

Spectroscopy study of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ obtained from mechanically activated $\text{Bi}_2\text{O}_3\text{--TiO}_2$ mixtures

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Abstract

Bismuth titanate, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders were prepared by mechanically assisted synthesis from their oxides. The diameter of obtained particles depends on time of milling. In order to understand the grain size effects on the crystal structure we measured X-ray, TEM analysis and Raman spectra. The effect of mechanical treatment on the grain size is quite evident: as the milling time increases (3, 6, 12 h), the powder becomes more activated and grain size decrease (7.3, 7.2, 6.9 nm). With reducing the grain size, quantum effects at the Raman spectra, is reflected in the mode position change against bulk crystal. And also, coagulation of each line appears, as well as a significant asymmetry of certain modes.

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1. Introduction

Bismuth titanate, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has been extensively studied for its ferroelectric and other excellent properties. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is a candidate material for high temperature piezoelectric applications, memory storage, and optical displays because of its high Curie temperature and electrooptical properties [1]. The properties and way of synthesis of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ have been reported in a number of papers, cited among others in references [2,3].

The layer structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ by the perovskite like $(\text{Bi}_2\text{Ti}_3\text{O}_{10})^{2-}$ layers sandwiched between two $(\text{Bi}_2\text{O}_2)^{2+}$ layers along its crystallographic *c* axis. In the Ti ions are enclosed by oxygen octahedral, which are linked through corners forming O–Ti–O linear chains. Bi ions occupy the spaces in the framework of TiO_6 octahedral.

In recent years, theoretically and experimentally has been investigated the grain size effects by ferroelectric bismuth titanate [4–6]. It is known that Raman scattering has a shorter characteristic length scale, which makes it a good probe to study structural properties associated with Nan regions of the mate-

rials. Raman scattering has been successfully used to study the phonon anomaly and phase transitions. We obtained the samples of bismuth titanate with the grain size below 16 nm by mechanical activation, that was better than literature data [5]. In this paper, we report our investigations of size effects on phase structural of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ nanocrystals. Changes in the crystal structure have been studied by X-ray diffraction and the Raman spectroscopy.

2. Experimental procedure

A synthetic procedure for preparation bismuth titanate $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ from bismuth oxide Bi_2O_3 and titanium oxide TiO_2 has been already described in previous papers [3,7]. 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 . Mechanically activated process was performed in air atmosphere in a planetary ball mill. 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} , for different milling time (1, 3, 6 and 12 h).

Characterization of the obtained samples was carried out by:

- X-ray diffraction analysis (XRD data for milled powders were collected using a Philips PH 1050, in range from 10° to 100° (increment 0.05°, exposition 12 s) automatic diffractometer with $\text{Cu K}\alpha$ graphite-monochromatized radiation ($\lambda = 0.15418 \text{ \AA}$).
- Room temperature Raman spectra in spectral range from 100 to 900 cm^{-1} , in back scattering geometry, were obtained by Micro Raman Chromex 2000

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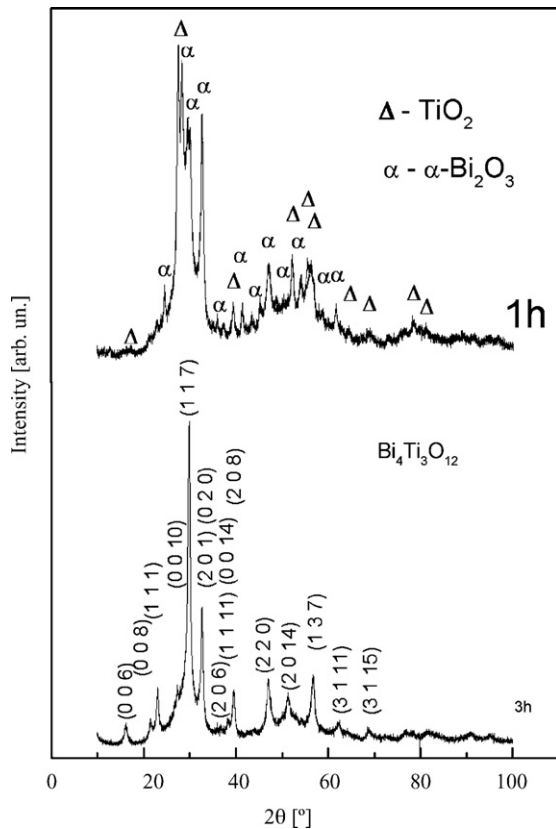


