

Properties of Aurivillius Phases in the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ – BiFeO_3 System

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Abstract—A number of new $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ compounds with integer and fractional m values are identified in the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ – BiFeO_3 system. All of the compounds are shown to have Aurivillius-type structures. The phase-transition and decomposition temperatures of the new and earlier known compounds of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ – BiFeO_3 system are determined. The linear thermal expansion coefficients of the synthesized compounds are evaluated using dilatometry, and their sintering onset temperatures are determined.

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INTRODUCTION

The $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ – BiFeO_3 system is known to contain a series of compounds with the general formula $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ [1–4]. These compounds have layered perovskite-like structures, first described by Aurivillius [1], in which fluorite-like bismuth–oxygen layers of thickness f and composition $\{(\text{Bi}_2\text{O}_2)^{2+}\}_\infty$ alternate with (001) perovskite-like slabs of composition $\{(\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+1})^{2-}\}_\infty$ and thickness $h = pm$ (Fig. 1). The values of f and h are related to the c cell parameter by $f + h = c/2$, m indicates the number of perovskite-like layers per slab and may take integer or fractional values, and p is the average thickness of the perovskite-like layers (Fig. 1). Fractional m values correspond to mixed-layer structures, which contain perovskite-like slabs of different thicknesses.

The compounds of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ – BiFeO_3 system combine ferroelectric, semiconducting, and ferromagnetic properties [2, 3], which makes them potentially attractive for producing composite films for information processing and storage applications [4].

The properties of the Aurivillius phases in the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ – BiFeO_3 system have not yet been studied in sufficient detail. Many researchers investigated only the end-members of the series in question—bismuth titanate and bismuth ferrite. Bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$), a semiconductor which is used in optical modulators and acoustic devices, has the structure of the $m = 3$ Aurivillius phase [5].

Bismuth ferrite, BiFeO_3 , is of interest as a basic magnetoelectric material, which is due in large part to its high electrical and magnetic ordering temperatures [6]. Since the crystal structure of bismuth ferrite has a rhombohedrally distorted perovskite cell, BiFeO_3 can

be regarded as a limiting case, $m = \infty$, of the layered perovskite-like structures in question. Note that this compound seems to be characterized by temperature-dependent nonstoichiometry [7–9], which notably impedes the synthesis of compounds containing BiFeO_3 -based perovskite-like structural components.

Isupov [10] and Srinivas *et al.* [11, 12] identified the compounds $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$, $\text{Bi}_6\text{Ti}_3\text{Fe}_2\text{O}_{18}$, $\text{Bi}_7\text{Fe}_3\text{Ti}_3\text{O}_{21}$, $\text{Bi}_8\text{Fe}_4\text{Ti}_3\text{O}_{24}$, and $\text{Bi}_9\text{Ti}_3\text{Fe}_5\text{O}_{27}$, which contain perovskite-like slabs with $m = 4, 5, 6, 7$, and 8 , respectively. Ismailzade *et al.* [13] described yet another compound of this family, $\text{Bi}_9\text{Ti}_6\text{FeO}_{27}$, whose structure is made up of alternating $m_1 = 3$ and $m_2 = 4$ perovskite-like slabs, so that the average number of perovskite-like layers per unit cell is $m = 3.5$. Note that most reports dealing with Aurivillius-type layered perovskite-like compounds are concerned primarily with the synthesis and structural details of such compounds.

The possibility of extending the $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ homologous series, pointed out by Isupov [10], has stimulated the search for new Aurivillius phases containing various perovskite-like slabs. Of particular interest is the synthesis of layered compounds containing very thick perovskite-like slabs, in the nanometer range, because such compounds are close in structural parameters to superlattices and can be regarded as structures intermediate between crystalline phases and nanoscale heterostructures.

