Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Journal of Solid State Chemistry 177 (2004) 4188–4196

JOURNAL OF SOLID STATE CHEMISTRY

www.elsevier.com/locate/jssc

Structural studies of five layer Aurivillius oxides: $A_2Bi_4Ti_5O_{18}$ (A = Ca, Sr, Ba and Pb)

Ismunandar[a,b], T. Kamiyama[a], A. Hoshikawa[a], Q. Zhou[c], B.J. Kennedy[c,*], Y. Kubota[d], K. Kato[e]

[a] Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba 305-0801, Japan
[b] Departemen Kimia, Institut Teknologi Bandung, Jl. Ganesa 10 Bandung, 40132, Indonesia
[c] The Centre for Heavy Metals Research, School of Chemistry, The University of Sydney, New South Wales 2006, Sydney, Australia
[d] Department of Environmental Sciences, Faculty of Science Osaka Women's University Daisen-cho 2-1, Sakai, Osaka 590-0035, Japan
[e] Japan Synchrotron Radiation Research Institute, 1-1-1 Kouto, Mikazuki-cho, Sayo-gun, Hyogo 67905198, Japan

Received 6 May 2004; received in revised form 21 July 2004; accepted 22 July 2004

Abstract

The room temperature structures of the five layer Aurivillius phases $A_2Bi_4Ti_5O_{18}$ (A = Ca, Sr, Ba and Pb) have been refined from powder neutron diffraction data using the Rietveld method. The structures consist of $[Bi_2O_2]^{2+}$ layers interleaved with perovskite-like $[A_2Bi_2Ti_5O_{16}]^{2-}$ blocks. The structures were refined in the orthorhombic space group $B2eb$ (SG. No. 41), $Z = 4$, and the unit cell parameters of the oxides are $a = 5.4251(2)$, $b = 5.4034(1)$, $c = 48.486(1)$; $a = 5.4650(2)$, $b = 5.4625(3)$, $c = 48.852(1)$; $a = 5.4988(3)$, $b = 5.4980(4)$, $c = 50.352(1)$; $a = 5.4701(2)$, $b = 5.4577(2)$, $c = 49.643(1)$ for A = Ca, Sr, Ba and Pb, respectively. The structural features of the compounds were found similar to $n = 2-4$ layers bismuth oxides. The strain caused by mismatch of cell parameter requirements for the $[Bi_2O_2]^{2+}$ layers and perovskite-like $[A_2Bi_2Ti_5O_{16}]^{2-}$ blocks were relieved by tilting of the TiO_6 octahedra. Variable temperature synchrotron X-ray studies for Ca and Pb compounds showed that the orthorhombic structure persisted up to 675 and 475 K, respectively. Raman spectra of the compounds are also presented.

Keywords: Aurivillius phase; Neutron powder diffraction; Synchrotron X-ray diffraction; $CaBi_4Ti_5O_{18}$; $SrBi_4Ti_5O_{18}$; $BaBi_4Ti_5O_{18}$; $PbBi_4Ti_5O_{18}$

1. Introduction

Aurivillius first reported a family of layered bismuth oxides, now referred to as the Aurivillius phases, more than 50 years ago when studying the Bi_2O_3–TiO_2 system [1]. Shortly afterwards, Smolenski and Subbarao recognized that many of the Aurivillius phases are ferroelectric [2,3]. In addition to their ferroelectric properties, some Aurivillius type oxides have been investigated for use as oxygen ion conductors [4] whilst others, such as Bi_2MoO_6, are employed as catalysts [5]. The Aurivillius phases, which have the general formula $Bi_2A_{n-1}B_nO_{3n+3}$, $n = 1, 2, 3, \ldots$ can be described as resulting from the regular stacking of $[Bi_2O_2]^{2+}$ slabs and perovskite-like $[A_{n-1}B_nO_{3n+3}]^{2-}$ blocks. The integer, n, describes the number of sheets of corner-sharing BO_6 octahedra forming the ABO_3-type perovskite blocks. The 12 coordinate perovskite-like A-site is typically occupied by a large cation such as Na^+, K^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Bi^{3+} or Ln^{3+} and the 6-coordinate perovskite-like B-site by smaller cations such as Fe^{3+}, Cr^{3+}, Ti^{4+}, Nb^{5+} or W^{6+}. Whereas the perovskite blocks offer large possibilities in terms of compositional flexibility, with numerous combinations of A and B cations observed, the cation sites in the $[Bi_2O_2]^{2+}$ layers are almost exclusively occupied by Bi^{3+}.