Fig. 1. XRD traces of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ prepared mechanochemical activation for 1 and 3 h.

using 532 nm of a frequency doubled Nd:YAG laser. The spectral resolution was 1 cm^{-1} . The average power density on the sample was about 2 mW/mm^2 .

- Transmission electron microscopy (TEM, Model Philips CM 200) 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 phase in synthesized $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powder.

2.1. Sample characterization

The $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase evolution prepared as stoichiometric composition was monitored by XRD. Fig. 1 is referred to the mixture of Bi_2O_3 and TiO_2 , milling for various times (1 and 3 h). It was evident that before mechanical activation, sharp peaks of crystalline Bi_2O_3 and TiO_2 did not trigger [3]. Also, for the mixture milled for 1 h, all the XRD reflections are attributed to the starting oxides. But, during 1 h of mechanical activation, the XRD pattern of milled powders shows the different progression. Significant structural changes had already observed after 1 h of milling. The formation of one new phase started during 1–3 h of milling— $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase. Upon 3 h of mechanical activation, the broadened peaks at 2θ angles around 16.2° , 21.3° , 23.2° , 27.9° , 30.0° , 37.9° , 39.2° , 46.9° , 50.9° , 57.3° , 62.0° and 68.8° can be attributed to formation of bismuth titanate (Fig. 1 for 3 h). All appearing peaks are very wide, as a result of downsizing and reduction of the grain size and of internal strain. In the period between 1 and 3 h of initial oxides milling, the expected $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase forms, which is shown at the diffractogram for the sample milled 3 h. At the diffractogram of the mixture milled 3 h, one can note all typical peaks of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ compound. The formed structure can be orthorhombic or tetragonal. However, in this case it is rather difficult to distinguish between these two structures based only on the observation of XRD data due to intense superposition of the broadened peaks. Peaks for orthorhombic and tetragonal structure are very close, which can be concluded from crystallographic cards (orthorhombic, JCPDS-card 12-0213; tetragonal, JCPDS-card 47-0398). And having in mind that the piques are wide, which is a consequence of milling, we cannot determine accurately what their

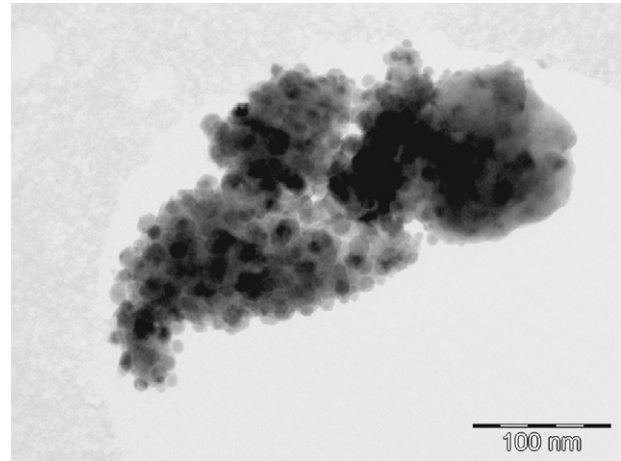


Fig. 2. TEM image of crystalline $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powder obtained after milling of 3 h.

crystal structure is. Therefore one can rightfully say that presences of both orthorhombic and tetragonal, i.e. monoclinic structures are possible.

However, the particle size of the powders was reduced, which is smaller than before milling [3,7]. The grain size was calculated using Scherrer's Eq. (1) [8] ((006) peak on Fig. 1):

$$B = \frac{\kappa\lambda}{\beta \cos \vartheta} \quad (1)$$

where B is the grain size, $\kappa = 0.9$ is shape factor, λ the X-ray wavelength, β the full width at half maximum of the diffraction line, and θ is the diffraction angle.

