

Aurivillius Phases in the $\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{BiFeO}_3$ System: Thermal Behaviour and Crystal Structure

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Dedicated to Professor Rüdiger Kniep on the Occasion of his 60th Birthday

Abstract. Four compounds of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{BiFeO}_3$ system with the formula $\text{Bi}_2\text{Bi}_{n-1}(\text{Ti,Fe})_n\text{O}_{3n+3}$, $n = 3, 4, 4.5$ and 6 were studied using high-temperature X-ray powder diffraction and differential thermoanalysis methods. The crystal structure of the $n = 6$ phase was refined by the Rietveld method. An unusual behaviour of thermal expansion attributed to an orthorhombic-to-tetragonal transformation was revealed. For all the compounds, the lattice parameter c vs temperature T dependence has three regions in the range of $T = 20 - 750$ °C interpreted as (1) expansion of the initial orthorhombic phase, (2) a pronounced structure reconstruction to the tetragonal phase, (3) an expansion of the tetragonal phase.

The crystal structure of $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$ based on 6-layer-perovskite blocks is proposed from X-ray powder diffraction data. The Rietveld refinement of the structure in the orthorhombic space group $F2mm$ with lattice parameters $a = 5.4699(3)$, $b = 5.4924(3)$, $c = 57.551(3)$ Å ($R_p = 9.4$, $R_{wp} = 11.9$, $R_{exp} = 4.7$, $R_B = 4.4$ %) shows that a distorted 6-layer model fits the data of $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$.

Keywords: Perovskite phases; Phase transitions; Thermal expansion; X-ray scattering

Introduction

The Aurivillius family of layered Bi-containing oxides is well known for its ferroelectric properties. Although these phases were first described more than 50 years ago [1] and their ferroelectric properties were found 10 years later by [2], layered perovskites still attract considerable interest in particular due to the recent observation of fatigue free behaviour and low coercive fields in thin films [3]. According to [4] Bi titanates are of great technological interest because of their applications as non-volatile ferroelectric memories and as high-temperature piezoelectric materials. Usually, crystal structures of these phases are described as a combination or intergrowth of $(\text{Bi}_2\text{O}_2)^{2+}$ layers and $(\text{A}_{n-1}\text{B}_n\text{O}_{3n+3})^{2-}$ perovskite-like blocks, where A is a twelve co-ordinated cation, e.g. Na, K, Ca, Sr, Ba, Pb, Bi, etc., and B is an octahedral cation such as Fe, Ti, Nb, Ta, Cr, etc. Here n is the number of octahedral layers in a perovskite-like block. The structural studies of these phases concern mainly the compounds with $n = 1 \dots 4$ or their intergrowth analogues.

Compounds from the $\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{BiFeO}_3$ system represent semiconducting, ferroelectric and ferromagnetic properties

[5, 7–9]. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($n=3$) shows high-electrical conductivity like $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ ($n=4$) [4]. For the latter, measurements of the magnetoelectric coefficient were reported in [6]. According to [7], $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ and $\text{Bi}_6\text{Ti}_3\text{Fe}_2\text{O}_{18}$ exhibit simultaneous electrical and magnetic ordering. The magnetic measurements of $\text{Bi}_8\text{Fe}_4\text{Ti}_3\text{O}_{24}$ ($n=7$) indicate antiferromagnetic behaviour for the compound [8]. An eight-layered compound $\text{Bi}_9\text{Fe}_5\text{Ti}_3\text{O}_{27}$ behaves like a superparamagnet [9] and transforms from that state to an antiferromagnetic state around 400 K.

In the $\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{BiFeO}_3$ system compounds with the general formula $\text{Bi}_2\text{Bi}_{n-1}(\text{Ti,Fe})_n\text{O}_{3n+3}$, $n = 3, 3.5, 4, 4.5, 5, 6, 8$ were synthesised by solid state reaction and characterised by X-ray diffraction (XRD) in [5]; the phases with $n = 4, 5$ and 8 were found before also in [10]. Diffraction data for the $n = 3, 4, 5, 8$ compounds were presented in the PDF database. The crystal structures of these compounds with $n = 3, 3.5, 4$ were determined in the orthorhombic system by [1, 11–14, and 21], respectively. The orthorhombic cell parameters, a and b , of these structures are in the range 5.40–5.47 Å. The number of perovskite-like layers varies along the [001] direction and the c value changes correspondingly: 32.8 Å ($n=3$) [11], 37.1 Å ($n=3-4$) [12], 41.2 Å ($n=4$) [14]. The structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ was determined both on the basis of an orthorhombic [22] and a monoclinic [15] space group.

Up to now the nature of the ferroelectric-paraelectric (FE-PE) transition is not fully resolved. Recently, a number of high temperature powder neutron diffraction (PND) studies has revealed that the initial polar orthorhombic structure transforms either into a non-polar orthorhombic,

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or into a non-polar tetragonal structure at a temperature coincident with the Curie temperature. The structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($n=3$) has been refined by the Rietveld method in the orthorhombic space group $B2cb$ (no.41) at 25, 500 and 650 °C and in the tetragonal space group $I4/mmm$ (no.139) at 800 °C [11]. For $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ ($n=4$) the polymorph phase transition from the polar space group $A2_1am$ (no.36) to the non-polar group $I4/mmm$ was studied in detail using PND data [17]. Its transition temperature determined as ~ 730 °C is coincident with the Curie temperature of the FE-PE transition. In contrast, two Sr-containing Aurivillius compounds, $\text{Sr}_{0.85}\text{Bi}_{2.1}\text{Ta}_2\text{O}_9$ ($n=2$) [16] and $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ ($n=4$) [14], do indeed undergo a two-step transition, proceeding from $A2_1am$ to $I4/mmm$ via an intermediate paraelectric orthorhombic $Amam$ (no.63) phase. Whereas the Sr-containing 2-layer phase $\text{SrBi}_2\text{Nb}_2\text{O}_9$ appears to transform directly to a tetragonal paraelectric phase $I4/mmm$ (no. 139) [17], the high-temperature synchrotron X-ray diffraction study [18] confirms that orthorhombic $\text{BaBi}_3\text{Ti}_4\text{O}_{15}$ ($A2_1am$) continuously transforms into a tetragonal structure at about 700 K. However, it was unclear whether an intermediate phase (space group $Amam$) exists over a very limited temperature range or not. So, the nature of the FE-PE transformation is not yet clear.

