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**Author:** Grzegorz Dercz, Jolanta Rymarczyk, Aneta Hanc, Krystian Prusik, R. Babilas, Lucjan Pająk, Jan Ilczuk

**Citation style:** Dercz Grzegorz, Rymarczyk Jolanta, Hanc Aneta, Prusik Krystian, Babilas R., Pająk Lucjan, Ilczuk Jan. (2008). Structural studies with the use of XRD and Mossbauer spectroscopy of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ . "Acta Physica Polonica A" (Vol. 114, nr 6 (2008), s. 1623-1629).



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Proceedings of the Polish Mössbauer Community Meeting 2008

# Structural Studies with the Use of XRD and Mössbauer Spectroscopy of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ Ceramic Powders Obtained by Mechanical Synthesis

G. DERCZ<sup>a,\*</sup>, J. RYMARCZYK<sup>b</sup>, A. HANC<sup>a</sup>, K. PRUSIK<sup>a</sup>,  
R. BABILAS<sup>c</sup>, L. PAJĄK<sup>a</sup> AND J. ILCZUK<sup>b</sup>

<sup>a</sup>Institute of Materials Science, University of Silesia  
Bankowa 12, 40-007 Katowice, Poland

<sup>b</sup>Department of Material Science, University of Silesia  
Żeromskiego 3, 41-200 Sosnowiec, Poland

<sup>c</sup>Institute of Engineering Materials and Biomaterials  
Silesian University of Technology  
Konarskiego 18a, 44-200 Gliwice, Poland

In this paper the structural and Mössbauer spectral properties of multi-ferroic ceramic  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  powders prepared by high-energy ball milling of polycrystalline precursor material (mixture of  $\text{Bi}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  powders) are presented. Mechanical synthesis was performed by high-energy vibratory mill. The X-ray diffraction methods were applied for the structure characterization of the studied samples. The parameters of diffraction line profiles were determined by PRO-FIT Toraya procedure. The crystallite sizes and lattice distortions were analyzed using the Williamson–Hall method. Investigations of hyperfine interactions in the studied materials were carried out by the Mössbauer spectroscopy. The powder morphology was analyzed by scanning electron microscopy and transmission electron microscopy techniques. It was found that during high-energy milling phase transitions, a decrease in crystallite size and amorphization process are observed.

PACS numbers: 61.05.Qr, 61.05.C-, 61.05.J-, 81.07.Bc, 81.20.Wk

## 1. Introduction

The  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  multiferroic ceramic can be applied for construction of different electronic devices of the new generation. This type of ceramics is promis-

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\*corresponding author; e-mail: grzegorz.dercz@us.edu.pl

ing owing to the possibility of their application as different types of memory elements [1]. The term multiferroic describes materials showing at least two ferroic states simultaneously in the same phase. In the multiferroic materials  $M_s$  (the ordering parameter of the magnetic system),  $P_s$  (the ordering parameter of the electric system) and  $\eta_s P_s$  (the ordering parameter of the elastic–magnetic system) can be changed by a magnetic field ( $H$ ), an electric field ( $E$ ) and by mechanical stress ( $\sigma$ ) [2–4]. The  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramic belongs to ferroelectromagnetics characterized by the presence of simultaneous magnetic and ferroelectric ordering [5–7]. This class of materials exhibits a spontaneous magnetization and polarization that can be switched on by an applied magnetic and electric field, respectively [8].

Majority of ferroelectromagnetics have a layer perovskite-like structure. Structures of this type were revealed for the first time in 1949 by Aurivillius [9]. The Aurivillius phases are layered bismuth oxides of general formula  $\text{Bi}_2\text{A}_{m-1}\text{B}_m\text{O}_{3m+3}$  ( $1 \leq m \leq 6$ ) formed by the regular stacking of  $[\text{Bi}_2\text{O}_2]^{2+}$  slabs and perovskite-like blocks  $[\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}]^{2-}$ , where A represents mono-, di-, or trivalent cations ( $\text{Bi}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ba}^{2+}$  or  $\text{Na}^+$ ) and B represents tetra-, penta-, or hexavalent cations of a transition metal ( $\text{Ti}^{4+}$ ,  $\text{Ta}^{5+}$ ,  $\text{Nb}^{5+}$  or  $\text{W}^{6+}$ ). This means that the layers made of chains of oxygen octahedrons with thickness  $m$  separated with bismuth–oxygen layers interleave with each other.

