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Comparative X-ray diffraction and Mössbauer spectroscopy studies of $BiFeO_3$ ceramics prepared by conventional solid-state reaction and mechanical activation

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The aim of this work was to prepare $BiFeO_3$ by modified solid-state sintering and mechanical activation processes and to investigate the structure and hyperfine interactions of the material. X-ray diffraction and Mössbauer spectroscopy were applied as complementary methods. In the case of sintering, $BiFeO_3$ phase was obtained from the mixture of precursors with 3 and 5 % excess of Bi_2O_3 during heating at 1023 K. Small amounts of impurities such as $Bi_2Fe_4O_9$ and sillenite were recognized. In the case of mechanical activation, the milling of stoichiometric amounts of Bi_2O_3 and Fe_2O_3 followed by isothermal annealing at 973 K resulted in formation of the mixture of $BiFeO_3$, $Bi_2Fe_4O_9$, sillenite and hematite. After separate milling of individual Bi_2O_3 and Fe_2O_3 powders, mixing, further milling and thermal processing, the amount of desired $BiFeO_3$ pure phase was significantly increased (from 70 to 90 %, as roughly estimated). From Mössbauer spectra, the hyperfine interaction parameters of the desired $BiFeO_3$ compound, paramagnetic impurities of $Bi_2Fe_4O_9$ and sillenite were determined. The main conclusion is that the lowest amount of impurities was obtained for $BiFeO_3$ with 3 % excess of Bi_2O_3, which was sintered at 1023 K. However, in the case of mechanical activation, the pure phase formed at a temperature by 50 K lower as compared to solid-state sintering temperature. X-ray diffraction and Mössbauer spectroscopy revealed that for both sintered and mechanically activated $BiFeO_3$ compounds, thermal treatment at elevated temperature led to a partial eliminating of the paramagnetic impurities.

Keywords: *bismuth ferrite; ceramics; sintering; mechanical activation; Mössbauer spectroscopy*

1. Introduction

Multiferroic materials are known from the sixties of the XX century when two research Russian groups of Smolenskii in St. Petersburg and Venevtsev in Moscow created one system with both ferroelectric and ferromagnetic properties [1]. One of the most frequently investigated multiferroics is bismuth ferrite $BiFeO_3$ (or BFO) which shows ferroelectric and antiferromagnetic properties at room temperature. The crystalline structure of this compound is well recognized in all forms, including monocrystals, polycrystalline material, or thin films. $BiFeO_3$ is reported to have a rhombohedrally distorted perovskite-like structure with a space group $R3c$ where the unit cell has parameters a = 3.96 Å and α = 89.5° [2] (or a = 5.58102(4) Å and c_{hex} = 13.8757(2) Å in the hexagonal setting [3]). The multiferroic properties of BFO are also well known, its phase transition temperatures are as follows: ferroelectric Curie temperature T_C = 1100 K and antiferromagnetic Néel temperature T_N = 640 K [3]. The presence of both ferroelectric and antiferromagnetic properties above an ambient temperature makes the BFO very attractive material from the application point of view.

Recently, an enhancement of multiferroic properties of BFO has attracted a great attention of researchers. One direction of investigations is an

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achievement of a large value of spontaneous polarization P_S. This was obtained in the case of epitaxial BFO thin films [4] or single crystals of BFO [5] for which the values of the ferroelectric remnant polarization exceeded 50 μC/cm^2. Second way is an enhancement of magnetic properties by modification of the BFO structure by addition of a small amount of Eu [6], Mn [7], Sc [8], La [9] or Nd [10].

Moreover, researches make every effort to synthesize BFO as pure phase in polycrystalline form. There are many preparation methods, from conventional solid-state-reaction (solid-state sintering) through the rapid-liquid-phase sintering [11], sol-gel route [12], solid-state ionic titration technique [13] and mechanical activation assisted synthesis [14, 15]. In most of cases the presence of impurity phases, mainly $Bi_2Fe_4O_9$, $Bi_{12}(Bi_{0.5}Fe_{0.5})O_{19.5}$ or $Bi_{25}FeO_{40}$ 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 [14] or nanocrystalline material [15]. In this technique the mechanical treatment is performed in the suitable ball mill and necessary thermal processing completes the formation of the ceramic phase. It was reported that in the case of the mechanically activated samples the calcination temperature was equal to 973 K and was lower by ~100 K as compared to the conventionally processed samples [14]. On the other hand, the authors of [15] have prepared BFO nanopowder during mechanochemical synthesis without any additional thermal treatment.