An important issue is to investigate mixed-layer compounds, which contain alternating perovskite-like slabs of different thicknesses. Since such compounds are close in chemical composition, samples prepared by solid-state reactions are, as a rule, characterized by phase inhomogeneity and disordered stacking of the slabs. The latter gives grounds to consider the

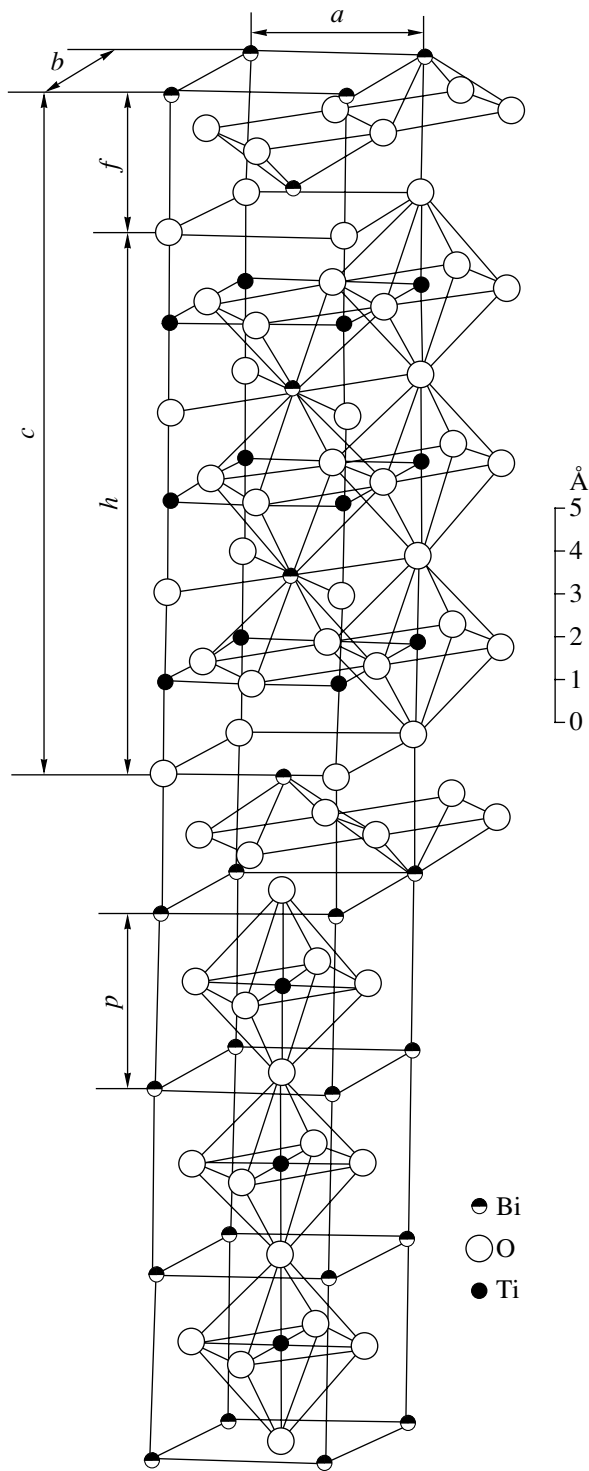


Fig. 1. Unit cell of $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ compounds, exemplified by $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

$\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ homologous series of Aurivillius phases as a phase of variable composition, $\text{AB}_{1-x}\text{O}_3$, where x is a rational number [4]. The compounds under consideration can then be thought of as peculiar solid solutions whose components are two-dimensional

structural blocks rather than atoms or ions. Note that the classification proposed by Gusarov [14] allows one to consider phases resulting from substitution (incorporation) of not only 0D but also 1D, 2D, and 3D structural units. At the same time, the possibility of quasi-continuous compositional changes across the $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ homologous series is still open to question.

The points raised above led us to synthesize new compounds with the general formula $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$, primarily those with fractional m , to determine their structure, and to investigate the thermal behavior of the new and earlier known layered perovskite-like compounds in the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ – BiFeO_3 system.

EXPERIMENTAL

Samples for this investigation were prepared from pure-grade bismuth oxide, analytical-grade iron(III) oxide, and extrapure-grade titanium(IV) oxide. The starting-mixture compositions were $(0.5n + 2)\text{Bi}_2\text{O}_3 + 0.5n\text{Fe}_2\text{O}_3 + 3\text{TiO}_2$ with $n = 0, 0.14, 0.17, 0.25, 0.67, 1, 1.5, 1.75, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5,$ and 6, which corresponds to a $\text{Bi}_4\text{Ti}_3\text{O}_{12} : \text{BiFeO}_3$ molar ratio of 1 : n and $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ compounds with $m = n + 3$.