By introducing  $\text{Fe}^{3+}$  cations into place B a group of compounds called ferroelectromagnetics with a general formula  $\text{Bi}_4\text{Bi}_{m-3}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$  ( $m = 1, 2, 3, 4, 5, 8$ ) can be obtained. The  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramic is a model ferroelectromagnetic of this type.

High-energy ball milling is a process in which elemental blends are milled to stimulate high-energy collisions among balls, thus achieving different types of reaction by diffusion at atomic and nanocrystalline levels [10, 11]. It is a well-established method for preparing extended solid solutions and amorphous, composite and nanocrystalline materials. Such preparation methods of nanostructured materials are promising for use at a production scale due to their simplicity and relatively low cost.

The aim of the present work is an attempt to prepare of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  multiferroic by mechanical synthesis. X-ray diffraction and the Mössbauer spectroscopy were used for structural analysis. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) methods were applied for the analysis of powder morphology.

## 2. Experimental

For synthesis of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  proceeds according to the following reaction:



The high-energy ball milling process was carried out in a vibratory mill SPEX 8000 CertiPrep Mixer/Mill type for 1 and 10 h under argon atmosphere. The balls to powder mass ratio was 5:1.

X-ray diffraction patterns were collected by X-Pert Philips diffractometer equipped with curved graphite monochromator on diffracted beam and a tube provided with copper anode and with the following slits (in the sequence from copper tube to proportional counter): Soller ( $2^\circ$ ), divergence ( $1/2^\circ$ ), antiscatter ( $1/2^\circ$ ), Soller ( $2^\circ$ ) and receiving (0.15 mm). The profiles of the diffraction lines were recorded by “step-scanning” mode in  $2\theta$  range from  $20^\circ$  to  $140^\circ$  and  $0.04^\circ$  step.

The values of full width at half maximum (FWHM) parameters of X-ray diffraction lines were determined using Toraya PRO-FIT procedure [12]. This procedure enables the determination of parameters of individual diffraction lines and applies Pearson VII function for the description of line profiles [13]. The NIST SRM660a (LaB<sub>6</sub> powder) was used for the determination of the instrumental line broadening. The crystallite sizes and lattice distortions were analyzed using the Williamson–Hall method [14]. The powder morphology was analyzed by SEM and TEM techniques. The above methods are standard ones in the studies of nanocrystalline materials [15–17].

Measurements of the  $^{57}\text{Fe}$  Mössbauer spectra were performed in transmission geometry by means of a constant spectrometer of standard design. The 14.4 keV gamma rays were provided by a 50 mCi source of  $^{57}\text{Co}/\text{Rh}$ . The spectra of the samples were measured at room temperature. Hyperfine parameters of the investigated spectra were related to the  $\alpha\text{-Fe}$  standard. Experimental spectrum shape was described with a transmission integral calculated according to the numerical Gauss–Legendre procedure.

### 3. Results and discussion

Qualitative phase analysis from X-ray data enabled the identification of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  (ICDD PDF 82-0063) and  $\text{Bi}_2\text{O}_3$  (ICDD PDF 72-0398) phases in the sample milled for 1 and 10 h (Fig. 1). Moreover, the X-ray diffraction investigations revealed that the 10 h milled sample contains both a crystalline and an amorphous phase. The presence of the broad diffraction halo at  $2\theta$  angles about  $29^\circ$  and  $50^\circ$  is characteristic of the amorphous structure. These effects indicate that high-energy ball milling causes the decrease in the crystallite size of the crystalline phase and increase in its lattice distortions.

As the result of 1 h milling process the crystallite size ( $D$ ) of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  and  $\text{Bi}_2\text{O}_3$  phases is equal to 18 nm and 14 nm, respectively. After rising the milling time to 10 h the crystallite size of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  increases to 23 nm. For  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  after 1 h and 10 h milling process the lattice distortions ( $\langle\Delta a/a\rangle$ ) are 0.18% and 0.11%, respectively. Increase in crystallite size and decrease in lattice distortions observed for  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  phase during high-energy milling indicating the presence of the amorphization process mainly concerns to oxide phases.

