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STRUCTURE INVESTIGATIONS OF $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ CERAMICS PREPARED BY FREE SINTERING PROCESS OF HIGH-ENERGY BALL MILLED NANOCRYSTALLINE PRECURSORS

ANALIZA STRUKTURY CERAMIKI $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ OTRZYMANEJ W PROCESIE SWOBODNEGO SPIEKANIA Z NANOKRYSTALICZNYCH PREKURSORÓW

The tested material was prepared in two stages. In the first stage polycrystalline precursor material (mixture of Bi_2O_3 , TiO_2 and Fe_2O_3 powders) was ground with the use of high-energy vibratory mill. The second stage was free sintering of ground precursor material conducted at $800^\circ\text{C}/5$ hours.

The X-ray diffraction methods were applied for the structure characterization of the examined samples. The parameters of diffraction line profiles were determined by PRO-FIT Toraya procedure. The crystallite sizes and lattice distortions were analyzed using Williamson-Hall method. Investigations of hyperfine interactions in the studied materials were carried out by Mössbauer spectroscopy. The powder morphology was analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques.

X-ray diffraction studies indicate the formation of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ phase during high-energy ball milling of the precursor mixture of component oxides. Thus the phase transition proceeds during high-energy ball milling. Moreover decrease of crystallite size and amorphization process are observed. Electron microscopy observations point out the presence of crystalline phase and of amorphous one. X-ray diffraction pattern reveals the crystallization of only one, $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ phase during free sintering process.

Keywords: Bismuth titanate, Multiferroic ceramics, Aurivillius phase, XRD, TEM, SEM

Materiał testowy zastał przygotowany dwuetapowo. W pierwszym etapie polikrystaliczne prekursory (mieszanina proszków: Bi_2O_3 , TiO_2 i Fe_2O_3) zostały poddane procesowi wysokoenergetycznego mielenia przy użyciu młynka wibracyjnego. Tak przygotowana mieszanina została poddana w drugim etapie swobodnemu spiekaniu przez 5 godzin w temperaturze 800°C .

W oparciu o badania rentgenowskie przeprowadzono analizę strukturalną ceramiki. Metodę Toraya wraz z procedurą PRO-FIT wykorzystano do analizy parametrów profili linii dyfrakcyjnych. Wyznaczone parametry FWHM (Full Width at Half Maximum) linii dyfrakcyjnych były wykorzystane przy oszacowywaniu wielkości kryształitów i zniekształceń sieciowych metodą Williamsona-Halla. Analizę parametrów nadsubtelnych badanych ceramiki przeprowadzono przy użyciu spektroskopii Mössbauera. Morfologia oraz mikrostruktura została zanalizowana przy użyciu skaningowej (SEM) oraz transmisyjnej mikroskopii elektronowej (TEM).

Jakościowa analiza fazowa wykazała tworzenie się podczas wysokoenergetycznego mielenia fazy $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$. Szczegółowa analiza dyfraktogramów rentgenowskich wykazała, iż materiał podczas mielenia ulega nanokrystalizacji oraz amorfizacji, co potwierdziły badania przy użyciu transmisyjnej mikroskopii elektronowej. Stwierdzono, że dwuetapowy proces przygotowania materiału badań ceramiki pozwolił na otrzymanie jednofazowej ceramiki zawierającej $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$.

1. Introduction

The term multiferroic describes materials showing at least two ferroic states simultaneously in the same phase. The $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ multiferroic ceramic is promising owing to the possibility of its application as different types of memory elements of the new generation [1]. The

$\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ ceramic belongs to ferroelectromagnetics characterized by the presence of simultaneous magnetic and ferroelectric ordering [2-3] This class of materials exhibits a spontaneous magnetization and polarization that can be induced on by an applied magnetic and electric field, respectively [4].

In the multiferroic materials M_s (the ordering pa-

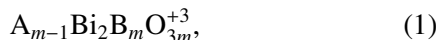
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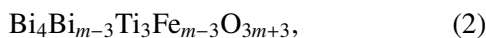
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parameter of the magnetic system), P_s (the ordering parameter of the electric system) and $\eta_s P_s$ (the ordering parameter of the elastic-magnetic system) can be changed by a magnetic field (H), an electric field (E) and by mechanical stress (σ) [5-6].