The starting reagents were ground and mixed in a vibratory mill and pressed into pellets, which were then fired in air in a Nabertherm furnace (Germany) in several steps, each at a higher temperature, with repeated intermediate grindings, or were heat-treated isothermally and then quenched. A more detailed description of the synthesis of compounds in the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ – BiFeO_3 system can be found in an earlier report [15].

After each step, the samples were examined by x-ray diffraction (XRD) on Siemens D-500HS and DRON-3 diffractometers ($\text{CuK}\alpha$ radiation).

Microstructural examination and chemical analysis were carried out by scanning electron microscopy (SEM) and electron probe x-ray microanalysis (EPXMA) using a CamScan MV2300 equipped with an Oxford Link microprobe system. The metal composition was deduced from analytical data, and the chemical formula of the oxide was inferred from the charge neutrality condition.

The thermal behavior of the samples was studied by differential thermal analysis (DTA) and differential scanning calorimetry (DSC). DTA scans were performed with a MOM Q-1500D Paulik–Paulik–Erdey thermoanalytical system in air at a heating rate of $7.5^\circ\text{C}/\text{min}$ and sample weights in the range 0.5–1.0 g. DSC measurements were conducted in a Netzsch STA 429 calorimeter in air at a heating rate of $10^\circ\text{C}/\text{min}$ and sample weights from 0.05 to 0.1 g. We determined the phase-transition (Curie) and decomposition temperatures of the synthesized compounds. The higher sensitivity of DSC compared to DTA led to a discrepancy between the characteristic temperatures determined by

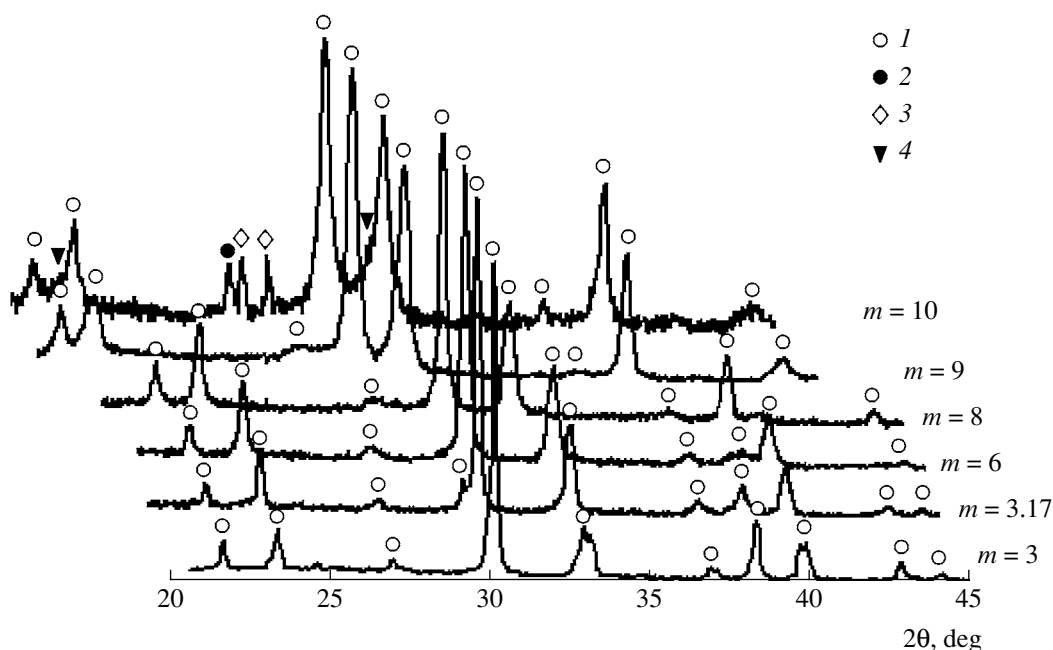


Fig. 2. XRD patterns of $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ compounds differing in the number of perovskite-like layers, m , in their structure (firing at 800°C for 24 h): (1) Aurivillius phases, (2) $\gamma\text{-Bi}_2\text{O}_3$, (3) $\text{Bi}_2\text{Fe}_4\text{O}_9$, (4) BiFeO_3 .

the two methods, which was associated in particular with the error of determination of the temperature: DTA curves were recorded on photographic paper, while DSC curves were digitized on a computer. As a consequence, the uncertainty in temperature was $\approx 1\text{--}2^\circ\text{C}$ in DSC and $\approx 10\text{--}15^\circ\text{C}$ in DTA. Another possible origin of the systematic discrepancy between the temperatures of thermal events determined by DTA and DSC was that the sample weight in DTA was 10 times that in DSC. This led to a significant broadening of DTA peaks, which is particularly undesirable if there are several thermal events close in temperature: the overlap of the corresponding peaks significantly increases the uncertainty in the temperature of the thermal event, determined from the intersection of tangents to the baseline and peak or as the maximum peak temperature in the DTA curve.

