

Hyperfine interactions in multiferroic mechanically activated BiFeO₃ compound

Streszczenie. W pracy przedstawiono wyniki badań strukturalnych i magnetycznych dla multiferroicznego związku BiFeO₃ otrzymanego w procesie aktywacji mechanicznej. Badania struktury i oddziaływań nadsubtelnych przeprowadzono odpowiednio metodami dyfrakcji promieniowania X oraz spektroskopii efektu Mössbauera.

Abstract. In this work the results of structural and magnetic investigations for multiferroic BiFeO₃ compound prepared by mechanical activation are presented. The structural analysis and hyperfine interactions investigations were performed by X-ray diffraction and Mössbauer spectroscopy, respectively. (Oddziaływania nadsubtelne w multiferroicznym związku BiFeO₃ otrzymanym w procesie aktywacji mechanicznej).

Słowa kluczowe: żelazian bizmutu, aktywacja mechaniczna, oddziaływania nadsubtelne, spektroskopia mössbauerowska

Keywords: bismuth ferrite, mechanical activation, hyperfine interactions, Mössbauer spectroscopy

Introduction

Bismuth ferrite BiFeO₃ (or BFO) is one of the most known multiferroics in which ferroelectric and antiferromagnetic ordering exist at room temperature. BiFeO₃ is reported to have a rhombohedrally distorted perovskite-like structure with space group *R3c* where the unit cell has parameters $a = 5.58102(4)$ Å and $c_{hex} = 13.8757(2)$ Å in the hexagonal setting [1]. The multiferroic properties of BFO are as follows: ferroelectric Curie temperature $T_C = 1100$ K and antiferromagnetic Néel temperature $T_N = 640$ K [1]. These properties result from the displacements of Fe³⁺, Bi³⁺ and O²⁻ ions from their positions in the ideal monomolecular perovskite structure as seen in Fig. 1 [2].

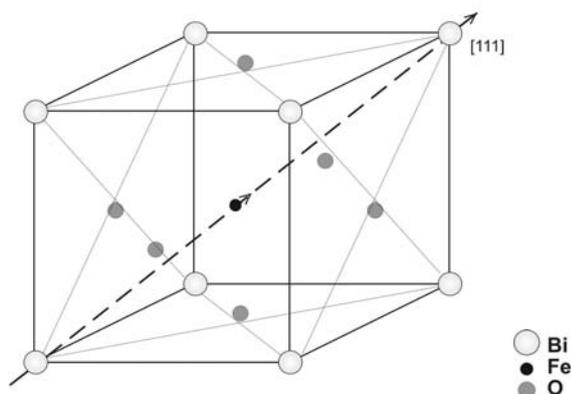


Fig. 1. The ideal monomolecular perovskite structure of BiFeO₃

The displacement of iron ion is equal to 0.23 Å from the centre of the oxygen octahedron along the [111] direction. Bismuth ions are also shifted along [111] axis by 0.62 Å [2]. Displacements of O²⁻ from their centrosymmetric positions are not definitely determined and no agreement concerning the values of the shifts exists in literature.

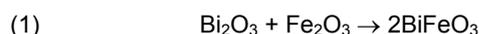
The possessing of both ferroelectric and antiferromagnetic properties above an ambient temperature makes the BFO very attractive material from the application point of view. Recently, researches make every effort to synthesize BFO as a pure phase in polycrystalline form. Among many preparation methods there are the conventional solid-state sintering, the rapid-liquid-phase sintering [3], sol-gel route [4] and solid-state ionic titration technique [5]. In most of cases the presence of impurity phases, mainly Bi₂Fe₄O₉ or Bi₂₅FeO₄₀ leads to poor ferroelectric behavior. Recently, the mechanical activation (MA) has been reported as an efficient method to prepare

the pure phase of BFO as polycrystalline [6] or nanocrystalline material [7]. In this technique the mechanical treatment is performed in the suitable ball mill and necessary thermal processing completes the formation of the ceramic phase.

In this work mechanical activation was performed in two manners: (1) mixing and milling of stoichiometric amounts of Bi₂O₃ and Fe₂O₃ followed by thermal treatment and (2) separate milling of individual Bi₂O₃ and Fe₂O₃ powders, mixing, further milling and thermal processing. The structure of BFO samples was examined using X-ray diffraction (XRD). The main goal of the present study was to determine hyperfine interactions parameters in the BFO obtained by MA using Mössbauer spectroscopy (MS).

