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

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The aim of the study was to determine the structure and hyperfine interactions of $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ multiferroic Aurivillius compounds prepared by mechanical activation process. X-ray diffraction and Mössbauer spectroscopy were applied as complementary methods. After the process of mechanical milling, desired Aurivillius phases were not formed, thus, thermal treatment needed to be applied. Heating the product of mechanical activation up to 993 K allowed to obtain Aurivillius phases with relatively large amount of non-reacted hematite. However, after the material was annealed at an elevated temperature of 1073 K, the content of not fully synthesized hematite was significantly reduced. Mössbauer spectroscopy confirmed that Aurivillius compounds remain in paramagnetic state at room temperature.

Keywords: *Aurivillius compounds; mechanical activation; Mössbauer spectroscopy*

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1. Introduction

According to the original definition given by Hans Schmid, multiferroics are materials that combine two or more of primary forms of ferroic order, i.e. ferroelasticity, ferroelectricity, ferromagnetism, and ferrotoroidicity [1]. The most appealing combination of those involves electric and magnetic ordering, as it opens great perspectives in terms of applications of such material, especially in the field of spintronics [2]. Multiferroic materials exhibit a magnetoelectric coupling ability, meaning that it is possible to control their magnetization by an external electric field as well as polarization by a magnetic field. However, the compounds exhibiting multiferroic properties above room temperature are very rare and include only some of perovskite oxides, such as BiFeO_3 .

Multiferroic ceramic Aurivillius compounds studied in this work and represented by the general formula $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$, are ferroelectric antiferromagnets with the structure of a layered crystal. The said structure consists of periodically arranged $\{(\text{Bi}_2\text{O}_2)^{2+}\}$ fluorite-like layers and m layers with a perovskite-like structure $\{(\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+1})^{2-}\}$. The m indicates the number of perovskite-like layers per slab and may take integer or fractional values, however, $m \leq 13$ [3]. The first member of the Aurivillius family is the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($m = 3$), a ferroelectric compound with high Curie temperature, $T_C = 948$ K [4]. BiFeO_3 can be regarded as a limiting case of layered perovskite-like structure with $m = \infty$, in which case the structure is not layered [3]. The Curie temperature of BiFeO_3 is equal to 1123 K, while the Néel temperature $T_N = 643$ K [5].

The standard method of preparing $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ ceramic compounds is

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solid-state sintering. Parameters, such as calcination temperature, sizes of particles of powdered precursors, temperature, time of sintering, etc., play an important role in the technological process. The choice of parameters determines the physical properties of the material, e.g. homogeneity, or microstructure.

Another promising alternative for the preparation of Aurivillius compounds is mechanical activation (MA). It is a high-energy ball milling process using a mixture of TiO_2 , Fe_2O_3 and Bi_2O_3 oxides as polycrystalline precursor materials. The mixture of the oxides is placed in a planetary ball mill. During a milling procedure, the linear velocities of the balls reach about 5 to 10 $\text{m}\cdot\text{s}^{-1}$ and consequently the force of the balls impact is unusually strong. As the result of balls colliding, powder particles are repeatedly fragmented, flattened, welded and fractured. Milling causes an increase in density of crystalline lattice defects, which significantly facilitates the diffusion of atoms of various components of the milled material between each other. The MA method allows to achieve various non-equilibrium phases, such as supersaturated solid solutions, nanostructures, metastable crystalline and quasi-crystalline phases as well as amorphous materials [6, 7]. The process of MA is carried out in an inert gas atmosphere, e.g. argon, to prevent oxidation of the material. In general, after mechanical activation, the compounds with complicated crystalline structure are not expected to form, thus, thermal processing of mechanically activated material is often required.

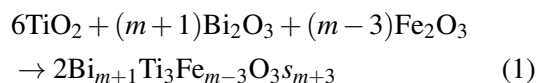
Mechanical activation process has several advantages over the standard solid-state sintering method. Firstly, it skips the calcination step at intermediate temperature, which simplifies the process. Secondly, the mechanically derived powders possess higher sinterability than powders synthesized by a conventional solid-state reaction. Preparing material with mechanical activation method seems to be promising at an industrial scale due to its simplicity and relatively low cost of processing.

The main aim of the study was to determine the hyperfine interactions parameters of $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ multiferroic Aurivillius

compounds with $m = 4$ to 8, obtained through mechanical activation and subsequent thermal treatment. The investigations of the structure and hyperfine interactions of the samples were carried out using X-ray diffraction (XRD) and Mössbauer spectroscopy (MS).