The thermal behavior of the synthesized compounds was also followed using a Netzsch DIL 402 ED dilatometer. The samples had the form of sintered disks 5 mm in diameter and 0.5–1.5 mm in thickness. The sintering onset temperature was evaluated as the temperature of the peak in the $\Delta l/l_0(T)$ curve. The linear thermal expansion coefficient α was measured in the range $200\text{--}400^\circ\text{C}$.

RESULTS AND DISCUSSION

Our results indicate that the $\text{Bi}_4\text{Ti}_3\text{O}_{12}\text{-BiFeO}_3$ system contains a large number of structurally similar $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ homologues. In addition to compounds with integer m values, the $\text{Bi}_4\text{Ti}_3\text{O}_{12}\text{-BiFeO}_3$

system contains compounds with ordered sequences of different perovskite-like slabs. One such compound is $\text{Bi}_{13}\text{FeTi}_9\text{O}_{38}$ ($m = 3.25$), containing alternating perovskite-like slabs with $m_1 = 3$, $m_2 = 3$, $m_3 = 3$, and $m_4 = 4$.

Figure 2 displays the XRD patterns of several samples prepared by firing at 800°C for 24 h. XRD results indicate that, under the conditions of this study, the samples with integer $m \leq 8$ consist of Aurivillius phases, with little or no impurity phases, whereas the samples with $m \geq 9$ contain reaction intermediates ($\gamma\text{-Bi}_2\text{O}_3$ and $\text{Bi}_2\text{Fe}_4\text{O}_9$) and a small amount of BiFeO_3 (Fig. 2), which has not been incorporated into the perovskite-like slabs of the layered structure shown in Fig. 1 for kinetic or thermodynamic (instability of the $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ Aurivillius phases with $m \geq 9$) reasons. Note that a similar situation holds in the synthesis of Aurivillius phases with fractional m values if the number of perovskite-like slabs of one kind differs markedly from the number of slabs of the other kind, e.g., at $m \approx 3.14$, which corresponds to the sequence of slabs $m = 3, 3, 3, 3, 3, 3, 4$ (Fig. 2).

Figure 3 shows the c cell parameter (along the normal to the perovskite-like layers) and in-plane unit-cell area S as functions of m .

As the number of perovskite-like layers increases, the c cell parameter rises almost linearly, which implies that the perovskite-like unit incorporated into the structure of the layered compound experiences only slight changes along the c axis with increasing m . It is of interest to note that the best fit straight line $c = 8.22m + 8.16$ (Fig. 3) has a rather large Pearson correlation moment, $R = 0.998$, which allows one to estimate the

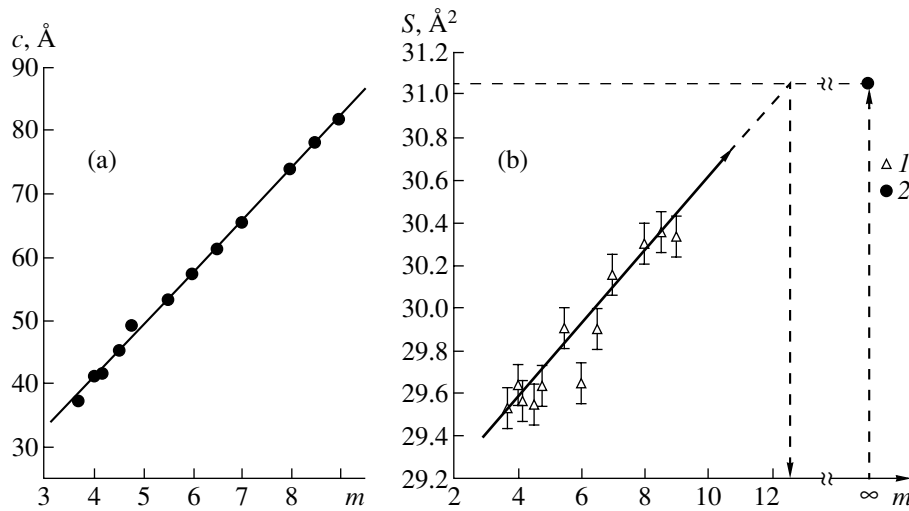


Fig. 3. (a) Lattice parameter c and (b) in-plane unit-cell area $S = ab$ as functions of the number of perovskite-like layers, m , in the crystal structure of $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ compounds: (1) Aurivillius phases, (2) BiFeO_3 .