TEM and high-resolution TEM (HRTEM) images and electron diffraction pattern shown in Figs. 2 and 3 indicate that the powder particles of the sample

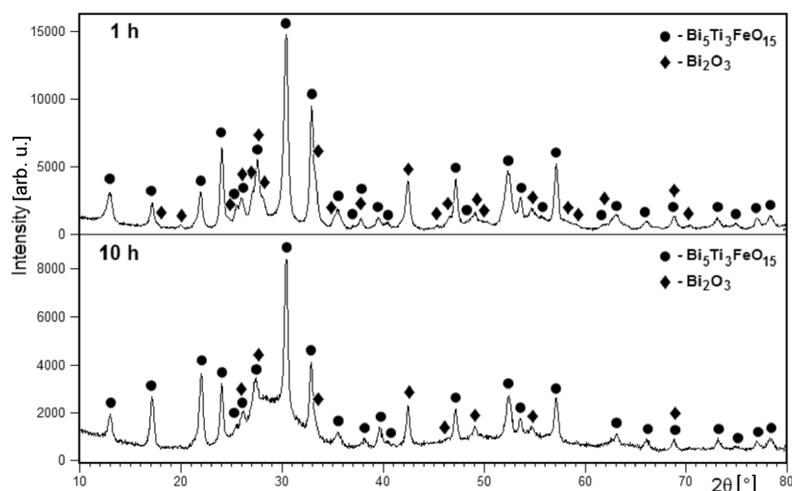


Fig. 1. X-ray diffraction patterns of precursor material mixture milled for 1 and 10 h.

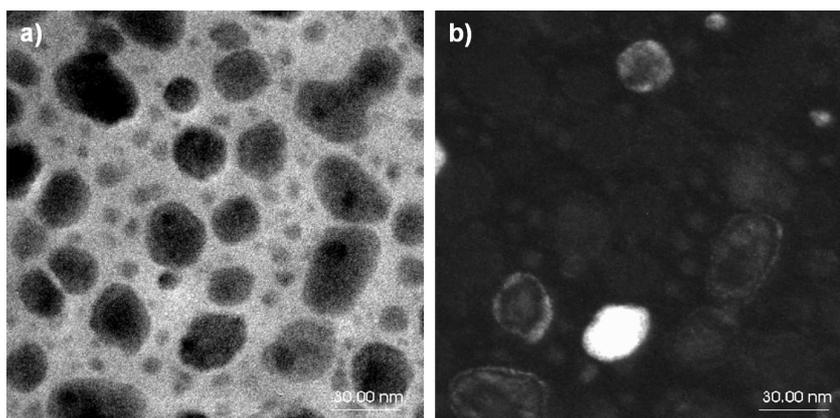


Fig. 2. TEM images of the sample milled for 10 h: (a) bright field, (b) dark field.

milled for 10 h contain nanosize particles which are immersed in an amorphous matrix. The particle size distribution is rather broad with particle diameter of the range from  $\approx 2$  nm to  $\approx 40$  nm. The above conclusions are confirmed by HRTEM image (Fig. 3). The electron microscopy results are in good correlation with the ones of the X-ray diffraction studies.

The Mössbauer spectra for samples after different milling time are shown in Fig. 4. Three distinct subspectra:  $\text{Fe}^{3+}$  Zeeman sextet (Z) and two ferric doublets (Q-1 and Q-2) were used in the fitting procedure (Table). Zeeman sextet (Z) can be attributed to desired  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  phase. Two ferric doublets can be associated with different phases: nanostructured hematite [18],  $(\text{Bi,Fe})_2\text{O}_3$  (which presents a sextet spectrum at room temperature for single crystalline samples [19]).

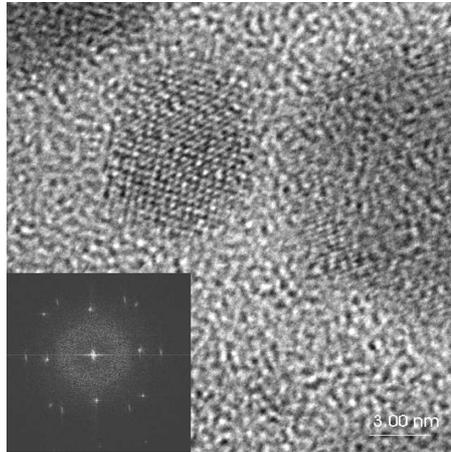


Fig. 3. HRTEM image of the sample milled for 10 h with electron diffraction pattern.