The present study is especially aimed at the investigation of the thermal behaviour of four Aurivillius phases with the general chemical formula $\text{Bi}_2\text{Bi}_{n-1}(\text{Ti},\text{Fe})_n\text{O}_{3n+3}$, $n = 3, 4, 4.5$ and 6 using high-temperature X-ray powder diffraction (HTXRD) and differential thermoanalysis (DTA) methods. Also, the structure of the compound $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$ will be refined using X-ray powder diffraction data and the Rietveld method.

Experimental

Polycrystalline samples were prepared using traditional solid-state technique from pure-grade Bi_2O_3 , analytical-grade Fe_2O_3 and extra-pure grade TiO_2 . From the initial mixture of $(0.5x+2)\text{Bi}_2\text{O}_3 + 0.5x\text{Fe}_2\text{O}_3 + 3\text{TiO}_2$, where $x = 0, 1, 1.5, 3$ corresponds to x mol of BiFeO_3 per 1 mol of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, the compounds with $n = 3, 4, 4.5$ and 6 , i. e. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$, $\text{Bi}_{11}\text{Ti}_6\text{Fe}_3\text{O}_{33}$ and $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$ were synthesized. The starting reagents were ground in a vibratory mill, pressed into tablets, and then heated in several steps each at higher temperature with intermediate regrindings between each steps. The synthesised materials were characterised by XRD using DRON 2 and D5000 powder diffractometers ($\text{CuK}\alpha$ radiation) and by scanning electron microscopy with ABT-55 [5]. The XRD data for the compounds with n mainly 4.5 and 6 were recently deposited by us in the PDF database (PDF # 54-240 and # 54-1044). The chemical composition of the compounds was determined using microprobe analysis on AX1000/S85 (Table 1). According to the electron microscopy data all powders contain a little amount of an additional phase with chemical composition indicated also in Table 1.

The thermal behaviour of the Aurivillius phases with $n = 3, 4, 4.5, 6$ under heating in air was studied by HTXRD using a DRON 3M diffractometer (NPO Burevestnik; 35 kV, 20 mA; $\text{CuK}\alpha$ $\lambda = 1.5418$ Å radiation, graphite monochromator and scintillation detector) in the temperature range 20 °C – 750 °C. The diffraction

Table 1 Chemical composition of $\text{Bi}_2\text{Bi}_{n-1}(\text{Ti},\text{Fe})_n\text{O}_{3n+3}$ from microprobe data for compounds of the $\text{Bi}_4\text{Ti}_3\text{O}_{12} - \text{BiFeO}_3$ system [5].

n	Nominal composition	Chemical composition (experimental data)	Additional phase
		Dominant phase	Additional phase
3	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	$\text{Bi}_4\text{Ti}_{3.02\pm 0.02}\text{O}_{12\pm 0.04}$	$\text{Bi}_2\text{Ti}_{4.01}\text{O}_{11.01}$
4	$\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$	$\text{Bi}_5\text{Ti}_{3.22\pm 0.06}\text{Fe}_{0.84\pm 0.16}\text{O}_{15.2\pm 0.13}$	$\text{Bi}_2\text{Ti}_{1.81}\text{Fe}_{2.22}\text{O}_{9.94}$
4.5	$\text{Bi}_{11}\text{Ti}_6\text{Fe}_3\text{O}_{33}$	$\text{Bi}_{11}\text{Ti}_{6.36\pm 0.12}\text{Fe}_{2.74\pm 0.11}\text{O}_{33.3\pm 0.08}$	$\text{Bi}_2\text{Ti}_{0.88}\text{Fe}_{3.16}\text{O}_{4.49}$
6	$\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$	$\text{Bi}_7\text{Ti}_{3.09\pm 0.08}\text{Fe}_{3.03\pm 0.17}\text{O}_{21.2\pm 0.10}$	$\text{Bi}_2\text{Ti}_{0.24}\text{Fe}_{3.77}\text{O}_9$

