

Hyperfine interactions and irreversible magnetic behavior in multiferroic Aurivillius compounds

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Abstract. In this work investigations of structure and magnetic properties of conventionally sintered $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ compounds with $4 \leq m \leq 8$ were performed using X-ray diffraction, Mössbauer spectroscopy and vibrating sample magnetometry. Room-temperature Mössbauer spectra of the compounds correspond to a paramagnetic state, however, low temperature measurements (80 K) reveal the antiferromagnetic state with a residual paramagnetic phase. Temperature dependencies of magnetic susceptibility, $\chi_\sigma(T)$, provided magnetic ordering temperatures and revealed an irreversibility in Aurivillius compounds with $m \geq 5$. In the case of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ compound the $\chi_\sigma(T)$ dependence shows a paramagnetic behavior down to 2 K. The $\text{Bi}_6\text{Ti}_3\text{Fe}_2\text{O}_{18}$ compound reveals a magnetic ordering at 11 K. The compounds with $m = 6-8$ show a magnetic ordering at temperatures higher than 200 K. Highly irreversible character of their temperature dependencies of χ_σ indicates a spin-glass type disordered magnetism with frustration due to a random distribution of Fe on Ti at their sites.

Key words: Aurivillius compounds • hyperfine interactions • magnetic properties • Mössbauer spectroscopy • multiferroics

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Introduction

Multiferroics in which ferroelectric and ferro(antiferro-) magnetic (and/or ferroelastic) properties are simultaneously combined in one material are a subject of intensive research due to prospective applications as, e.g. next-generation memory storage materials [11]. The Aurivillius phases of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ - BiFeO_3 system are described by the general formula $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ where m denotes the number of perovskite-like layers per slab and $3 \leq m \leq 13$ [5]. With increasing m significant changes occur in the physical properties of these materials, e.g. the lattice parameter c of the orthorhombic unit cell increases from 32.80 Å for $m = 3$ up to 81.25 Å for $m = 9$ [5]. The compounds are semiconductors with two phase transitions in the temperature ranges of 933–1033 K and 1073–1123 K confirmed by differential scanning calorimetry and temperature dependencies of dielectric constant [4]. It was found that the ferroelectric Curie temperature T_C increases with m number, then decreases for $m = 4-6$ and for $m > 6$ a plateau in the dependence $T_C(m)$ can be observed [5].

While the structure, thermal stability and electric properties of the Aurivillius compounds are relatively well known, their magnetic properties are still not well recognized. At room temperature these compounds combine the ferroelectric and antiferromagnetic prop-

erties. The antiferromagnetic Néel temperature increases with m from 80 K for $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ up to about 300 K for $\text{Bi}_9\text{Ti}_3\text{Fe}_5\text{O}_{27}$. On the other hand, $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$ and $\text{Bi}_8\text{Ti}_3\text{Fe}_4\text{O}_{24}$ compounds are antiferromagnetic materials showing weak ferromagnetism at room temperature, as reported in [8]. Investigations of hyperfine interactions in the Aurivillius compounds performed earlier by the authors of the present work revealed that at room temperature the Aurivillius compounds for $m = 4-8$ are paramagnetic materials [2, 7]. Mössbauer spectra which were paramagnetic doublets for all the compounds have been numerically fitted by two components, i.e. two doublets with similar values of quadrupole splitting ($\Delta \sim 0.30 \text{ mm}\cdot\text{s}^{-1}$) and isomer shifts $\delta \sim 0.23 \text{ mm}\cdot\text{s}^{-1}$ and $\delta \sim 0.40 \text{ mm}\cdot\text{s}^{-1}$, respectively. These two doublets in the spectra reflect two nonequivalent octahedral Fe^{3+} cation sites, i.e. in the inner B(1) oxygen octahedron inside the slab and in the outer B(2) octahedron near the fluorite-like $\{(\text{Bi}_2\text{O}_2)^{2+}\}$ layer (Fig. 1). In both cases iron ions substitute Ti ions. The recent Mössbauer spectroscopy investigations performed at room temperature by Lomanova *et al.* have revealed the dependence of Fe ions distribution over the nonequivalent sites on the number of perovskite-like layers in the Aurivillius compounds [6]. It was shown that up to $m = 5$ iron ions are distributed over B(1) and B(2) sites in an ordered manner, while the outer B(2) sites of the perovskite-like block are preferentially occupied by ions with a larger