average thicknesses of the perovskite layers, $p \approx 4.11$ Å, and fluorite-like layers, $f \approx 4.08$ Å, in the homologous series under consideration. The thickness of the BiFeO_3 perovskite layer (Fig. 1) evaluated from the effective ionic radii of Fe^{3+} (VI) and O^{2-} (VI) [16] is $p = 2(0.75 + 1.26) \approx 4.08$ Å, which is rather close to the p deduced from the best fit straight line in Fig. 3a.

With increasing m , the in-plane unit-cell area approaches that in BiFeO_3 (Fig. 3b). Extrapolation of $S = ab$ as a function of m indicates that, at $m \approx 12$ –13, S is close to that in the perovskite-like structure of BiFeO_3 (Fig. 3).

Consequently, the existence of Aurivillius phases with a thickness of the perovskite-like slab $h \approx 37$ Å in the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ – BiFeO_3 system appears unlikely. This is also evidenced by the fact our attempts to synthesize

compounds with $m \geq 9$ led to the formation of impurity phases (Fig. 2).

According to SEM and EPXMA results, the samples were homogeneous, and their chemical compositions coincided with the starting-mixture compositions to within the error of determination. The composition of each sample was determined as an average of several measurements at different points, and the error of determination was evaluated as the standard deviation. An important point is that the compositions of $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ compounds were very close to the nominal ones at high values of m because the difference in composition between compounds close in m decreases with increasing m . As an example, Table 1 lists the chemical compositions of some of the synthesized $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ compounds with large m . Coupled with XRD data, the good agreement between the sample compositions and intended stoichiometry indicates that all of the synthesized compounds (Table 1) are Aurivillius phases with a layered perovskite-like structure.

Taking into account the experimental uncertainties in the lattice parameters and elemental compositions of the samples, we conclude that, with increasing m , the structure of the layered perovskite-like compounds under consideration and, consequently, their formation energy approach those of BiFeO_3 , a perovskite-like compound with a nonlayered structure. This suggests that the stability of the many-layered Aurivillius phases in the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ – BiFeO_3 system decreases as the number of layers rises.

Figure 4 shows the DSC curves of some of the synthesized compounds. The thermal events above 900°C are the decomposition of the $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ compounds, as evidenced by the irreversible character of the process, associated with the extremely slow

Table 1. EPXMA results for several samples

Number of perovskite-like layers, m	Nominal composition	Chemical composition according to EPXMA data
5.5	$\text{Bi}_{13}\text{Fe}_5\text{Ti}_6\text{O}_{39}$	$\text{Bi}_{13.4 \pm 0.1}\text{Fe}_{4.9 \pm 0.2}\text{Ti}_{6.1 \pm 0.1}\text{O}_{41.1 \pm 0.4}$
6	$\text{Bi}_7\text{Fe}_3\text{Ti}_3\text{O}_{21}$	$\text{Bi}_{7.4 \pm 0.3}\text{Fe}_{3.0 \pm 0.2}\text{Ti}_{3.0 \pm 0.2}\text{O}_{21.5 \pm 0.2}$
7	$\text{Bi}_8\text{Fe}_4\text{Ti}_3\text{O}_{24}$	$\text{Bi}_{8.0 \pm 0.1}\text{Fe}_{4.2 \pm 0.2}\text{Ti}_{2.8 \pm 0.3}\text{O}_{23.7 \pm 0.3}$
9	$\text{Bi}_{10}\text{Fe}_6\text{Ti}_3\text{O}_{30}$	$\text{Bi}_{10.1 \pm 0.3}\text{Fe}_{5.9 \pm 0.1}\text{Ti}_{3.0 \pm 0.2}\text{O}_{30.0 \pm 0.2}$

kinetics of the synthesis of these compounds from the melt. The solidus temperatures of all the synthesized compounds are listed in Table 2. Thermal analysis results indicate that the thermal stability of $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ compounds decreases with increasing m , which lends support to the above assumptions. Note that the DSC curves of the many-layered compounds show the same events as are observed at a smaller number of perovskite-like layers in the structure (Fig. 4). This suggests that the decomposition of the layered perovskite-like compounds in the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ - BiFeO_3 system can be thought of as sequential peritectic decomposition into compounds of the same homologous series with a smaller number of perovskite-like layers in their structure.