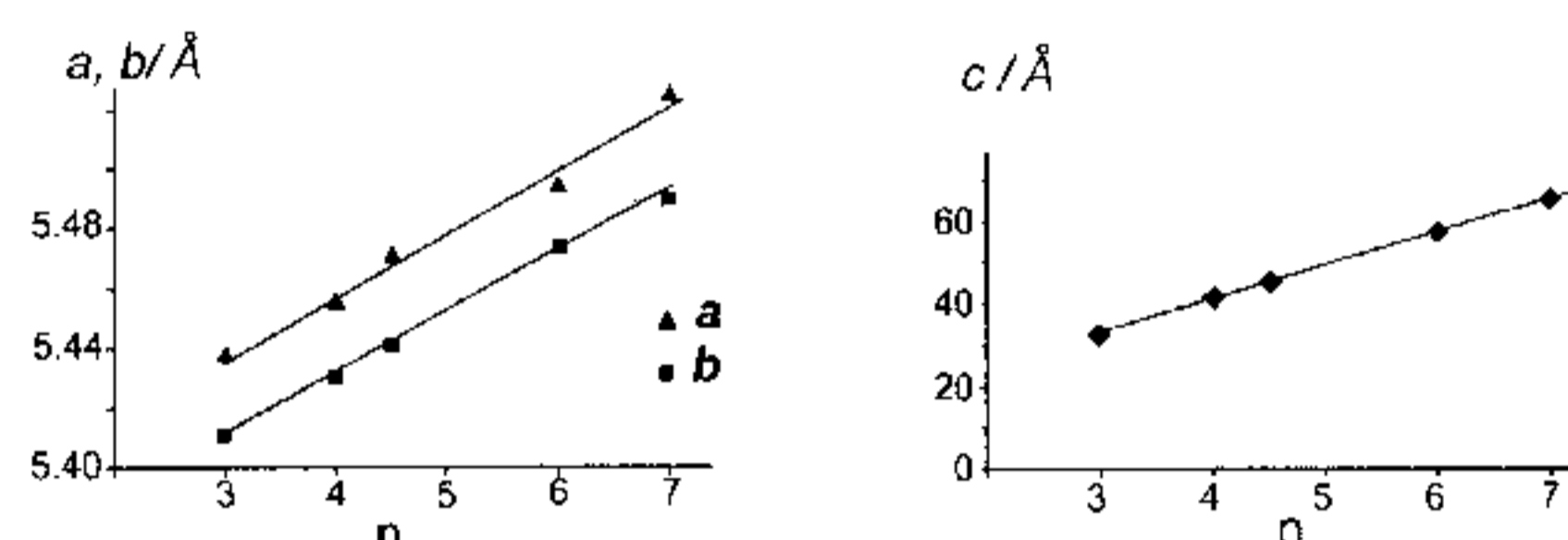


Figure 1 Orthorhombic cell parameters a, b, c as a function of the number of octahedral layers (n) in a perovskite-like block.

data for the Rietveld refinement was collected at room temperature on a D5000 powder diffractometer ($\text{CuK}\alpha$ -radiation, air atmosphere, step-scan mode with step width 0.01° in 2θ). The structure refinement has been carried out with the program Rietica 1.7.1 [19]. All samples have also been investigated by DTA in the range of temperatures 20 °C – 1300 °C.

Thermal behaviour of Aurivillius phases of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{BiFeO}_3$ system

At room temperature the orthorhombic cell parameters increased linearly with increasing number of octahedral layers in a perovskite-like block (Fig. 1).

The temperature dependence of the cell parameters for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($n=3$), $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ ($n=4$), $\text{Bi}_{11}\text{Ti}_6\text{Fe}_3\text{O}_{33}$ ($n=4.5$), and $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$ ($n=6$), as derived from powder HTXRD data, is shown in Fig. 2 a, b, c, d respectively. For comparison, the data for the $n = 3$ phase from [11] and for $n = 4$ from [14] are designated by 'x' in Fig. 2. Since the cell parameters a and b (5.46 ± 0.03 Å) and hence the reflection pairs hkl, khl are very close to each other in the compounds studied, it is difficult to determine a and b values accurately. To define the point where the orthorhombic cell parameters a and b become equal to each other, we analyzed the changes of the full width at half maximum (FWHM) with temperature for unique reflections and for reflection pairs. For example, for $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ ($n=4$) the FWHM of the unique reflection 119 ($I/I_0 = 100\%$) practically does not change under heating: 0.33° in 2θ at 20 °C and 0.31° at 640 °C, whereas the FWHM of the reflection pair 200 and 020 ($I/I_0 = 30\%$) decreased from 0.45° (2θ) at room temperature up to 0.31° at 680 °C (Fig. 3b). We suppose that in that point ($a = b$) the orthorhombic structure transforms into a tetragonal one.

The dependence c vs T for the compounds with $n = 3, 4, 4.5$ and 6 could be divided into three ranges: (1) the low-

