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Antiferromagnetic spin glass-like behavior in sintered multiferroic Aurivillius $Bi_{m+1}Ti_3Fe_{m-3}O_{3m+3}$ compounds

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ABSTRACT

The structure, hyperfine interactions and magnetic properties of the series of multiferroic $Bi_{m+1}Ti_3Fe_{m-3}O_{3m+3}$ Aurivillius compounds with $m=4$–8 were studied using X-ray diffraction, ^{57}Fe Mössbauer spectroscopy and vibrating sample magnetometry. Samples were prepared by the conventional solid-state sintering method. Bulk magnetic measurements showed that for $m=4$ the compound is paramagnetic down to 2 K while in the compound with $m=5$ the antiferromagnetic type transition was observed at 11 K. In the case of compounds with $m=6$–8 much more complex magnetic behavior was found. For these compounds a gradual spin freezing and antiferromagnetic spin glass-like ordering were observed on decreasing temperature. The temperature of spin glass freezing was determined as 260, 280 and 350 K for $m=6$, 7 and 8, respectively. Room-temperature Mössbauer spectra of all the compounds studied confirm their paramagnetic state. However, liquid nitrogen and liquid helium temperature measurements reveal magnetic ordering with a residual paramagnetic phase contribution for the compounds with $m=5$–8.

1. Introduction

Multiferroics are materials in which ferroelectric and ferro (antiferro-)magnetic (and/or ferroelastic) properties are simultaneously combined. Recently, the development of various technologies of producing multiferroics may be observed which is connected with the promising applications of these materials [1–6]. Until now, however, the microscopic mechanism of coexistence in multiferroics the magnetic and ferroelectric ordering is not well recognized, especially in systems with perovskite-like structure, therein Aurivillius compounds.

The Aurivillius phases of the $Bi_4Ti_3O_{12}$–$BiFeO_3$ system are described by the general formula $Bi_{m+1}Ti_3Fe_{m-3}O_{3m+3}$. These compounds have layered perovskite-like structure, in which fluorite-like bismuth–oxygen layers $\{(Bi_2O_2)^{2+}\}$ alternate with (0 0 1) perovskite-like slabs $\{(Bi_{m+1}Ti_3Fe_{m-3}O_{3m+1})^{2-}\}$ [7,8]. The m value indicates the number of perovskite-like layers per slab and may take integer or fractional values, however $m\leq 13$ [8]. It was found that with increasing the number of perovskite-like layers significant changes in the physical properties of these materials occurred.

The structure and thermal stability of the Aurivillius phases of the $Bi_4Ti_3O_{12}$–$BiFeO_3$ system are relatively well known and based on the structural models and databases reported in literature [8–10]. The orthorhombic unit cell of the Aurivillius $Bi_4Ti_3O_{12}$ compound ($m=3$) published by Lomanova et al. [8] has two bismuth–oxygen layers of the thickness $f\cong 4.08$ Å and three perovskite-like layers of the average thickness $p\cong 4.11$ Å. The slab consisting of m layers has the thickness $h=pm$. Parameters f and h satisfy the relationship $f+h=c/2$, where c denotes the lattice parameter of the orthorhombic elemental cell. It was found that with increasing m number the lattice parameter c increases from 32.80 Å for $m=3$ up to 81.25 Å for $m=9$ while the a and b parameters are of the order of 5.40/5.47 Å [8,10]. Thermal analysis performed for the Aurivillius phases of the $Bi_4Ti_3O_{12}$–$BiFeO_3$ system has shown that thermal stability of these compounds decreases with increasing m number. Moreover, during heating the structural phase transitions from orthorhombic to tetragonal system has been observed in the temperature ranges coinciding with the temperatures of ferroelectric–paraelectric transitions [8,10].

