

Mössbauer studies of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ electroceramic prepared by mechanical activation

Streszczenie. W pracy przedstawiono wyniki badań dla multiferroicznej elektroceramiki $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ otrzymanej podczas procesu aktywacji mechanicznej (mielenie wysokoenergetyczne polikrystalicznych proszków Bi_2O_3 , TiO_2 i Fe_2O_3). Badania struktury i oddziaływań nadsubtelnych przeprowadzono metodami dyfrakcji promieniowania X oraz spektroskopii efektu Mössbauera.

Abstract. The present work involves the structure analysis and the determination of hyperfine interactions parameters of multiferroic $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ electroceramic, prepared by high-energy ball milling of polycrystalline precursors (mixture of the Bi_2O_3 , TiO_2 and Fe_2O_3 simple oxides). This analysis was performed by X-ray diffraction and Mössbauer spectroscopy. (**Badania mössbauerowskie elektroceramiki $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ otrzymanej w procesie aktywacji mechanicznej.**)

Słowa kluczowe: związki Aurivilliusa, aktywacja mechaniczna, oddziaływania nadsubtelne, spektroskopia mössbauerowska.

Keywords: Aurivillius compounds, mechanical activation, hyperfine interactions, Mössbauer spectroscopy.

Introduction

Materials on the basis of bismuth ferrite BiFeO_3 are of substantial interest because of applications in magnetoelectric devices, i.e. as different types of memory elements of new generation [1]. Magnetoelectric effect has been predicted by P. Curie in 1894 on the basis of symmetry conditions. This effect concerns materials which can be polarized electrically by placing them in a magnetic field and magnetically by placing them in an electric field [2]. Bismuth iron titanate $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ is an example of ferroelectromagnetic material, otherwise known as multiferroic, in which both ferroelectric and antiferromagnetic ordering exist simultaneously. Electroceramic $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ is Aurivillius phase of BiFeO_3 - $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ system. The elementary cell of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ presented in Fig. 1 is built from fluorite-like bismuth-oxygen layers $\{(\text{Bi}_2\text{O}_2)^{2+}\}$ alternate with (001) perovskite-like slabs $\{(\text{Bi}_4\text{Ti}_3\text{O}_{10})^{2-}\}$ [3].

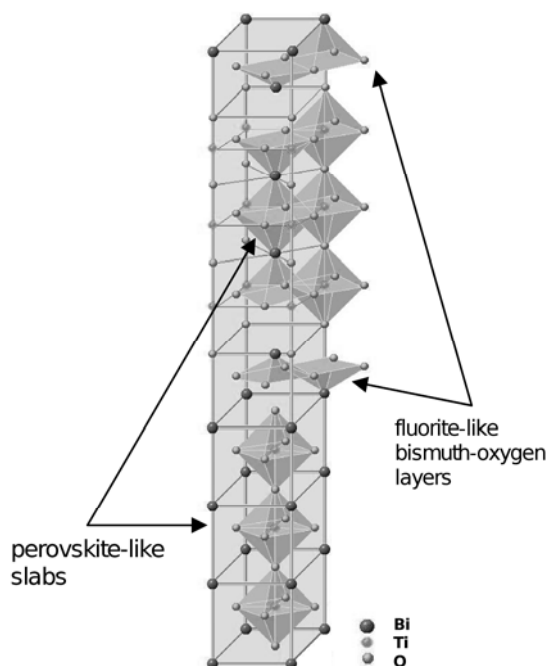


Fig. 1. The elementary cell of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [3]

In the case of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ the elementary cell contains four perovskite-like layers per slab, in which three oxygen-

octahedra have Ti ion at the centre and one octahedron has Fe ion [4, 5].

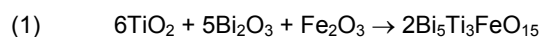
The materials with the Aurivillius structure are promising from the applications point of view. Their properties make possible the wide practical use of these materials in the electronics industry and electrical engineering. Useful properties of Aurivillius compounds are connected with the appropriate chemical composition and deformations of the crystalline structure, such as the ions displacements caused by temperature, electric field or the oxygen octahedral chains rotation. In such materials the magnetization can be controlled by the electric field and vice versa: the electric polarization can be steering by the magnetic field.

