



Effect of BaTiO₃ concentration on structural and magnetic properties of mechanically activated BiFeO₃-BaTiO₃ system

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Abstract. In this research, the mechanical activation method is proposed as an alternative process of preparation of the (BiFeO₃)_{1-x}-(BaTiO₃)_x solid solutions with various concentrations of barium titanate ($x = 0.1 \div 0.9$). However, mechanical milling itself does not allow obtaining the desired products and additional thermal treatment is needed to complete the solid-state reaction. In the present studies, X-ray diffraction and ⁵⁷Fe Mössbauer spectroscopy were applied as complementary methods in order to study the structural and magnetic properties of materials. The investigations revealed that an increase of BaTiO₃ concentration causes changes in the crystal-line and hyperfine magnetic structure of the studied (BiFeO₃)_{1-x}-(BaTiO₃)_x system.

Keywords: solid solutions • mechanical activation • X-ray diffraction • Mössbauer spectroscopy

Introduction

Multiferroic materials have attracted much attention for years because of their potential technological applications such as magnetic field sensors [1] or energy harvesting devices [2]. Bismuth ferrite, BiFeO₃, is one of such multiferroic materials, in which ferroelectricity and antiferromagnetism coexist at room temperature. The BiFeO₃ has a ferroelectric phase transition temperature, $T_C \sim 1100$ K [3] and antiferromagnetic ordering, with a transition temperature, $T_N \sim 640$ K [4]. BiFeO₃ is known to have a distorted perovskite structure with rhombohedral space group $R\bar{3}c$ [5] and the spontaneous polarization along the $\langle 111 \rangle$ direction. The main problem during synthesis of pure BiFeO₃ compound is the formation of undesired secondary phases, as the crystalline structure of bismuth ferrite is not stable. One of the commonly appearing impurities in BiFeO₃ is Bi₂Fe₄O₉. The synthesis of BiFeO₃-BaTiO₃ system is expected to solve the problem of structural instability of bismuth ferrite. The standard method of preparation of BiFeO₃-BaTiO₃ solid solutions is the solid-state sintering [4, 6–8]. Another promising technology is the mechanical activation (MA) as an alternative method of formation of (BiFeO₃)_{1-x}-(BaTiO₃)_x system with various concentration of barium titanate, x . However, mechanical milling itself does not allow obtaining the desired solid solutions and the subsequent heat treatment plays a key role in the process.

In the present work, the (BiFeO₃)_{1-x}-(BaTiO₃)_x solid solutions with $x = 0.1 \div 0.9$ have been prepared by mechanical activation and subsequent isothermal

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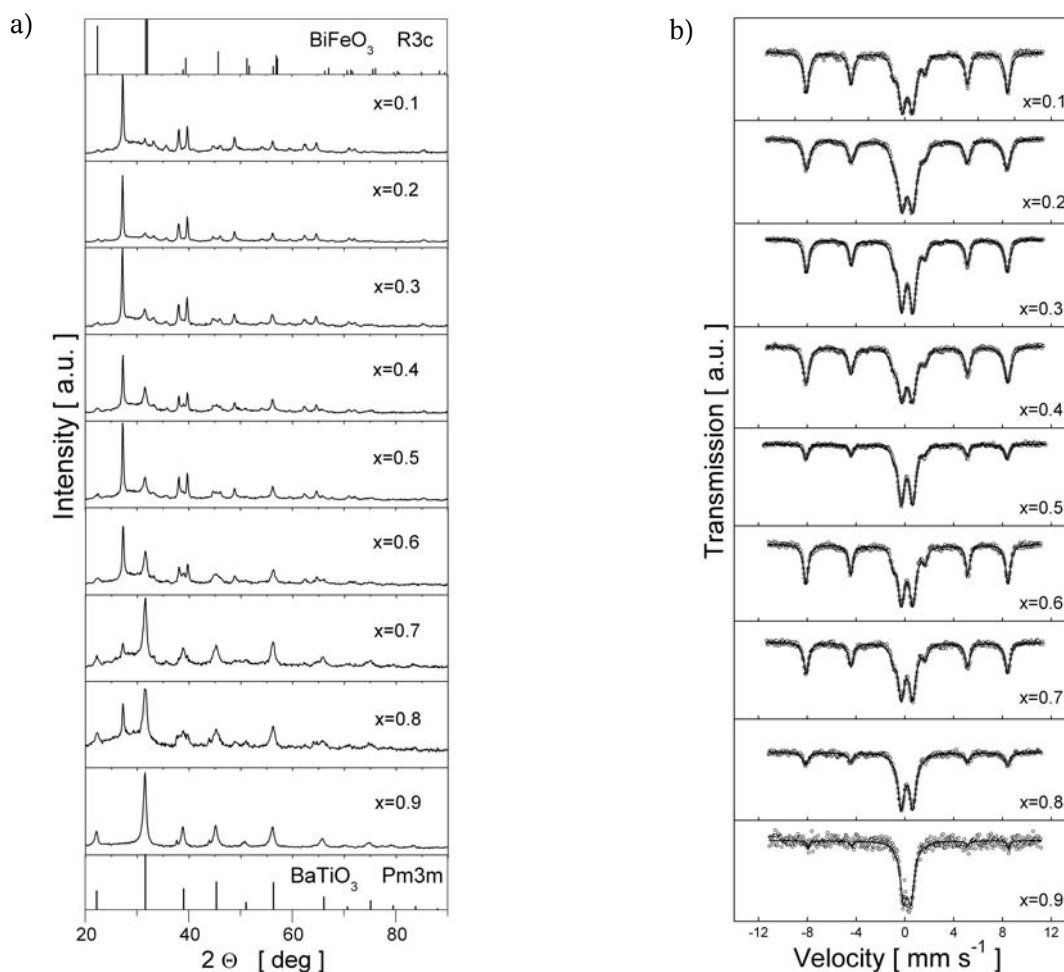