Recently there has been renewed interest in the ferroelectric properties of the Aurivillius phases. In particular $SrBi_2Ta_2O_9$ and $Bi_3Ti_4O_{15}$ have been found to

---

*Corresponding author. Fax: +61-2-9351-3329.
E-mail address: kennedyb@chem.usyd.edu.au (B.J. Kennedy).

0022-4596/$ - see front matter Crown Copyright © 2004 Published by Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2004.07.032

exhibit large spontaneous polarizations over a wide temperature range, making them ideal candidates for use in information medium such as nonvolatile computer memories [6]. This has prompted numerous structural studies of these types of oxides in order to establish the relationship between their desirable ferroelectric properties and structure (e.g., [7–10]). A second area of interest has been the observation that the dielectric constants of the Aurivillius oxides typically show a broad maximum at the Curie temperature. It was long postulated that this is a consequence of disorder between Bi from the $[Bi_2O_2]^{2+}$ layers and the perovskite-like *A*-type cations [3]. Considerable effort has been directed toward identifying and understanding the factors that influence the extent of cation disorder in the $n=2$ compounds, that is, in the oxides of the type $ABi_2M_2O_9$ ($A=$ Ca, Sr, Ba, Pb and $M=$ Nb, Ta) [11–13]. For the $n=2$ Nb oxides the extent of cation disorder is greatest in $PbBi_2Nb_2O_9$ due to the similar stereochemistry of the isoelectronic Pb^{2+} and Bi^{3+} cations. Replacing the Pb with an alkaline-earth cation (Ca, Sr or Ba) considerably reduces the extent of cation disorder, although it does not eliminate it [8]. The persistence of cation disorder in these oxides reflects the local bonding effects between the perovskite-like slabs and the $[Bi_2O_2]^{2+}$ layers. Cation disorder has also been identified in some $n=3$ oxides including $LnBi_2Ti_3O_{12}$ [14].

In comparison to the $n=2$ oxides very little is known about the higher order $n=4$ or 5 oxides. Aurivillius and Subbarao first reported the synthesis and ferroelectric behavior of the $n=5$ oxides $A_2Bi_4Ti_5O_{18}$ ($A=$ Sr, Ba and Pb) in 1962 [15–17]. There were conflicting reports about the existence of single phase samples of $Ba_2Bi_4Ti_5O_{18}$, Subbarao reported that this is in fact a mixture of the four layer oxide $BaBi_4Ti_4O_{15}$ and $BaTiO_3$ while Aurivillius claimed $Ba_2Bi_4Ti_5O_{18}$ could be obtained as a single phase. Recently Irie et al. reported the preparation and ferroelectric properties of single crystals of $A_2Bi_4Ti_5O_{18}$ ($A=$ Ba and Pb) [18]. They indexed the patterns of both compounds in *B*2*ab* with $a \approx b \approx 5$ Å and $c \approx 50$ Å, no other structural parameters were reported. The structure of some $n=3$ and $n=4$ oxides have recently been described from powder neutron diffraction studies [10,19].

High resolution diffraction studies have demonstrated that the majority of Aurivillius phases do not adopt the prototype tetragonal structure at room temperature, rather tilting of the perovskite-like BO_6 octahedra, together with displacement of the cations relative to the Bi_2O_2 layers, lowers the symmetry to either orthorhombic or monoclinic. Indeed the main structural basis for the ferroelectricity is the displacement of the perovskite A-type cations within the perovskite-like layers, along the crystallographic *a*-axis with respect to the chains of corner sharing BO_6 octahedra. This corresponds to a [110] displacement referred to the parent *I*4/*mmm*.

In order to retain the unit cell, with the *c*-axis perpendicular to the structural layers, it has been customary to select the direction of spontaneous polarization along the *a*-axis. This results in the widespread use of non-standard settings of the space groups with an *A*-centered lattice for compounds with even values of *n* and a *B*-centered lattice for compounds with *n* odd. For example the room temperature structure of $SrBi_2Ta_2O_9$, an $n=2$ Aurivillius oxides is described in $A2_1/am$, while that of the $n=3$ oxide $Bi_3Ti_4O_{12}$ is in space group *B2eb*. In both cases upon increasing the temperature the tilting of the BO_6 octahedra is reduced and the structure ultimately becomes tetragonal in *I*4/*mmm*.