It is known that the structure and physical properties of materials prepared by mechanical activation (mechanochemical synthesis, mechanical alloying) often depend on the milling conditions (type of mill, number and size of balls, atmosphere of process, etc.). It may be noted that investigations of the properties of $BiFeO_3$ prepared by MA method are still rare in the literature reports. Thermo-gravimetric analysis of BFO samples confirmed the weight loss caused by the evaporation of Bi [14]. Moreover, as reported in [11], the initial size of powder particles of Bi_2O_3 and Fe_2O_3 had an influence on the formation of single-phase BFO ceramics. All the mentioned reasons inspired us to prepare BFO by two methods, with small modifications as compared with those reported in literature. The first one was conventional solid-state sintering in which the amount of Bi_2O_3 constituent was slightly increased. The second method was mechanical activation assisted synthesis performed in two manners: (1) mixing and milling of stoichiometric amounts of Bi_2O_3 and Fe_2O_3 followed by thermal treatment and (2) separate milling of individual Bi_2O_3 and Fe_2O_3 powders, mixing, further milling and thermal processing.

The structure of BFO samples prepared by these two methods was examined using X-ray diffraction (XRD). The main goal of this work was to determine hyperfine interactions parameters in the samples obtained by both preparation techniques to compare them with each other and with the literature data. Mössbauer spectroscopy (MS) was used to characterize hyperfine interactions.

2. Experimental details

The studied $BiFeO_3$ compound was prepared by the conventional solid-state route and mechanical activation methods.

In the first technique, the appropriate amounts of reagent-grade oxide powders, viz. Fe_2O_3, and Bi_2O_3 (all 99.9 % purity, Aldrich Chemical Co.) were weighted and mixed in an agate mortar. The amount of Bi_2O_3 was slightly increased by 3 and 5 % above the stoichiometric composition. Next, the powders were thoroughly mixed in a ball mill and pressed into 20 mm diameter stainless-steel die under the pressure $p = 300$ MPa. The green bodies were then placed in an alumina crucible and fired in air at temperature $T_S = 993$ K for $t = 10$ h. After calcination, the compacts were re-milled, pressed into discs of 10 mm in diameter at $p = 600$ MPa, and then sintered at a temperature of 1023 K for 10 h in a sealed alumina crucible (pressureless sintering). The heating and cooling rates were 5 Kmin^{-1}. All the samples were furnace-cooled to room temperature.

In the case of mechanical activation method, the stoichiometric amounts of the Fe_2O_3 and Bi_2O_3 oxides were placed 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. The samples for measurements were taken after 5, 10, 20, 50 and 100 h of milling. After the MA process the mixture was annealed isothermally in a furnace at 973 K in air for 1 h. The second MA process (MA II) was performed as follows: (1) stoichiometric amounts of the Fe_2O_3 and Bi_2O_3 oxides were milled separately up to 10 h in air, (2) next, the powders were mixed and milled together during 50 h in air, (3) thermal treatment of the obtained mixture 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 sintered samples was examined using the Philips PW3710 diffractometer with CoK_α radiation, while the mechanically activated samples were analyzed by the Rigaku MiniFlex II diffractometer with CuK_α radiation. The phase and structural analysis of the recorded X-ray patterns was performed with an X'Pert HighScore Plus computer programme equipped with the newest ICSD data base using Rietveld method of the crystalline structure refinement.

MS studies were carried out at room temperature in standard transmission geometry using a source of ^{57}Co in a chromium matrix. The compacts of the sintered $BiFeO_3$ compounds were crushed and powdered in a mortar. All the samples from MA processes were in a powder form. The absorbers for Mössbauer spectroscopy measurements were prepared using a self-adhesive transparent foil. A 25-µm-thick metallic iron foil was taken as a standard for calibration of the spectrometer.

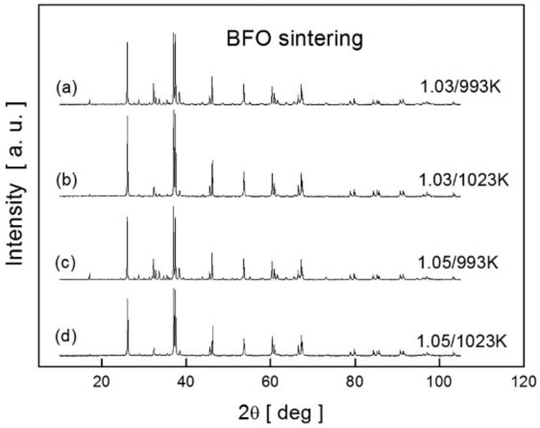


Figure 1. X-ray diffraction patterns (CoK_α radiation) of conventionally processed BFO: sample with 3 % excess of Bi_2O_3 (a) calcined at 993 K and (b) sintered at 1023 K; sample with 5 % excess of Bi_2O_3 (c) calcined at 993 K and (d) sintered at 1023 K.

