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Spectroscopy study of $Bi_4Ti_3O_{12}$ obtained from mechanically activated Bi_2O_3–TiO_2 mixtures

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Abstract

Bismuth titanate, $Bi_4Ti_3O_{12}$ 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 balk crystal. And also, coagulation of each line appears, as well as a significant asymmetry of certain modes.

Keywords: Mechanochemical synthesis; Crystal structure and symmetry; X-ray diffraction; Light absorption and reflection

1. Introduction

Bismuth titanate, $Bi_4Ti_3O_{12}$ has been extensively studied for its ferroelectric and other excellent properties. $Bi_4Ti_3O_{12}$ 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 $Bi_4Ti_3O_{12}$ have been reported in a number of papers, cited among others in references [2,3].

The layer structure of $Bi_4Ti_3O_{12}$ by the perovskite like $(Bi_2Ti_3O_{10})^{2-}$ layers sandwiched between two $(Bi_2O_2)^{2+}$ 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 materials. 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 $Bi_4Ti_3O_{12}$ 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 $Bi_4Ti_3O_{12}$ 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 Cu Kα graphite-monochromatized radiation (λ = 0.15418 Å).
- 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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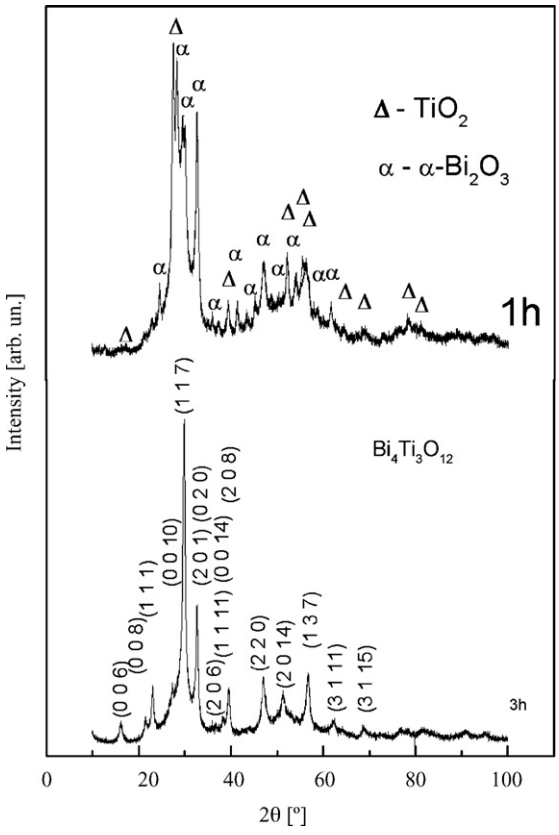

Fig. 1. XRD traces of $Bi_4Ti_3O_{12}$ prepared mechanochemical activation for 1 and 3 h.

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 carry 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 $Bi_4Ti_3O_{12}$ powder.

2.1. Sample characterization

The $Bi_4Ti_3O_{12}$ phase evolution prepared as stoichometric 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 1h, 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—$Bi_4Ti_3O_{12}$ 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 $Bi_4Ti_3O_{12}$ phase forms, which is shown at the difractogram for the sample milled 3 h. At the difractogram of the mixture milled 3 h, one can note all typical peaks of $Bi_4Ti_3O_{12}$ 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

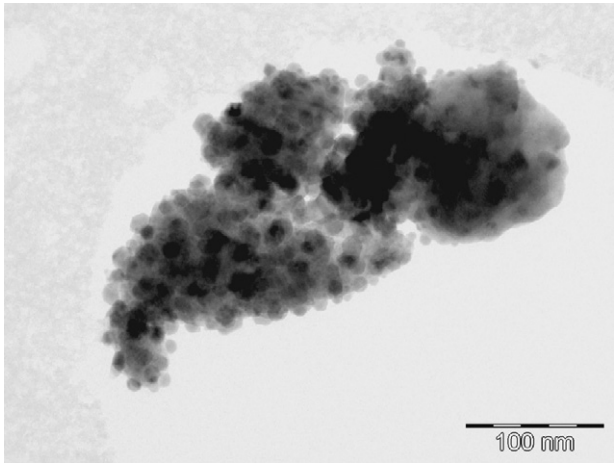

Fig. 2. TEM image of crystalline $Bi_4Ti_3O_{12}$ powder obtained after milling of 3 h.

crystal structure is. Therefore one can righteously 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] ((0 0 6) 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.

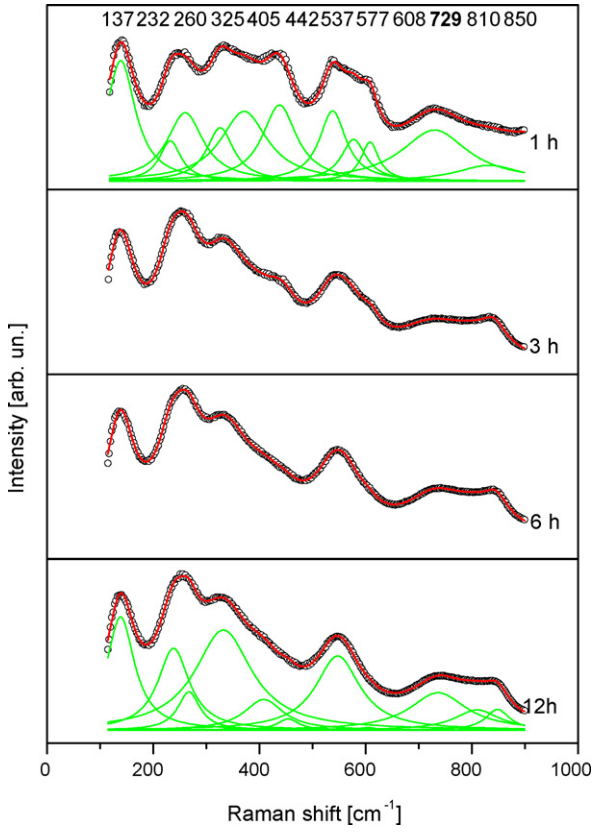

Fig. 3. Raman spectra of the $Bi_4Ti_3O_{12}$ samples prepared mechanochemical activation for 1, 3, 6 and 12 h at room temperature.