As stated above the BO_6 octahedra are tilted relative to each other. These two structural features, cation displacement and BO_6 tilting act in concert to lower the symmetry from tetragonal however they are not linked and there is no reason to suppose that both modes will condense at precisely the same temperature. Rather it is probable that these modes will condense successively and the two end member phases will be linked by an intermediate phase. Using powder neutron diffraction methods Macquart and Lightfoot have independently shown that the $A2_1am$ to *I*4/*mmm* transition in the $n=2$ Aurivillius phases $SrBi_2Ta_2O_9$ [20] and $Sr_{0.85}Bi_{2.1}Ta_2O_9$ [21] proceeds via an intermediate paraelectric *Amam* phase in each case. That is, upon cooling from the *I*4/*mmm* phase the tilting of the octahedra occurs before the cation displacement. The same sequence is reported to occur in $PbBi_2M_2O_9$ ($M=$ Nb, Ta) [20] the $n=4$ Aurivillius oxide $SrBi_4Ti_4O_{15}$ [10]. Zhou and Kennedy recently reported evidence for an intermediate phase in $Bi_4Ti_3O_{12}$ [23].

Numerous studies have now been reported on structures and phase transitions in the simpler $n=2$ or 3 oxides. Very little is known about the larger $n=4$ or 5 oxides. Recently we reported a brief communication describing the structure of one example [24]. Here we describe the results of high-resolution synchrotron and neutron powder diffraction and Raman spectroscopic studies of the family of $n=5$ oxides $A_2Bi_4Ti_5O_{18}$ ($A=$ Ca, Sr, Ba and Pb).

2. Experimental

Polycrystalline samples of $A_2Bi_4Ti_5O_{18}$ ($A=$ Ca, Sr, Ba and Pb) were prepared by the solid state reaction of stoichiometric quantities of the appropriate alkaline earth carbonate ($A=$ Ca, Sr and Ba) or PbO_2 with Bi_2O_3, and TiO_2. The heating sequence was 850 °C/24 h, 1000 °C/24 h and 1100 °C/24 h with the samples being reground every 24 h. Powder X-ray diffraction (XRD) data collected, on a Siemens D5000 diffractometer using non-monochromatic CuK_α radiation, did not show the presence of any unexpected peaks suggesting the oxides were single phase. No evidence for any sample inhomogeneity was observed using both scanning electron microscopy and energy dispersive X-ray analysis. Room- and variable temperature ($300 < T < 1000$ K) powder synchrotron XRD measurements were carried out on the large Debye–Scherrer camera installed on BL02B2 at SPring-8. Sample temperatures were controlled by N_2 gas flow system installed at the experimental station and were stabilized to within 1 K during the measurement [25]. For the synchrotron diffraction measurements the samples were housed in 0.2 mm dia quartz capillaries and the X-ray wavelength was 0.5 Å. Neutron powder diffraction data were measured at 295 K for ca. 3 h on the time-of-flight neutron diffractometer Vega [26] at the pulsed spallation neutron facility KENS. The samples were contained in cylindrical vanadium cells 9.2 mm in diameter, 20 mm in height, with wall thickness 150 μm. The Rietveld refinement from the neutron data used RIETAN-2001T [27], whilst those from the synchrotron X-ray data were undertaken with the computer program RIETICA [28].

The solid state Raman spectra were recorded over the range 0–3600 cm^{-1} using a Bruker RFS100 FT-Raman spectrometer, which employed a Nd:YAG laser emitting at 1064 nm as the excitation source. Solid samples were prepared by grinding the powdered solid and pressing it into an aluminum disc. Raman spectra were collected at resolution of 4 cm^{-1} by the co-addition of 16 continuous scans using a laser power of 130 mW.

3. Structure refinements

It has previously been established that the three oxides $A_2Bi_4Ti_5O_{18}$ (A = Sr, Ba, Pb) are ferroelectric at room temperature. This demonstrates that the structures cannot be described in space group $I4/mmm$ since this is a centrosymmetric tetragonal space group that does not support ferroelectricity. Examination of the room temperature synchrotron diffraction patterns of both $Ca_2Bi_4Ti_5O_{18}$ and $Pb_2Bi_4Ti_5O_{18}$ showed clear evidence that the symmetry was lower than tetragonal, whereas for $Sr_2Bi_4Ti_5O_{18}$ and $Ba_2Bi_4Ti_5O_{18}$ the room temperature synchrotron diffraction patterns could be adequately described by a tetragonal model.

The lowering of symmetry from tetragonal in the Aurivillius phases is typically associated with rotations of the perovskite-like BO_6 octahedra that may or may not be accompanied by cation displacements. While such rotations may be responsible for the lowering of the cell metric, they generally do not give rise to any additional strong reflections. The movement of the light oxygen atoms, responsible for the rotation or tilting of the BO_6 octahedra, is best studied by neutron rather than X-ray methods in these types of oxides. The powder neutron diffraction patterns of all four compounds showed some very weak reflections that could only be indexed by an expansion of the *ab* plane as occurs when the BO_6 octahedra are tilted. Careful examinations of the raw diffraction data revealed a number of reflections that violated an F-centered orthorhombic cell ruling out an alternate ferroelectric orthorhombic space group $F2mm$, but were accounted for in the orthorhombic $B2eb$ space group. We did not find any evidence for weak $hk0$ (k odd) reflections indicating the loss of the b-glide in $B2eb$. Rae et al. observed such reflections in their study of $Bi_4Ti_3O_{12}$ indicating the loss of the b-glide and they concluded the structure of $Bi_4Ti_3O_{12}$ is monoclinic at room temperature in $B1a1$ [29]. Not only did we not observe such reflections, attempted structural refinements from either the neutron of high resolution synchrotron diffraction data in the monoclinic space group showed $\beta = 90°$. Accordingly we concluded that the structure of the four compounds is orthorhombic in space group $B2eb$.