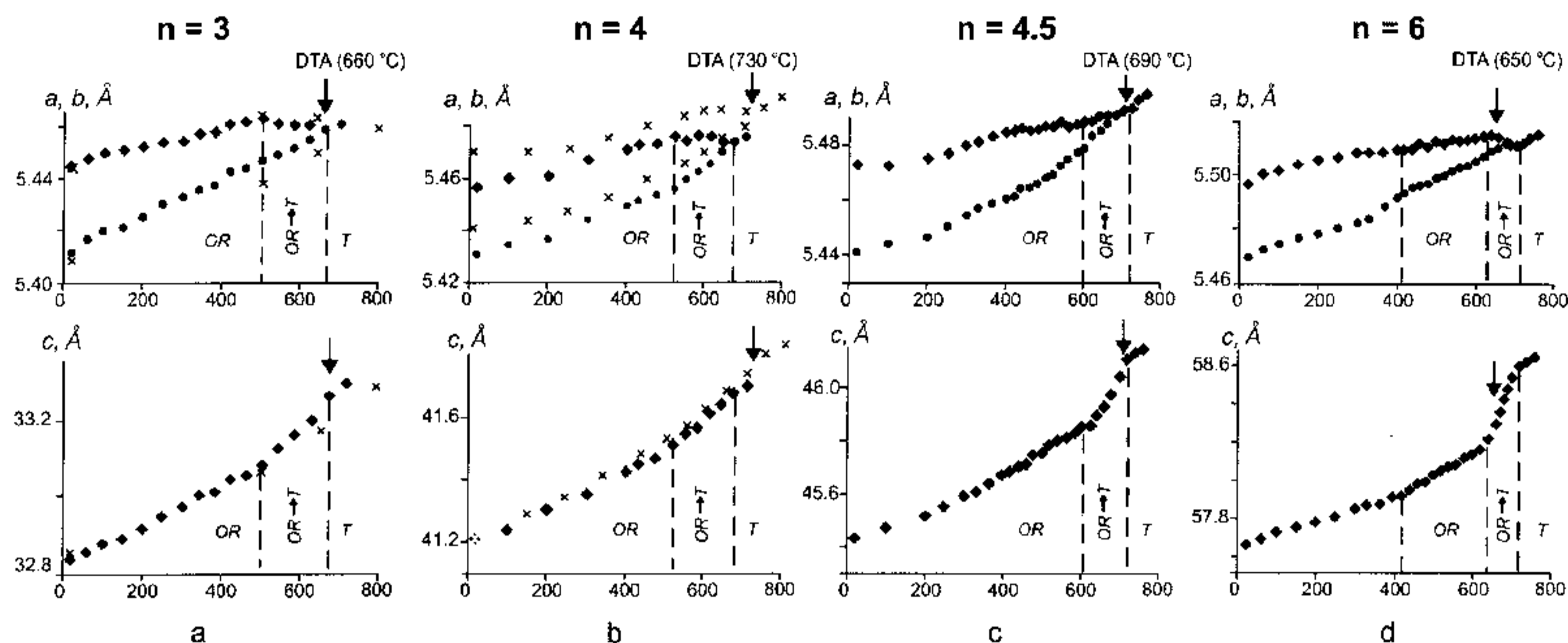


Figure 2 Orthorhombic cell parameters a , b , c as a function of temperature (abscissa in $^{\circ}\text{C}$): (a) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($n=3$), (b) $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ ($n=4$), (c) $\text{Bi}_{11}\text{Ti}_6\text{Fe}_3\text{O}_{33}$ ($n=4.5$), (d) $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$ ($n=6$).

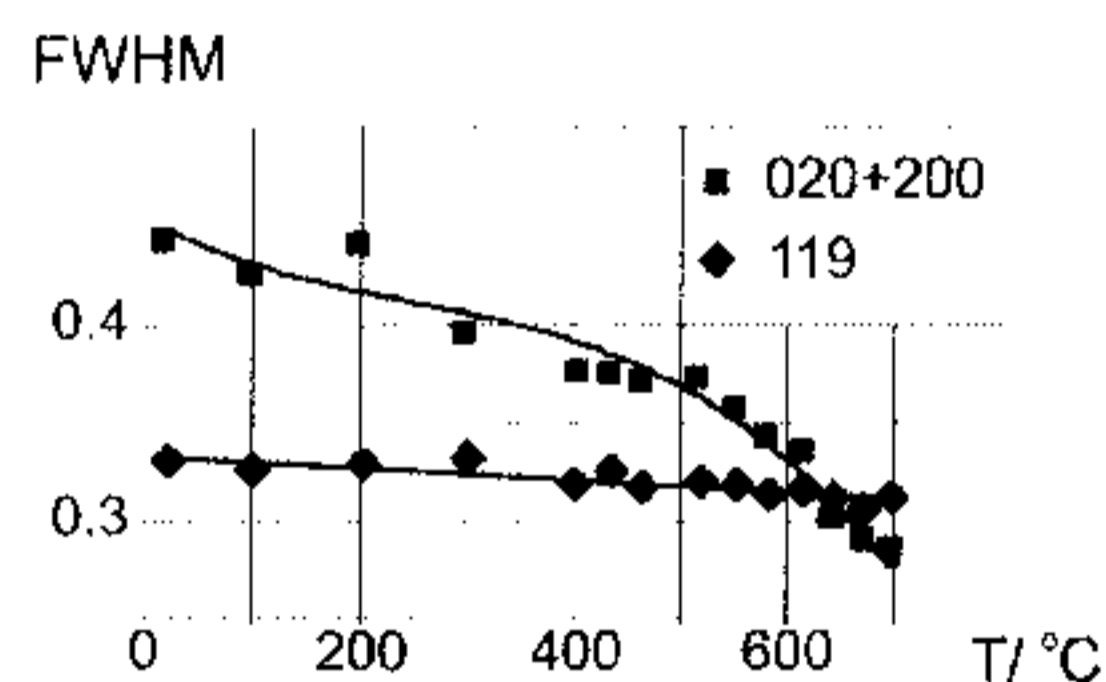


Figure 3 Temperature dependence of the full width at half maximum (FWHM) for the unique reflection 119 and for the reflection pair 020, 200 of the compound $n=4$.