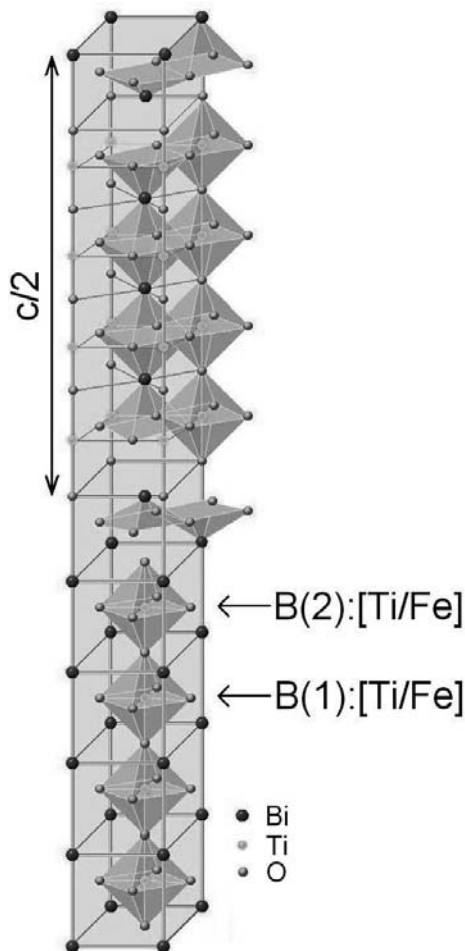


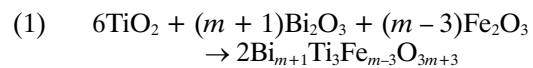
Fig. 1. The unit cell of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ [5, 6]; B(1):[Ti/Fe] and B(2):[Ti/Fe] are respectively the inner and the outer oxygen octahedrons where Fe ions substitute Ti ions.

charge. The ordered distribution of ions over B(1) and B(2) sites is disturbed with increasing thickness of the perovskite-like block. At $m \geq 7$, the distribution of Fe^{3+} and Ti^{4+} ions over the inner and outer sites of the perovskite-like block tends to become random [6].

The aim of this work was to investigate the hyperfine interactions and magnetic properties in the Aurivillius compounds with $m = 4-8$ at liquid nitrogen (LN), temperature. X-ray diffraction (XRD), Mössbauer spectroscopy (MS) and vibrating sample magnetometry (VSM) were applied to the respective series of $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ samples prepared by the solid-state sintering method.

Experimental details

The Aurivillius $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ compounds were prepared by a conventional solid-state synthesis route. The appropriate amounts of reagent-grade oxide powders, viz. Fe_2O_3 , Bi_2O_3 , and TiO_2 (all 99.9% purity) were mixed together in an agate mortar and pestle to give the desired composition and thus provide conditions for the following solid state reactions:



with $m = 4-8$. After pressing the mixtures in 20 mm diameter pellets they were placed in an alumina crucible and fired in air at temperature $T_s = 993 \text{ K}$ for $t = 2 \text{ h}$. After calcination, the pellets were re-milled, pressed into discs of 10 mm in diameter and then sintered at a temperature higher than T_s , i.e. 1123 K for $m = 4, 6, 7, 8$ and 1253 K for $m = 5$. Sintering process lasted 2 h in a sealed alumina crucible (free sintering method), with heating and cooling rates of 5 K min^{-1} . All the samples were furnace-cooled to room temperature.