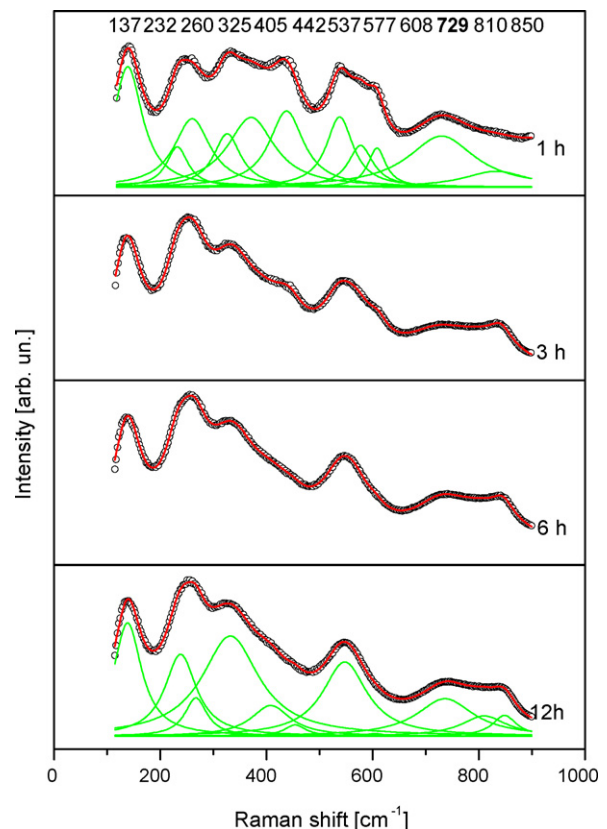


Fig. 3. Raman spectra of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ samples prepared mechanochemical activation for 1, 3, 6 and 12 h at room temperature.

During 1 h of milling the particle size of the mixture decreases further too less than 15 nm. In the milling period from 1 to 3 h, it appears that the formation of the amorphous phase is completed and a steady-state is reached. Thus, no significant structural changes occurred after prolonged milling up to 12 h. The effect of mechanical treatment on the grain size is quite evident: as the milling time increases (3, 6, 12 h), the powder becomes more activated and grain size decrease (7.3, 7.2, 6.9 nm). And in spirit of all that absolute error was usual [9]. Also, these results mean that the crystal structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ changes from the orthorhombic structure to tetragonal structure with decreasing the grain size. If we compared the obtained value of the grain size to the data from literature, we would see that they are considerably smaller, and conclusion is that it is a result, i.e. an advantage of the way of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ synthesis.

TEM image of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powder milled for 3 h are presented in Fig. 2. The image present in Fig. 2 reveal that the specimens consists of nanocrystalline particles with crystallite size less than 20 nm that is in agreement with XRD study. The difference in electron diffraction pattern for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders milled 3, 6 and 12 h is not significant, that is in agreement with XRD study [9].

3. Results and discussion

The non-polarized Raman spectra of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders formed during different milling time (1–12 h), in the spectral range from 100 to 900 cm^{-1} at room temperature are shown

in Fig. 3. Experimental results are presented by circles. Full lines are result of application of deconvolution, which will be described later. The spectrum of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ which is obtained by milling of 1 h of length in the mill, exhibit intense modes at about 137, 260, 325, 405, 442, 537, 577, 608, 729 and 850 cm^{-1} , together with weak features at about 232 and 810 cm^{-1} .

As we told in Section 2.1, by increasing the milling time, the grain size is being reduced. When reducing the grain size, quantum effects are coming to the forefront. At the Raman spectra, this apparition is reflected in the mode position change against bulk crystal (137, 232, 260 and 577 cm^{-1}). And also, coagulation of each line appears, as well as a significant asymmetry of certain modes. Therefore, what happens is the overlapping of modes, which form complex wide structures. These apparitions make the analysis of spectra significantly more complex. This is especially expressed for modes which are in spectral range from 729 to 850 cm^{-1} .