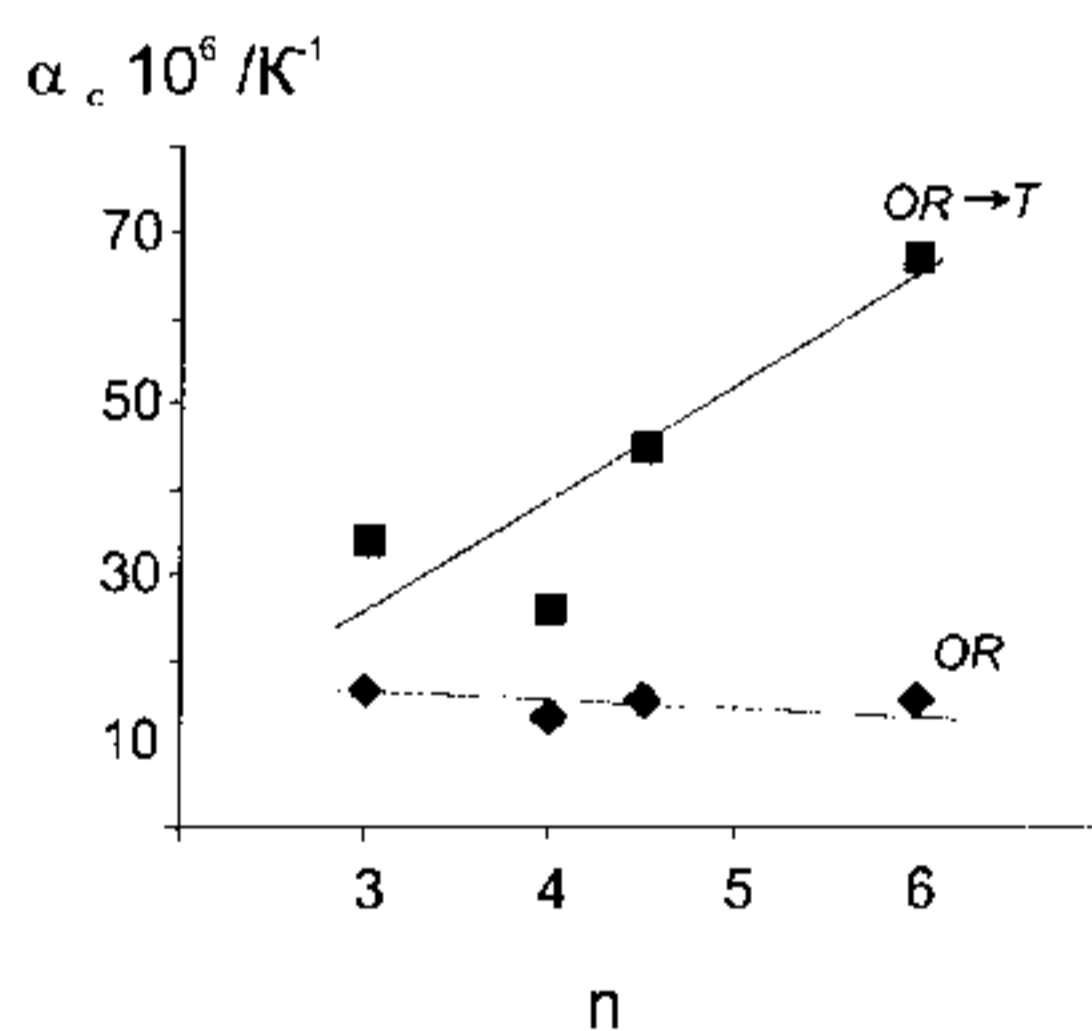


Figure 4 Linear thermal expansion coefficient α_c as a function of the number of octahedral layers n for the orthorhombic (OR) and intermediate region (OR \rightarrow T).

temperature orthorhombic (OR) region with lower thermal expansion, (2) the intermediate orthorhombic \rightarrow tetragonal (OR \rightarrow T) region with greater expansion and (3) the high-temperature tetragonal (T) region with lower thermal expansion. The thermal expansion coefficient α_c calculated for the intermediate region is about 2–4 times larger than that for low-temperature orthorhombic phases (Fig. 4). It should be noted that the high-temperature neutron diffrac-

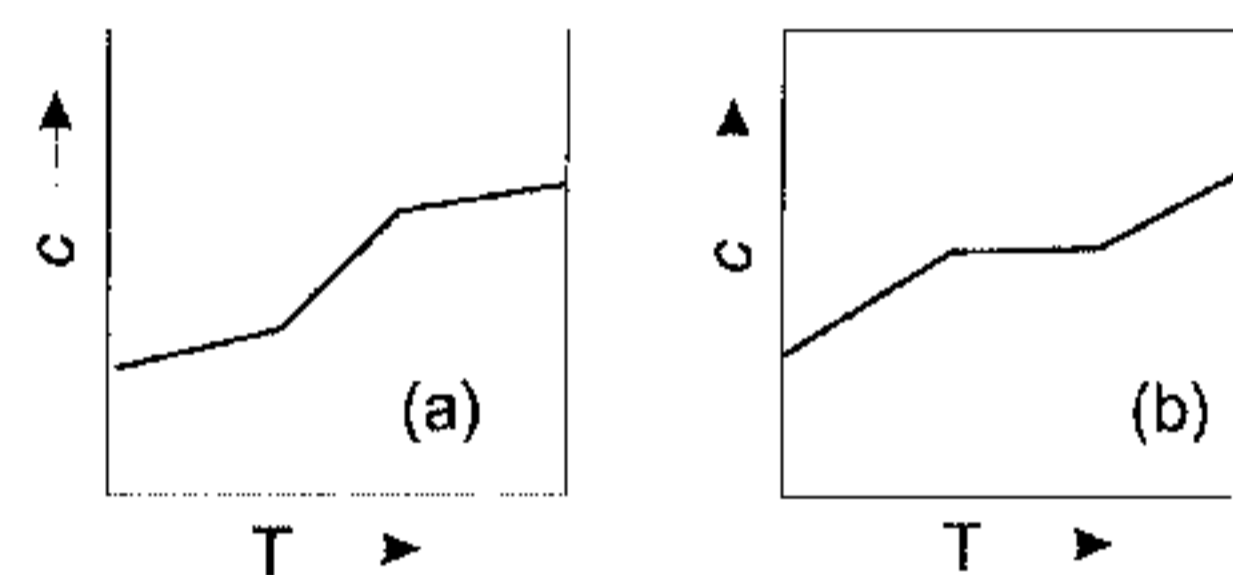


Figure 5 Typical temperature dependence of the cell parameter c of Bi- (a) and Sr-containing (b) Aurivillius phases.

tion data for $n=3$ and $n=4$ from [11, 14] are in agreement with our HTXRD data (Fig. 2, x). As reported by [11, 14] for $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$, according to the Rietveld refinement at elevated temperatures there is no evidence of any intermediate phase: only the direct transformation from the FE orthorhombic into the PE tetragonal phase is noted. Thus we assume that this unusual c vs. T dependence could be interpreted as follows: firstly the orthorhombic modification expands under heating, then the same or a similar orthorhombic structure rebuilds towards tetragonal symmetry. We see that cell parameters a and b become closer to each other, whereas along the c direction the structure expands significantly. Obviously, the $(\text{Ti,Fe})\text{O}_6$ octahedral axis becomes parallel to the c direction. So, we observed the region (OR \rightarrow T) of thorough structure reconstruction. At further heating we saw presumably the expansion of the high-temperature tetragonal phase.

