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Structure and Mössbauer Spectroscopy Studies of Multiferroic Mechanically Activated Aurivillius Compounds

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X-ray diffraction and ^{57}Fe Mössbauer spectroscopy were applied as complementary methods to investigate the structure and hyperfine interactions of the Aurivillius compounds prepared by mechanical activation and subsequent heat treatment. Preliminary milling of precursors enhanced the diffusion process and pure Aurivillius compounds were obtained at lower temperature as compared with conventional solid-state sintering technology (lower at least by 50 K). All the investigated Aurivillius compounds are paramagnetic materials at room temperature.

1. Introduction

Multiferroics are the materials which exhibit at least two ferroic states simultaneously. Especially interesting from the application point of view is the group of magnetoelectrics in which both ferroelectric and magnetic ordering coexist [1]. They attract a lot of interest due to their possible applications as sensors, actuators and digital memory elements [2]. The most frequently investigated multiferroic compound is $BiFeO_3$. It offers ferroelectric and antiferromagnetic ordering at relatively high temperatures. However, the existence of spin cycloid in this compound averages out a linear magnetoelectric coupling. The Aurivillius compounds, described by the general formula $Bi_{m+1}Ti_3Fe_{m-3}O_{3m+3}$, have layered perovskite-like structure where m value indicates the number of perovskite-like layers per slab [3–5]. Each member of family can be viewed as an atomic stacking of the ferroelectric $Bi_4Ti_3O_{12}$ compound and the multiferroic $BiFeO_3$, so the Aurivillius compounds offer magnetoelectric coupling. It was found that some physical properties depend on the m number, i.e. lattice parameter of the orthorhombic elemental cell, ferroelectric Curie temperature, antiferromagnetic Néel temperature [4, 6–9].

In order to obtain the Aurivillius compounds mainly the conventional solid-state route is used. Appropriate amounts of reagent-grade oxide powders are mixed together, pressed, calcinated and sintered. However, various purity and gradation of started oxides, various temperatures of calcination and sintering, etc. may be the reason for the large discrepancies in some physical prop-

erties reported in the literature. Even the structural models for the Aurivillius compounds are not well known, some databases have been reported in the sixties of the 20th century [10]. Moreover, not always the obtained materials are single-phased compounds. Only the first member of the Aurivillius family, i.e. $Bi_5Ti_3FeO_{15}$ compound is thermally stable, other compounds with increasing m number may contain admixtures of adjacent phases with $m \pm 1$, as it was reported in our previous investigations [11].

In this work mechanical activation (MA) method is proposed as an alternative technology for production of $Bi_{m+1}Ti_3Fe_{m-3}O_{3m+3}$ Aurivillius compounds. Our previous investigations have shown that after mixing of the oxides and milling them in the planetary ball mill the desired Aurivillius compounds have not been formed. The subsequent thermal treatment was necessary. After heating the mechanically activated mixture from the room temperature up to 993 K or isothermal annealing in a furnace at 1073 K, the desired Aurivillius compounds with $m = 4 \div 8$ have been obtained, however, in some cases small amount of unreacted hematite has been registered by the Mössbauer spectroscopy (MS) [12, 13]. The aim of this work was to modify the mechanical activation technology in order to obtain pure Aurivillius compounds. X-ray diffraction (XRD) and MS were applied as complementary methods to get information about structure and hyperfine interactions of the materials.

2. Experimental details

The appropriate amounts of reagent-grade oxide powders, viz. Fe_2O_3, Bi_2O_3, and TiO_2 were first milled separately during 10 h in air. The milling process was performed in the stainless-steel vial of a Fritsch P5 Pulverisette planetary ball mill equipped with hardened steel balls. The ball-to-powder weight ratio was

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10:1. Next powders were mixed and milled together during 50 h in air in the same ball mill. Synthesis of $Bi_{m+1}Ti_3Fe_{m-3}O_{3m+3}$ Aurivillius compounds with $m = 4 \div 8$ proceeded according to the following reaction:

$$(m-3)Fe_2O_3 + (m+1)Bi_2O_3 + 6TiO_2 \rightarrow$$

$$2Bi_{m+1}Ti_3Fe_{m-3}O_{3m+3}. \tag{1}$$
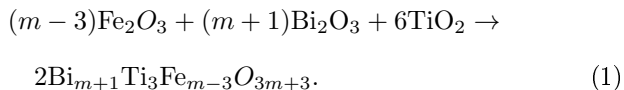
After mechanical activation process isothermal annealing in a furnace was performed in air at 1073 K during 1 h.