In that case, Raman spectra are often analyzed with the help of a Lorentzian and Gaussian curves [10]. Our interest is quantitative analysis with a partial discussion of trend, and we assume that all lines are of Lorentzian type (Eq. (2)). Solid lines in Fig. 3,

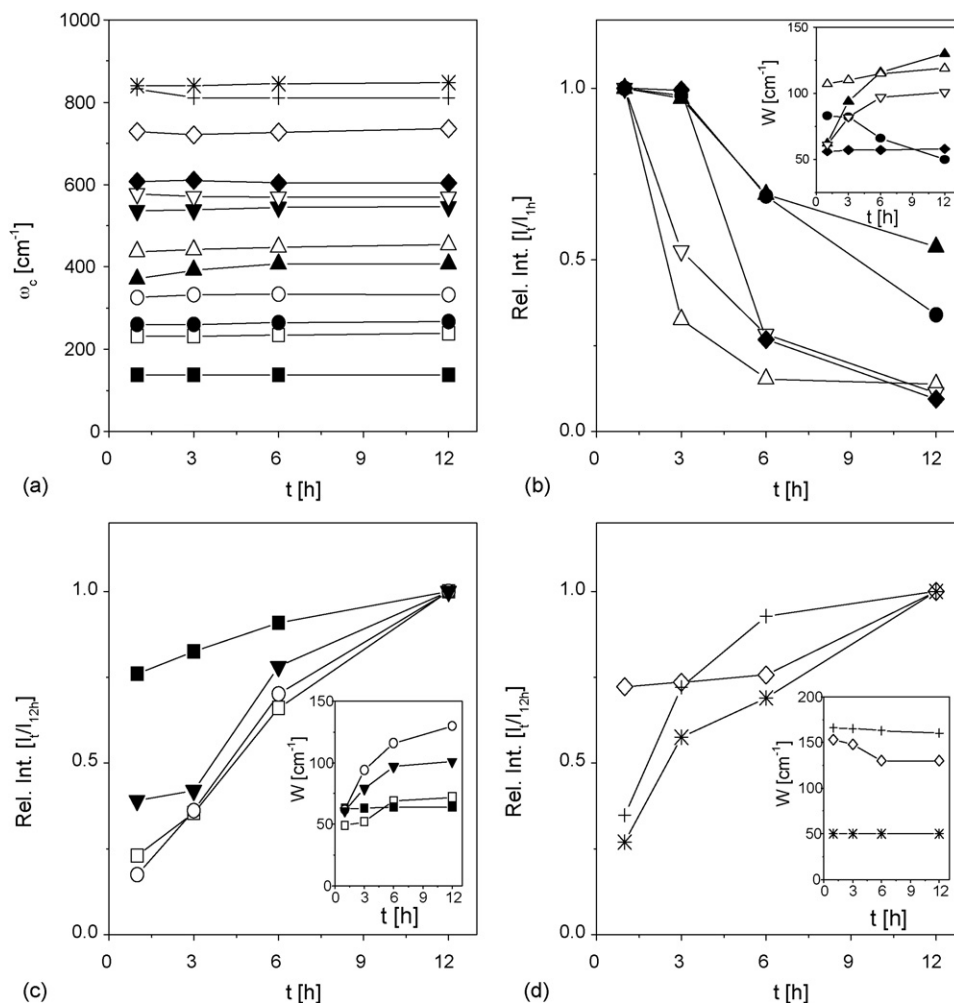


Fig. 4. (a) position of Raman modes. Relative intensity of modes at: (b) 260, 405, 442, 577, 608; (c) 137, 232, 325, 537; (d) 729, 810, 850. Insets: corresponding half-widths.

was obtained by adding 12 different profiles:

$$I(\omega) = I_0 + \frac{2A}{\pi} \frac{W}{4(\omega - \omega_c)^2 + W^2} \quad (2)$$

Here I is a line intensity, I_0 a height of the baseline, ω_c a position of the maximum, W a half-width of the peak and A a parameter that depends on W . The typical line shape obtained by deconvolution is present in Fig. 2 for 1 and 12 h of mill. The results of the analysis were given in Fig. 4.