3. Results

3.1. Results of X-ray diffraction studies

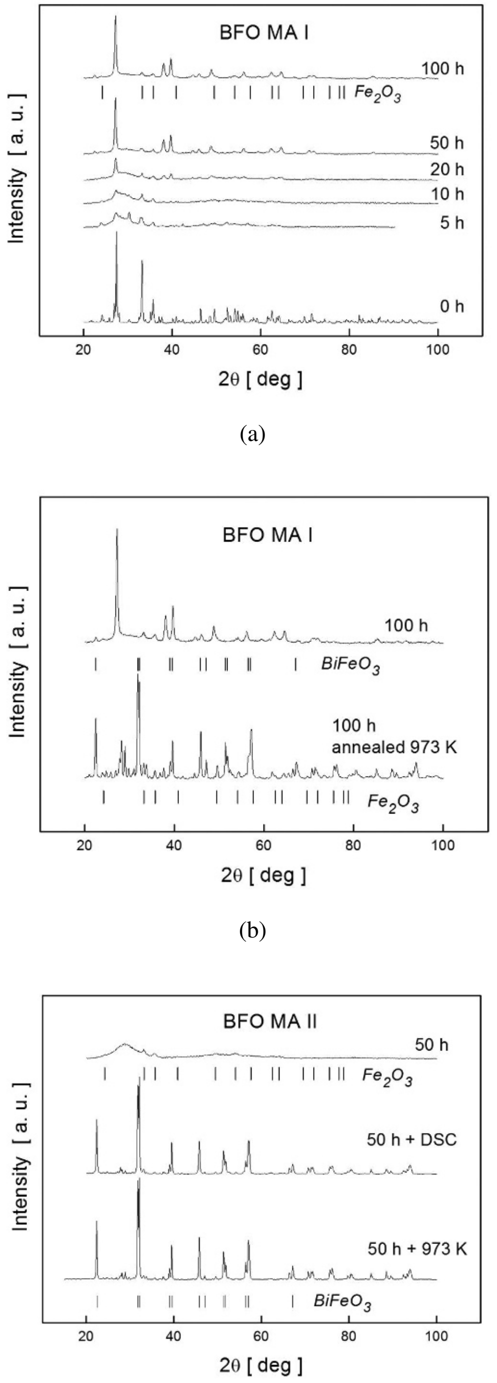
The XRD patterns for the first set of the samples, i.e. obtained by the conventional sintering method are shown in Fig. 1. Majority of the most intensive peaks belong to $BiFeO_3$ (bismuth iron (III) oxide, bismuth ferrite) compound. Their 2θ angle positions were compared with the newest ICSD data base [16]. Unfortunately, some diffraction lines with low intensity were also visible. These peaks in the fitting procedure were attributed to: $Bi_2Fe_4O_9$ – dibismuth tetrairon (III) oxide [17] and $Bi_{12.5}Fe_{0.5}O_{19.5}$, $Bi_{25}FeO_{40}$ – sillenite [18]. Detailed results of the phase and structural analysis are listed in Table 1. It may be noted that the lattice parameters determined for the BFO investigated in this work are in good agreement with the data base (the reported in [16] values of a = b vary from 5.5650 Å to 5.5888 Å, the value of c varies from 13.7854 Å to 13.8690 Å). Moreover, the contribution of the impurity phases is smaller in the case of the samples sintered at 1023 K as compared to the samples calcined at 993 K. The average values of crystallite sizes were estimated using Scherrer formula and they are as follows: 94(10) nm and 95(10) nm for BFO with 3 % excess of Bi_2O_3, sintered at 993 and 1023 K, respectively and 85(10) nm and 96(10) nm for BFO with 5 % excess of Bi_2O_3, sintered at 993 and 1023 K, respectively. The mean level of internal strains is of the order of 0.15(1) % for all the samples of sintered BFO.

Table 1. Structural parameters of $BiFeO_3$ and impurity compounds prepared by sintering and mechanical activation methods; a, b, c, α, β, γ – lattice parameters, A – weight fraction of the suitable phase; uncertainty of the values are given in parentheses for the last significant number.