2. Experimental details

A powder mixture of bismuth, titanium, and iron oxides (all of 99.9 % purity) was subjected to MA process in order to obtain $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ Aurivillius compounds. Synthesis of $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ proceeds according to the following reaction:



As-mixed powders were milled in a Fritsch Pulverisette P5 type high-energy ball mill under an argon atmosphere. The mixture of the oxides was placed into a stainless-steel vial together with hardened steel balls. MA processes were continued for up to 50 h.

Thermal processing of the obtained mixtures was performed in a two-way manner: (1) heating from the room temperature up to 993 K in a calorimeter under an argon atmosphere with a rate of 20 $\text{K}\cdot\text{min}^{-1}$ and (2) isothermal annealing in a furnace at 1073 K in air for 1 h.

XRD measurements were performed using a Rigaku diffractometer working in a continuous scanning mode with $\text{CuK}\alpha$ radiation. Basing on the XRD patterns, the lattice constants were determined from the shift of the diffraction lines. Refinement of the elementary cell parameters was performed using the Rietveld method.

Measurements of the ^{57}Fe Mössbauer spectra were performed in transmission geometry by utilizing a POLON spectrometer working in a constant acceleration mode at room temperature. The 14.4 keV gamma rays were provided by a 25 mCi source of ^{57}Co in a chromium matrix. The isomer shifts values determined from Mössbauer spectra of the samples are given with respect to the standard $\alpha\text{-Fe}$.

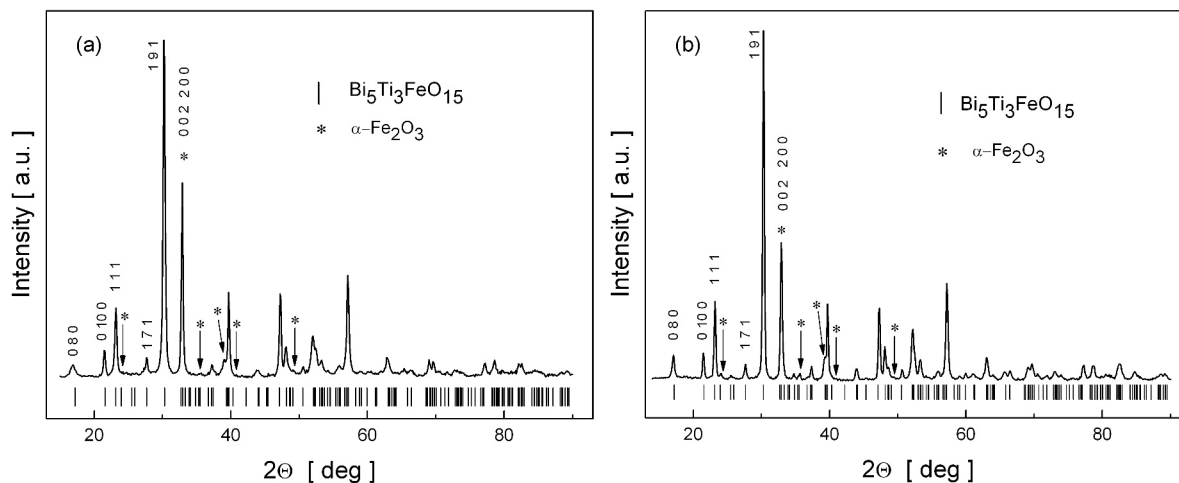


Fig. 1. XRD patterns of the $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ compound after mechanical activation and (a) heating up to 993 K; and (b) annealing at 1073 K. The bars show the diffraction lines positions for the $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ compound according to the card No. 01-082-0063.

Table 1. Structural data for $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ Aurivillius compounds; m – number of perovskite-like layers, T – temperature of thermal processing, a , b , c – lattice parameters.