The crystalline structure of the mechanically activated as well as isothermally annealed samples was analyzed using the Philips PW 1830 diffractometer with CuK_α radiation. The phase analysis of the recorded X-ray patterns was performed with an X'Pert HighScore Plus computer programme equipped with the ICDD PDF2 database.

MS studies were carried out at room temperature in standard transmission geometry using a source of ^{57}Co in a rhodium matrix. The absorbers were prepared using a self-adhesive transparent foil. A 25 μm thick metallic iron foil was taken as a standard for calibration of a spectrometer.

3. Results and discussions

Preliminary milling of the oxides aimed activation of the powders to make them more reactive during subsequent mixture milling. In the registered XRD patterns of Fe_2O_3, Bi_2O_3, and TiO_2 only the broadening of diffraction lines was observed. The average crystallite sizes estimated roughly by the Scherrer formula are of the order of 20 nm for all the precursors. Figure 1 presents the set of XRD patterns for the investigated mixtures of oxides after 50 h of milling.
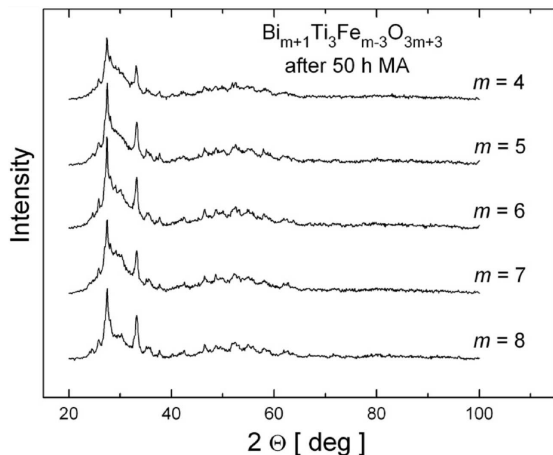

Fig. 1. XRD patterns of mechanically activated $Bi_{m+1}Ti_3Fe_{m-3}O_{3m+3}$ compounds after 50 h.

It may be observed that milling process of preliminary activated powders led to the formation of some amorphous/nanocrystalline phase but not the desired Aurivillius compounds. It may be seen that some diffraction peaks emerge from the background of amorphous

halo. These peaks may come from α-Bi_2O_3 and α-Fe_2O_3 phases. After isothermal annealing of mechanically activated powders, the Aurivillius compounds were obtained. As seen in Fig. 2 all the main diffraction lines belong to the Aurivillius compounds, smaller peaks marked by stars come from the impurity phase. Small broadening and shifts of diffraction lines may be observed with an increasing m number. From broadening of lines using the Scherrer formula the average crystallite sizes were estimated and they are listed in Table. Shifts of lines, towards both lower and higher 2Θ angles are the reason of increase in the volume of the orthorhombic unit cell (as reported in literature c parameter increases from 32.80 Å for $m = 3$ up to 81.25 Å for $m = 9$ while a and b parameters are of the order of 5.40 Å [4, 6]).
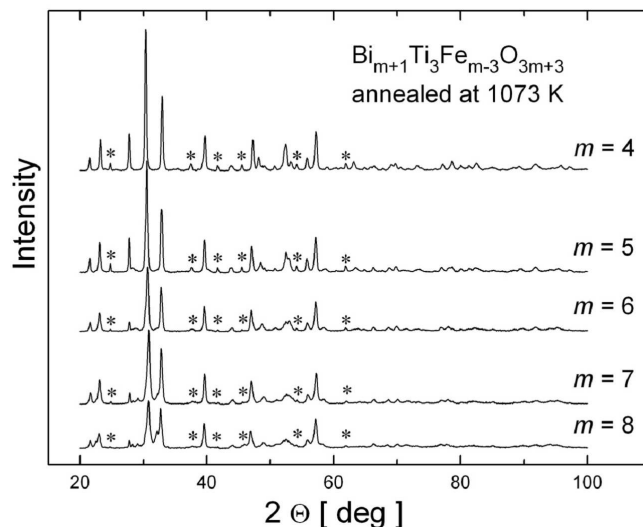