Specimen/ method	Space group	a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]	A [%]	Compound
1.03	P b a m (55)	7.9723(4)	8.4440(4)	6.0063(3)	90	90	90	14.8(2)	$Bi_2Fe_4O_9$
993 K	I 2 3 (197)	10.1790(1)	10.1790(1)	10.1790(1)	90	90	90	18.2(1)	$Bi_{12.5}Fe_{0.5}O_{19.5}$
sintering	R 3 c (161)	5.57814(4)	5.57814(4)	13.8679(1)	90	90	120	67.1(1)	$BiFeO_3$
1.03	P b a m (55)	7.972(2)	8.442(2)	6.008(1)	90	90	90	5.8(2)	$Bi_2Fe_4O_9$
1023 K	I 2 3 (197)	10.1658(4)	10.1658(4)	10.1658(4)	90	90	90	7.9(1)	$Bi_{25}FeO_{40}$
sintering	R 3 c (161)	5.57809(4)	5.57809(4)	13.8675(1)	90	90	120	86.3(2)	$BiFeO_3$
1.05	P b a m (55)	7.9714(3)	8.4436(3)	6.0053(2)	90	90	90	19.3(2)	$Bi_2Fe_4O_9$
993 K	I 2 3 (197)	10.1803(1)	10.1803(1)	10.1803(1)	90	90	90	17.3(2)	$Bi_{25}FeO_{40}$
sintering	R 3 c (161)	5.57809(4)	5.57809(4)	13.8672(1)	90	90	120	63.4(2)	$BiFeO_3$
1.05	P b a m (55)	7.979(2)	8.441(2)	6.006(1)	90	90	90	4.7(3)	$Bi_2Fe_4O_9$
1023 K	I 2 3 (197)	10.1651(3)	10.1651(3)	10.1651(3)	90	90	90	9.1(2)	$Bi_{25}FeO_{40}$
sintering	R 3 c (161)	5.57875(4)	5.57875(4)	13.8691(1)	90	90	120	86.2(4)	$BiFeO_3$
Annealed	P b a m (55)	7.950(4)	8.440(3)	6.000(3)	90	90	90	12.2(3)	$Bi_2Fe_4O_9$
973 K	I 2 3 (197)	10.132(5)	10.132(5)	10.132(5)	90	90	90	4.8(8)	$Bi_{25}FeO_{40}$
MA II	R 3 m (160)	5.5745(4)	5.5745(4)	13.8588(6)	90	90	120	83.0(7)	$BiFeO_3$

Fig. 2 presents XRD patterns for two sets of mechanically activated BFO. In the first case, (MA I series), the stoichiometric mixture of Bi_2O_3 and Fe_2O_3 was milled up to 100 h. As shown in Fig. 2a, the diffraction peaks of non-milled Bi_2O_3 and Fe_2O_3 are systematically broadened and shifted, giving after 5 and 10 h of milling the patterns characteristic of nanocrystalline/amorphous material. However, prolonged milling for 20, 50 and 100 h has not caused a complete amorphization of the mixture, but the formation of some unrecognized crystalline phase. This phase may be a mixture of hematite and $Bi_xFe_yO_z$ compound with unknown composition. It may be noted that the main diffraction peaks of hematite (2θ angles near 33.2 and 35.7°) have not disappeared in the patterns for the samples milled for 50 and 100 h (the angle positions of lines for Fe_2O_3 are marked in Fig. 2a). This means that not a whole amount of hematite has been dissolved in Bi_2O_3. Moreover, the phase formed after 100 h of MA is not a pure BFO, as indicated in Fig. 2b (the angle positions of lines for pure $BiFeO_3$ are marked for comparison [19]). 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 $Bi_2Fe_4O_9$ phase are also visible. Small amount of hematite as impurity is also possible. The estimated contribution of the desired BFO is about 70 % and the average crystallite sizes of this compound determined using Scherrer formula are 45(10) nm.

During the second series of mechanical activation, (MA II), after 10 h of separate milling of each oxide, Bi_2O_3 and Fe_2O_3 were crumbled up to nanometer level. The average crystallite sizes, D, and the mean level of internal strains, e, determined by the Williamson-Hall method [20] are as follows: D = 22(10) nm and e = 0.5(1) % for both oxides. These crumbled oxides were mixed together and milled for 50 h. The XRD pattern of the sample obtained after the milling is presented in Fig. 2c. It may be noted that during this experiment the amorphous-like structure has been formed (top pattern), however small peaks coming from hematite are also visible. Heat treatment, in the calorimeter as well as in the furnace, allowed obtaining BFO phase with about 10 % of impurities, i.e. $Bi_2Fe_4O_9$ phase (the angular positions of diffraction lines are in agreement with [21]). After the thermal treatment, the average crystallite sizes of $BiFeO_3$ phase increased and the mean level of internal strains significantly decreased. The determined values are as follows: D = 70(25) nm, e = 0.07(1) % for heated



