow size distribution. For this purpose, submicron or even nanosized ferroelectric $Bi_4Ti_3O_{12}$ powders have been synthesized by various wet-chemistry methods in the last decades, including chemical co-precipitation [10], sol-gel process [11], hydrothermal synthesis [12], molten salt [13], etc. Although significant progress has been achieved, there are problems. For example, sol-gel process uses metal alkoxides as the starting materials, which are very expensive and extremely sensitive to the environmental conditions such as moisture, light and heat. Co-precipitation processes involve repeated washing in order to eliminate the anions coming from

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the precursor salts used, making the process complicated and very time consuming.

Mechanochemical synthesis, which is also known as mechanical alloying [14], has been recently employed to prepare nano-sized oxides and compounds. The most significant characteristic of this technique is that the formation of the designed compounds is due to the reactions of oxide precursors which are activated by mechanical energy, instead of the heat energy required in the conventional solid-state reaction process. The novel mechanical technique is superior to both the conventional solid-state reaction and the wet-chemistry-based processing routes for several reasons. Firstly, it uses low-cost and widely available oxides as starting materials and skips the calcinations step at an intermediate temperature, leading to a simpler process [15]. Secondly, it takes place at room temperature in well sealed containers, thus effectively alleviating the loss of the volatile components, such as bismuth. Furthermore, due to their nanometer scale size and very high homogeneity, mechanochemically derived ceramic powders demonstrate much better sinterability than those synthesized by the conventional solid-state reaction and wet-chemical processes. Also, the high-energy milling can greatly improve the reactivity of precursors by reducing the phase formation temperatures of $Bi_4Ti_3O_{12}$ and many Arivillius family ferroelectrics [16].

In this letter, preparation of $Bi_4Ti_3O_{12}$ from their oxide mixture via a ball milling process will be reported. Characterization and properties of $Bi_4Ti_3O_{12}$ ceramics derived by mechanochemical synthesis will be discussed.

Experimental Procedure

A synthesis procedure for preparation $Bi_4Ti_3O_{12}$ from bismuth oxide (Bi_2O_3, Fluka, p.a.99, 8%) and titanium oxide (TiO_2, in rutil crystal form, Carlo Erba p.a 99%) has been already described in paper [17]. Mechanically activated process was performed in a planetary ball mill for 0, 60, 120 and 360 min.

The X-ray diffraction data for milled powders were collected using a Rigaku® RINT2000 diffractometer (42kV X 120mA) with Cu k_α radiation ($\lambda_{k\alpha1}$ = 1.5405Å, $\lambda_{k\alpha2}$ = 1.5443Å, $I_{k\alpha1}/I_{k\alpha2}$ = 0.5), 2θ range between 15° and 110°, step size of 0.02°(2θ), divergence slit = 0.5 mm, receiving slit = 0.3 mm. Scanning electron microscopy (SEM, Model JOEL-5300) was used to study particle size and powder morphology of activated powders and microstructure of sintered pellets. The pellets were prepared by pressing at 210 MPa and sintered in closed system at 850 and 1000°C during 4-24 h. The average crystallite size of the milled powders was estimated using the Sherrer formula. Specific sample surface areas were determined based on isotherms of nitrogen adsorption using the BET method (Sorptomatic 1990) [18].

Results and Discussion

The $Bi_4Ti_3O_{12}$ phase evolution was monitored by X-ray analysis. The mechanically activated powders (Figure 1) 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. 1), 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. It indicates that upon grinding the solid-state reaction between initial oxides starts. After 120 minutes of milling, the broadened peaks were separated in few main peaks indicating the formation orthorhombic perovskite $Bi_4Ti_3O_{12}$ phase, which can be concluded from crystallographic

cards (orthorhombic, JCPDS-card 12-0213). The crystallite size was calculated using Scherrer's equation [19] ((111) peak on Fig. 1). During 2 h of milling the crystallite size of the mixture decreases further to less than 15 nm. If we compared the obtained value of the crystallite size to the data from literature [19], we would see that they are considerably smaller, and conclusion is that it is a result, i.e. an advantage of the way of $Bi_4Ti_3O_{12}$ synthesis. The crystalline phase $Bi_4Ti_3O_{12,}$ formed after 120 min of milling time, possesses rather small amounts of amorphous phase, which shows a small increase upon 360 minutes of milling.