The purity of the phases and the chemical composition were checked using the EDS (energy dispersive spectroscopy) method which confirmed conservation of the compounds chemical composition of the compounds with a relative accuracy of $\pm 3\%$.

Phase composition and structure of the compounds were analyzed by an Empyrean PANalytical diffractometer using CuK_α radiation and a graphite monochromator at the diffracted beam and a Philips PW3710-type X-ray diffractometer with CoK_α radiation. Both the phase and structural analysis of the recorded X-ray patterns were performed by the 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 LN temperature in standard transmission geometry using a source of ^{57}Co in a rhodium or a chromium matrix. A 25- μm -thick metallic iron foil was taken as a standard for calibration of a spectrometer.

The field cooled-zero field cooled (FC-ZFC) DC (direct current) mass magnetic susceptibility (χ_c) curves in a field of 100 Oe were measured in the temperature range from 2 K or 10 K up to 350 K using the vibrating sample magnetometer (VSM) option of the quantum design physical property measurement system (PPMS-9).

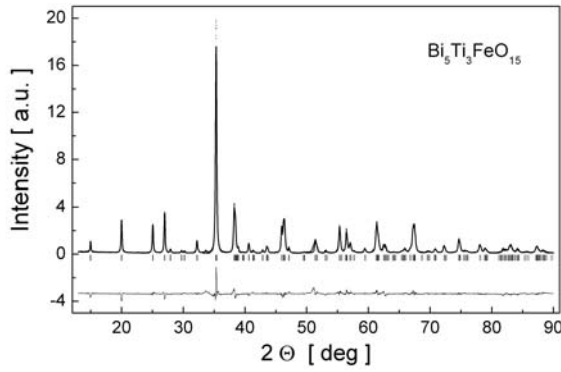


Fig. 2. Fitted XRD pattern of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ compound.

Results and discussion

The detailed analysis of XRD patterns shows that only in the case of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ compound the obtained sample is a single-phase material. The result of numerical fitting by the Rietveld method based on the respective structural model [1] with the $Fm\bar{2}m$ (no. 42) space group is presented in Fig. 2.

The lattice parameters determined from the pattern are as follows: $a = 5.4389 \pm 0.0011 \text{ \AA}$, $b = 5.4649 \pm 0.0009 \text{ \AA}$ and $c = 41.2706 \pm 0.0067 \text{ \AA}$ and they agree well with the reported data [1, 5]. All the other Aurivillius compounds, with $m = 5-8$, appeared to contain some amounts of adjacent phases besides the main one. For example, the Rietveld analysis of XRD pattern for $\text{Bi}_6\text{Ti}_3\text{Fe}_2\text{O}_{18}$ shows that the mass contribution of the main phase is of 63%, while the adjacent phases in the amount of 13% of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ and 24% of $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$ constitute the rest. The lattice parameter c of the main phases depends linearly on m according to the formula $c = 8.39m + 7.41$ which is similar to that reported in [5] (i.e. $c = 8.22m + 8.16$).