A large majority of ferroelectromagnetics have a layer perovskite-like structure, revealed for the first time in 1949 by Aurivillius and Subbaro [7] and described in 1969 according to a general formula:



where big cations A are: Ba^{2+} , Sr^{2+} , Ca^{2+} , Bi^{3+} , Pb^{4+} , and B are cations of transient metals: Ti^{4+} , Nb^{5+} , Ta^{5+} , Mo^{6+} , W^{6+} , Fe^{3+} , Mn^{2+} , m designates the number of perovskite layers along the thickness [6-13]. This means that the layers are composed of chains of oxygen octahedrons with thickness m separated by bismuth-oxygen layers laying alternately with each other. By introducing Fe^{3+} cations into the place of B a group of compounds called ferroelectromagnetics can be obtained with a general formula:



where: $m = 1, 2, 3, 4, 5, 8$.

The $Bi_5Ti_3FeO_{15}$ ceramics can be regarded as a model of this type of ferroelectromagnetics.

High-energy ball milling (HEBM) has appeared to be an important route for processing continuous extended solid solutions, amorphous, composites and nanocrystalline materials [8-11]. This is a process in which elemental blends are milled to stimulate high-energy collisions among balls, thus achieving different types of reactions by diffusion at atomic and nanocrystalline levels.

The aim of the present work is an attempt to prepare of $Bi_5Ti_3FeO_{15}$ multiferroic ceramic exhibiting a layer perovskite-like structure of the type according to formula (2) where $m = 4$, by mechanical synthesis and free sintering process. X-ray diffraction and Mössbauer spectroscopy were used for structural analysis. The SEM and TEM methods were applied for the analysis of powder morphology and microstructure, respectively.

2. Experimental details

The tested material was prepared in two stages. In the first stage high-energy ball milling process was carried out in a vibratory mill SPEX 8000 CertiPrep Mix-

er/Mill type for 1 and 10 hours under argon atmosphere. The balls to powder mass ratio was 5:1. The second stage of the technology was the free sintering process conducted at 800°C for 5 hours. The synthesized powder was subjected to pressing giving discs of 10 mm in diameter.

X-ray diffraction patterns were collected by X-Pert Philips diffractometer equipped with 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°), divergence (1/2°), antiscatter (1/2°), Soller (2°) and receiving (0.15 mm). The profiles of the diffraction lines were recorded by "step-scanning" mode in 2θ range from 20° to 140° and 0.04° step.

The values of *FWHM* (Full Width at Half Maximum) 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_6 powder) was used for the determination of the instrumental line broadening. The crystallite sizes and lattice distortions were analyzed using Williamson-Hall method [14]. The powder morphology and microstructure was analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. The above methods are standard ones in the studies of nanocrystalline materials [15-17].

Measurements of the ^{57}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 50mCi source of $^{57}Co/Rh$. The spectra of the samples were measured at room temperature. Hyperfine parameters of the investigated spectra were related to the α -Fe standard. Experimental spectrum shape was described with a transmission integral calculated according to the numerical Gauss-Legendre's procedure.

3. Results and discussion

Morphology of powder sample milled for 1 and 10 hours, revealed the decrease of the size of powder particles with the increase of the milling time (Fig. 1). SEM images show that milled material is of branched, rather loose skeleton type structure.