A structural model was then created from the archetypal tetragonal model described by Aurivillius for $Ba_2Bi_4Ti_5O_{18}$. The positions of the heavy atoms were initially established for each of the four compounds using the room temperature synchrotron diffraction data and the resulting models were then refined from the appropriate powder neutron diffraction data. For the three compounds $A_2Bi_4Ti_5O_{18}$, A = Sr, Ba and Pb these refinements rapidly converged and the final R-factors and lattice parameters are listed in Table 1. The atomic coordinates and isotropic displacement parameters are listed in Table 2. In the case of $Ca_2Bi_4Ti_5O_{18}$ the refinements converged to higher than usual R-factors, Table 1. Examination of the Rietveld plots showed this to be a consequence of problems modeling the shape of a number of reflections, Fig. 1. We believe this is most likely a consequence of anisotropic peak broadening as

Table 1
Selected structural and refinements data for $A_2Bi_4Ti_5O_{18}$ (A = Ca, Sr, Ba and Pb).

	Ca	Sr	Ba	Pb
a (Å)	5.4251(2)	5.4647(2)	5.4985(3)	5.4700(2)
b (Å)	5.4034(1)	5.4625(2)	5.4980(4)	5.4575(2)
c (Å)	48.486(1)	48.8515(7)	50.3524(8)	49.6434(7)
Volume (Å^3)	1421.32(7)	1458.23(7)	1522.3(1)	1482.07(3)
$2(a-b)/(a+b)$	4.01×10^{-3}	4.58×10^{-4}	1.82×10^{-4}	2.27×10^{-3}
T	0.97	1.00	1.06	1.02
R_p	6.36	4.67	4.37	3.76
R_{wp}	7.98	6.06	5.51	4.80
R_{Bragg}	2.47	2.17	2.94	2.26
GOF	2.59	1.43	1.97	1.46

Note. The structures were refined in space group $B2cb$, $Z = 4$.

Table 2
Atomic coordinates and isotropic atomic displacement parameters (Å^2) for $A_2Bi_4Ti_5O_{18}$ (A = Ca, Sr, Ba and Pb), all atoms are in general position 8*b* except, Ti(1) in 4*a*