The diameter of obtained particles depends on time of milling. The effect of mechanical treatment on the crystallite size is quite evident: as the milling time increases (2 and 6 h), the powder becomes more activated and crytallite size decrease (14.9 and 7.2 nm) (Tab. 1).

Tab.I. The values of crystallite size and specific surface area of BIT powders prepared with excess of 3 wt % Bi_2O_3 upon mechanical activation of 120 min and 360 min.

sample	crystallite size, nm	specific surface area, $m^2 g^{-1}$
120 min	14.9	13.1
360 min	7.2	9.6

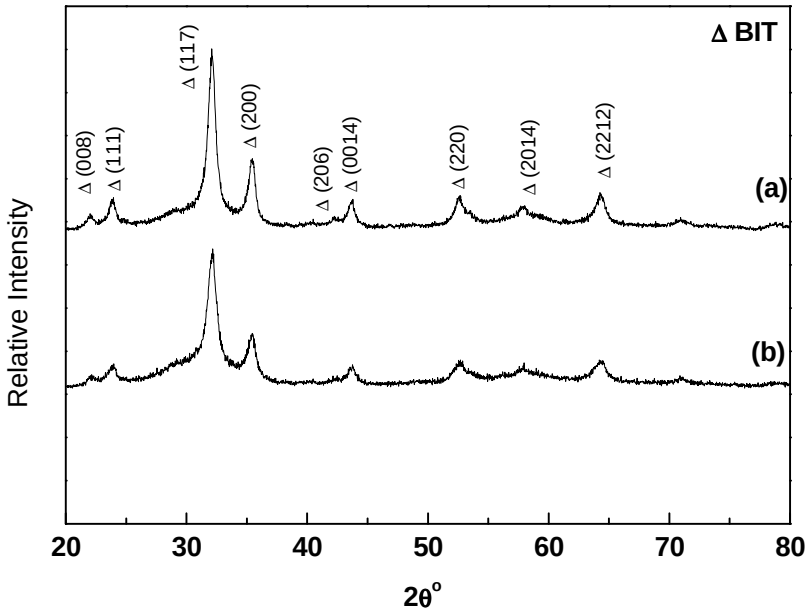

Fig. 1 XRD traces of BIT prepared with excess of 3 wt % Bi_2O_3 upon mechanical activation of a) 120 and b) 360 min.

The specific surface area powder mixtures of BIT, prepared with excess of $Bi_2O_{3,}$ 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 value of specific surface area is lower compared to the ific surface area value obtained with prolongation of milling time. When BIT becomes the dominant phase in the milling sample form, mechanically assisted synthesis process is

dominant to the secondary agglomeration process due to the milling, which corresponds to the increasing of the value of specific surface area, from 5.6 $m^2 g^{-1}$ at the beginning of milling to 13.1 $m^2 g^{-1}$ after 120 min. On the contrary, the decrease trend of specific surface area to 9.6 $m^2 g^{-1}$ can be seen after milling for 360 min as a result of secondary agglomeration processes (Tab. I).

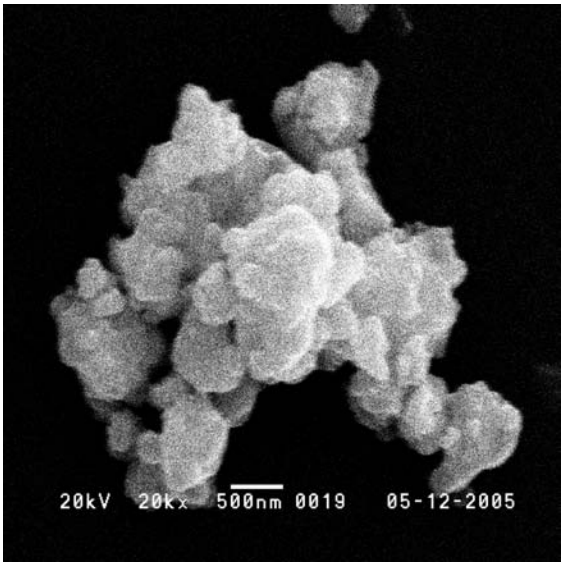

Fig. 2 SEM micrographs showing BIT powders derived from 120 min of mechanical activation**.**