| Compound | m | T [K] | Space group | a 10^{-10} [m] | b 10^{-10} [m] | c 10^{-10} [m] | Weight fraction [%] |
|--|------|------------|----------------|-----------------------|-----------------------|-----------------------|------------------------|
| $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ | 4 | 993 | Fmm2 (42) | 5.429(7) | 5.449(7) | 41.42(2) | 60 |
| | | | R-3c (167) | 5.3161(5) | 5.3161(5) | 11.437(2) | 40 |
| | 1073 | Fmm2 (42) | 5.4277(9) | 5.4456(8) | 41.286(5) | 90 | |
| | | R-3c (167) | 5.3285(4) | 5.3285(4) | 11.9868(6) | 10 | |
| $\text{Bi}_6\text{Ti}_3\text{Fe}_2\text{O}_{18}$ | 5 | 993 | Fmm2 (42) | 5.46(2) | 5.44(2) | 49.63(3) | 67 |
| | | | R-3c (167) | 4.9879(3) | 4.9879(3) | 13.9153(7) | 33 |
| | 1073 | Fmm2 (42) | 5.450(3) | 5.460(3) | 49.61(1) | 70 | |
| | | R-3c (167) | 5.9537(9) | 5.9537(9) | 14.166(4) | 30 | |
| $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$ | 6 | 993 | Fmm2 (42) | 5.445529 | 5.466406 | 40.726590 | 90 |
| | | | R-3c (167) | 5.31(2) | 5.31(2) | 11.5(2) | 10 |
| | 1073 | Fmm2 (42) | 5.458(2) | 5.472(2) | 57.56(2) | 100 | |
| | | R-3c (167) | – | – | – | 0 | |
| $\text{Bi}_8\text{Ti}_3\text{Fe}_4\text{O}_{24}$ | 7 | 993 | Fmm2 (42) | 5.465(2) | 5.478(2) | 57.40(2) | 90 |
| | | | R-3c (167) | 5.208(4) | 5.208(4) | 14.08(8) | 10 |
| | 1073 | Fmm2 (42) | 5.465(2) | 5.478(2) | 57.40(2) | 95 | |
| | | R-3c (167) | 5.208(4) | 5.208(4) | 14.08(8) | 5 | |

3. Results and discussion

XRD measurements allowed for a set of patterns to be obtained for the samples after MA process, and subsequent heating up to 993 K or isothermal annealing at 1073 K. As an example,

XRD patterns of the $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ compound are presented in Fig. 1.

Preliminary analysis of each diffractogram was conducted under the assumption that a single-phase Aurivillius compound was formed. Using Rietveld

refinement method, the lattice constants were determined from diffractograms assuming Fmm2 space group. The resulting values are as follows: a and b are about 5.4×10^{-10} m, while the c parameter depends linearly on m value, as it can be seen in Fig. 2. The observed linear dependence (determined for the annealed samples) is very similar to those reported for conventionally sintered Aurivillius compounds in [8] ($c = 8.39m + 7.41$) or in [3] ($c = 8.22m + 8.16$).

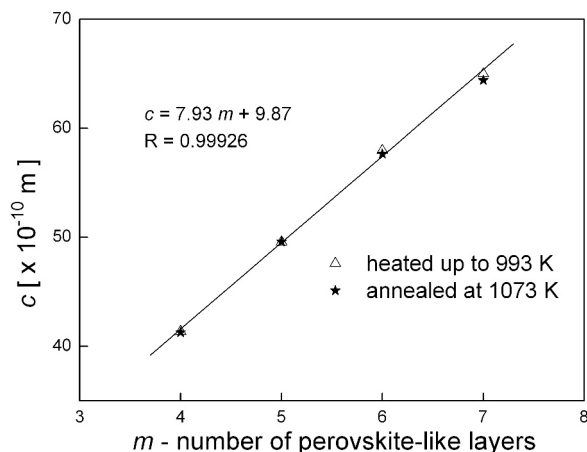


Fig. 2. Lattice parameter c of Aurivillius compounds as a function of the number of perovskite-like layers m.

Further investigations performed using Mössbauer spectroscopy indicated the necessity of conducting the XRD analysis with the account of two phases, i.e. given Aurivillius compound and hematite. MS proved that not all hematite reacted during the thermal processing. On the other hand, it is well known that bismuth evaporates from the mixture during technological process and consequently, the overabundance of hematite is to be expected. Thus, each XRD pattern was elaborated as a superposition of two diffractograms, i.e. first characteristic of the predominant Aurivillius phase (with Fmm2 space group) and the second of hematite (with R-3c space group). Detailed results of phase analysis are listed in Table 1. The determined lattice parameters for hematite are in agreement with data in the literature [9].