Atom	*x*	*y*	*z*	*B*
A = Ca				
Bi(1)/*A*(1)	0	0.995(3)	0.0425(2)	0.8(2)
Bi(2)	0.980(4)	−0.018(2)	0.2238(1)	1.0(2)
Bi(3)/*A*(2)	−0.022(7)	0.006(3)	0.1278(2)	2.5(2)
Ti(1)	0.010(7)	0	$\frac{1}{2}$	0.6
Ti(2)	0.004(6)	0.001(6)	0.4191(3)	0.6
Ti(3)	−0.002(5)	0.006(4)	0.3342(2)	0.6
O(1)	0.197(2)	0.224(3)	0.0062(2)	0.6(3)
O(2)	0.237(5)	0.244(3)	0.2489(2)	0.6
O(3)	−0.048(4)	0.044(3)	0.2973(2)	1.0(3)
O(4)	0.969(4)	0.944(2)	0.3804(1)	0.6
O(5)	0.953(4)	0.067(2)	0.4586(2)	0.6
O(6)	0.236(5)	0.256(3)	0.0754(3)	1.5(3)
O(7)	0.177(4)	0.200(2)	0.9145(2)	0.6
O(8)	0.220(5)	0.243(3)	0.8453(2)	0.6
O(9)	0.250(6)	0.269(3)	0.1619(2)	0.6
A = Sr				
Bi(1)/*A*(1)	0	0.000(2)	0.0421(1)	0.9(1)
Bi(2)	0.003(2)	−0.021(2)	0.2241(1)	1.6(1)
Bi(3)/*A*(2)	0.002(4)	0.004(2)	0.1297(1)	1.6(1)
Ti(1)	0.011(5)	0	$\frac{1}{2}$	0.6
Ti(2)	0.013(4)	0.994(4)	0.4168(2)	0.6
Ti(3)	0.018(3)	0.007(5)	0.3314(2)	0.6
O(1)	0.290(3)	0.254(2)	0.0021(3)	0.6
O(2)	0.266(3)	0.246(2)	0.2491(2)	0.5(1)
O(3)	0.005(3)	0.020(4)	0.2960(1)	1.2(2)
O(4)	0.041(4)	0.966(3)	0.3790(1)	0.6
O(5)	0.042(3)	0.041(3)	0.4598(2)	1.0(2)
O(6)	0.262(3)	0.230(2)	0.0776(2)	0.6
O(7)	0.316(2)	0.295(2)	0.9182(2)	0.6
O(8)	0.263(3)	0.251(2)	0.8413(2)	0.6
O(9)	0.282(2)	0.257(2)	0.1630(2)	0.7(2)
A = Ba				
Bi(1)/*A*(1)	0	0.963(7)	0.0432(1)	3.4(1)
Bi(2)	0.991(4)	−0.003(4)	0.2251(1)	1.9(1)
Bi(3)/*A*(2)	−0.004(4)	0.000(6)	0.1306(1)	2.2(1)
Ti(1)	0.000(6)	0	$\frac{1}{2}$	0.6
Ti(2)	−0.002(4)	0.001(7)	0.4162(2)	0.6
Ti(3)	0.000(5)	0.999(6)	0.3300(2)	0.6
O(1)	0.246(4)	0.252(4)	0.0014(5)	1.3(2)
O(2)	0.255(5)	0.256(5)	0.2497(4)	0.4(1)
O(3)	−0.022(4)	0.991(6)	0.2958(1)	1.0(2)
O(4)	0.004(4)	0.998(5)	0.3801(1)	0.40(9)
O(5)	0.015(4)	0.021(7)	0.4603(1)	1.6(2)
O(6)	0.268(4)	0.264(3)	0.0785(4)	0.6
O(7)	0.250(4)	0.250(4)	0.9193(3)	1.3(2)
O(8)	0.264(4)	0.268(3)	0.8374(3)	0.5(2)
O(9)	0.264(4)	0.259(3)	0.1618(3)	0.6
A = Pb				
Bi(1)/*A*(1)	0	0.998(2)	0.04314(6)	1.93(7)
Bi(2)	0.016(2)	−0.006(1)	0.22481(6)	0.74(7)
Bi(3)/*A*(2)	0.000(2)	0.002(2)	0.13000(6)	0.94(8)
Ti(1)	0.025(6)	0	$\frac{1}{2}$	0.6
Ti(2)	0.020(3)	0.997(3)	0.4164(1)	0.6
Ti(3)	0.014(3)	0.004(3)	0.3305(1)	0.6
O(1)	0.304(3)	0.264(2)	0.0015(3)	1.2(2)
O(2)	0.268(3)	0.248(3)	0.2497(2)	0.6
O(3)	0.046(2)	0.010(2)	0.2961(1)	0.7(1)
O(4)	0.028(3)	0.983(2)	0.3796(1)	0.9(1)
O(5)	0.041(2)	0.044(2)	0.4601(1)	1.9(2)
O(6)	0.270(2)	0.232(2)	0.0775(2)	0.7(2)
O(7)	0.320(3)	0.284(2)	0.9194(2)	1.2(2)
O(8)	0.272(2)	0.246(2)	0.8399(2)	0.4(1)
O(9)	0.281(2)	0.247(2)	0.1624(2)	0.6

a result of stacking faults along the *c*-axis. Despite these problems with the refinement the final structural model for $Ca_2Bi_4Ti_5O_{18}$, Table 2, appears chemically reasonable. Selected bond distances, TiO_6 rotation angles and bond valence sums for the four oxides are given in Tables 3–5, respectively.

During the refinements we observed that the displacement parameters for the Ti atoms at the center of the TiO_6 octahedra were unusually small and occasionally negative. Similar problems have been observed by other workers; see for example Ref. [19]. We believe his problem arises from the small magnitude of displacements observed for the atoms at the center of the octahedra, a feature also noted in a number of simple ABO_3 perovskites (see for example Ref. [30]), possibly coupled with experimental errors associated with absorption. In the final refinements the displacement parameters for the Ti atoms were fixed at a reasonable positive value and these were not varied. On occasions the displacement parameters for one of the oxygen atoms become physically unreasonable, when this was observed these were reset to a finite positive value and the refinements recommenced.