The high-temperature data for $\text{BaBi}_3\text{Ti}_4\text{O}_{15}$, as reported by [18], allows the same division in the evaluation of cell parameters on heating to be made like in our Bi-phases. In [14, 16, 17] another character of structure transformation was observed for Sr-containing Aurivillius phases. The c cell parameter vs. temperature variation is shown schematically in Fig. 5a and 5b for Bi (this work) – and for Sr-containing phases. Both curves exhibit two kinks, but in the case of the Bi-phase the structure within the intermediate region has a

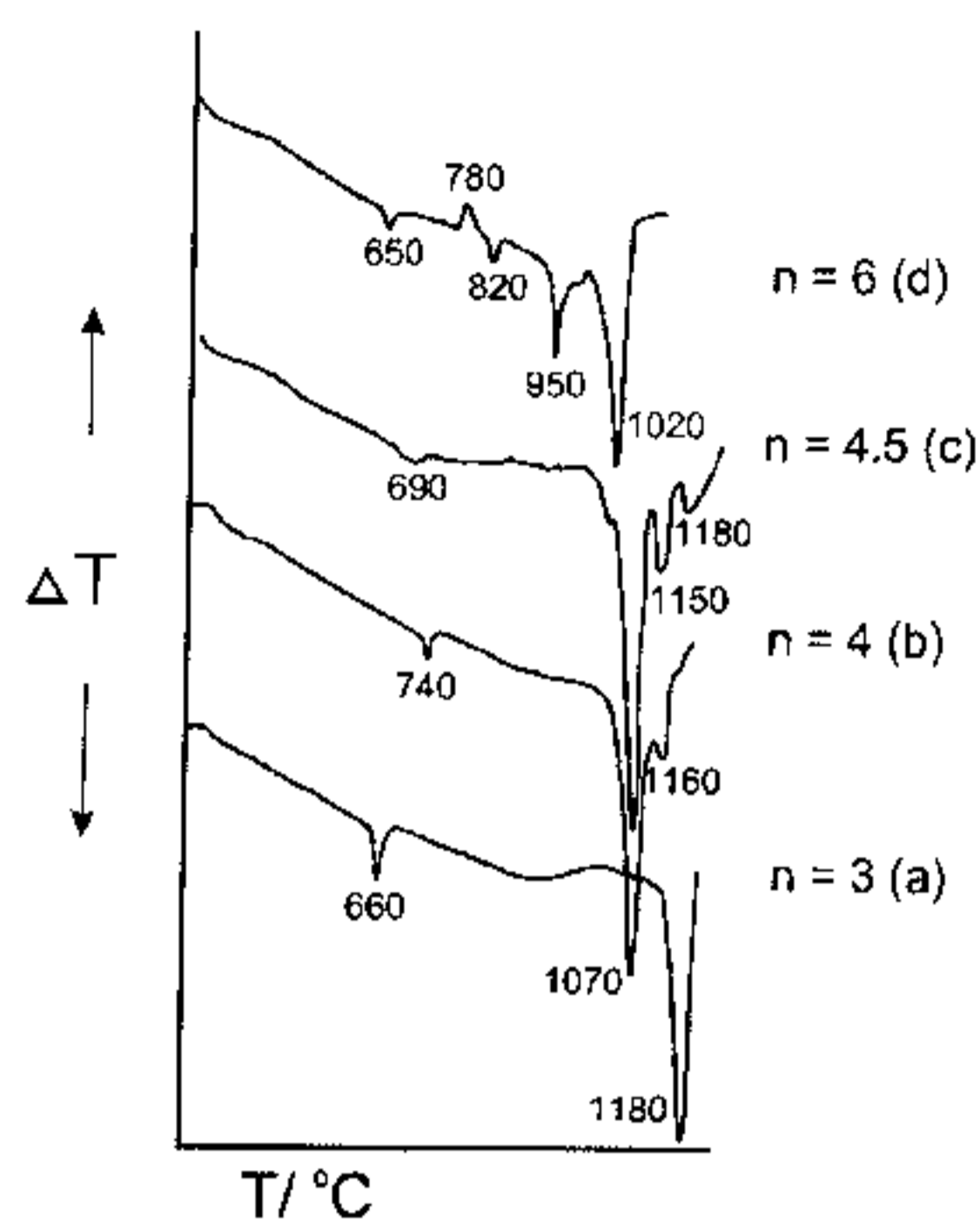


Figure 6 Differential thermoanalysis (DTA) data for (a) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($n=3$), (b) $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ ($n=4$), (c) $\text{Bi}_{11}\text{Ti}_6\text{Fe}_3\text{O}_{33}$ ($n=4.5$), (d) $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$ ($n=6$). $\Delta T = T_s - T_r$ temperature difference between sample, T_s , and reference, T_r . Changes of ΔT shown indicate endothermic reactions.

greater value of thermal expansion, whereas for Sr-phases almost zero expansion is observed.

The DTA results are presented in Fig. 6. A weak endothermic effect was observed in the range of temperatures 650–740 °C for all samples studied. It could be associated with an OR \rightarrow T transformation. Generally, the DTA endothermic effect is in good agreement with HTXRD data (Fig. 2). For example, the temperature of the DTA endothermic effect (660 °C), of the $a = b$ point (670°) and of the Curie temperature (675°) are practically equal to each other for the $n = 3$ phase.

So, the HTXRD data represent a new region (OR \rightarrow T) of intensive structure reconstruction for all compounds investigated. The evaluation of the cell parameters for the $n = 6$ phase revealed a more complicated character. Actually, on the c vs T temperature dependence we could define one more point near 400 °C, where the dependence changes its slope.

A crystal structure model of $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$ ($n=6$)

As far as we are aware, there is only one crystal structural study of the Aurivillius phase $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ with the c parameter 57.99 Å that could be attributed to a 6 layer-structure [20]. A careful single crystal structural analysis made it clear that it is indeed the intergrowth phase with Bi-TiNbO_7 ($n=2$) and $\text{Bi}_2\text{Ti}_3\text{O}_{10}$ ($n=3$) slabs [20].

