

Mössbauer Spectroscopy Studies of Multiferroic (BiFeO₃)_{1-x}-(BaTiO₃)_x Solid Solutions Prepared by Mechanical Activation

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X-ray diffraction and ⁵⁷Fe Mössbauer spectroscopy were applied as complementary methods in order to investigate the structure and hyperfine interactions of (BiFeO₃)_{1-x}-(BaTiO₃)_x solid solutions prepared by mechanical activation and subsequent heat treatment.

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1. Introduction

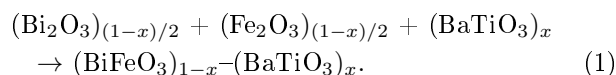
Multiferroics which simultaneously exhibit ferroelectric and ferro-/antiferromagnetic and/or ferroelastic properties are the subject of intensive research due to their potential applications in new types of magnetoelectric devices and next-generation memory storage materials [1]. Until now the best recognized multiferroic compound is bismuth ferrite BiFeO₃ in which at room temperature coexist both ferroelectric and antiferromagnetic ordering. Because the spiral spin structure leads to vanishing of the macroscopic magnetization, the linear and quadratic magnetoelectric effect is not observed in this material [2]. Synthesis of bismuth ferrite with other oxides (e.g. with barium titanate BaTiO₃) allows to obtain new ceramic materials with interesting structural, electric, and magnetic properties and with high level of magnetoelectric coupling.

In this work the results of studies on (BiFeO₃)_{1-x}-(BaTiO₃)_x solid solutions are presented for $x = 0.1-0.3$. The samples were prepared by mechanical activation (MA) and subsequent heat treatment. X-ray diffraction (XRD) and ⁵⁷Fe Mössbauer spectroscopy (MS) were applied as complementary methods in order to investigate the structure of material and hyperfine interactions parameters. The aim of the studies was to determine the influence of BaTiO₃ contents on the structure and hyperfine interactions in the investigated solid solutions.

2. Experimental details

High purity (99.9%) powders of Bi₂O₃, Fe₂O₃, and BaTiO₃ were used as precursor materials in order to obtain (BiFeO₃)_{1-x}-(BaTiO₃)_x solid solutions with $x =$

0.1–0.3, according to the following reaction:



The powder mixture was weighted and milled in a high-energy ball mill type Fritsch Pulverisette P5 (stainless steel balls of 10 mm diameter, 10:1 ball-to-powder weight ratio) under argon atmosphere during 2, 5, 10, 20, 50, and 100 h. After milling process thermal treatment of the mechanically activated solid solutions was performed in order to complete the solid-state reaction. The isothermal annealing was performed in a furnace at 1073 K and at 1173 K for 1 h in air.

XRD measurements were carried out using a RIGAKU Miniflex2 diffractometer working in a continuous scanning mode with Cu K_α radiation.

Measurements of the ⁵⁷Fe Mössbauer spectra were made using transmission geometry with a 20 mCi source of ⁵⁷Co in a rhodium. The spectrometer was calibrated using α -Fe foil at room temperature.

3. Results and discussion

X-ray diffraction studies conducted at early stage of MA process (from 2 to 20 h of MA) showed that the peaks attributed to Bi₂O₃ broadened. It can be due to the dissolving of hematite in Bi₂O₃ phase lattice structure and the formation of BiFeO₃ as well as some non-stoichiometric Bi_xFe_yO_z phases. Moreover, diffraction lines of BaTiO₃ disappeared. After 50 h of MA (for $x = 0.1$ and 0.3) and after 100 h for $x = 0.2$ the steady-state was reached and the products of milling consisted of a mixture of not completely dissolved Fe₂O₃ and Bi_xFe_yO_z phases. The main peak visible in the diffraction pattern at 27.2 degrees (see example for $x = 0.1$ in Fig. 1a) can be fitted to Bi₂Fe₄O₉ phase. However,

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because of the overlapping of the diffraction lines characteristic for $\text{Bi}_2\text{Fe}_4\text{O}_9$, $\text{Bi}_{24}\text{Fe}_2\text{O}_{39}$, and $\text{Bi}_{25}\text{FeO}_{40}$ compounds it is difficult to determine precisely which phase was formed during MA process. Isothermal annealing at 1073 K allowed to obtain BiFeO_3 phase with dissolved BaTiO_3 , i.e. solid solution $0.9\text{BiFeO}_3\text{-}0.1\text{BaTiO}_3$. However, the temperature of treatment was not enough to complete the dissolution of hematite (small peaks of Fe_2O_3 are visible on XRD pattern beside those produced by BiFeO_3 , see Fig. 1b).

