

Structure and hyperfine interactions of multiferroic $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ ceramics prepared by mechanical activation

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Abstract. The structure and hyperfine interactions in the $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$, $\text{Bi}_6\text{Ti}_3\text{Fe}_2\text{O}_{18}$ and $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$ multiferroic ceramics were studied using X-ray diffraction and Mössbauer spectroscopy. Samples were prepared by mechanical activation process in a high-energy ball mill from a mixture of TiO_2 , Fe_2O_3 and Bi_2O_3 oxides as polycrystalline precursor materials. The mechanical milling process was completed by thermal processing. A pure single-phased material was obtained in the case of $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$ compound. The proposed mechanical activation technology allows to produce the Aurivillius compounds at lower temperature, by about 50 K, as compared to the solid-state sintering method.

Key words: Aurivillius compounds • hyperfine interactions • mechanical activation • Mössbauer spectroscopy

Introduction

Multiferroics are materials which exhibit the coexistence of at least two ferro-properties (ferroelectric, ferro(antiferro-)magnetic, ferroelastic, etc.) [6]. These materials are of substantial interest for new types of magnetoelectric device applications [7]. The finding of new compounds in which multiferroic properties exist at a convenient range of temperature (i.e. near room temperature) is intense and desirable work of many scientists. Until now, the best recognized multiferroic compound is bismuth ferrite BiFeO_3 , and the methods of preparation from the conventional solid-state sintering through the rapid-liquid-phase sintering, sol-gel route, solid-state ionic titration technique and epitaxial deposition of thin films are successfully applied to obtaining a single-phased material. On the basis of BiFeO_3 , the other multiferroic materials may be prepared, e.g. Aurivillius compounds or solid solutions.

The materials studied in this work are ceramic Aurivillius phases of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ - BiFeO_3 system, first described in [1]. The general formula of these compounds is $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$, where m indicates the number of perovskite-like layers $\{(\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+1})^{2-}\}$ per slab alternated with fluorite-like bismuth-oxygen layers $\{(\text{Bi}_2\text{O}_2)^{2+}\}$ [4]. At room temperature, these compounds combine the ferroelectric and antiferromagnetic properties.

To obtain pure single-phased multiferroic Aurivillius compounds the conventional solid-state sintering technology is often used. In this method the oxides of bismuth, titanium and iron in the appropriate stoichiometric

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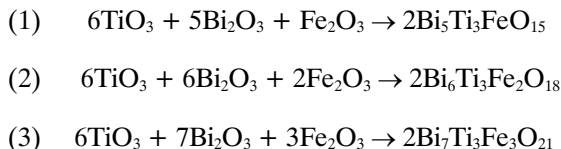
proportions are wet-mixed with ethyl alcohol, C_2H_5OH , in containers of polyamide in a planetary mill for $t = 24$ h. As grinding media zirconium-yttrium balls with a diameter of 10 mm are used. After drying, the mixtures are pressed on a hydraulic press in a steel matrix under pressure, $p = 300$ MPa, and the discs with a diameter of 20 mm are formed. The obtained green bodies are then placed in an alumina crucible and synthesized in the resistance furnace at a temperature of about $T_s = 993$ K for a certain time. After synthesis, the compacts are re-milled, pressed into discs of 10 mm in diameter and then sintered at temperature higher than T_s during 2 h with heating and cooling rates of 5 K min^{-1} .

In this work the mechanical activation (MA) is proposed as an alternative method of synthesis of the Aurivillius compounds. The earlier studies performed by the authors of this work showed such a possibility in the case of $Bi_6Ti_3Fe_5O_{27}$ compound [5]. In the MA technology the weighed mixture of the oxides is placed into the stainless-steel vial planetary ball mill equipped with hardened or stainless-steel balls. During milling, the linear velocities of the balls are of the order of 5–10 m/s and consequently the force of the balls impact is unusually great. In the result of balls collisions, powder particles are repeatedly fragmented, flattened, welded, fractured and disconnected. Milling causes an increase of the density of the crystalline lattice defects, what makes the diffusion of atoms of various components of the milled material among each other very easy. MA is the method allowing to obtain various non-equilibrium phases, such as supersaturated solid solutions, nanostructures, metastable crystalline and quasi-crystalline phases and amorphous materials. Process of MA is carried out in the inert gas atmosphere, e.g. argon or helium. Several advantages can be listed for the MA technology. Firstly, it uses low-cost and widely available oxides as the starting materials and skips the calcination step at an intermediate temperature, leading to a simplifying of the process. Secondly, the synthesis may take place at a temperature lower than that used in the sintering process. Furthermore, the mechanically derived powders possess a higher sinterability than those powders synthesized by a conventional solid-state reaction and most wet-chemical processes. Such preparation methods of materials are promising for use on a production scale due to their simplicity and relatively low cost.