Fig. 1. (a) XRD patterns and (b) MS spectra registered for all the studied $(\text{BiFeO}_3)_{1-x}(\text{BaTiO}_3)_x$ mixtures after 100 h of mechanical activation.

annealing. X-ray diffraction (XRD) and Mössbauer spectroscopy (MS) were applied as complementary methods to monitor the process of formation of the desired solid solutions. The aim of this study was to find the relationship between the content of BaTiO_3 and the structural and magnetic properties in BiFeO_3 - BaTiO_3 system.

Experimental details

High-purity (above 99.9%) oxides of $\alpha\text{-Bi}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ and barium titanate BaTiO_3 were used to prepare solid solutions $(\text{BiFeO}_3)_{1-x}(\text{BaTiO}_3)_x$ with $x = 0.1 \div 0.9$ by the mechanical activation method. The powder mixture was milled in a high-energy ball mill of planetary type Fritsch Pulverisette P5. The vial and balls were made from stainless-steel. The ball-to-powder weight ratio was 10:1. The powders were ball milled for 2, 5, 10, 20, 50 and 100 h. Subsequent thermal treatment of the mechanically activated samples was carried out in order to complete the solid-state reaction. The isothermal annealing was performed in a resistance furnace at 1073 K for 1 h in air. The X-ray diffraction patterns were recorded at room temperature using a RIGAKU Miniflex2 diffractometer working in a continuous scanning mode with

$\text{CuK}\alpha$ radiation. Mössbauer spectra were registered at room temperature in transmission geometry with a ^{57}Co source in a rhodium matrix. The spectrometer was calibrated using $\alpha\text{-Fe}$ foil at room temperature.

Results and discussion

X-ray diffraction and Mössbauer spectroscopy techniques were used to investigate structural and magnetic properties of mechanically activated samples of BiFeO_3 - BaTiO_3 system. XRD patterns (not presented here) recorded for the samples milled for shorter periods (2–50 h) revealed shifts and broadening of diffraction peaks of the constituent oxides. Figure 1a shows the diffraction patterns registered for all the studied mixtures after 100 h of MA. It may be noted that the angular positions of the diffraction lines are not compatible with neither BiFeO_3 nor BaTiO_3 . In all patterns, the peaks originating from un-reacted $\alpha\text{-Bi}_2\text{O}_3$, BaTiO_3 and $\alpha\text{-Fe}_2\text{O}_3$ are present. Some changes in XRD patterns may be observed for $x \geq 0.4$. The peak near 32° systematically increases its intensity with increasing of x , while the peak near 27° disappears at $x = 0.9$. It may be concluded that during MA process, the desired $(\text{BiFeO}_3)_{1-x}(\text{BaTiO}_3)_x$ solid solutions were

not formed. Broadened diffraction peaks may be attributed to fragmentation and/or amorphization of the material.