Mössbauer spectroscopy studies confirmed and complemented X-ray diffraction results. In Fig. 3a, Mössbauer spectra of the oxides mixture for preparing the $\text{Bi}_8\text{Ti}_3\text{Fe}_4\text{O}_{24}$ compound are presented as a function of milling time. Each spectrum for 10, 20 and 50 h is a superposition of six lines and paramagnetic doublet. The six-line component originates from the hematite, which is confirmed by the hyperfine interactions parameters (isomer shift $\delta = 0.38(1) \text{ mm}\cdot\text{s}^{-1}$, quadrupole shift $2\varepsilon = -0.21(4) \text{ mm}\cdot\text{s}^{-1}$ and hyperfine magnetic field induction $B_{hf} = 51.36(3)\text{T}$). The obtained values correspond well with data reported for hematite in [9]. Paramagnetic doublet in the centre of MS spectra is attributed to the $\text{Bi}_8\text{Ti}_3\text{Fe}_4\text{O}_{24}$ compound. From Fig. 3b it can be noticed that after additional thermal processing, when the main Aurivillius phase was formed, the contribution of the doublet to the whole MS spectrum increases. However, the sextet from hematite is still visible in MS spectra though its intensity is relatively small. It is reasonable to add, that the annealing at elevated temperature, i.e. 1073 K resulted in the formation of the $\text{Bi}_8\text{Ti}_3\text{Fe}_4\text{O}_{24}$ compound with smaller amount of hematite as compared with thermal process conducted at lower temperature of 973 K.

The sextet from the hematite was registered for all the heated $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ Aurivillius compounds (Fig. 4a). In the case of the annealed samples (Fig. 4b) the amount of the hematite is significantly lower and there is no trace of hematite in the spectrum for the compound with $m = 6$.

It is known that the Néel temperature of the Aurivillius compounds depends on m value, however, for all the compounds investigated in this paper it is lower than room temperature [10, 11]. Therefore, paramagnetic doublets in MS spectra are to be expected. The hyperfine interactions parameters of doublets for the samples after MA process and after thermal processing are as follows: isomer shift $\delta = 0.36(2) \text{ mm}\cdot\text{s}^{-1}$ and quadrupole splitting $2\varepsilon = 0.58(2) \text{ mm}\cdot\text{s}^{-1}$. The obtained values of the 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 (within the margin of experimental error) as those reported for

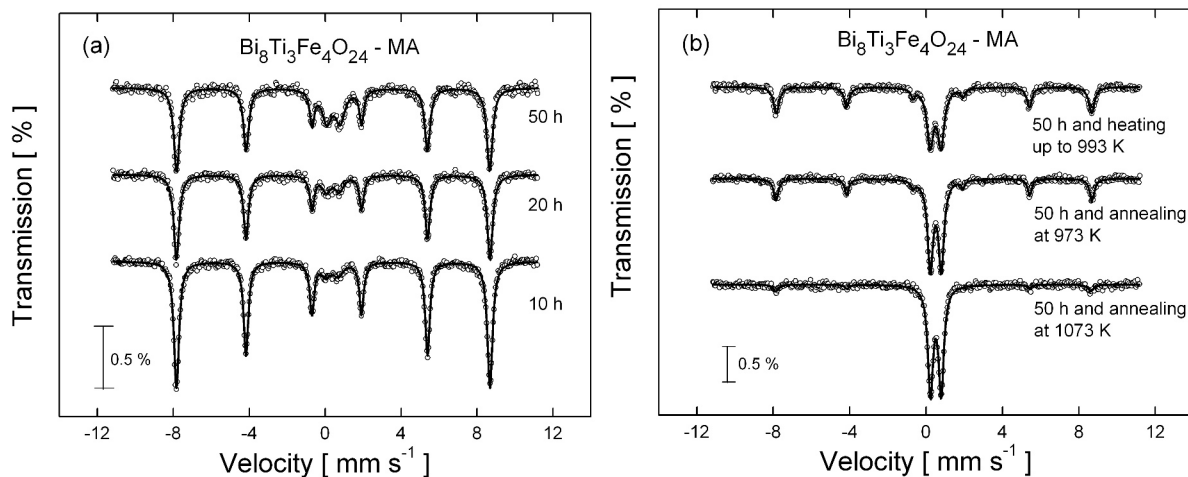


Fig. 3. Fitted room-temperature Mössbauer spectra of the mechanically activated $\text{Bi}_8\text{Ti}_3\text{Fe}_4\text{O}_{24}$ Aurivillius compound after various milling times (a) and after thermal treatment (b).