Experimental details

Mechanical activation of the stoichiometric amounts of the Fe₂O₃ and Bi₂O₃ oxides (all 99.9% purity, Aldrich Chemical Co.) was performed according to the solid-state reaction:



MA processes were carried out into the hardened steel vial of a Fritsch P5 Pulverisette planetary ball mill equipped with hardened steel balls. The ball-to-powder weight ratio was 10:1. In the first process (MA I) both oxides were milled together up to 100 h under an air atmosphere. After the MA process the mixture was annealed isothermally in a furnace at 973 K in air for 1 h. In the second MA process (MA II), the Fe₂O₃ and Bi₂O₃ oxides were milled separately up to 10 h in air and then the powders were mixed and milled together during various times up to 50 h in air. Thermal processing of the obtained mixtures was performed in two ways: (a) heating from the room temperature up to 993 K in a calorimeter (DSC) under an argon atmosphere with the rate of 20 Kmin⁻¹ and (b) isothermal annealing in a furnace at 973 K in air for 1 h. The crystalline structure of the mechanically activated samples was analyzed by the Rigaku MiniFlex II diffractometer with CuK_α radiation. MS studies were carried out at room temperature in standard transmission geometry using a source of ⁵⁷Co in a chromium matrix. A 25-μm-thick metallic iron foil was taken as a standard for calibration of a spectrometer.

Results and discussion

In Fig. 2 the XRD patterns of mechanically activated Fe₂O₃ and Bi₂O₃ oxides for various milling times are presented together with the pattern for annealed mixture. It

may be seen that during milling process the diffraction peaks are broadened and shifted. After 100 h MA I the formation of the new crystalline phase may be observed, however it is not a pure BFO. To complete the solid-state reaction the isothermal annealing process at 973 K was performed. Unfortunately, besides the main BFO phase the diffraction peaks coming from impurity $\text{Bi}_2\text{Fe}_4\text{O}_9$ phase are also visible. The estimated contribution of the desired BFO is about 70 % and the average crystallite sizes of this compound determined using Scherrer formula are 45 nm +/- 10 nm.

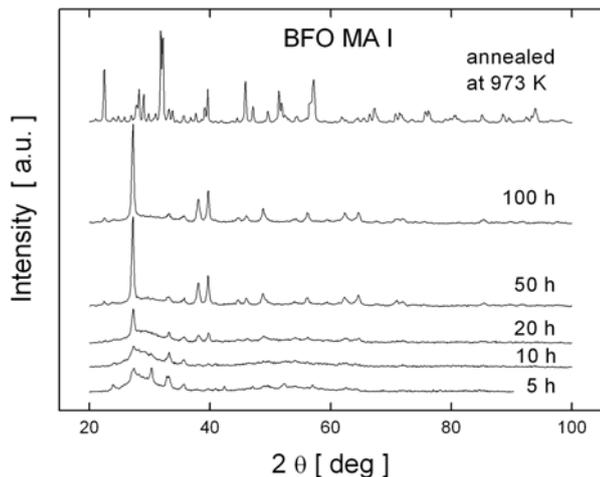


Fig.2. X-ray diffraction patterns of the Fe_2O_3 and Bi_2O_3 oxides mixture milled for different times and annealed at 973 K.

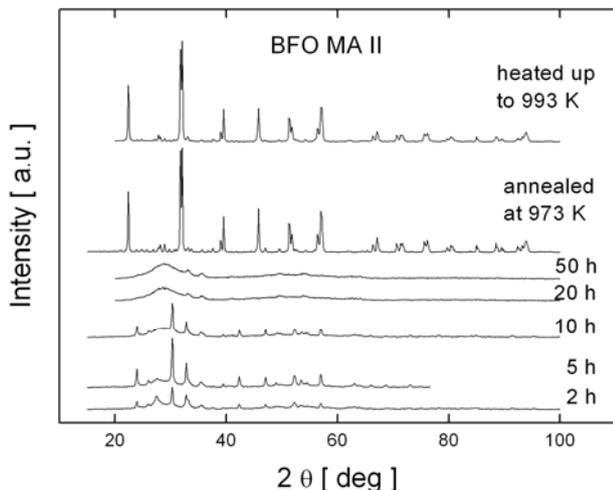


Fig.3. X-ray diffraction patterns of the initially milled Fe_2O_3 and Bi_2O_3 oxides, then mechanically activated during different times and subsequently annealed at 973 K and heated up to 993 K.