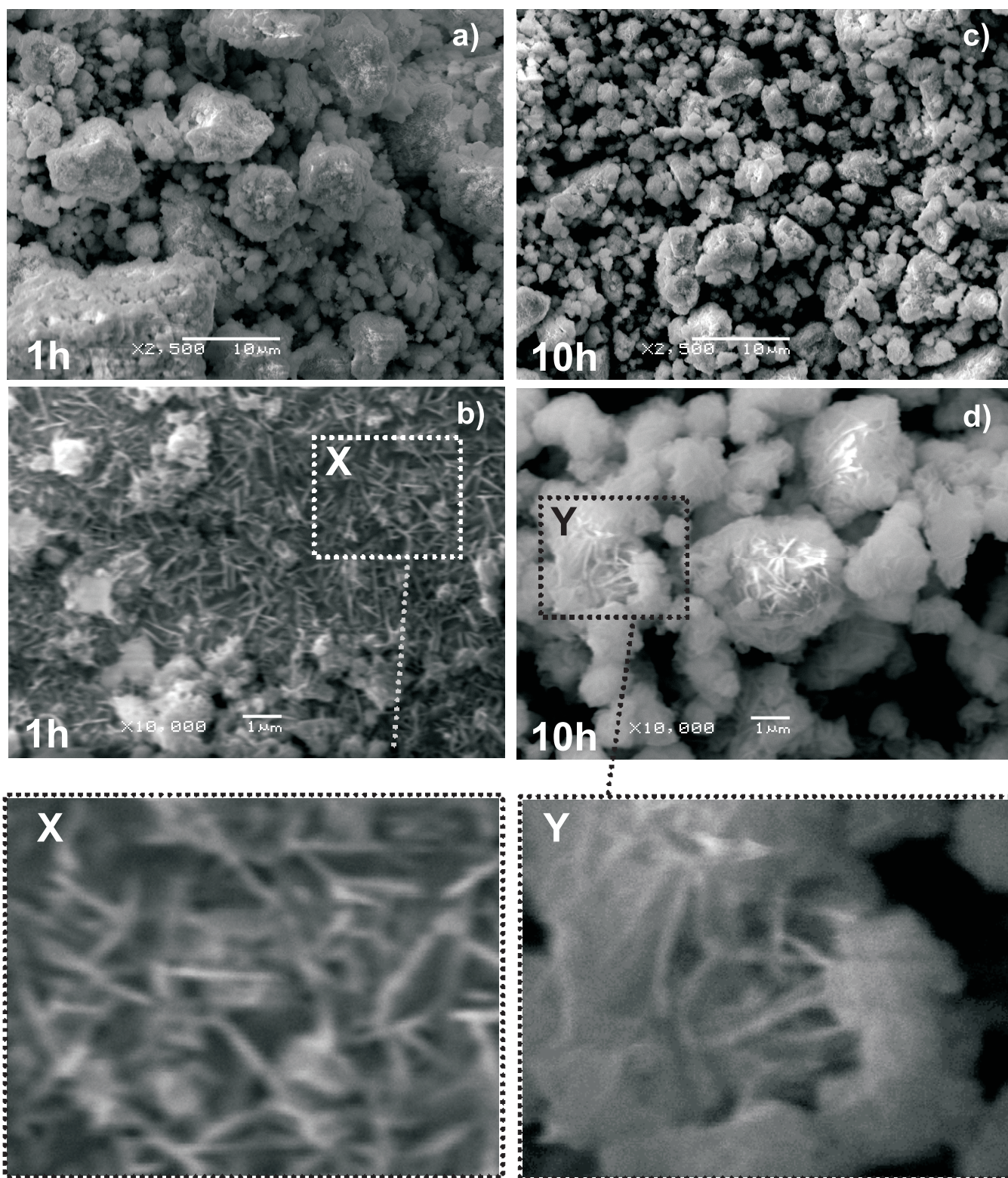


Fig. 1. The SEM images of samples ground for 1 (a, b) and 10 (c, d) hours and large images of the X and Y regions

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

The X-ray diffraction analysis reveals the presence of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ (ICDD PDF 82-0063) and Bi_2O_3 (ICDD PDF 72-0398) phases in the samples milled for 1 and 10 hours (Fig. 2).