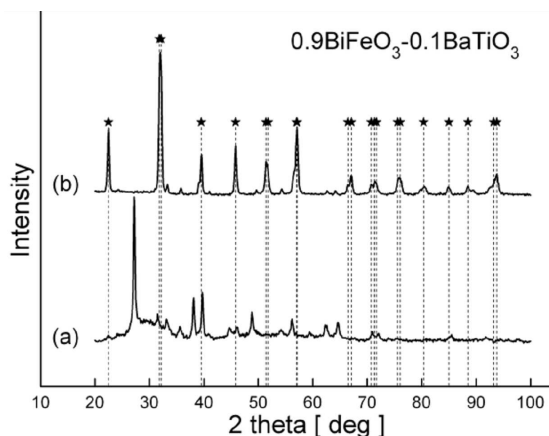


Fig. 1. X-ray diffraction patterns for $0.9\text{BiFeO}_3\text{-}0.1\text{BaTiO}_3$ solid solution: (a) after mechanical activation during 100 h and (b) after 100 h MA and isothermal annealing at 1073 K; asterisks and dotted lines denote the positions of diffraction lines for pure BiFeO_3 according to JCPDS PDF card no. 20-0169.

Thermal treatment at elevated temperature (1173 K) allowed $(\text{BiFeO}_3)_{1-x}\text{-(BaTiO}_3)_x$ solid solutions to form; however, with a small amount of impurity phases. All the main diffraction lines are produced by BiFeO_3 with dissolved BaTiO_3 (Fig. 2). Dissolution of BaTiO_3 is proven by the shift of the peaks identified as BiFeO_3 phase towards lower 2θ angles with the increase of barium titanate amount in the initial powder mixtures. The lattice parameters of the obtained solid solutions with rhombohedral crystalline lattice were determined after $K\alpha_2$ stripping using the Rachinger method [3] and applying DHN PDS numerical program. Their values are as follows: $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ (space group $R3c$) and $a = b = 5.5887(20)$ Å, $c = 13.7756(40)$ Å, for $x = 0.1$, $a = b = 5.6105(35)$ Å, $c = 13.7756(70)$ Å, for $x = 0.2$ and $a = b = 5.6370(20)$ Å, $c = 13.7996(40)$ Å, for $x = 0.3$. The obtained results agree well with the data reported for $(\text{BiFeO}_3)_{1-x}\text{-(BaTiO}_3)_x$ solid solutions prepared using other methods, i.e. molten salt and solid-state sintering, respectively [2, 4].

The Mössbauer spectroscopy measurements confirmed the results of X-ray diffraction. The spectra revealed that after MA process the obtained material is not a desired solid solution but a mixture of hematite and some other phase (Fig. 3a). The six lines visible in the

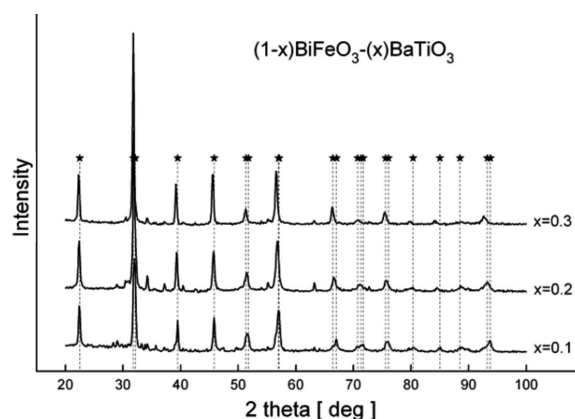


Fig. 2. X-ray diffraction patterns for $(\text{BiFeO}_3)_{1-x}\text{-(BaTiO}_3)_x$ solid solutions after MA and isothermal annealing at 1173 K; asterisks and dotted lines denote the positions of diffraction lines for pure BiFeO_3 according to JCPDS PDF card no. 20-0169.

spectra originate from hematite, which is confirmed by the hyperfine interactions parameters (isomer shift relative to α -iron $\delta = 0.36(1)$ mm s $^{-1}$, quadrupole shift $2\varepsilon = -0.10(2)$ mm s $^{-1}$ and hyperfine magnetic field induction $B_{\text{hf}} = 51.42(4)$ T). The double line may be attributed to the paramagnetic compound $\text{Bi}_2\text{Fe}_4\text{O}_9$ (dibismuth tetrairon oxide) whose hyperfine interactions parameters ($\delta = 0.30(2)$ mm s $^{-1}$ and the quadrupole splitting $\Delta = 0.92(3)$ mm s $^{-1}$) are similar to those reported in [5]. Thus, both methods, XRD and MS, indicate that during MA process $\text{Bi}_2\text{Fe}_4\text{O}_9$ compound was formed and that part of hematite is insoluble phase.