(a)

(b)

(c)

Figure 2. X-ray diffraction patterns (CuK_α radiation) of mechanically activated BFO: (a) for a mixture of Bi_2O_3 and Fe_2O_3 from MA I process; (b) after 100 h MA I and annealing; (c) after 50 h MA II, subsequent heating in calorimeter (DSC) up to 993 K and annealing in a furnace at 973 K.

material and D = 72(24) nm, e = 0.02(1) % for annealed sample. Detailed phase and structural analysis using Rietveld method was performed only for the sample milled for 50 h and annealed at 973 K in the furnace and the results are listed in Table 1. In comparison to the sintered samples, the lattice parameters of BFO phase prepared by MA method differ about 0.005 Å for a = b and about 0.01 Å for c. The obtained values agree well with the database [16].

Summarizing the results obtained from XRD measurements, it may be stated that both conventional solid-state reaction and mechanical activation methods make possible to prepare $BiFeO_3$ with various level of impurity phases.

3.2. Results of Mössbauer studies

Mössbauer spectra collected for sintered BFO are presented in Fig. 3. It may be seen that the spectra are the superposition of two kinds of components, i.e. six-line (sextet) and double-line (doublet). The best computer-fitting parameter (Chisq) was achieved when two sextets and two doublets were assumed in the fitting procedure. The hyperfine interaction parameters determined from the spectra are as follows: IS – *I*somer *S*hift relative to α-iron, QS – *Q*uadrupole *S*hift of the magnetically split spectra or *Q*uadrupole *S*plitting of the paramagnetic doublet, B_{hf} – induction of the hyperfine magnetic field, Γ – half width at half maximum of spectral lines. In the fitting procedure the quadrupole shift for the sextet was defined as: QS = $(P_2-P_1)/4-(P_6-P_5)/4$, where P_i denotes the position of i – spectral line in the velocity scale [22]. The hyperfine interactions parameters for sintered BFO are listed in Table 2 together with the data for mechanically activated samples and the literature data [2, 3, 6, 23]. On the base of XRD results mentioned above and the reported data, two sextets may be attributed to $BiFeO_3$. One of the doublet (D1) has the isomer shift and quadrupole splitting similar to that for $Bi_2Fe_4O_9$, i.e. IS = 0.24(1) mms^{-1} and QS = 0.36(1) mms^{-1}, as reported in [24]. It may be concluded that the second doublet (D2) may originate from sillenite. Moreover, as seen from Fig. 3, the amount of the impurity phases (e.g. relative contribution of the doublets to the whole Mössbauer spectrum) is smaller in the case of the samples sintered at 1023 K as compared to the samples calcined at 993 K. This observation agrees well with the results of XRD studies.

Fig. 4 presents Mössbauer spectra for mechanically activated BFO for two sets of samples. Spectra for the mixtures milled during MA I process for 10, 20 and 50 h are not presented here. The numerical fitting of the spectra was performed with one sextet and one doublet, the values of the hyperfine interactions parameters obtained from fitting are listed in Table 2. The obtained parameters for the sextet are similar to those for hematite (for example B_{hf} = 51.75 T, IS = 0.37 mm s^{-1}, $2\varepsilon = -0.197$ mm s^{-1} [25]; or $B_{hf} = 51.9 \pm 0.1$ T, IS = 0.38 ± 0.01 mm s^{-1}, $\varepsilon = -0.09 \pm 0.01$ mm s^{-1} [26]; or $B_{hf} = 51.4 \pm 0.3$ T, IS = 0.37 ± 0.02 mm s^{-1}, $\varepsilon = -0.09 \pm 0.01$ mm s^{-1} [27]; ε means quadrupole shift). As proved by XRD measurements (Fig. 2a, b), the phase formed after 100 h of MA is not a pure BFO and the amount of hematite is small. The most intensive diffraction peak near 27.2° belongs neither to BFO nor to hematite (Fig. 2b). However, two peaks near 39 and 39.5° and other peaks with smaller intensity prove the beginning of BFO formation. So, the components in the Mössbauer spectrum, both the sextet and the doublet may be attributed to the bismuth iron oxides of unknown chemical composition $Bi_xFe_yO_z$ with small amount of hematite Fe_2O_3. After isothermal annealing of the sample, in the Mössbauer spectrum, the sextets are clearly separated (bottom spectrum in Fig. 4a) and the spectral lines are narrower as compared to the lines in the spectrum for the sample milled for 100 h (see Table 2). Besides two sextets which may be attributed to the desired BFO compound, two doublets and a sextet from hematite were fitted to the spectrum. The hyperfine interaction parameters of the doublets are similar to those of sintered samples, i.e. $Bi_2Fe_4O_9$ and sillenite.