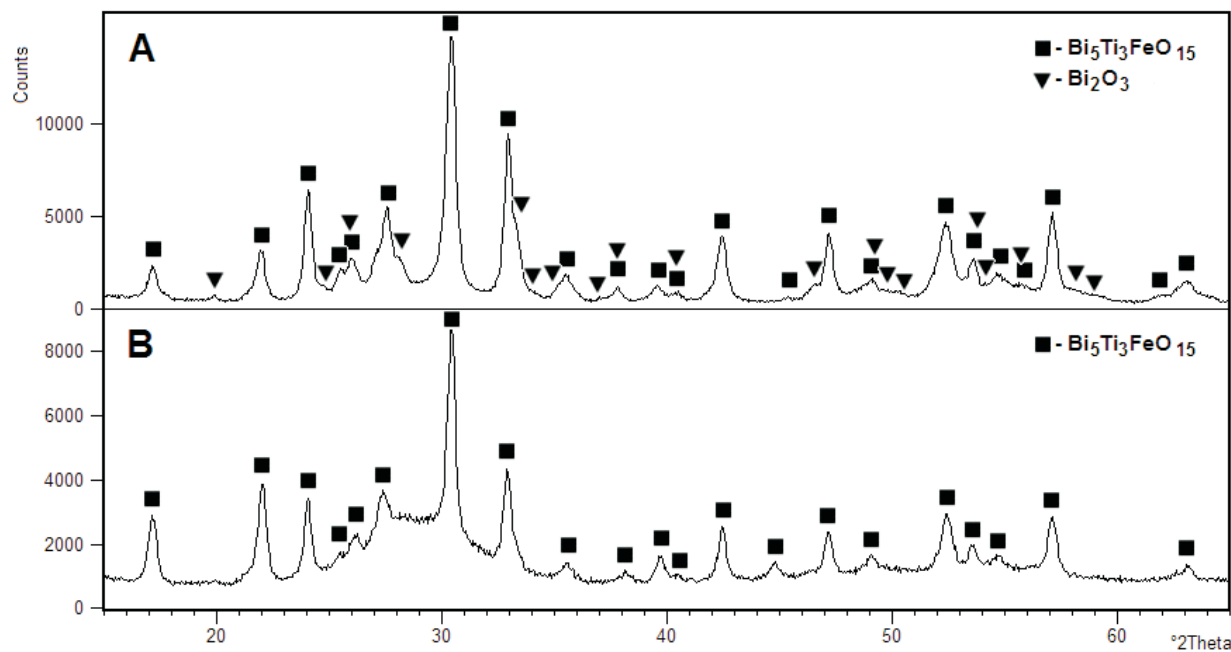


Fig. 2. X-ray diffraction patterns of precursor material milled for 1 (A) and 10 hours (B)

Detailed analysis of the X-ray diffraction patterns revealed that the 10 hour milled sample contains both a crystalline phase and amorphous one (diffraction halo at 2θ angles about 29° and 50°). From the analysis of Williamson-Hall plot (not presented here) it can be concluded that the crystallite size (D) of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ phase produced during milling process increases with the increase of the milling time and is equal to 18 nm and 23 nm for the samples milled for 1 and 10 hours, respectively. On the other hand the lattice distortion ($\langle \Delta a/a \rangle$) is equal to 0.18% and 0.11% for the

samples milled for 1 and 10 hours, respectively. From Mössbauer and XRD studies it can be concluded that the synthesis of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ phase during milling process is not complete. Shorter milling time gives smaller amount of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ phase of smaller crystallite size and larger lattice distortion. However longer milling time causes probably partial amorphization of oxide phases (Fig. 2). Above results were confirmed by HRTEM image and electron diffraction pattern shown in Fig. 3; sample milled for 10 hours contains nanosize particles which are “immersed” in amorphous matrix.