Fig. 2. XRD patterns of $Bi_{m+1}Ti_3Fe_{m-3}O_{3m+3}$ compounds after 50 h of mechanical activation and isothermal annealing at 1073 K. The peaks from $Bi_{12}TiO_{20}$ impurity phase are marked by stars.

TABLE I

Results from XRD and MS studies; m — number of perovskite-like layers in the Aurivillius compounds, FWHM — full width at half maximum of the most intensive diffraction line, D — average crystallite size estimated using the Scherrer formula, Γ — half width at half maximum of spectral lines from Mössbauer spectrum.

m	FWHM [deg]	D [nm]	Γ [mm s^{-1}]
4	0.268	49	0.19(4)
5	0.340	34	0.19(3)
6	0.380	30	0.26(3)
7	0.429	25	0.27(3)
8	0.466	23	0.26(5)

Detailed phase analysis was performed for all the samples. In Fig. 3 the results of this analysis are shown for the $Bi_5Ti_3FeO_{15}$ compound, as an example. The main $Bi_5Ti_3FeO_{15}$ phase constitutes 95%, the rest 5% comes

from the impurity phase, recognized as $Bi_{12}TiO_{20}$. On the basis of the performed XRD studies it may be stated that the applied technology allowed obtaining the Aurivillius compounds. In all cases the whole amount of hematite reacted with other oxides. Unfortunately, some other impurity phase was also formed besides the desired Aurivillius compounds. It may be noted (Fig. 2) that intensity of the diffraction lines from impurity phase systematically decreased with the increase of m number. In all cases the amount of impurity is relatively small (lower than 5%). Moreover, Aurivillius phases were formed by mechanical activation and subsequent thermal treatment at the temperature lowered by 50–200 K as compared to the temperature of conventional sintering method. As reported in [14], the Aurivillius compounds with reproducible physical properties have been prepared by sintering at various temperatures in the range of 1123–1313 K. It may be supposed that after mechanical activation described above the powders of the Aurivillius compounds may be sintered even at 1073 K.
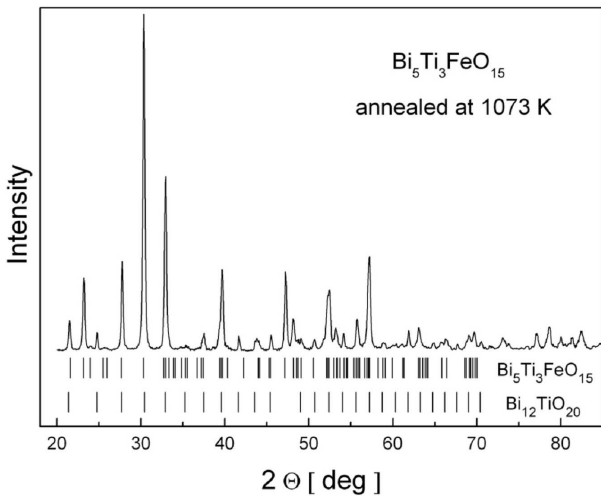

Fig. 3. XRD pattern with phase analysis for the $Bi_5Ti_3FeO_{15}$ compound; the vertical bars below the XRD pattern denote positions of reflections for $Bi_5Ti_3FeO_{15}$ according to PDF2 card no. 01-082-0063 and for $Bi_{12}TiO_{20}$ – card no. 00-034-0097.