As follows from earlier results [3–5, 7], the peaks between 650 and 750°C in the DSC curves of the $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ compounds correspond to their Curie temperatures. Figure 5 shows the Curie temperature t_C of these compounds as a function of the number of perovskite-like layers, m , in their structure. It seems likely that t_C is determined by the Fe content of the perovskite-like layers (BiFeO_3 content). In going from $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, containing no Fe, to compounds containing approximately 50 mol % BiFeO_3 ($m \approx 4$), the Curie temperature rises. As the Fe content increases further, t_C gradually decreases and then plateaus starting at $m \approx 6$.

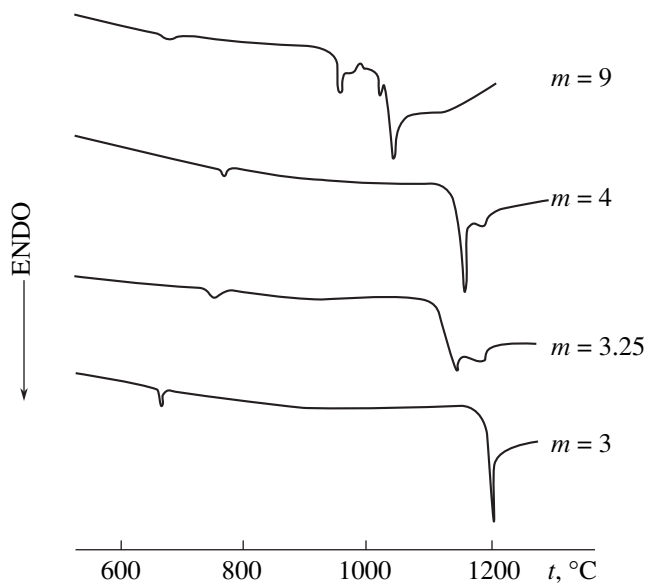


Fig. 4. DSC curves of several samples.

The present t_C data are at variance with the results reported by Hervoches and Lightfoot [17]. According to their findings, t_C increases steadily with m (Fig. 5) and approaches the Curie temperature of BiFeO_3 : $t_C = 850^\circ\text{C}$. Note however that, according to Morozov *et al.* [7] and Hoizumi *et al.* [8], BiFeO_3 does not exist at this

Table 2. Thermal analysis and dilatometry data

Compound	m	Solidus temperature, °C		$\alpha \times 10^{-6}, \text{K}^{-1}$
		DSC	DTA	
$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	3	1170	1170	11 ± 1
$\text{Bi}_{13}\text{FeTi}_9\text{O}_{38}$	3.25	1100	1100	6 ± 4
$\text{Bi}_9\text{Ti}_6\text{FeO}_{27}$	3.5	–	1090	–
$\text{Bi}_{14}\text{Fe}_2\text{Ti}_9\text{O}_{42}$	3.67	1100	1080	13 ± 2
$\text{Bi}_5\text{FeTi}_3\text{O}_{15}$	4	1100	1070	10 ± 1
$\text{Bi}_{11}\text{Fe}_3\text{Ti}_6\text{O}_{33}$	4.5	1080	1030	17 ± 7
$\text{Bi}_{17}\text{Fe}_2\text{Ti}_9\text{O}_{52}$	4.75	1070	–	13 ± 3
$\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$	5	980	1000	13 ± 3
$\text{Bi}_{13}\text{Fe}_5\text{Ti}_6\text{O}_{39}$	5.5	990	1000	7 ± 3
$\text{Bi}_7\text{Fe}_3\text{Ti}_3\text{O}_{21}$	6	980	950	–
$\text{Bi}_{29}\text{Fe}_{13}\text{Ti}_{12}\text{O}_{87}$	6.25	980	–	11 ± 1
$\text{Bi}_{15}\text{Fe}_7\text{Ti}_6\text{O}_{45}$	6.5	970	970	–
$\text{Bi}_8\text{Fe}_4\text{Ti}_3\text{O}_{24}$	7	980	950	12 ± 2
$\text{Bi}_{17}\text{Fe}_9\text{Ti}_6\text{O}_{51}$	7.5	970	–	10 ± 0
$\text{Bi}_9\text{Fe}_5\text{Ti}_3\text{O}_{27}$	8	980	950	10 ± 0
$\text{Bi}_{19}\text{Fe}_{11}\text{Ti}_6\text{O}_{57}$	8.5	970	–	9 ± 1
$\text{Bi}_{10}\text{Fe}_6\text{Ti}_3\text{O}_{30}$	9	970	960	9 ± 1