In order to determine the magnetic ordering temperatures the low field (100 Oe) FC and ZFC DC susceptibilities, χ_σ , were measured as a function of temperature down to 2 K for the compounds $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ and $\text{Bi}_6\text{Ti}_3\text{Fe}_2\text{O}_{18}$ and down to 10 K for $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$, $\text{Bi}_8\text{Ti}_3\text{Fe}_4\text{O}_{24}$ and $\text{Bi}_9\text{Ti}_3\text{Fe}_5\text{O}_{27}$. The results of measurements are presented in Fig. 3. In the case of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ compound (Fig. 3a) a Curie-Weiss type dependence was observed down to the lowest temperatures with no indication of any magnetic transition. In the case of $\text{Bi}_6\text{Ti}_3\text{Fe}_2\text{O}_{18}$ the FC and ZFC curves start to diverge at about 225 K (as seen in Fig. 3b from the differential curve), however, a much stronger divergence is observed below 10 K, suggesting an additional magnetic transition in this temperature range. Defining the magnetic transition temperature as corresponding to the inflection point of the $\chi_\sigma(T)$ dependence, the temperature of this additional antiferromagnetic type transition about 11 K was found from the ZFC curve. In the case of $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$, $\text{Bi}_8\text{Ti}_3\text{Fe}_4\text{O}_{24}$ and $\text{Bi}_9\text{Ti}_3\text{Fe}_5\text{O}_{27}$ compounds the FC and ZFC curves start to diverge strongly at about 260, 280 and 340 K for $m = 6, 7$ and 8 , respectively (Fig. 3c–e). Such a behavior where the FC and ZFC curves diverge is characteristic of a “glassy” magnetic state of the material and the bifurcation temperature usually corresponds to the spin glass freezing. The FC curves below the bifur-

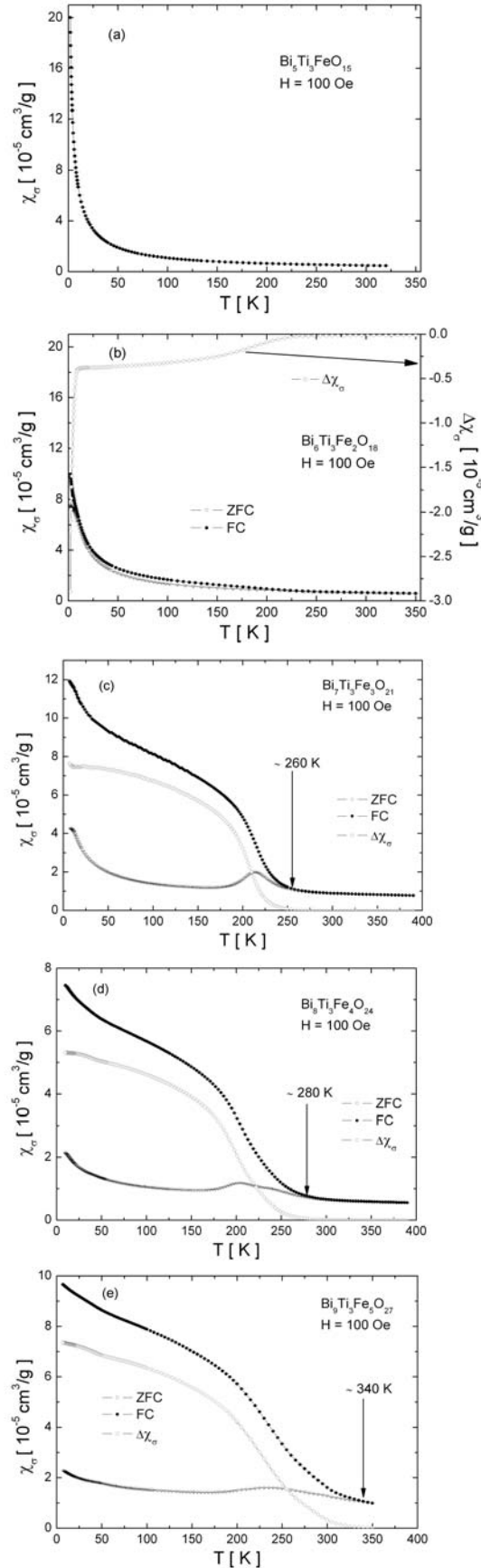


Fig. 3. Temperature dependencies of FC and ZFC DC mass magnetic susceptibility (χ_σ) for (a) $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$, (b) $\text{Bi}_6\text{Ti}_3\text{Fe}_2\text{O}_{18}$, (c) $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$, (d) $\text{Bi}_8\text{Ti}_3\text{Fe}_4\text{O}_{24}$ and (e) $\text{Bi}_9\text{Ti}_3\text{Fe}_5\text{O}_{27}$; $\Delta\chi_\sigma (= \chi_\sigma^{\text{FC}} - \chi_\sigma^{\text{ZFC}})$ denotes the differential curve. Vertical arrows denote the irreversibility temperatures.