The standard method for preparation of ceramics is a solid-state sintering. However, equally promising technology is a mechanical activation (MA). It is a high-energy ball milling process in which elemental precursors are repeatedly fragmented, flattened, welded and fractured. Such a preparation method may be used in an industrial scale.

The aim of this work was to investigate the hyperfine interactions in multiferroic Aurivillius phase $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ prepared by MA. The investigations of the structure and magnetic properties of the samples were performed using X-ray diffraction (XRD) and Mössbauer spectroscopy (MS).

Experimental details

$\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ ceramic powder was prepared by the high-energy ball milling in a Fritsch Pulverisette P5 planetary ball mill, using hardened steel medium (vial and balls). Three simple oxides, viz. Bi_2O_3 , TiO_2 and Fe_2O_3 were weighted and mixed together according to the following solid-state reaction:



The ball-to-powder weight ratio was 10:1. The total weight of the powders was 10 g. For selected times the milling process was interrupted and a small amount of the milled powders was taken out for further examinations.

Thermal treatment of the mechanically activated $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ compound was performed in two ways: (1) heating from the room temperature up to 993 K in a calorimeter (Perkin Elmer DSC 7) under an argon atmosphere with the rate of 20 K per min and (2) isothermal annealing in a furnace at 973 and 1073 K for 1 h in vacuum.

XRD measurements were carried out using a Philips PW 1830 diffractometer working in a continuous scanning mode with $\text{CuK}\alpha$ radiation.

Mössbauer spectroscopy studies were carried out on POLON spectrometer in the transmission geometry at room temperature. The source ^{57}Co in a Cr matrix with an activity of about 10 mCi was used. Hyperfine interactions parameters of the investigated material were related to the $\alpha\text{-Fe}$ standard.

Results and discussion

Fig. 2 shows the XRD patterns of the powders mechanically activated for various milling times.

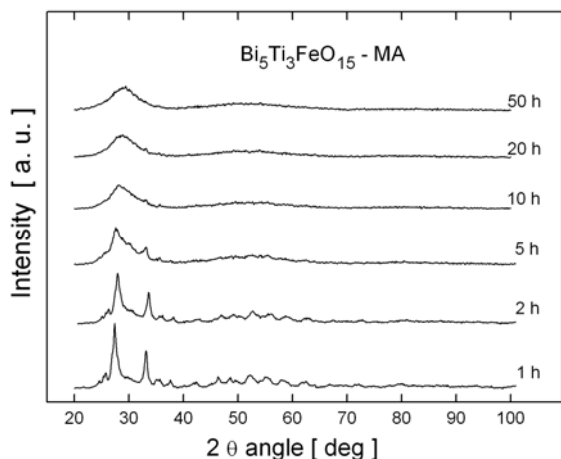


Fig.2. X-ray diffraction patterns of the oxides mixture milled for different times

It may be seen that the diffraction peaks are shifted and broadened as the milling time increases. It means that during milling the crystalline phases systematically transform into nanocrystalline and/or amorphous state (amorphous halo near $2\theta = 30^\circ$ is visible for the samples milled for 10, 20 and 50 h). After heating up to 993 K and isothermal annealing at 973 K the desired $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ compound was formed what is proved by XRD patterns presented in Fig. 3 (the angular positions of diffraction peaks are marked by short vertical lines according to database [6]). The crystallite sizes were analyzed using the Debye-Scherrer method. It was found that the average crystallite sizes of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ compound heated up to 993 K are about 30 nm while those of compound annealed at 973 K are 40 nm.