Fig. 3 presents XRD patterns of the initially milled Fe_2O_3 and Bi_2O_3 oxides up to the nanometer level (~20 nm) and subsequently mechanically activated during 2-50 h. It may be noted that after 50 h MA II the mixture is practically amorphous. After thermal treatment the desired BFO phase is formed in 90 %, as roughly estimated from XRD patterns. About 10 % of material makes impurity phase $\text{Bi}_2\text{Fe}_4\text{O}_9$. After thermal processing the average crystallite sizes of BiFeO_3 phase are as follows: 70 nm +/- 25 nm for heated material and 72 nm +/- 24 nm for annealed sample. Detailed phase and structural analysis using Rietveld method performed for the sample milled for 50 h and annealed at 973 K allowed determining the lattice

parameters as follows $a = 5.5745(4)$ Å, $c = 13.8588(6)$ Å. The obtained values agree well with the data base [8].

Mössbauer spectroscopy confirmed XRD results. Spectra for mixtures milled during MA I process for 10-100h are a superposition of one sextet and one doublet (Fig. 4).

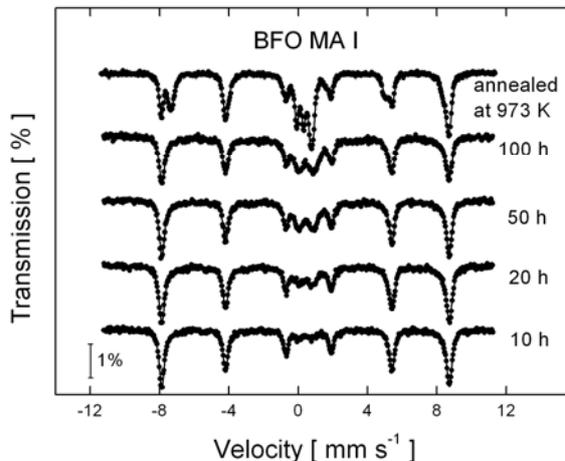


Fig.4. Room-temperature Mössbauer spectra of the Fe_2O_3 and Bi_2O_3 oxides milled for different times and annealed at 973 K.

Both sextet and doublet may be attributed to the bismuth iron oxides with unknown chemical composition $\text{Bi}_x\text{Fe}_y\text{O}_z$ with small amount of hematite Fe_2O_3 . After isothermal annealing of the sample, in the Mössbauer spectrum sextets are clearly separated (top spectrum in Fig. 4). Besides two sextets attributed to the desired BFO compound, two doublets and sextet from hematite were fitted to the spectrum. The numerical fitting of the experimental spectra allowed obtaining the hyperfine interactions parameters of each component. They are listed in Table 1.

Table 1 Hyperfine interactions parameters of BiFeO_3 compound prepared by MA I process: IS – isomer shift relative to α -iron, QS – quadrupole splitting for the doublet (D) and quadrupole shift for the sextet (S), B_{hf} – hyperfine magnetic field; uncertainty of the values are given in parentheses for the last significant number.

Milling time	IS [mm/s]	QS [mm/s]	B_{hf} [T]	Component/compound
10 h	0.28(2)	0.39(2)	—	D
MA I	0.37(1)	-0.09(1)	51.63(1)	S
20 h	0.31(1)	0.39(1)	—	D
MA I	0.37(1)	-0.09(1)	51.62(1)	S
50 h	0.33(1)	0.41(1)	—	D
MA I	0.37(1)	-0.09(1)	51.56(1)	S
100 h	0.35(1)	0.44(1)	—	D/ $\text{Bi}_x\text{Fe}_y\text{O}_z$
MA I	0.37(1)	-0.09(1)	51.49(1)	S/ $\text{Bi}_x\text{Fe}_y\text{O}_z$ + Fe_2O_3
100 h MA I + annealing at 973 K	0.16(1)	0.39(1)	—	D 1/ $\text{Bi}_2\text{Fe}_4\text{O}_9$
	0.44(1)	-0.27(1)	—	D 2/ sillenite
	0.38(1)	0.16(1)	49.43(2)	S 1/ BFO
	0.39(1)	-0.06(1)	49.17(2)	S 2/ BFO
	0.37(1)	-0.09(1)	51.73(1)	S 3/ hematite

The obtained parameters for Fe_2O_3 , $\text{Bi}_2\text{Fe}_4\text{O}_9$, sillenite $\text{Bi}_{25}\text{FeO}_{40}$ and BFO are in good agreement with the literature data [9-12].