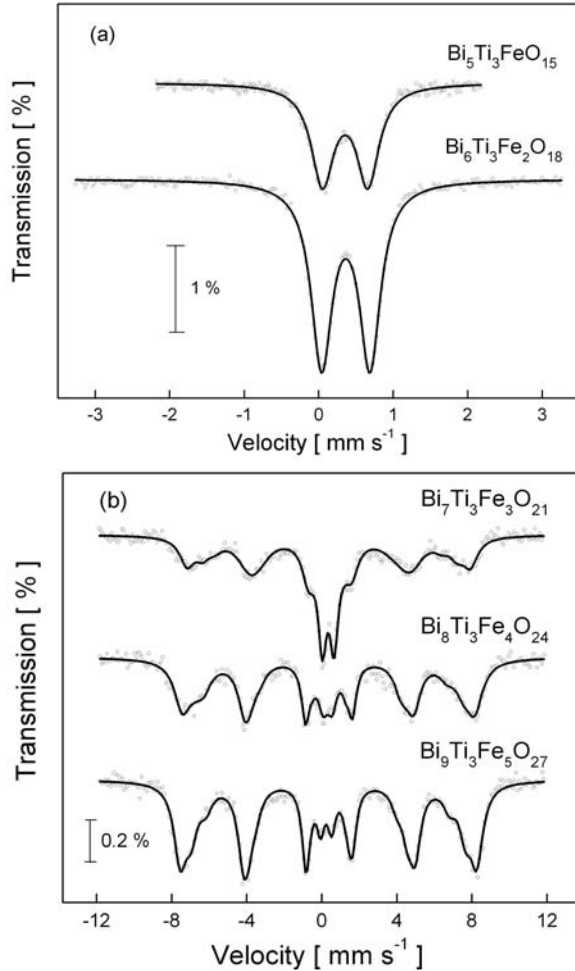


Fig. 4. Liquid nitrogen-temperature Mössbauer spectra of (a) $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ and $\text{Bi}_6\text{Ti}_3\text{Fe}_2\text{O}_{18}$, (b) $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$, $\text{Bi}_8\text{Ti}_3\text{Fe}_4\text{O}_{24}$ and $\text{Bi}_9\text{Ti}_3\text{Fe}_5\text{O}_{27}$ compounds.

cation temperature show an increase similar to that in ferro- or ferrimagnets, whereas the ZFC curves show a broad peak there. The magnetic ordering temperatures were determined as the mean value of the maximum of first derivative of the ZFC $\chi_c(T)$ dependence and the zero of second derivative of the FC $\chi_c(T)$ function. The obtained results are as follows: 241 K for $m = 6$, 204 K for $m = 7$ and 235 K for $m = 8$. These values do not agree with the literature data concerning the Néel temperature for the Aurivillius compounds ($T_N = 195, 220$ and 300 K for $m = 6, 7$ and 8, respectively) [8, 10]. The observed discrepancy can be attributed to differences in sample preparation procedures, concerning, e.g. temperatures of calcination and sintering as compared with those reported in the literature.