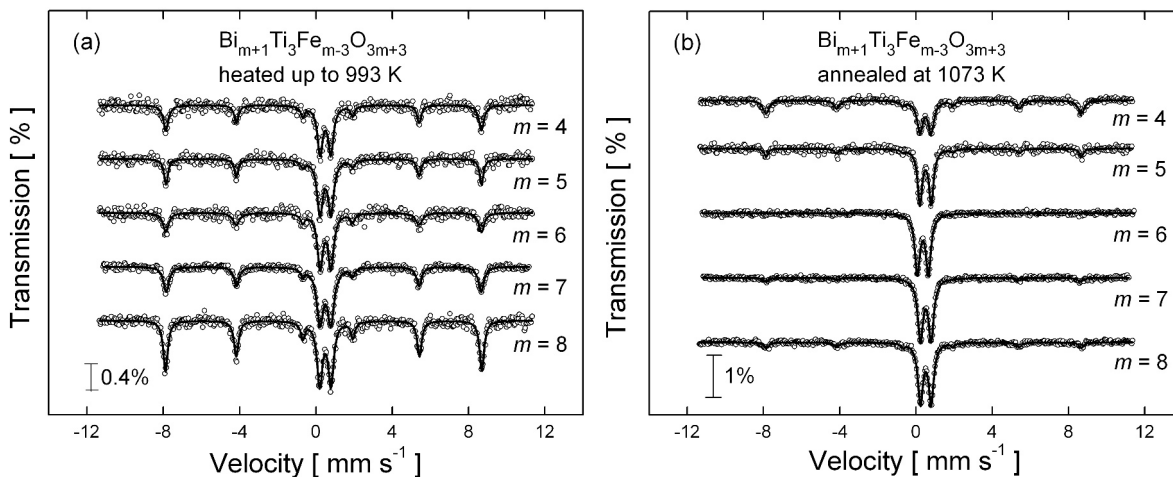


Fig. 4. Fitted room-temperature Mössbauer spectra of $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ Aurivillius compounds after mechanical activation process and (a) heating up to 993 K, (b) isothermal annealing at 1073 K.

conventionally sintered samples [8, 12]. The determined value of isomer shift is typical of the trivalent iron, Fe^{3+} . Iron ions substitute Ti ions in the center of the oxygen octahedra. Non-zero value of quadrupole splitting proves that the nearest neighbourhood of ^{57}Fe isotopes generates the electric field gradient with no spherical symmetry. The half widths at half maximum of spectral lines for the doublets are about $0.16 \text{ mm}\cdot\text{s}^{-1}$. Both isomer shift and quadrupole splitting parameters practically do not depend on the number of perovskite-like layers in Aurivillius compounds.

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 can be estimated from XRD patterns (Table 1). Similar estimation of the contribution of the given phase from the Mössbauer spectrum is possible only under the assumption that each phase has the same value of Debye-Waller factor. The contribution of the Aurivillius phase with the suitable m number was estimated from the area of spectral lines for the heated and annealed samples (Fig. 5).

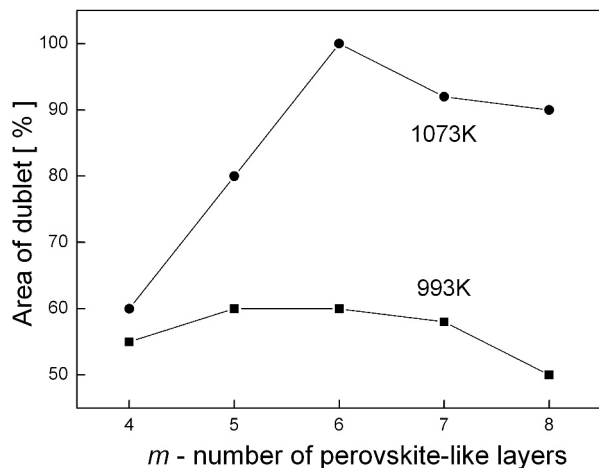


Fig. 5. The contribution of Aurivillius compound estimated from the area of spectral lines of Mössbauer spectrum.

Except from the case of the compound with $m = 6$, all the contributions of Aurivillius phases are underestimated. This may be due to larger Debye-Waller factor for hematite than that for the Aurivillius phase. Although the results from XRD and MS do not overlap it can be stated that the thermal processing of the milled material at elevated temperature is more effective in obtaining the desired Aurivillius compound. It is worth noting that in the case of mechanical activation, the pure phase may be formed at a temperature of 50 to 200 K lower as compared to sintering temperatures in the standard solid-state technology (similar Aurivillius compounds were obtained at sintering temperatures of 1123 to 1313 K, as reported in [8, 12]).

4. Conclusions

X-ray diffraction and MS techniques allowed us to determine structural properties and hyperfine interactions parameters of the $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ Aurivillius compounds prepared using mechanical activation method. The resulting materials exhibit similar properties as the conventionally sintered Aurivillius compounds.

On the basis of the performed research it can be clearly stated that only in the case of the $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$ compound a single-phase material was successfully obtained by mechanical activation process and subsequent annealing at 1073 K. However, in most cases not entire amount of hematite reacted during the thermal processing, which was the result of bismuth evaporation from the mixture during the technological process.

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