In the case of the second process of mechanical activation, MA II, Mössbauer spectra were computer fitted using two doublets and three sextets. The hyperfine interactions parameters for all components are listed in Table 2. It may be noted (Fig. 4b) that the contribution of the doublets in the spectra for thermally treated samples is significantly smaller than in the case of the sample milled for 100 h in MA I process and annealed at 973 K (Fig. 4a). As proved by XRD studies, the sample consisting of Bi_2O_3 and Fe_2O_3, which were at first milled separately and subsequently milled together for 50 h, was in the amorphous and/or nanocrystalline state. Two of three sextets may be attributed to the nanostructured BFO compound in which small reduction of B_{hf} values may be observed (Table 2). After thermal treatment, the values of IS, QS and B_{hf} parameters for these two sextets changed and they became similar to the parameters of BFO prepared by sintering. It may be seen (Fig. 4 b) that the main part of the Mössbauer spectrum for the sample heated in the calorimeter up to 993 K as well as the sample annealed at 973 K, comes from the sextets originating from desired BFO, however, small amount of hematite is still visible. The results obtained in this work for mechanically activated BFO are in good agreement with the data reported for high-energy ball milled $BiFeO_3$ reported in [6] (Table 2). The authors observed about 97 % of pure BFO with 3 % impurity of γ-Bi_2O_3.

As previously, paramagnetic doublets in the spectra can be attributed to the impurity phases of $Bi_2Fe_4O_9$ and sillenite. The most interesting observation is that the level of paramagnetic impurities is the lowest in the case of mechanically activated BFO, subsequently heated in a calorimeter.

4. Discussion and conclusions

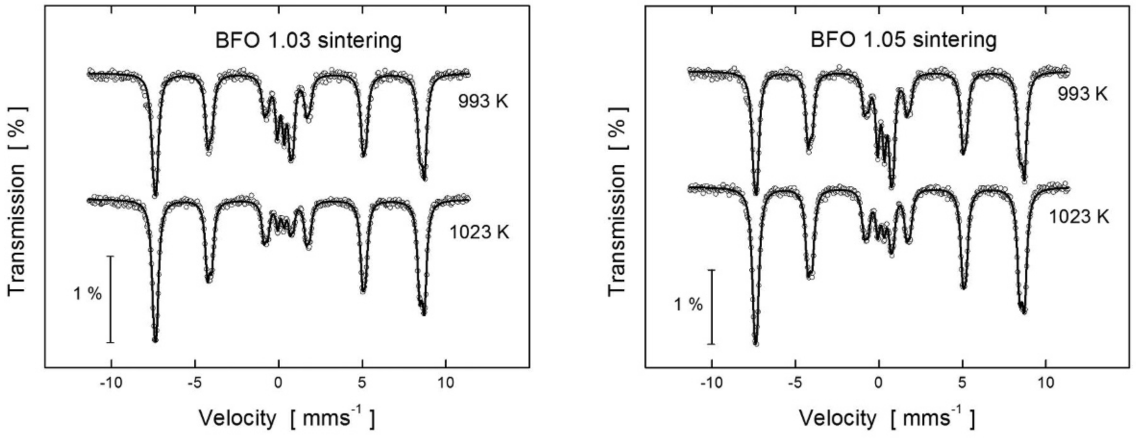
Both XRD and MS measurements provided information about phase composition of the processed materials. In the case of XRD, the weight fraction of the suitable phase may be calculated from XRD patterns by a computer program. Similar estimation of the contribution of the given phase from the Mössbauer spectrum is not possible because each phase should have the same value of Debye-Waller factor whereas the crystalline lattices of the recognized phases are various (different local environment of the ^{57}Fe nuclei). So, the com-

Table 2. Hyperfine interactions parameters of $BiFeO_3$ and impurity compounds prepared by sintering and mechanical activation methods: 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, Γ − half width at half maximum of spectral lines, Chisq – fitting parameter; uncertainty of the values are given in parentheses for the last significant number. Literature data are added.