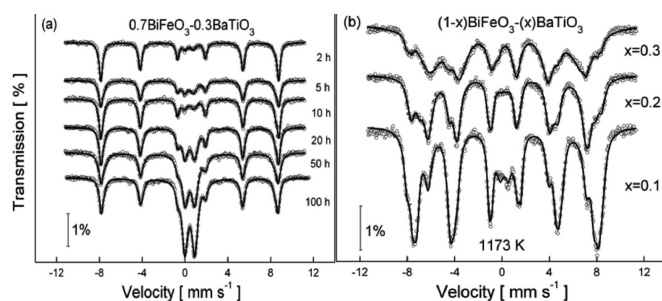


Fig. 3. Fitted room-temperature Mössbauer spectra of: (a) $0.7\text{BiFeO}_3\text{-}0.3\text{BaTiO}_3$ as a function of milling time and (b) $(\text{BiFeO}_3)_{1-x}\text{-(BaTiO}_3)_x$ solid solutions after MA and isothermal annealing at 1173 K for various contents of BaTiO_3 .

Annealing at higher temperature allowed to obtain solid solutions. The spectra measured for the investigated samples are presented in Fig. 3b. As the contents of BaTiO_3 increases in the solid solutions, the spectra broaden, reflecting the disorder in the superexchange magnetic interactions resulting from the random distribution of Fe^{3+} ions which may substitute Ti^{4+} ions within the structure of $(\text{BiFeO}_3)_{1-x}\text{-(BaTiO}_3)_x$.

All the spectra were numerically fitted using continuous distribution of hyperfine magnetic field (Fig. 4). In the fitting procedure the parameters for the doublet caused by the impurity $\text{Bi}_2\text{Fe}_4\text{O}_9$ phase were fixed. It is visible that the distributions are relatively broad and some maxima are more separated. The peak of hematite (field ≈ 51 T) is visible in all distributions; however, its intensity is significantly smaller than for other components. The average values of the hyperfine magnetic field induction $\langle B_{\text{hf}} \rangle$ were determined from the distributions (values are given in Fig. 4). It may be noted that $\langle B_{\text{hf}} \rangle$ decreases as the contents of BaTiO_3 in solid solutions increases. The obtained result reflects weakening of the inherent strength of magnetic interactions associated with increasing spin disordering. Our observation agrees well with the data reported earlier for analogous solid solutions obtained by molten salt method [2] and solid-state sintering [2, 4].

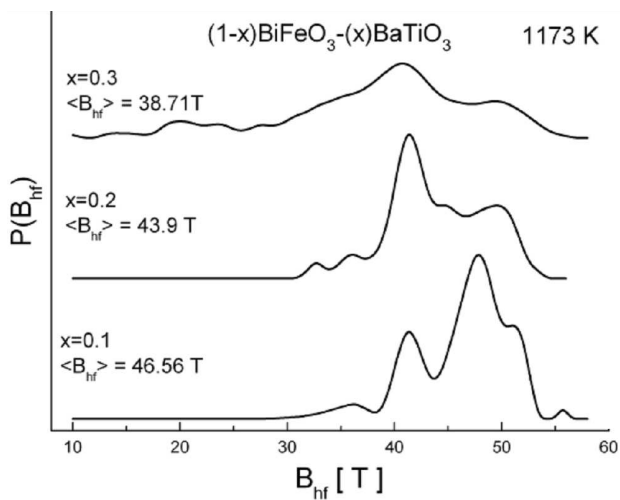


Fig. 4. Hyperfine magnetic field distributions for $(\text{BiFeO}_3)_{1-x}-(\text{BaTiO}_3)_x$ solid solutions after MA and isothermal annealing at 1173 K for various contents of BaTiO_3 ; $P(B_{\text{hf}})$ — probability in arbitrary units.

4. Conclusions

The solid solutions of $(\text{BiFeO}_3)_{1-x}-(\text{BaTiO}_3)_x$ were prepared with different amount of BaTiO_3 , employing mechanical activation technology. X-ray diffraction and Mössbauer spectroscopy allowed to monitor technological process and obtain information about structure and hyperfine interactions in the studied multiferroic materials. By using the MS technique and knowledge of the hyperfine interactions parameters it is possible to determine which phases were formed during preparation.

Increase of BaTiO_3 concentration causes changes in the crystalline structure of solid solutions as well as in hyperfine magnetic structure. The decrease of hyperfine magnetic fields proves a gradual magnetic phase transformation from a more-ordered spin structure for $x = 0.1$ to an increasingly spin disordered magnetic phase for $x = 0.3$.

It may be added that long-time milling usually results in contamination of the milled powder by iron coming from the steel balls and vial. However, previously performed measurements revealed that Fe content after 100 h of milling under the applied processing conditions does not exceed 1 at.%. The improvement of mechanical activation technology (for example by applying tungsten carbide balls) in order to obtain more homogeneous solid solutions will be the subject of our further investigations.

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