As it was reported earlier, room-temperature MS spectra for the samples sintered at various temperatures from 1123–1313 K range were paramagnetic doublets [2] what proves that all the Aurivillius compounds studied have their T_N temperatures lower than room temperature. In Figure 4 the Mössbauer spectra measured at liquid nitrogen temperature are shown. The paramagnetic doublets constituting the spectra for $m = 4$ and 5 compounds (Fig. 4a) confirm our magnetometric results showing that these compounds have their T_N temperatures lower than the liquid nitrogen temperature. Below the Néel temperature of the compound

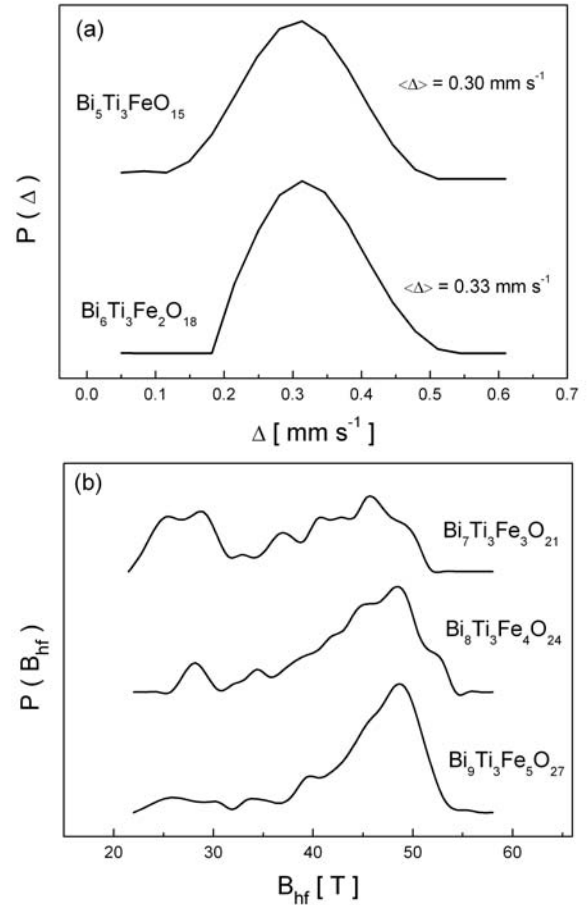


Fig. 5. (a) Distributions of the quadrupole splitting for $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ and $\text{Bi}_6\text{Ti}_3\text{Fe}_2\text{O}_{18}$ compounds and (b) distributions of the hyperfine magnetic field induction for $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$, $\text{Bi}_8\text{Ti}_3\text{Fe}_4\text{O}_{24}$ and $\text{Bi}_9\text{Ti}_3\text{Fe}_5\text{O}_{27}$ compounds.

we should observe magnetically splitted MS spectrum of a six-line pattern, expected for the hyperfine magnetic interaction much stronger than the quadrupolar one. Such patterns can be seen in Fig. 4b for $m = 6–8$ compounds, however, besides the six-line component a quadrupole doublet appears in the spectra. This means that some additional paramagnetic phase is present in the samples. There are three possible explanations of the paramagnetic component. Firstly, the doublet may be due to the superparamagnetic relaxation phenomena expected in the vicinity of the magnetic transition. Secondly, it may be an evidence that not all the iron magnetic moments are antiferromagnetically ordered at liquid nitrogen temperature. Finally, an admixture of phases with $m = 4$ or 5 to the $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$, $\text{Bi}_8\text{Ti}_3\text{Fe}_4\text{O}_{24}$ and $\text{Bi}_9\text{Ti}_3\text{Fe}_5\text{O}_{27}$ compounds can be present.

The numerical fitting of the spectra was performed assuming a distribution of the hyperfine interactions parameters which is justified for random occupation of Fe and Ti sites. In the case of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ and $\text{Bi}_6\text{Ti}_3\text{Fe}_2\text{O}_{18}$ compounds the obtained distributions of quadrupole splitting are presented in Fig. 5a together with the average value of the quadrupole splitting $\langle \Delta \rangle$. In the case of compounds with $m = 6–8$, the doublet representing the paramagnetic phase was fixed and the hyperfine magnetic field distributions were derived using the Hesse-Rübartsch method. The doublet components have the following parameters: $\delta = 0.44 \text{ mm}\cdot\text{s}^{-1}$, $\Delta =$