Specimen/ method	IS [mm/s]	QS [mm/s]	B_{hf} [T]	Γ [mm/s]	Chisq	Component/ compound
1.03 993 K sintering	0.15(1)	0.38(1)	–	0.13(1)	2.0	D 1/ $Bi_2Fe_4O_9$
	0.44(1)	−0.27(1)	–			D 2/ sillenite
	0.40(1)	0.15(1)	49.89(1)	0.17(1)		S 1/ BFO
	0.39(1)	−0.07(1)	49.59(2)			S 2/ BFO
1.03 1023 K sintering	0.16(1)	0.37(1)	–	0.13(1)	1.3	D 1/ $Bi_2Fe_4O_9$
	0.45(1)	−0.28(1)	–			D 2/ sillenite
	0.39(1)	0.16(1)	49.84(1)	0.16(1)		S 1/ BFO
	0.39(1)	−0.06(1)	49.47(1)			S 2/ BFO
1.05 993 K sintering	0.16(1)	0.39(1)	–	0.14(1)	1.7	D 1/ $Bi_2Fe_4O_9$
	0.44(1)	−0.27(1)	–			D 2/ sillenite
	0.39(1)	0.16(1)	49.86(1)	0.16(1)		S 1/ BFO
	0.39(1)	−0.07(1)	49.57(1)			S 2/ BFO
1.05 1023 K sintering	0.17(1)	0.38(1)	–	0.16(1)	1.3	D 1/ $Bi_2Fe_4O_9$
	0.44(1)	−0.28(1)	–			D 2/ sillenite
	0.39(1)	0.16(1)	49.85(1)	0.17(1)		S 1/ BFO
	0.39(1)	−0.06(1)	49.48(1)			S 2/ BFO
10 h MA I	0.28(2)	0.39(2)	–	0.31(3)	1.0	D
	0.37(1)	−0.09(1)	51.63(1)	0.17(1)		S
20 h MA I	0.31(1)	0.39(1)	–	0.34(2)	1.4	D
	0.37(1)	−0.09(1)	51.62(1)	0.18(1)		S
50 h MA I	0.33(1)	0.41(1)	–	0.33(2)	1.5	D
	0.37(1)	−0.09(1)	51.56(1)	0.18(1)		S
100 h MA I	0.35(1)	0.44(1)	–	0.41(1)	1.7	D/ $Bi_xFe_yO_z$
	0.37(1)	−0.09(1)	51.49(1)	0.20(1)		S/ $Bi_xFe_yO_z$ + Fe_2O_3
100 h MA I annealed at 973 K	0.16(1)	0.39(1)	–	0.13(1)		D 1/ $Bi_2Fe_4O_9$
	0.44(1)	−0.27(1)	–		1.3	D 2/ sillenite
	0.38(1)	0.16(1)	49.43(2)	0.13(1)		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
50 h MA II	0.23(4)	0.43(4)	–	0.21(1)	1.4	D 1/ $Bi_2Fe_4O_9$
	0.37(1)	−0.27(1)	–			D 2/ sillenite
	0.36(2)	0.08(2)	48.93(14)	0.16(1)		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 DSC up to 993 K	0.14(4)	0.37(3)	–	0.15(4)	1.4	D 1/ $Bi_2Fe_4O_9$
	0.40(6)	−0.20(6)	–			D 2/sillenite
	0.38(1)	0.15(1)	49.65(2)	0.14(1)		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 annealed at 973 K	0.16(1)	0.38(1)	–	0.12(1)	1.2	D 1/ $Bi_2Fe_4O_9$
	0.44(1)	−0.27(1)	–			D 2/ sillenite
	0.39(1)	0.16(1)	49.62(2)	0.14(1)		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

Continuation of Table 2

Specimen/ method	IS [mm/s]	QS [mm/s]	B_{hf} [T]	Γ [mm/s]	Chisq	Component/ compound
sintering	0.24 0.17	−0.045 0.20	49.8 50.1	–	–	Ref. [23] measured at 100 K
sintering	0.38	0.057	49.686	–	–	Ref. [2] measured at RT
sintering	0.48 0.48	−0.065 0.175	54.37 54.68	0.34	–	Ref. [2] measured at 80 K
polycrystalline	– –	−0.031 0.196	54.019 54.355	–	0.91	Ref. [3] measured at 90 K
polycrystalline	– –	−0.048 0.171	49.579 49.931	–	1.39	Ref. [3] measured at RT
MA	0.39 0.39	−0.055 0.16	49.2 49.5	0.34 0.29	–	Ref. [6] measured at RT



(a) (b)