The aim this work was to obtain the multiferroic Aurivillius $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ compounds with $m = 4-6$ using the MA technology and to compare the structure and hyperfine interactions parameters with those reported for similar compounds prepared by the solid-state sintering method. X-ray diffraction (XRD) and Mössbauer spectroscopy (MS) were applied as complementary methods.

Experimental details

Powders of bismuth, titanium, and iron oxides were used as precursor materials. The suitable amounts of the powders were weighed and mixed together to obtain the $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ compounds with $m = 4-6$, according to the following reactions:



The weighed powder was milled in a high-energy ball mill Fritsch Pulverisette P5 type (stainless steel balls of 6 mm diameter, 10:1 ball-to-powder weight ratio) under an argon atmosphere during 1, 2, 5, 10, 20 and 50 h. After milling process the thermal treatment of the mechanically activated compounds was performed. The heating of the powders was carried out from room temperature up to 993 K in a calorimeter Perkin Elmer DSC 7 under an argon atmosphere with a rate of 20 K per min. The isothermal annealing was performed in a furnace at 1073 K for 1 h in air. In both cases the resulted compounds were in the powder form.

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

Measurements of the ^{57}Fe Mössbauer spectra were performed in a transmission geometry by means of a constant-acceleration POLON spectrometer of standard design. The 14.4 keV gamma rays were provided by a 20 mCi source of ^{57}Co in a rhodium or a chromium matrix. The spectrometer was calibrated using α -Fe at room temperature and the isomer shifts (IS) for all the samples were determined in relation to α -Fe at room temperature.

Results and discussion

X-ray diffraction measurements were performed for all mixed powders at the different stages of milling. The obtained XRD patterns allowed to monitor the process of the compound formation. As an example, Figure 1 shows the X-ray diffraction patterns of powder mixture milled for various times to obtain the $Bi_7Ti_3Fe_3O_{21}$ compound. It may be seen that with increasing milling time, the diffraction peaks are systematically broadened, which shows the gradual grain size reduction. In the patterns for the sample milled for 20 and 50 h the broad halo near $2\theta = 30^\circ$ may be observed. It means that the

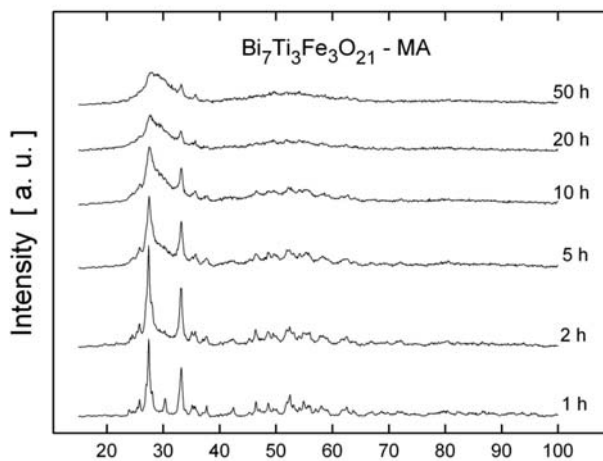


Fig. 1. X-ray diffraction patterns of the powders milled for various times to obtain the $Bi_7Ti_3Fe_3O_{21}$ compound.

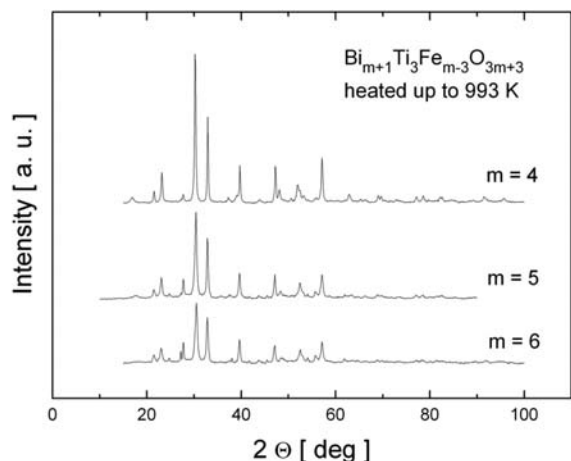


Fig. 2. XRD patterns of $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ compounds after mechanical activation and heating up to 993 K.

desired compound was formed as nanocrystalline or amorphous material. Unfortunately, small diffraction peaks visible on the halo background indicate that not whole hematite reacted with other oxides during milling process. Similar observations were made for $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ and $\text{Bi}_6\text{Ti}_3\text{Fe}_2\text{O}_{18}$ compounds.