In the case of the MA II process (Fig. 5) MS spectra were computer fitted using two doublets and three sextets. Two of three sextets may be attributed to the nanostructured BFO compound; however, small amount of hematite is still visible. As previously, paramagnetic doublets in the spectra are attributed to the impurity phases $\text{Bi}_2\text{Fe}_4\text{O}_9$ and sillenite. All the values of hyperfine interactions parameters listed in Table 2 are in good agreement with the literature data [1-2, 12-13].

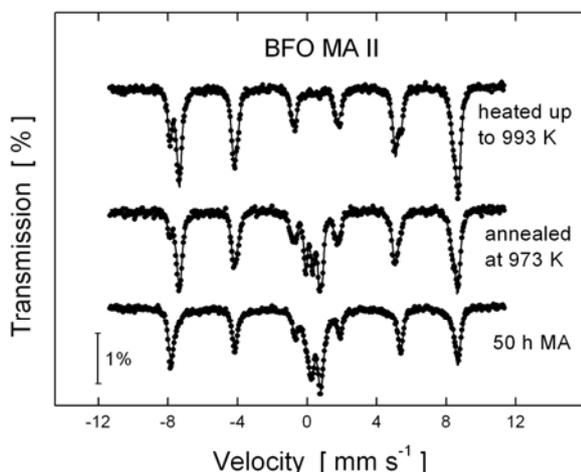


Fig.5. Room-temperature Mössbauer spectra of the initially milled Fe_2O_3 and Bi_2O_3 oxides, then mechanically activated during 50 h and subsequently annealed at 973 K and heated up to 993 K.

Table 2 Hyperfine interactions parameters of BiFeO_3 compound prepared by MA II process: IS – isomer shift relative to α -iron, QS – quadrupole splitting for the doublet (D) and quadrupole shift for the sextet (S), B_{hf} – hyperfine magnetic field; uncertainty of the values are given in parentheses for the last significant number.

Milling time and thermal treatment	IS [mm/s]	QS [mm/s]	B_{hf} [T]	Component/compound
50 h MA II	0.23(4)	0.43(4)	—	D 1/ $\text{Bi}_2\text{Fe}_4\text{O}_9$
	0.37(1)	-0.27(1)	—	D 2/ sillenite
	0.36(2)	0.08(2)	48.93(14)	S 1/ BFO-nano
	0.36(1)	-0.17(1)	49.19(9)	S 2/ BFO-nano
	0.38(1)	-0.09(1)	51.40(1)	S 3/ hematite
50 h MA II + heating up to 993 K	0.14(4)	0.37(3)	—	D 1/ $\text{Bi}_2\text{Fe}_4\text{O}_9$
	0.40(6)	-0.20(6)	—	D 2/sillenite
	0.38(1)	0.15(1)	49.65(2)	S 1/ BFO
	0.39(1)	-0.04(1)	49.31(2)	S 2/ BFO
	0.38(1)	-0.10(1)	51.69(2)	S 3/ hematite
50 h MA II + annealing at 973 K	0.16(1)	0.38(1)	—	D 1/ $\text{Bi}_2\text{Fe}_4\text{O}_9$
	0.44(1)	-0.27(1)	—	D 2/ sillenite
	0.39(1)	0.16(1)	49.62(2)	S 1/ BFO
	0.38(1)	-0.05(1)	49.23(2)	S 2/ BFO
	0.38(1)	-0.09(1)	51.75(6)	S 3/ hematite

Conclusions

Mechanical activation method allowed obtaining the desired BFO compound with small amount of impurities. The gradual heating in the calorimeter seems to be more effective method in terms of an amount of paramagnetic impurities. The values of the hyperfine magnetic fields for mechanically activated BFO are smaller than those for conventionally sintered samples. This is mainly due to the reduced grain sizes to the nanometer level as well as the residual strains introduced into the sample during mechanical milling process. Moreover, desired BFO phase

was formed by mechanical activation and subsequently thermal processing at the temperature lower by 30-50 K as compared to the conventional sintering method.

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