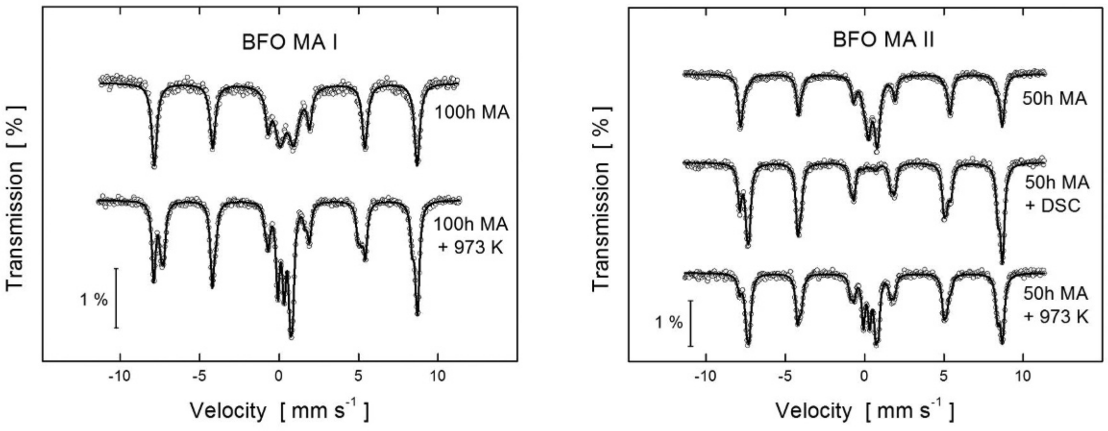
Figure 3. Room-temperature Mössbauer spectra for conventionally processed BFO: (a) samples with 3 % excess of Bi_2O_3 calcined at 993 K and sintered at 1023 K; (b) samples with 5 % excess of Bi_2O_3 calcined at 993 K and sintered at 1023 K.

parison of the results from XRD and MS methods may be only qualitative.

Comparing the results for sintered BFO compound it may be stated that the lowest amount of impurities (about 14 %) was obtained from the mixtures with both 3 and 5 % excess of Bi_2O_3 during sintering at 1023 K (see Table 1). On the other hand, as it may be seen in Mössbauer spectra, the relative contribution of the components coming from impurities, i.e. doublets, is smaller in the case of the sample with 3 % excess of Bi_2O_3.

In the case of mechanical activation method, the MA II process gave better results. The gradual heating of mechanically activated BFO in the calorimeter seems to be more effective method in terms of an amount of paramagnetic impurities. However, in this case the amount of hematite impurity is larger than in the case of annealing process.

Comparing the MS spectra both for sintered and mechanically activated BFO compound it may be seen that with increasing the temperature of thermal treatment the spectra become more magnetic, i.e. the doublet components become smaller. This effect may be connected with the grain sizes. As mentioned, the average crystallite sizes estimated from XRD analysis are of the order of nanometers (i.e. $\leq$ 100 nm) both for sintered and mechanically activated and thermally treated BFO. How-



(a) (b)

Figure 4. Room-temperature Mössbauer spectra for mechanically activated BFO: (a) after 100 h MA I process and annealed at 973 K; (b) after 50 h MA II process, subsequently heated in calorimeter (DSC) up to 993 K and annealed in a furnace at 973 K.

ever, each sample is characterized by a distribution of the crystallite sizes, so within a given sample the particles smaller and larger than the average ones are possible. Upon thermal treatment at higher temperature the agglomeration process leads to the formation of larger particles, which obtain magnetic properties similar to those for bulk material (in bulk samples the average grain sizes are larger than 245 nm as reported in [28]). Thermal processing of the samples, however, does not remove the impurities.

Summarizing the obtained results, it may be stated that in spite of some problems with production of pure $BiFeO_3$ compound by the proposed modified methods some interesting observations were made. First of them concerns the values of the hyperfine magnetic fields which for mechanically activated BFO (but not thermally treated) are smaller than those for conventionally sintered samples. This is mainly due to the grain sizes reduced to the nanometer level as well as the residual strains introduced into the sample during mechanical milling process. The second one is that the paramagnetic components in Mössbauer spectra originate both from impurity phases and the smallest particles within the BFO samples. Thermal treatment at elevated temperature leads to partial eliminating of the paramagnetic component. Moreover, the desired BFO phase is formed by mechanical activation and subsequent thermal processing at the temperature lowered by 30 – 50 K as compared to the temperature of conventional sintering method.

It may be concluded that both technologies allowed us to obtain BFO compound containing impurities. The lowest amount of $Bi_2Fe_4O_9$ and sillenite was achieved for the sample with 3 % excess of Bi_2O_3 and sintered at 1023 K. It is worth emphasizing that the problem of impurities during preparation of the polycrystalline BFO by various methods should be examined using XRD together with Mössbauer spectroscopy. The sensitivity of MS method is larger than X-ray measurements and this makes possible to reveal not only small amount of impurities (which are not detectable by XRD method) but simultaneously determine their magnetic properties. Mössbauer spectroscopy may be used as a method for detecting both pure BFO phase and impurity compounds containing iron.

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