Mössbauer spectroscopy confirmed the results of XRD measurements. All Mössbauer spectra (not presented here) registered for (BiFeO₃)_{1-x}-(BaTiO₃)_x with given x and after a milling period between 2 and 50 h were a superposition of sextet (originating from hematite) and doublet. Figure 1b presents MS spectra for all the compositions after 100 h of MA process. It may be seen that the spectra consist of six-line pattern and doublet in the central part of the spectrum. The numerical fitting of MS spectra was performed using one sextet and one doublet with the parameter χ^2 in the range of 1.1–2.0. The hyperfine interaction parameters of the sextet are characteristic for hematite (isomer shift IS = 0.38(2) mm·s⁻¹, quadrupole shift 2ε = -0.20(3) mm·s⁻¹ and hyperfine magnetic field induction B_{hf} = 51.4(1) T) and agree well with the literature data [9]. The doublets have values of isomer shifts between 0.28(2) and 0.32(2) mm·s⁻¹ and quadrupole splitting between 0.62(2) and 0.94(2) mm·s⁻¹. They can be assigned probably to metastable Bi_xFe_yO_{1-x-y} ternary oxide with unknown composition.

Based on the performed XRD and MS studies, we may conclude that mechanical milling itself do not allow obtaining the desired solid solutions and the subsequent heat treatment is necessary to complete the solid-state reaction.

Heat treatment changes the situation significantly. Figures 2a and 2b present XRD patterns

and Mössbauer spectra registered for all the studied (BiFeO₃)_{1-x}-(BaTiO₃)_x samples after MA and isothermal annealing at 1073 K. It may be seen that diffraction lines (Fig. 2a) are relatively narrow, testifying better crystal structure after heat treatment. The angular positions of diffraction peaks for all the compositions are similar; however, in the range of $x = 0.1 \div 0.3$, some peaks are split (peak at $2\theta \sim 56^\circ$ is shown as an example in the right panel of Fig. 2a). The diffractograms for the specimens with $x \leq 0.3$ were fitted assuming rhombohedrally distorted perovskite structure with $R3c$ space group characteristic for BiFeO₃. An increase of BaTiO₃ concentration causes structural transformation from rhombohedral to cubic symmetry in the range of $0.3 < x < 0.4$, which is evidenced by the disappearance of the splitting of diffraction peaks (see right panel in Fig. 2a for $x = 0.3$ and 0.4) and shift of peaks towards smaller angles with increasing of x . After transformation, the cubic symmetry ($Pm3m$ space group) is maintained up to $x = 0.9$.

Isothermal annealing at 1073 K allowed to obtain (BiFeO₃)_{1-x}-(BaTiO₃)_x solid solutions with a relatively low number of secondary phases. Traces of hematite Fe₂O₃ were visible in diffractograms for $x = 0.2 \div 0.7$, while the peak at $2\theta = 34^\circ$ was recognized as belonging to the hexagonal barium ferrite BaFe₁₂O₁₉ (Fig. 2a).

The results of Mössbauer spectroscopy studies are presented in Fig. 2b. The sextet with hyperfine interactions parameters characteristic for the hematite was visible practically in all MS spectra (only for