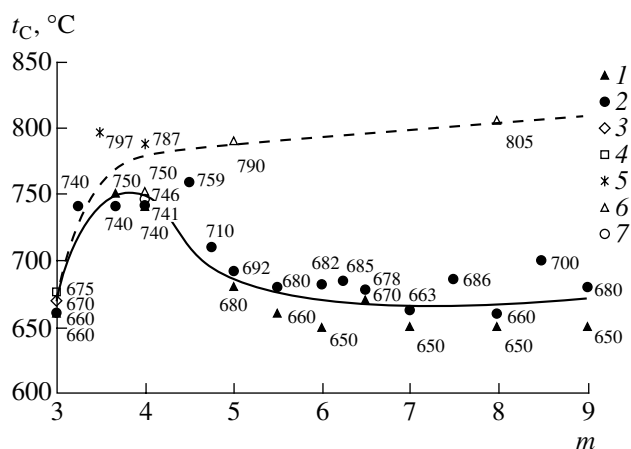


Fig. 5. Curie temperature as a function of the number of perovskite-like layers, m : (1, 2) this work, (3–7) earlier results; (1) DTA data, (2) DSC data, (3) [10], (4) [13], (5) [17], (6) [18], (7) [19].

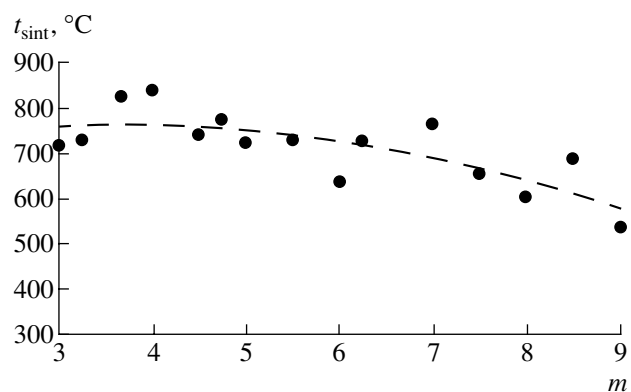


Fig. 6. Sintering activation temperature as a function of the number of perovskite-like layers, m .

temperature, so the $t_C = 850^\circ\text{C}$ for BiFeO_3 appears to be an overestimated value.

The thermal expansion data for the $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ compounds demonstrate that α depends very little on the number of perovskite-like layers in their structure (Table 2). The average α of the compounds studied is $(11 \pm 2) \times 10^{-6} \text{ K}^{-1}$.

The sintering onset temperature t_{sint} of the samples was between 500 and 850°C . As the number of perovskite-like layers increases, t_{sint} gradually decreases (Fig. 6), which provides indirect evidence that the thermal stability of the $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ compounds decreases with increasing m .

CONCLUSIONS

A number of new compounds differing in the thickness of the perovskite-like slab were identified in the $\text{Bi}_4\text{Ti}_3\text{O}_{12}\text{-BiFeO}_3$ system. Our results demonstrate that, as the number of perovskite-like layers in their

structure increases, the in-plane unit-cell area approaches that in BiFeO_3 . Our estimates suggest that the number of perovskite-like layers in the structure of such compounds cannot be greater than $m \approx 12\text{--}13$.

Increasing the number of perovskite-like layers reduces the thermal stability of the $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ compounds, which undergo sequential peritectic decomposition into layered compounds of the same homologous series with smaller m . The sintering onset temperature of the $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ compounds also decreases with increasing m .

The linear thermal expansion coefficient of these compounds depends very little on the number of perovskite-like layers in their structure.

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