Main difference in obtaining nanocrystal powders $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ from mechanically activated $\text{Bi}_2\text{O}_3\text{--TiO}_2$ mixture, in regard to obtaining the same through other procedures of synthesis [4,5] or bulk crystals is in simultaneous coexistence of both orthorhombic and tetragonal structure.

The Raman selection rules in orthorhombic $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ with space group $Fmmm$ allow 24 Raman active modes of different symmetries ($6A_g + 2B_{1g} + 8B_{2g} + 8B_{3g}$) [10], while in tetragonal case $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ allow 16 ($6A_{1g} + 2B_{1g} + 8E_g$) [11]. However, only 12 Raman bands are clearly observed. The position of the Raman modes, obtained by deconvolution, is presented on the Fig. 4a. Marks that are used have been kept on other illustrations too. The position change with increase of milling times, is expressed for modes at about 405, 537, 729 cm^{-1} . The position change of other modes is within measurement and analysis error (about 5%).

The change in relatively intensity (I_t/I_{12h}) of the mode at 260, 405, 442, 577 and 608 cm^{-1} , are presented in Fig. 4b, together with corresponding half-width changing. In increasing the milling time, decrease of relative intensity has been noted at all modes. At the same time, half-width grows, except for the mode on 260. These modes are a consequence of the existence of orthorhombic structure in samples. Same modes have been noted at bulk crystal at same frequency. In increasing the milling time, share of this phase decreases, and the intensity of these modes becomes proportionally smaller. Only five modes are registered which correspond to this structure, probably due to possible overlap of the same symmetry vibrations or the weak features of some Raman bands [10].

The change in relatively intensity (in this case I_t/I_{12h}) of the mode at 137, 232, 325 and 537 cm^{-1} , are presented in Fig. 4c, and attributed to the internal vibration modes of TiO_6 octahedron [5]. Our results are in good agreement with trend about which Du and others had spoken in their paper [5]. In increasing the milling time, increase of relative intensity has been noted at all modes. We can see that the corresponding half-width increase with increasing milling time. Unique behavior of half-width for both groups of modes shows that in the entire volume of samples, with the increase of the milling time, grains of ever smaller dimensions are being formed, and in nano-band, they lead to expansion of the lines. Changes in relative intensity of some components probably could be caused by structural change (orthorhombic \leftrightarrow tetragonal structures).

Especially Fig. 4d illustrates results of deconvolution for modes at 729, 810 and 850 cm^{-1} . Their relative intensity grows

with the increase of the milling time, which is typical for modes deriving from tetragonal structure. It is unusual that the half-width decreases. Reasons for such a trend can be different. Mode at 729 cm^{-1} , as far as we know, has not been recorded yet, not for a single group of samples $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Mode at 850 cm^{-1} , has been described in the literature as anti-symmetric so far [4]. Asymmetry was more rendered in samples with smaller grain size. As opposed to them, we described the antisymmetry of this mode introducing one more mode at about 810 cm^{-1} into analysis. We have obtained overlapping of the experimental and theoretic spectrum. However, it seems that some changes occurred in this part of the spectrum, caused by the way of sampling. It is possible that surfaces of the grains and interaction between them have significant impact on the shape of these lines.

4. Conclusions

In this paper we have used X-ray diffraction, TEM and Raman spectroscopy to obtain the structural properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, prepared by mechanically assisted synthesis. In addition to record of reduction in grain size with the increase of milling time, effects are also noted (change of position, relative intensity and half-width of Raman modes), which indicate changes in the structure, caused by nan dimensioned grains. Main difference in obtaining Raman spectra of nanocrystal powders $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ from mechanically activated $\text{Bi}_2\text{O}_3\text{--TiO}_2$ mixture, in regard to obtaining Raman spectra of samples the same through other procedures of synthesis or bulk crystals to compete in simultaneous existence Raman lines which correspond to both orthorhombic and tetragonal structure.

Acknowledgements

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