Having this in mind, it is possible to assume that after 120 min, the mechanochemical reaction and the crystallization of formed BIT is almost finished and the breaking process of formed particles is dominant compared to secondary agglomeration. This is in agreement with XRD results.

The existence of powder agglomerates and change in their size are confirmed with SEM analysis (Fig. 2). The strong agglomeration of powders was noticeable with a mostly pyramidal agglomerate shape. In order to determine the individual particle size it was excluded the smallest agglomerates were magnified while it was rather difficult to evaluate the correct value.

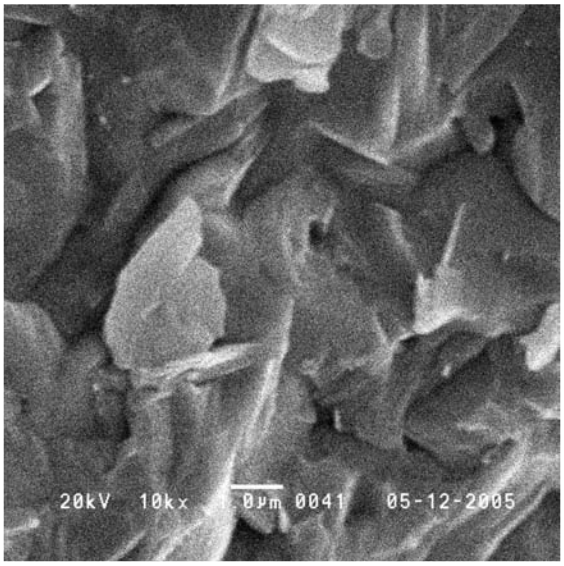

Fig. 3 The microstructure of $Bi_4Ti_3O_{12}$ sintered at 1000 ^oC for 12h.

Fig. 3 shows the microstructure of the $Bi_4Ti_3O_{12}$ ceramics prepared from BIT

powders obtained by mechanical activation after 120 min and with 3 wt % excess of Bi_2O_3 and sintered at 1000°C for 12 h. A closed system and protective atmosphere of Bi_2O_3 powders was used. The sample exhibits a plate-like grain structure.

The obtained results indicated that nano-sized powder synthesized by high-energy ball milling process had a better sinterability than those prepared by other methods, showing the advantage of the mechanochemical process over conventional solid-state reactions and chemical processes.

Conclusion

$Bi_4Ti_3O_{12}$ ceramics has been successfully prepared from nano-sized powders obtained by mechanochemical synthesis via a high-energy ball milling process. The BIT prepared with excess of Bi_2O_3 and milled 2 h shows the orthorhombic crystalline structure. The crystallite size was less than 15 nm. It is shown that Bi_2O_3 has the dominant role in formation of bismuth titanate phase during mechanical activation of starting oxides and during mechanochemical synthesis. BIT ceramics obtained from powders prepared by milling process have a plate-like structure. The mechanochemical process has an advantage because of using low-cost and widely available oxides as starting materials and skips the calcination step at an intermediate temperature, leading to a simplified process.

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Садржај: *Бизмут-титанат, $Bi_4Ti_4O_{12}$ (BIT) прах нановеличине је успешно синтетизован поступком високо енергетске механохемијске активације. Процес BIT фазе, кристална структура, микроструктура, величина кристалита и специфична површина су извешене мерењем са XRD, SEM и BET методом. BIT млевен током 2 h има орторомбичну кристалну структур са малом количином аморфне фазе. Микроструктура $Bi_4Ti_3O_{12}$ керамике добије не синтеровањем на 1000 ^oC за 12h је плочаста.*

Кључне речи: *Бизмут титанат, керамички прах, механохемијска синтеза.*