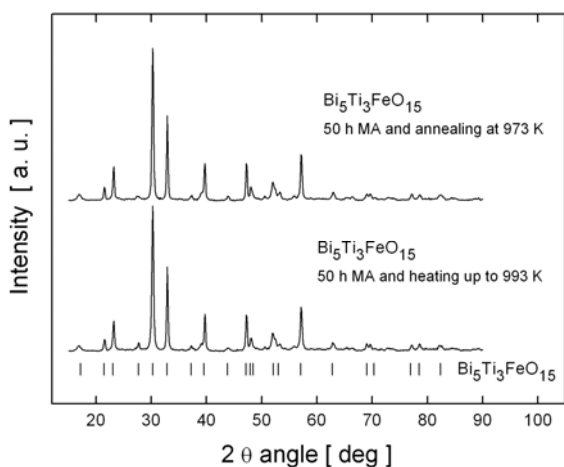


Fig.3. XRD patterns of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ compound after mechanical activation and heating up to 993 K and annealing at 973 K

Mössbauer spectra of the oxides mixture after various milling times are presented in Fig. 4. It may be seen that spectrum for 2 h is a sextet that is characteristic for hematite. Spectra for 10 and 50 h are a superposition of the six lines and paramagnetic doublet in the centre. The numerical fitting of the spectra allowed determining the hyperfine interactions parameters which are listed in Table 1. The six-line component originates from the hematite and the paramagnetic doublet is attributed to the $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ electroceramic.

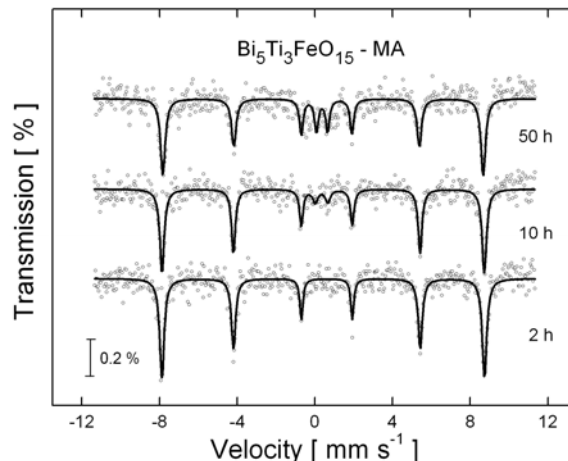


Fig.4. Room-temperature Mössbauer spectra of mechanically activated $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ electroceramic after various milling times

Table 1. Hyperfine interactions parameters of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ after MA and after thermal treatment; IS – isomer shift relative to $\alpha\text{-iron}$, QS – quadrupole splitting of the doublet (D), Δ – quadrupole shift of the sextet (S), B_{hf} – hyperfine magnetic field.

	IS [mm/s]	QS [mm/s]	Δ [mm/s]	B_{hf} [T]	Remarks
2 h MA	0.38(1)	–	0.10(1)	51.69(33)	S – hematite
10 h MA	0.20(5) 0.37(1)	0.32(5) –	– 0.10(1)	– 51.65(38)	D – $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ S – hematite
50 h MA	0.23(2) 0.37(1)	0.29(2) –	– 0.10(1)	– 51.34(47)	D – $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ S – hematite
Annealed at 973 K	0.36(1) 0.37(1)	0.28(1) –	– 0.11(1)	– 51.50(39)	D – $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ S – hematite
Annealed at 1073 K	0.36(1) 0.37(1)	0.29(1) –	– 0.11(1)	– 51.47(61)	D – $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ S – hematite
Heated up to 993 K	0.36(1) 0.37(1)	0.28(1) –	– 0.11(1)	– 51.46(51)	D – $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ S – hematite

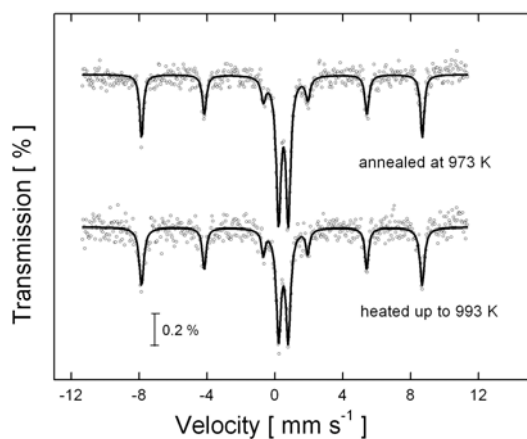


Fig.5. Room-temperature Mössbauer spectra of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ mechanically activated and annealed at 973 K and heated up to 993 K

Fig.5 presents MS spectra for $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ mechanically activated and thermally treated. It may be noted that besides the paramagnetic doublet in the centre of the spectra the sextet from the hematite is still visible for the heated as well as for the annealed sample. The contribution of the doublet is larger than the sextet.