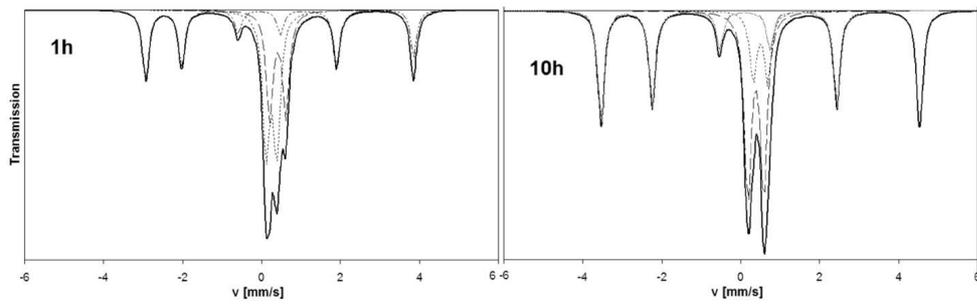


Fig. 4. Mössbauer spectra for the samples ground for 1 and 10 h.

TABLE

Hyperfine parameters of the milled samples.  $B_{\text{hf}}$  — hyperfine magnetic field, IS — isomer shift, QS — quadrupole splitting, A — concentration of phases.

Milling time [h]	Subspectra	$B_{\text{hf}}$ [kGs] $\pm 3$ [kGs]	IS [mm/s] $\pm 0.02$ [mm/s]	QS [mm/s] $\pm 0.02$ [mm/s]	A [%] $\pm 2$ [%]
1	Z	113	0.25	0.27	39
	Q-1		0.41	0.43	26
	Q-2		0.34	0.39	35
10	Z	126	0.29	0.23	71
	Q-1		0.49	0.37	11
	Q-2		0.38	0.43	18

The kinetics of the formation of the desired  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  phase during high-energy ball milling can be derived from the analysis of the Mössbauer spectra.

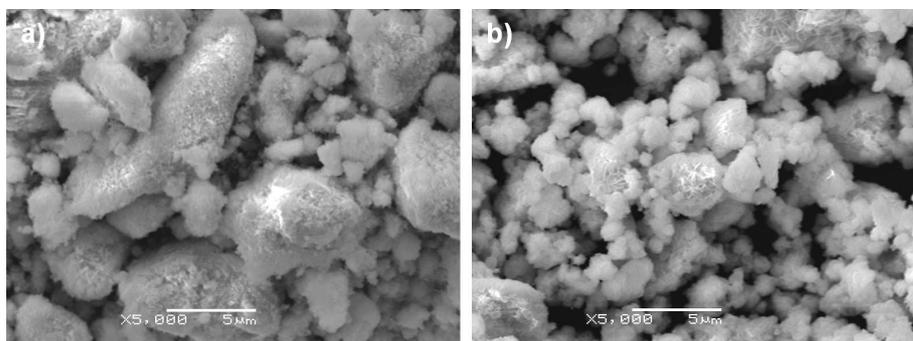


Fig. 5. The SEM images of ground sample for 1 (a) and 10 (b) h.

The content of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  phase is equal to about 40% after 1 h milling and increases to about 70% after 10 h milling.

Figure 5 shows the SEM images of the sample milled for 1 and 10 h. The decrease in grain size with the increase in the milling time is observed. Moreover, the SEM images revealed agglomerated fine-grained powder. The images presented in Fig. 5 point to the branched, rather loose structure of skeleton type.

#### 4. Conclusions

The investigations performed on the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  phase prepared by mechanical synthesis in high-energy ball mill allowed us to formulate the following conclusions:

- X-ray diffraction studies point to the formation of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  phase during high-energy ball milling of the precursor mixture of bismuth, titanium, and iron oxides.
- The Mössbauer spectroscopy confirmed the formation of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramic phase during milling process and revealed the presence of the remainder hematite and bismuth oxide ( $\text{Bi}_2\text{O}_3$ ) enriched in iron.
- High-energy ball milling process causes the increase in the crystallite size and decrease in lattice distortion of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  phase. Amorphization process concerns mainly the oxide phases.
- Electron microscopy studies indicate the presence of the crystalline phase and of the amorphous one. Moreover, the agglomeration of powder particles is observed.
- The applied investigation methods appeared to be very complementary for a more accurate structure characterization of the studied ceramic.

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