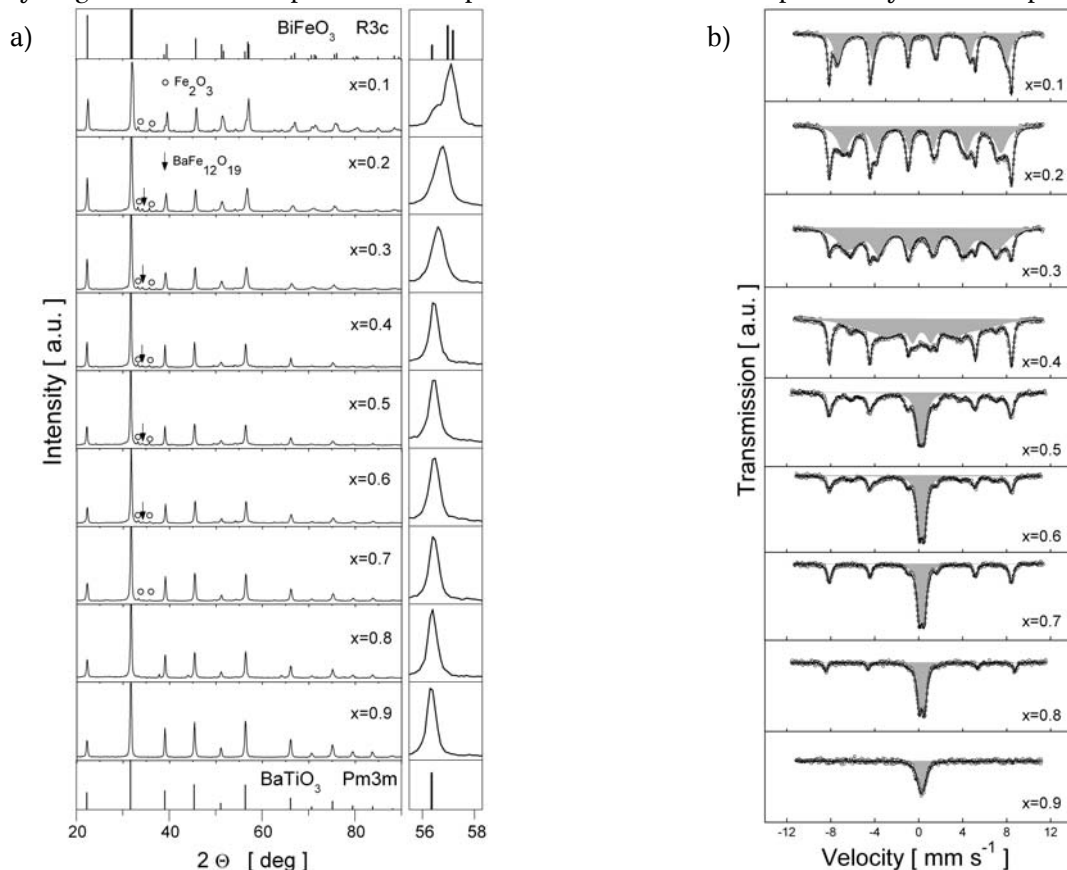


Fig. 2. (a) XRD patterns and (b) MS spectra registered for all the studied (BiFeO₃)_{1-x}-(BaTiO₃)_x solid solutions after 100 h of mechanical activation and isothermal annealing at 1073 K.

$x = 0.9$, there was no sextet from Fe_2O_3). Numerical fitting of the spectra was performed by a discrete method. For the sample with $x = 0.1$, the Mössbauer spectrum was fitted with two sextets, that is, one corresponding to the $(\text{BiFeO}_3)_{0.9}\text{-(BaTiO}_3)_{0.1}$ solid solution ($B_{\text{hf}} = 47.9(1)$ T) and the second related to hematite ($B_{\text{hf}} = 51.7(2)$ T). In the case of $x = 0.2 \div 0.6$, the number of components of the spectra significantly increased. Besides the components from hematite and suitable solid solution, five sextets originating from $\text{BaFe}_{12}\text{O}_{19}$ compound were fitted to the spectra (the sextets have B_{hf} values equal to 39.9, 41.1, 48.6, 50.4 and 51.2 T [10]).

In Fig. 2b, the component from the desired $(\text{BiFeO}_3)_{1-x}\text{-(BaTiO}_3)_x$ solid solution is shown as grey sextet, which transforms to the doublet for $x > 0.4$. This correlates with the structural transformation from rhombohedral to cubic system. The hyperfine magnetic field systematically decreases from $B_{\text{hf}} = 47.9(1)$ T for $x = 0.1$ to $B_{\text{hf}} = 32.4(2)$ T for $x = 0.4$. An increase in BaTiO_3 concentration corresponds to a decrease of the average number of Fe ions per formula unit. Thus, the average distance between the neighbouring Fe ions increases, which results in a weakening of the superexchange Fe-O-Fe interactions and decreasing of B_{hf} .

The doublets visible in MS spectra for the samples with $x > 0.4$ are due to $(\text{BiFeO}_3)_{1-x}\text{-(BaTiO}_3)_x$ solid solutions in paramagnetic state. It may be noted that the Mössbauer spectra for the samples with $x \geq 0.4$ should not exhibit quadrupole splitting since the crystalline lattice of material shows cubic symmetry. On the other hand, an appearance of different atomic configurations in the studied solid solutions breaks the spherical symmetry of EFG seen by ^{57}Fe nuclear probes and causes non-zero values of QS. The numerical fitting is allowed obtaining the QS values of the order of $0.45(2)$ $\text{mm}\cdot\text{s}^{-1}$ for $x = 0.4 \div 0.8$. The last solid solution with $x = 0.9$ has significantly smaller $\text{QS} = 0.34(2)$ $\text{mm}\cdot\text{s}^{-1}$.

Conclusions

It was shown that it is possible to produce $(\text{BiFeO}_3)_{1-x}\text{-(BaTiO}_3)_x$ solid solutions employing mechanical activation technology with subsequent thermal treatment in a wide range of constituent concentration ($x = 0.1 \div 0.9$). The obtained materials are characterized by perovskite-type structure. X-ray diffraction and Mössbauer spectroscopy allowed monitoring the technological process and obtaining information about structure and hyperfine

interactions in the studied materials. Structural transformation from rhombohedral to cubic symmetry occurs for $x = 0.4$. Moreover, the structural change is accompanied by transition from magnetic ordering to the paramagnetic state of solid solutions $(\text{BiFeO}_3)_{1-x}\text{-(BaTiO}_3)_x$.

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