For $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$ we propose here a structural model based on 6-layered perovskite blocks (Fig. 7). The model was constructed with starting coordinates being derived from those of the $F2mm$ (no.42) 4-layer $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ structure [13] by the incorporation of two additional octahedral layers ($2 \times \text{BiFeO}_3$) to the 4-layer-block. $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$ was

refined in the orthorhombic space groups $F2mm$ and $A2_1am$ with the code Rietica, since the structure of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ was also reported having $F2mm$ [13] as well as $A2_1am$ symmetry [14]. The results obtained in these groups are similar to each other what did not enable us to distinguish them. Finally, we applied the more symmetrical group $F2nm$ (Table 2). The background was modelled using a 5th order polynomial approximation. The peak-profile was described by a pseudo-Voigt function. The displacement parameters for Ti/Fe atoms as well as for the oxygen atoms were constrained to be each equal in order to stabilise the refinement. As it is noted in the Table 1, according to the microprobe data, the initial sample contained the admixture (<5 %) of a phase with the composition $\text{Bi}_2\text{Ti}_{0.24}\text{Fe}_{3.77}\text{O}_9$. So we used the positional parameters of the orthorhombic compound $\text{Bi}_2\text{Fe}_4\text{O}_9$ (space group $Pbam$ (no.55)) [23] for this additional phase. The profile parameters and the unit cell ($a=7.840(3)$ Å, $b=8.445(4)$ Å, $c=5.958(3)$ Å) only were refined for the add-phase. The best Rietveld refinement (Fig. 7) was achieved with reliability factors (R-values) listed in Table 2.

Selected bond distances are presented in Table 4. Relatively high R-factors are probably caused by structural defects. The FWHM for the 00l reflections is two to three times larger than that for other maxima. Obviously, the number of layers in a block is not constant in the structure, but the 6-layer phase dominates. Since X-ray diffraction is much more efficient for the localisation of heavy Bi atoms than for O atoms, the values of the estimated standard deviations for atomic parameters and, correspondingly, for the interatomic distances especially of oxygen atoms are much larger than that of Bi atoms (Table 4).

The structure of $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$, as any other Aurivillius structure, could also be described in terms of crystal chemistry with oxocentered anions [24] as an alternation of perovskite blocks and Bi-O layers build up from OBi_4 tetrahedra by sharing of edges (Fig. 7).

Table 2 Crystallographic data for $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$.

Formula	$\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$
Temperature (in °C)	22
Space group	$F2mm$ (no.42)
Z	4
Formula weight (in mass units)	2110
Density D_{calc} (in 10^3kg/m^3)	7.74
a (in Å)	5.4699(3)
b (in Å)	5.4924(3)
c (in Å)	57.551(3)
V (in Å ³)	1729.0
2 θ range (in °)	10.0–95.0
Step size (in °2 θ)	0.01
Radiation	$\text{CuK}\alpha$
R_p (in %)	9.4
R_{wp} (in %)	11.9
R_B (in %)	4.4
R_{exp} (in %)	4.7
χ^2	6.5
No. of reflections ($\alpha_1 + \alpha_2$)	528
No. of variables	52