The Mössbauer studies confirmed structural results. After 50 h of milling all the spectra of the Aurivillius compounds consisted of the sextet and the doublet (in Fig. 4 the spectrum for $Bi_5Ti_3FeO_{15}$ is presented as an example). Poor statistics of the spectrum is caused by the high absorption of gamma radiation by the bismuth and small amount of iron in the sample. The six lines visible in the spectrum (light-grey component in Fig. 4) originate from hematite which is confirmed by the hyperfine interactions parameters (i.e. isomer shift relative to α-iron $\delta = 0.37(1)$ mm s^{-1}, quadrupole shift $2\varepsilon = -0.18(2)$ mm s^{-1} and hyperfine magnetic field induction $B_{hf} = 50.9(7)$ T). The double line (grey component in Fig. 4) may be attributed to the paramagnetic $Bi_5Ti_3FeO_{15}$ compound which starts to form during

milling process. The hyperfine interactions parameters for the doublet determined from the numerical fitting of the spectrum are as follows: $\delta = 0.27(2)$ mm s^{-1} and $\Delta = 0.61(3)$ mm s^{-1}.
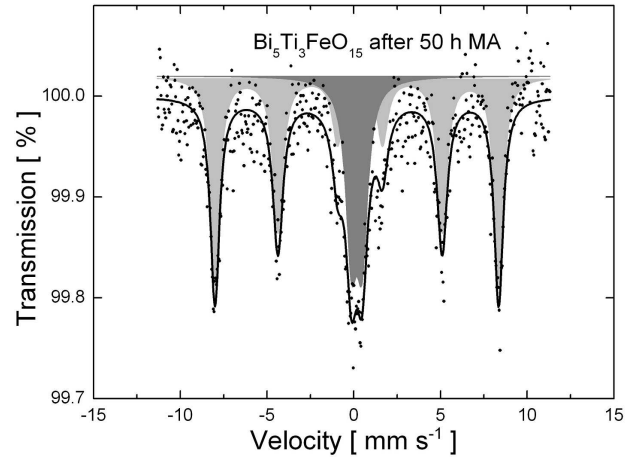

Fig. 4. Fitted room-temperature Mössbauer spectrum of $Bi_5Ti_3FeO_{15}$ compound after 50 h of mechanical activation.

After thermal treatment changes in MS spectra are clearly visible (Fig. 5). After annealing of mechanically activated powders the desired Aurivillius compounds are formed and they are all paramagnetic at room temperature. There is no trace of the hematite component. The hyperfine interactions parameters for the doublets are as follows: $\delta = 0.35(1)$ mm s^{-1} and $\Delta = 0.56(2)$ mm s^{-1} for each m number. It may be noted that these parameters are the same as those obtained for the Aurivillius compounds prepared conventionally by solid-state sintering method [11] and they are independent of m number. The width of spectral lines for doublets increases with an increasing m number (see Table) which correlates with the decrease of the average crystallite sizes of the Aurivillius compounds.
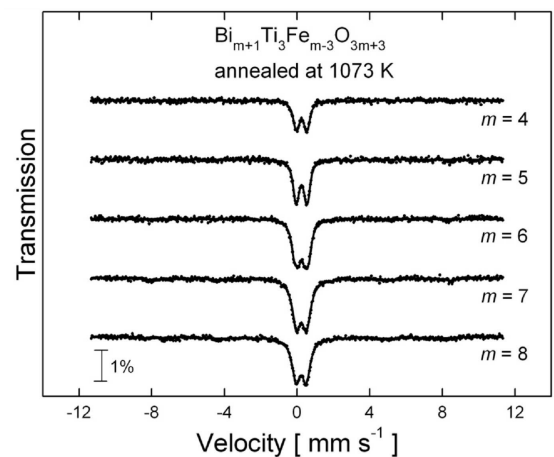

Fig. 5. Fitted room-temperature Mössbauer spectra of $Bi_{m+1}Ti_3Fe_{m-3}O_{3m+3}$ compounds after 50 h of mechanical activation and isothermal annealing at 1073 K.

4. Conclusions

It was shown that mechanical activation with subsequent isothermal annealing is a good technology to produce multiferroic Aurivillius compounds. X-ray diffraction and Mössbauer spectroscopy are complementary methods which allow monitoring of technological process and obtaining the information about structure and magnetic properties of the material.

It may be supposed that preliminary milling of precursors enhances the diffusion process. To complete solid-state reaction and obtaining pure Aurivillius compounds heat treatment is necessary; however, temperature of annealing is lower as compared with conventional solid-state sintering technology.

Acknowledgments

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