The thermal treatment of MA powders should complete the compound formation. As seen in Fig. 2, the heating of the final product of the MA process from the room temperature up to 993 K in a calorimeter did not supply the pure single-phased $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ compounds. All well-visible diffraction peaks with high intensity belong to the main phase, i.e. the suitable Aurivillius compound, and their angle positions agree well with database [2]. However, small peaks from the hematite hidden in the background and superimposed with the main peaks still indicate not completed reaction.

The annealing process performed in a furnace at 1073 K resulted in the formation of a single-phased $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$ compound. In the case of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ and $\text{Bi}_6\text{Ti}_3\text{Fe}_2\text{O}_{18}$, very small peaks from non-reacted hematite was registered and recognized (Fig. 3).

Summarizing the results obtained from XRD analysis it may be stated that milling process alone is not enough to produce the Aurivillius compounds. Additional thermal treatment allows to obtain the compounds with a relatively high purity. The materials are nanocrystalline

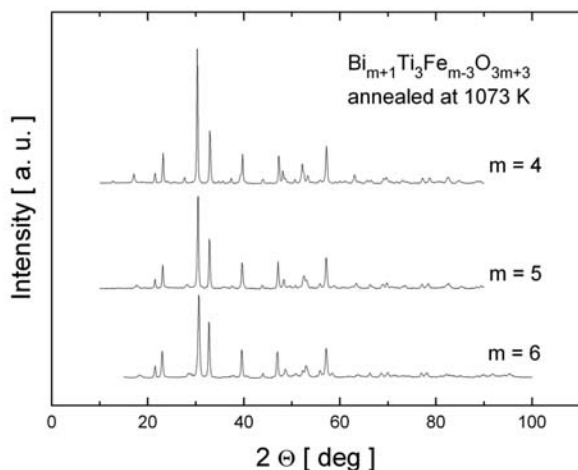


Fig. 3. XRD patterns of $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ compounds after mechanical activation and isothermal annealing at 1073 K.

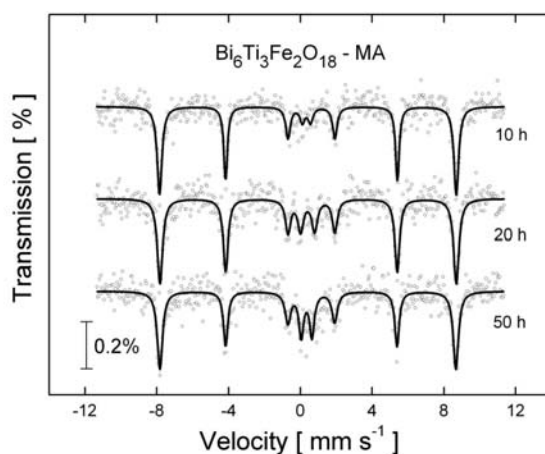


Fig. 4. Room-temperature Mössbauer spectra of mechanically activated $\text{Bi}_6\text{Ti}_3\text{Fe}_2\text{O}_{18}$ Aurivillius compound after various milling times.

as proved by analysis using the Scherrer formula. It was found that the average crystallite sizes of the compounds heated up to 993 K are about 30, 27 and 23 nm for $m = 4, 5, 6$, respectively, while those of compounds annealed at 1073 K are about 40, 64 and 36 nm.

Mössbauer spectroscopy confirmed and completed XRD results. As seen in Fig. 4 for the $\text{Bi}_6\text{Ti}_3\text{Fe}_2\text{O}_{18}$ sample, MS spectra registered after various milling times consist of the paramagnetic doublet, which originates from the desired phase, and the discrete sextet from he-