Electric properties of the Aurivillius compounds of the $Bi_4Ti_3O_{12}$–$BiFeO_3$ system are also relatively well known. These

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compounds are semiconductors with two phase transitions confirmed by thermal investigations and temperature dependence of dielectric constant [11]. However, phase transition temperatures determined from differential scanning calorimetry for compounds with $m=3$–9 are slightly different from those of literature [[11] and references therein]. Moreover, various values of ferroelectric Curie temperature T_C may be found in the literature [8] and references therein, [12–14]. It was reported that T_C increases with m number, then decreases for $m=4$–6 and for $m>6$ a *plateau* in the dependence $T_C(m)$ may be observed [8]. The discrepancies in published data may be connected with some differences in preparation of the compounds (various purity and gradation of started oxides, various temperatures of calcination and sintering, etc.) and the fact that not always the obtained materials are single-phased compounds. Only few scientists prove experimentally that their samples are not single-phased, for example a small amount of additional phases in powdered Aurivillius compounds was recognized and reported by Krzhizhanovskaya et al. in [10] or recently by Lomanova et al. in [15].

A slight disorder or lack of data may be found when it comes to magnetic properties of the Aurivillius compounds of the $Bi_4Ti_3O_{12}$–$BiFeO_3$ system. At room temperature these compounds combine the ferroelectric and antiferromagnetic properties. The antiferromagnetic Néel temperature increases with m number and is equal to 80 K for $Bi_5Ti_3FeO_{15}$, 160 K for $Bi_6Ti_3Fe_2O_{18}$, 195 K for $Bi_7Ti_3Fe_3O_{21}$ and 220 K for $Bi_8Ti_3Fe_4O_{24}$ [12–14]. For $Bi_9Ti_3Fe_5O_{27}$ there is no agreement in the literature data on Néel temperature, it is greater than 300 K [14] or it is about 360 K, as suggested in [16]. However, investigations performed earlier by the authors of the present work revealed that at room temperature $Bi_9Ti_3Fe_5O_{27}$ as well as other Aurivillius compounds for $m=4$–7 are paramagnetic materials [17,18]. On the other hand, $Bi_7Ti_3Fe_3O_{21}$ and $Bi_8Ti_3Fe_4O_{24}$ compounds are antiferromagnetic materials showing weak ferromagnetism at room temperature, as reported by Srinivas et al. on the basis of the magnetic hysteresis loop measurements [13,14].

In the light of the discrepancies in literature magnetic data there is the necessity of systematic investigations of magnetic properties of Aurivillius compounds of the $Bi_4Ti_3O_{12}$–$BiFeO_3$ system. In this work X-ray diffraction (XRD), ^{57}Fe Mössbauer spectroscopy (MS) and vibrating sample magnetometry (VSM) were applied as complementary methods to investigate the series of $Bi_{m+1}Ti_3Fe_{m-3}O_{3m+3}$ samples synthesized by the solid-state sintering method. The aim of MS study was to determine the hyperfine interactions in Aurivillius compounds with $m=4$–8 at room, RT, liquid nitrogen, LN, and liquid helium, LHe temperatures. Temperature dependencies of magnetic susceptibility, $\chi_\sigma(T)$, and hysteresis loops allowed to reveal the irreversible magnetic behavior in Aurivillius compounds and to determine the values of the coercive fields, H_C, in these compounds.

2. Experimental details

The Aurivillius $Bi_{m+1}Ti_3Fe_{m-3}O_{3m+3}$ compounds with $m=4$–8 were prepared by the conventional solid-state route in a form of compacts of 10 mm in diameter. The appropriate amounts of reagent-grade oxide powders, viz. Fe_2O_3, Bi_2O_3, and TiO_2 (all 99.9% purity) were used in preparation procedure. The general formula of solid state reaction may be described as follows:

$$6TiO_2+(m+1)Bi_2O_3+(m\text{–}3)Fe_2O_3\rightarrow 2Bi_{m+1}Ti_3Fe_{m-3}O_{3m+3}. \quad (1)$$

More details of synthesis have been reported earlier in [17,18]. The purity of the phases and the chemical composition was checked using EDS (Energy Dispersive Spectroscopy) method which confirmed conservation of the compounds chemical composition with a relative accuracy of ±3%.