0.32 mm·s⁻¹, $\Gamma = 0.32$ mm·s⁻¹ for Bi₇Ti₃Fe₃O₂₁ compound; $\delta = 0.34$ mm·s⁻¹, $\Delta = 0.24$ mm·s⁻¹, $\Gamma = 0.33$ mm·s⁻¹ for Bi₈Ti₃Fe₄O₂₄ and $\delta = 0.32$ mm·s⁻¹, $\Delta = 0.28$ mm·s⁻¹, $\Gamma = 0.32$ mm·s⁻¹ for Bi₉Ti₃Fe₅O₂₇. The obtained hyperfine magnetic field distributions are relatively broad and the average value of the magnetic field induction $\langle B_{\text{hf}} \rangle$ increases with number of the perovskite-like layers from $\langle B_{\text{hf}} \rangle = 35.83$ T for $m = 6$, to $\langle B_{\text{hf}} \rangle = 43.91$ T for $m = 8$ (see Fig. 5b).

Results of MS and VSM measurements complement each other and both studies show that the single-phase Aurivillius Bi₅Ti₃FeO₁₅ compound does not show any indication of magnetic ordering down to 2 K. The second member of the Aurivillius family, corresponding to $m = 5$, exhibits antiferromagnetic type transition at 11 K for the majority of Bi₆Ti₃Fe₂O₁₈ phase, however, some admixture of the Bi₇Ti₃Fe₃O₂₁ phase may explain signatures of a second transition at much higher temperature, i.e. 225 K where FC and ZFC curves start to diverge. This is consistent with Mössbauer spectroscopy results if one assumes that a small amount of magnetic Bi₇Ti₃Fe₃O₂₁ phase is not detectable in MS measurement at liquid nitrogen temperature. In the light of this supposition, the mentioned above contributions of the adjacent phases determined from XRD patterns using the Rietveld method can be regarded as overestimated. In the case of Bi_{*m*+1}Ti₃Fe_{*m*-3}O_{3*m*+3} compounds with $m = 6-8$ highly irreversible character of $\chi_o(T)$ indicates a spin-glass type disordered magnetism with frustration due to a random distribution of Fe and Ti on their sites.

It is worth mentioning that only Kizhaev *et al.* [3], who reported Mössbauer spectra for Bi₉Ti₃Fe₅O₂₇, explained that magnetic transition in this compound has not sharp but a progressive character, while the other authors gave the definite Néel temperatures for the Aurivillius compounds [8–10]. It may be supposed that our Aurivillius phases with $m = 6-8$ exhibit a relaxational behavior and that magnetic transition occurs at a broad range of temperatures. The relaxation properties of the compounds may be due to the structural disorder, i.e. stacking faults in the sequence of the perovskite-like layers and mixed phases.

Conclusions

Preparation of a single Aurivillius phase with the specified stoichiometry is the task with the difficulty rising strongly with increasing number of layers in the unit cell. Only the Bi₅Ti₃FeO₁₅ compound was obtained as a single phase and thermally stable material. With increasing number of perovskite-like layers the thermal stability of materials decreases and the majority of phase may be admixed with the adjacent ones. Despite the phase contaminations and structural imperfection, an interesting magnetic behavior may be observed for the Aurivillius compounds. In the case of the first member

of the family with $m = 4$ paramagnetic properties are conserved down to 2 K. The next one with $m = 5$ orders antiferromagnetically at about 11 K. For the following three compounds with $m = 6, 7$ and 8 a much complex magnetic behavior is observed. Both Mössbauer spectroscopy results and magnetic measurements allow us to state that magnetic transition from paramagnetic to antiferromagnetic ordering occurs at a broad range of temperatures. The complex magnetic behavior may be explained by the relaxational nature of the hyperfine interactions as well as a possibility of admixture of adjacent phases to the major one. The distributions of the hyperfine interactions parameters indicate a random distribution of Fe on the inner and outer oxygen octahedrons in the perovskite-like layers.

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