Comparison of the structures and stiochiometry suggest that the $A(2)$ site near $z \approx \frac{1}{4}$, that is within the Bi_2O_2 layers, contains only Bi cations. Refinement of the site occupancies for $Ca_2Bi_4Ti_5O_{18}$, chosen since the XRD contrast is largest between Ca and Bi, using the powder XRD data supports this suggestion. The coordination of this atom obtained in the final refinement using the powder neutron diffraction data showed the BVS for this site to be ≈ 3 indicative of full occupancy by Bi(III). Similar results were obtained for the Sr containing compound. Next the possibility that the alkaline earth, or lead, cations preferentially occupied one of the other available sites ($z \approx 0$ or $\frac{1}{8}$) was investigated. For all compounds the refinements did not indicate a preference of the alkaline earth for either site, irrespective of the initial site occupancies chosen for the refinements. It was concluded that there was a statistical distribution of Bi and the alkaline earth (or lead) cations on both sites. The final refinements using the powder neutron diffraction data were made using this assumption. With the exception of the Ca oxide the effective BVS for the two sites are similar suggesting the assumption of a random distribution is valid.

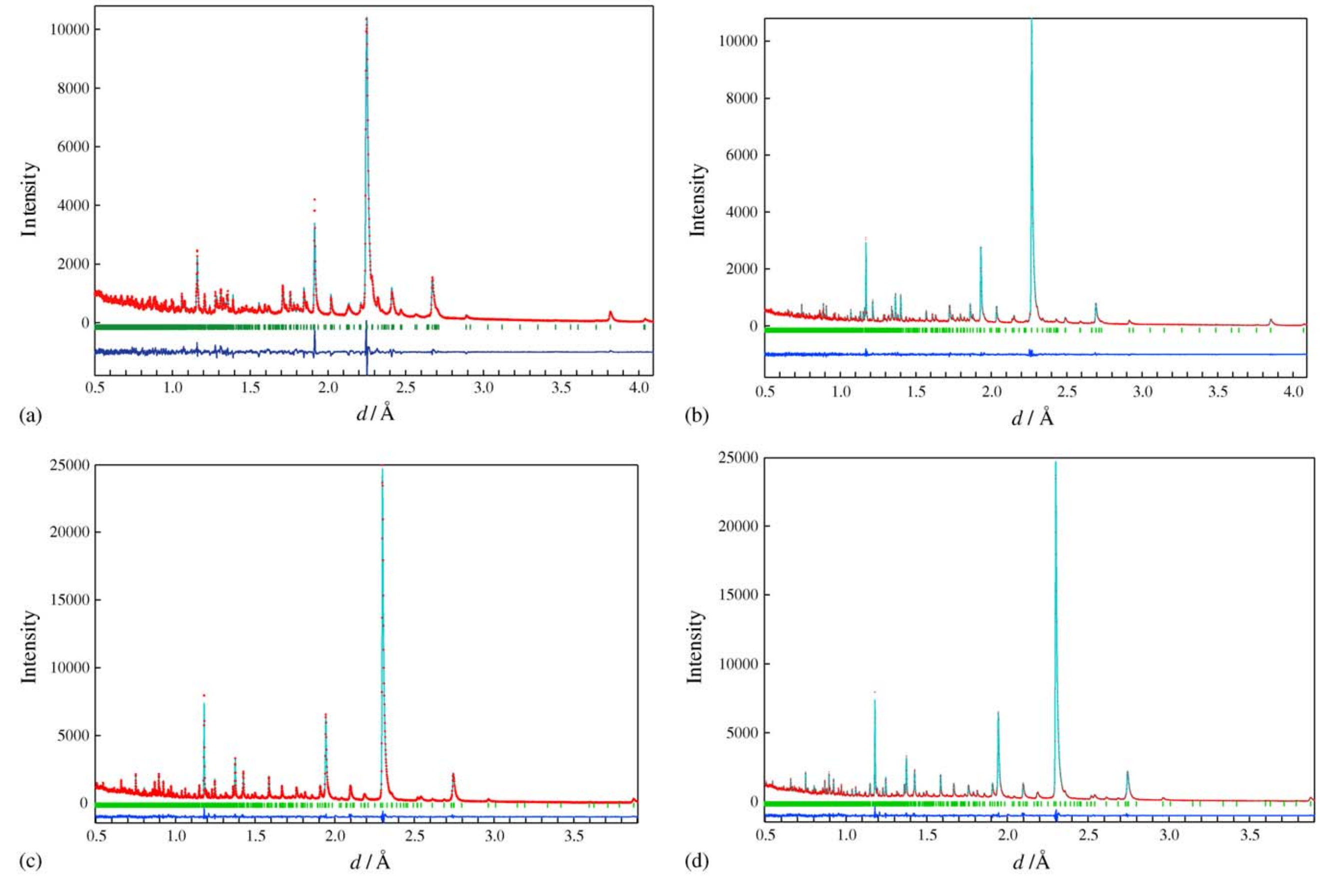

Fig. 1. Rietveld refinement plot showing the observed (×), calculated (solid line) neutron diffraction profiles and their difference for $A_2Bi_4Ti_5O_{18}$ (A = Ca, Sr, Ba and Pb) at room temperature. The tick marks show the positions of the allowed Bragg reflections in space group *B2cb*.