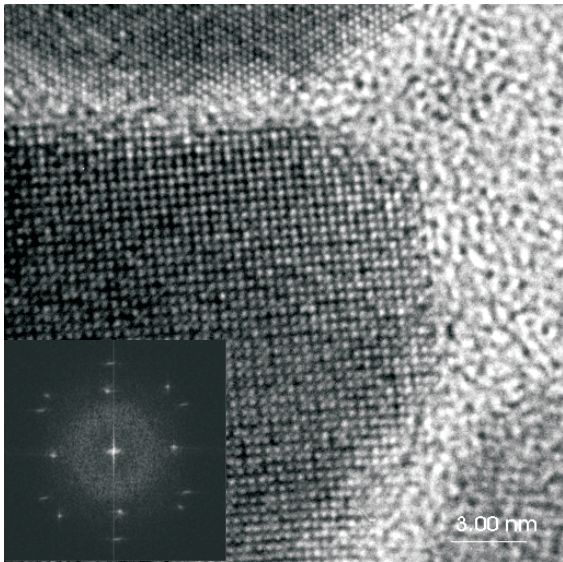


Fig. 3. HRTEM image of sample milled 10 hours and electron diffraction pattern

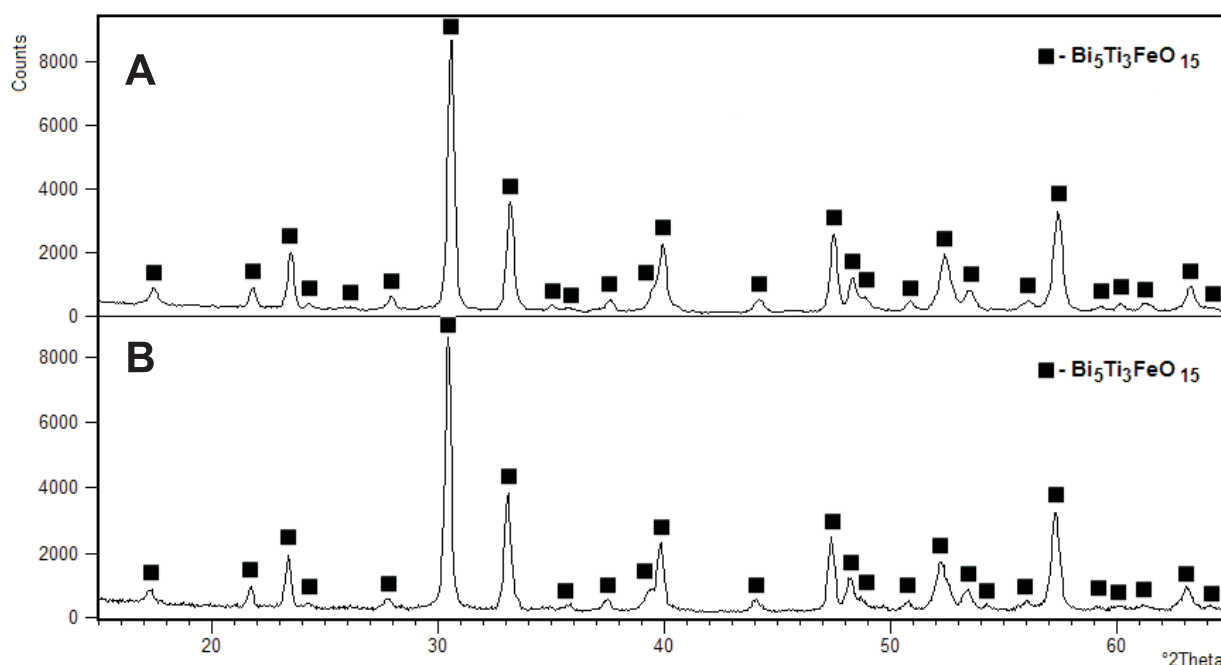


Fig. 4. X-ray diffraction patterns of ceramics obtained after free sintering process at 800°C for 5 h of samples milled for 1 (A) and 10 hours (B)

The X-ray diffraction investigations of the samples obtained by free sintering process performed at 800°C (using the mixture of precursor oxides) milled for 1 and 10 hours enabled the identification of only one crystalline phase – $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ (ICDD PDF 82-0063) (Fig. 4). The crystallite size of this phase is above 100 nm. This means that the synthesis of required phase can be regarded as complete.

4. Conclusions

- Free sintering process performed on the previously milled samples gives complete crystallization of the material in the form of only single, $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ microcrystalline phase.
- X-ray diffraction analysis performed during high-energy ball milling processes of the precursor mixture of bismuth, titanium, and iron oxides revealed the formation of nanocrystalline $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ phase.
- Shorter milling time gives smaller amount of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ phase of smaller crystallite size and larger lattice distortion. Amorphization process is also observed and probably can be concerned mainly to the oxide phases.
- Mössbauer spectroscopy conducted prior to sintering confirm at the formation of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ ceramic phase during milling process and reveal the presence of remains of Fe_2O_3 and Bi_2O_3 enriched in iron.

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