The obtained results induced us to perform the annealing process at the higher temperature, i.e. at 1073 K. Fig.6 presents XRD pattern of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ compound after mechanical activation and annealing at 1073 K. It may be stated that main phase is the desired $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ electroceramic, however small amount of the hematite still exists in the sample. It may be supposed that not a whole amount of hematite reacted during thermal processing or small quantity of iron-oxides impurities from the milling media was introduced into the sample. On the other hand it is known that bismuth evaporates from the mixture during technological process [7] and consequently the overabundance of hematite is expected.

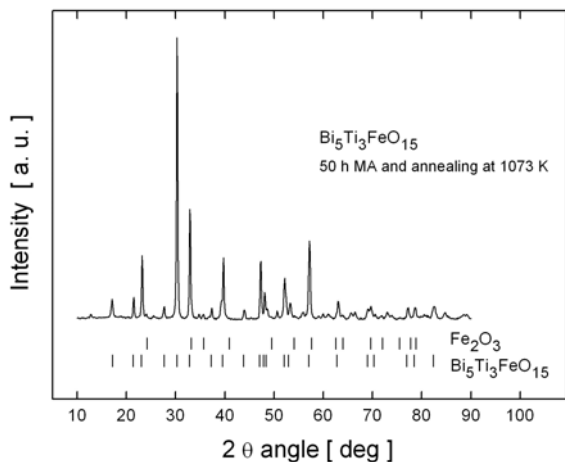


Fig.6. XRD pattern of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ compound after mechanical activation and annealing at 1073 K; short vertical lines are marked at angular positions of diffraction peaks for hematite and $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ according to databases [8] and [6], respectively

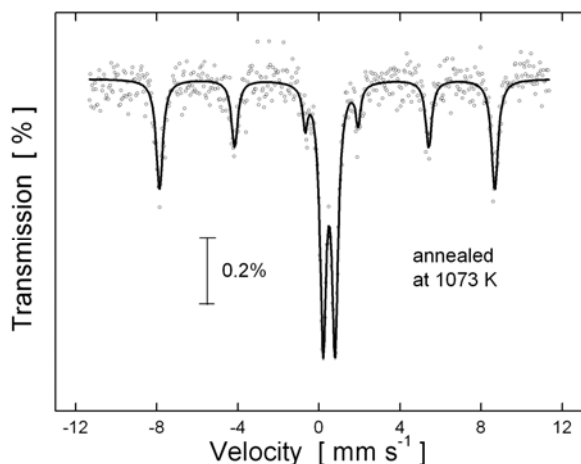


Fig.7. Room-temperature Mössbauer spectrum of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ mechanically activated and annealed at 1073 K

Mössbauer measurement confirmed the XRD results. Fig.7 presents the spectrum for $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ compound after mechanical activation and annealing at 1073 K. It may be seen that besides the paramagnetic doublet which originates from the desired $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ compound the sextet from hematite is still visible in the spectrum.

The hyperfine interactions parameters determined from the spectra for $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ compound mechanically activated and thermally treated are presented in Table 1. The obtained results agree well with the data for conventionally sintered ceramic [9].

Conclusions

Mechanical activation allows obtaining $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ electroceramic; however, technological process must be improved. X-ray diffraction and Mössbauer spectroscopy as complementary techniques may be used to monitoring of technological process. Mechanical activation as well as solid-state sintering give the possibility to produce single-phased compound. The heat treatment plays an important role in both cases. In the conventional solid-state route, the sintering at various temperatures under the pressure is the consecutive stage of the process. Mechanical activation seems to be a simpler method; however the final product of milling requires thermal treatment to complete the solid-state reaction. The values of hyperfine interaction parameters of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ electroceramic were determined firstly for mechanically activated samples, in accordance with the knowledge of the authors. The improvement of technological process will be the subject of further investigations.

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