The refined lattice parameters show that whilst $Ba_2Bi_4Ti_5O_{18}$ is metrically tetragonal (although the symmetry is strictly orthorhombic) at room temperature the remaining three oxides have an appreciable orthorhombic distortion. Irie and co-workers recently reported that $Ba_2Bi_4Ti_5O_{18}$ is pseudo tetragonal with $a = 5.496$ and $b = 5.494$ Å, and whilst they concluded that the correct space group is *B*2*ab* (an alternate setting of *B2eb*) they neither showed the diffraction data nor gave the refined structural parameters. This situation is somewhat similar to that observed in $BaBi_2Nb_2O_9$ which is tetragonal and ferroelectric at room temperature. Macquart and co-workers concluded, based on both neutron and high-resolution synchrotron diffraction data, that the appropriate space group for $BaBi_2Nb_2O_9$ is $I4m$ [22]. Clearly neutron diffraction is critical to identify the appropriate symmetry of these types of oxides. This has the further advantage of considerably enhancing the precision in the refined lattice parameters listed for the present compounds, Table 1, through the observation, and use of the weak superlattice reflections that distinguish space group *B2eb* from $I4/mmm$ in refining these.

4. Structural features

The observed cell parameters are in good agreement with values reported previously [16,17]. Fig. 2 compares the structures of $Ca_2Bi_4Ti_5O_{18}$ and $Ba_2Bi_4Ti_5O_{18}$. It is immediately apparent from this figure that the structure of BBT-5 is much less distorted that of CBT-5. The local environments of the three crystallographically distinct Ti atoms are noticeably different. As has been observed in other Aurivillius oxides the outermost MO_6 octahedra are highly distorted, even in BBT-5. Considering the $Ti(3)O_6$ octahedra as tetragonal then the two "axial" Ti-O distances are very different. The Ti(3) atom is displaced away from the equatorial plane formed by two O(8) and two O(9) atoms, towards O(3). As evident from Fig. 2 this O(3) atoms interacts with a Bi(2) atom within the $[Bi_2O_2]$ layer. This results in the axial Ti(3)–O(3) distance being much, ≈0.5 Å, shorter than the *trans* axial Ti(3)–O(4) distance. Despite this highly distorted environment bond valence sum calculations for Ti(3) show, with the obvious exception of CBT-5, the valence in this site to be unexceptional. The O(4) atoms links the $Ti(3)O_6$ and $Ti(2)O_6$ octahedra and there is an

Table 3
Selected bond distances (Å) for $A_2Bi_4Ti_5O_{18}$ (A = Ca, Sr, Ba and Pb)