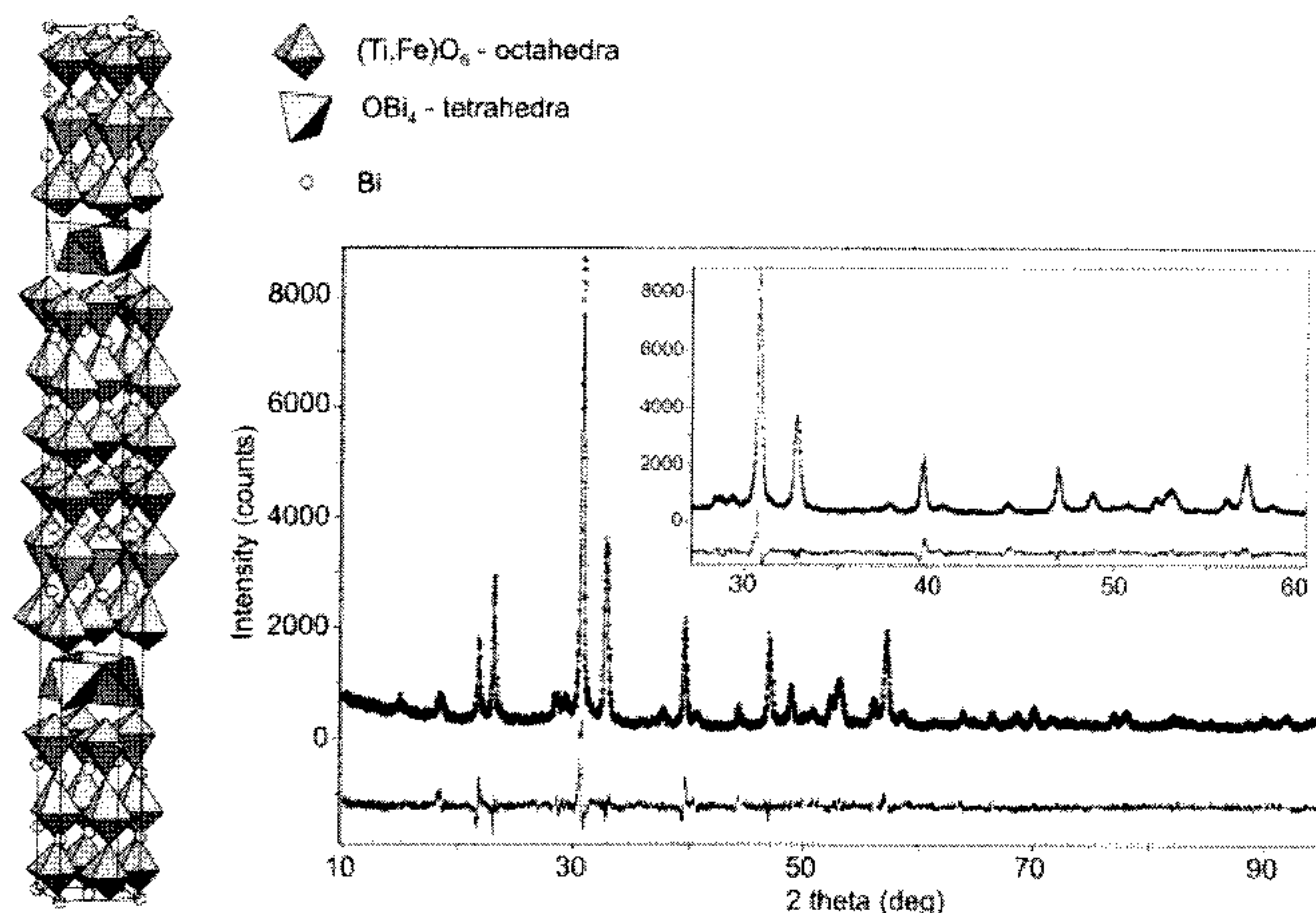


Figure 7 Model of crystal structure of $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$ and the Rietveld data plot (+ observed pattern, solid line for simulated pattern, bottom line for difference).

Table 3 Atomic parameters for $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$

Atom	x	y	z	B_{iso} (in \AA^2)
Bi1	0.0	0.0	0.0	0.48(17)
Bi2	0.0	-0.002(2)	0.0737(1)	0.62(16)
Bi3	0.0	-0.013(3)	0.1473(1)	0.75(17)
Bi4	0.0	-0.013(2)	0.2251(2)	1.53(15)
Ti1(Fe1)*	0.0	0.021(7)	0.3138(2)	0.64(2)
Ti2(Fe2)*	0.0	0.053(5)	0.3954(3)	0.64(2)
Ti3(Fe3)*	0.0	0.025(7)	0.4671(3)	0.64(2)
O1	0.0	0.629(20)	0.0	0.6(35)
O2	0.294(19)	0.805(18)	0.972(1)	0.6
O3	0.0	0.607(15)	0.934(1)	0.6
O4	0.199(13)	0.828(15)	0.402(1)	0.6
O5	0.0	0.058(17)	0.356(1)	0.6
O6	0.226(18)	0.723(16)	0.312(1)	0.6
O7	0.0	0.554(18)	0.212(1)	0.6
O8	0.25	0.234(40)	0.25	0.6

Ti/Fe sites are considered to be occupied at random by Ti/Fe=0.5/0.5

Conclusions

The HTXRD study of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$, $\text{Bi}_{11}\text{Ti}_6\text{Fe}_3\text{O}_{33}$ and $\text{Bi}_7\text{Fe}_3\text{Ti}_3\text{O}_{21}$ showed an unusual behaviour of the cell parameters especially for the c vs T dependence. For all compounds studied three temperature regions could be distinguished: {1} the low-temperature OR region of the thermal expansion of the initial orthorhombic phase, {2} the OR \rightarrow T intermediate region of structure reconstruction; {3} the thermal expansion of the resulting tetragonal phase T. The linear coefficient of thermal expansion along the c direction within the intermediate region is 2-4 times larger than that for the OR as well as for the T phase. This is caused by a structural reconstruction. No evidence of a structural phase transition was found. For the 6-layer structure an additional temperature region has been observed,

Table 4 Selected bond lengths of the $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$ structure

Atom pair	Bond length (in \AA)	Atom pair	Bond length (in \AA)
Bi1 - Bi1'	3.8758*4	Ti1 - O5	2.46(6)
Bi2	4.2415(2)*2	O6	1.99(7) * 2
		O6'	1.93(7) * 2
		O7	1.51 (6)
Bi2 - Bi2'	3.8758*4	(Ti1 - O)	1.97
Bi3	4.2338(2)	Ti2 - O3	2.26(8)
		O4	1.68(5) * 2
Bi3 - Bi3'	3.8758*4	O4'	2.26(5) * 2
Bi4	4.4792(2)	O5	2.23(7)
		(Ti2 - O)	2.06
Bi4 - Bi4'	3.8758*4	Ti3 - O1	1.97(3)
Bi4''	3.9702(2)*2	O2	2.24(11) * 2
Bi4'''	3.9624 (2) *2	O2'	1.67(11) * 2
		O3	1.93 (8)
		(Ti3 - O)	1.95
Bi1 - O1	2.04 (12)	Bi2 - O2	3.25 (4)*2
O1'	2.82 (3)*2	O2'	3.32 (5)*2
O2	2.52 (4)*4	O3	2.18 (8)
O2'	2.60 (5)*4	O3'	2.84(2)*2
O1	3.45 (12)	O3''	3.39 (8)
(Bi1 - O)	2.63	O4	2.36(8)*2
		O4'	2.55 (9)*2
		(Bi2 - O)	2.85
Bi3 - O4	3.37(6)*2	Bi4 - O8	2.41(18)*2
O4'	3.56(8)*2	O8'	2.42(18)*2
O5	2.36(9)	O6	2.81(11)*2
O5'	2.77(2)*2	O6'	3.01(11)*2
O5''	3.14(9)	O7	2.51(9)
O6	2.93(9)*2	O7'	2.87(2)*2
O6'	3.12(11)*2	O7''	3.21(9)
(Bi3 - O)	3.08	(Bi4 - O)	2.49

which could be associated with an intermediate OR phase.

The structure of $\text{Bi}_7\text{Fe}_3\text{Ti}_3\text{O}_{21}$ has been refined in the orthorhombic space group $F2mm$ using X-ray powder diffraction data. The 6-layer model for this structure is build up

by the incorporation of two additional octahedral layers ($2 \times \text{BiFeO}_3$) to the 4-layer-block of $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ structure.

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