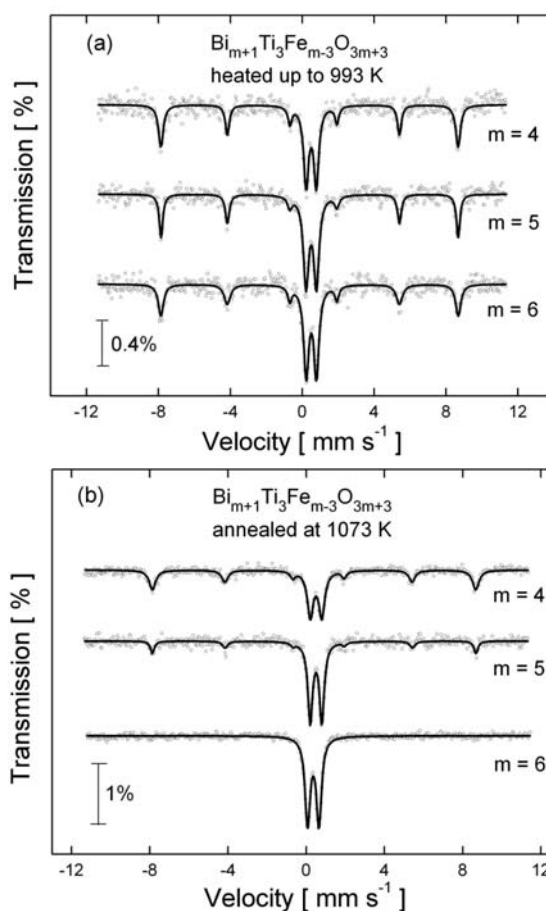


Fig. 5. Room-temperature Mössbauer spectra of Aurivillius compounds after mechanical activation process and (a) heating up to 993 K; (b) isothermal annealing at 1073 K.

Table 1. Hyperfine interactions parameters of $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ for $m = 4-6$ after MA process and after thermal treatment, IS – isomer shift relative to α -iron, QS – quadrupole splitting of the doublet, Δ – quadrupole shift of the sextet, B_{hf} – hyperfine magnetic field induction; uncertainties of the parameters are given in parentheses for the last significant numbers

Specimen / method	$\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$			$\text{Bi}_6\text{Ti}_3\text{Fe}_2\text{O}_{18}$			$\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$					
	IS (mm/s)	QS (mm/s)	Δ (mm/s)	B_{hf} (T)	IS (mm/s)	QS (mm/s)	Δ (mm/s)	B_{hf} (T)	IS (mm/s)	QS (mm/s)	Δ (mm/s)	B_{hf} (T)
50 h MA	0.23(2)	0.29(2)	–	51.34(47)	0.20(2)	0.30(2)	–	51.33(53)	0.37(1)	0.28(1)	–	51.49(75)
50 h MA	0.37(1)	–	–0.10(1)	–	0.37(1)	–	–0.10(1)	–	0.37(1)	–	–0.10(1)	–
heated up to 993 K	0.36(1)	0.28(1)	–	51.46(51)	0.36(1)	0.29(1)	–	51.44(46)	0.35(1)	0.28(1)	–	51.72(57)
50 h MA annealed at 1073 K	0.37(1)	–	–0.11(1)	–	0.38(1)	–	–0.10(1)	–	0.37(1)	–	–0.11(1)	–
	0.36(1)	0.28(1)	–	51.50(39)	0.36(1)	0.30(1)	–	51.50(91)	0.36(1)	0.29(1)	–	–
	0.37(1)	–	–0.11(1)	–	0.38(2)	–	–0.12(2)	–	–	–	–	–

matite. Similar observations were made for $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ and $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$ samples after the MA process.

After additional thermal processing, when the main Aurivillius phases were formed, the contribution of the doublet to the whole MS spectra increases, as seen in Fig. 5. The sextet from the hematite is still visible for all the heated samples (Fig. 5a), while in the case of the annealed samples the amount of the hematite is significantly smaller and there is no trace of hematite in the spectrum for $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$ compound (Fig. 5b).

The numerical analysis of the spectra allowed determining the hyperfine interactions parameters. During the fitting procedure, the Lorentzian shape of spectral lines was assumed and the Mössbauer spectra have been developed with one doublet and one sextet. Parameters are listed in Table 1 for $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ compounds with $m = 4-6$ both obtained by the MA process and thermally processed. The parameters for the sextet are characteristic of the hematite. The values of the hyperfine interactions parameters for mechanically activated and thermally treated $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ compounds are the same (in the limit of the error) as those reported for conventionally sintered samples at temperatures 1123–1313 K [3].

Conclusions

On the basis of the performed investigations it may be stated that the mechanical activation method with completed thermal processing allows to obtain the $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ Aurivillius compounds. In most cases not a whole amount of hematite reacted during thermal processing what is connected with the bismuth evaporation from the mixture during technological process and consequently, the overabundance of hematite is expected. However, in the case of $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$ a single-phased material was successfully obtained. This means that mechanical activation as the technological process needs further tests and improvements.

X-ray diffraction and Mössbauer spectroscopy as complementary methods allowed to determine the structural and hyperfine interactions parameters of the Aurivillius compounds. The comparison of the obtained results with the data for the conventionally sintered compounds allows to state that by the mechanical activation technology it is possible to produce the Aurivillius compounds at lower temperature, by at least 50 K, as in the case of the solid-state sintering method.

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