Phase composition and structure of the compounds were analyzed by Empyrean PANalytical diffractometer using CuK_α radiation and a graphite monochromator at the diffracted beam and Philips PW3710-type X-ray diffractometer with CoK_α radiation. Both the phase and structural analysis of the recorded XRD patterns were performed by Rietveld refinement method based on FullProf software and an X'Pert HighScore Plus computer program equipped with the newest ICSD data base.

MS studies were carried out at RT and LN (80 K) temperatures with POLON spectrometer in standard transmission geometry using a source of ^{57}Co in a rhodium or a chromium matrix. In the case of measurements at liquid helium the absorber was kept at 7 K using Janis Research Co. Inc. SVT-400M cryostat. A temperature stability was of the order of 0.01 K. Spectrum was collected applying MsAa-3 spectrometer of the RENON Co. For all measurements the compacts of the investigated compounds were crushed and powdered in a mortar. The absorbers were prepared using a self-adhesive transparent foil (for RT and LN measurements). For LHe measurements powdered compound was mixed with B_4C fine powder and then lightly pressed between mylar sheets aluminized on both sides. Absorber was mounted in a cryostat on the gold-plated copper holder equipped with the thermometer. A 25-μm-thick metallic iron foil was taken as a standard for calibration of both spectrometers.

The field cooled–zero field cooled (FC–ZFC) dc magnetization values in a field of 100 Oe as well as magnetization loops up to 80 kOe were measured in the temperature range from 2 K or 10 K up to 350 K using the vibrating sample magnetometer option of the Quantum Design physical property measurement system (PPMS-9). Additional measurements for $Bi_5Ti_3FeO_{15}$ compound were performed in 1 kOe down to 10 K.

3. Results

3.1. Crystalline structure of Aurivillius compounds

The detailed results of the crystalline structure investigations of Aurivillius compounds for $m=4$, 6, 7 and 8 have already been published elsewhere [17,18]. As X-ray diffraction studies proved, the samples fired at 993 K contained a little amount of non-reacted hematite, however, sintering of compounds at elevated temperatures, i.e. 1123–1313 K allowed to obtain Aurivillius phases. Complementing those data we present the Rietveld refined XRD patterns of $Bi_5Ti_3FeO_{15}$ and $Bi_6Ti_3Fe_2O_{18}$ compounds in Fig. 1.

The detailed analysis of XRD patterns shows that only in the case of $Bi_5Ti_3FeO_{15}$ compound the obtained sample is a single-Aurivillius phase, well crystallized material. The numerical fitting by the Rietveld method was based on the respective structural model [19,20] with the *Fm2m* (no. 42) space group. All the other compounds, with $m=5$–8, appeared to contain some amounts of adjacent Aurivillius phases besides the main one. As an example, the results of Rietveld analysis of XRD pattern for $Bi_6Ti_3Fe_2O_{18}$ compound for which structural models for the main and the adjacent Aurivillius phases were available are presented in Fig. 1 (b). The inset in Fig. 1(b) shows a broad and structured peak composed of the reflections (0 0 8), (0 0 10) and (0 0 12) belonging to $Bi_5Ti_3FeO_{15}$ (*Fm2m*, No. 42, [19,20]), $Bi_6Ti_3Fe_2O_{18}$ (*F2mm*, No. 42, [21,22]) and $Bi_7Ti_3Fe_3O_{21}$ (*F2mm* No. 42, [10,23]) Aurivillius phases, respectively.

The lattice parameters a, b and c determined for the main phases as a function of m number are presented in Fig. 2. The obtained linear dependence $c(m)$ described by the formula $c=8.39m+7.41$ is very similar to that reported in [8] and allows to estimate the average thickness of perovskite-like layer as $p\cong 4.19$ Å.