A	Ca	Sr	Ba	Pb
Bi_2O_2 layer				
Bi(2)–O(2)	2.23(2)	2.21(2)	2.25(1)	2.27(2)
–O(2)	2.33(2)	2.32(2)	2.29(1)	2.30(2)
–O(2)	2.31(2)	2.33(2)	2.34(1)	2.31(2)
–O(2)	2.33(2)	2.37(2)	2.38(1)	2.31(2)
–O(3)	2.76(2)	2.73(2)	2.87(1)	2.77(3)
–O(3)	3.05(2)	3.07(2)	2.92(1)	2.84(2)
–O(3)	3.21(2)	2.87(2)	3.02(1)	3.01(1)
–O(3)	2.58(2)	2.89(2)	2.97(1)	3.08(2)
Average	2.60	2.60	2.63	2.61
A(1)/Bi(1)–O(1)	2.40(2)	2.62(1)	2.96(3)	2.63(2)
–O(1)	2.78(2)	2.78(1)	2.95(3)	2.79(2)
–O(1)	2.85(2)	2.88(1)	2.88(3)	3.01(2)
–O(1)	3.22(2)	3.03(1)	2.87(3)	3.15(2)
–O(5)	2.33(2)	2.97(2)	2.62(3)	2.51(2)
–O(5)	2.48(2)	2.51(2)	2.89(3)	2.97(2)
–O(5)	3.10(2)	2.50(2)	2.50(2)	2.96(2)
–O(5)	2.99(2)	2.95(2)	2.84(2)	2.49(2)
–O(6)	2.48(2)	2.57(1)	2.55(3)	2.59(1)
–O(6)	2.53(2)	2.63(1)	2.73(3)	2.60(1)
–O(7)	2.53(2)	2.46(1)	2.70(3)	2.39(1)
–O(7)	3.16(2)	3.06(1)	2.70(3)	2.97(1)
Average	2.74	2.75	2.77	2.76
A(2)/Bi(3)–O(4)	2.40(3)	2.97(2)	2.75(2)	2.66(1)
–O(4)	3.06(3)	2.57(2)	2.84(4)	2.89(1)
–O(4)	2.70(2)	2.54(2)	2.78(2)	2.92(2)
–O(4)	2.80(2)	2.96(2)	2.82(2)	2.63(2)
–O(6)	3.13(2)	3.15(1)	3.18(1)	3.24(1)
–O(6)	3.20(2)	3.21(1)	3.35(1)	3.24(1)
–O(7)	2.57(1)	2.79(1)	3.19(2)	3.40(1)
–O(7)	3.10(2)	3.32(1)	3.17(1)	2.91(1)
–O(8)	2.29(2)	2.36(2)	3.64(3)	2.38(1)
–O(8)	2.38(2)	2.44(2)	2.41(2)	2.51(1)
–O(9)	2.39(2)	2.39(2)	2.58(2)	2.41(1)
–O(9)	2.63(2)	2.62(1)	2.41(3)	2.61(1)
Average	2.72	2.78	2.93	2.82
Ti(1)–O(1) × 2	1.82(2)	1.85(2)	1.87(2)	1.87(3)
–O(1) × 2	2.11(2)	2.03(2)	2.00(1)	2.00(3)
–O(5) × 2	2.06(1)	1.98(1)	2.01(2)	2.01(1)
Average	2.00	1.95	1.96	1.96
Ti(2)–O(4)	1.91(1)	1.85(1)	1.82(1)	1.83(1)
–O(5)	1.97(2)	2.11(1)	2.23(1)	2.18(1)
–O(6)	1.84(3)	1.87(2)	2.00(3)	1.87(3)
–O(6)	2.03(3)	2.01(2)	1.94(4)	2.01(2)
–O(7)	1.88(3)	1.95(3)	1.94(4)	1.92(3)
–O(7)	2.09(3)	2.01(2)	1.96(4)	2.01(3)
Average	1.95	1.97	1.98	1.97
Ti(3)–O(3)	1.82(2)	1.72(1)	1.73(1)	1.72(1)
–O(4)	2.27(2)	2.35(1)	2.52(1)	2.44(1)
–O(8)	1.89(3)	1.96(2)	1.97(4)	1.91(3)
–O(8)	2.05(3)	1.97(2)	1.99(4)	2.03(4)
–O(9)	1.88(3)	1.93(2)	1.96(4)	1.91(2)
–O(9)	2.01(3)	2.04(2)	2.01(4)	2.05(2)
Average	1.99	2.00	2.03	2.01

Table 4
Various angle measuring tilting of TiO_6 octahedra for $A_2Bi_4Ti_5O_{18}$ (A = Ca, Sr, Ba and Pb)

A	Ca	Sr	Ba	Pb
Ti(2)–Ti(1)–Ti(2)	179.0(3)	179.7(3)	179.2(3)	179.2(3)
Ti(1)–Ti(2)–Ti(3)	179.7(3)	178.6(3)	179.2(3)	179.0(3)
O(1)–O(1)–O(1)	154.4(3)	171.4(3)	174.5(3)	173.1(3)
O(6)–O(7)–O(6)	155.4(3)	165.3(3)	173.6(3)	166.9(3)
O(8)–O(9)–O(8)	163.8(3)	170.2(3)	178.8(3)	174.8(3)

Table 5
BVS for $A_2Bi_4Ti_5O_{18}$ (A = Ca, Sr, Ba and Pb)

A	Ca	Sr	Ba	Pb
A(1)/Bi(1)[a]	2.47	2.57	2.84	2.60
Bi(2)	3.07	2.97	2.82	2.96
A(2)/Bi(3)[a]	2.65	2.82	2.59	2.51
Ti(1)	3.91	4.22	4.12	4.12
Ti(2)	4.24	4.10	4.02	4.13
Ti(3)	4.05	4.14	3.95	4.11

[a] $r_o = r_o(\mathrm{Bi}) + r_o(A)/2$.

“inductive” effect that effectively shortens the Ti(2)–O(4) distance relative to the corresponding *trans* Ti(2)–O(5) distance. The four equatorial distances and the BVS for the Ti(2) site was also unexceptional. Ti(1) is located on a mirror plane and consequently the two axial Ti(1)–O(5) distances are equal.

The structure refinements suggest both Ti(3) and Ti(2) are severely overbonded in CBT-5, while the $A2$/Bi3 site is somewhat underbonded. Haluska and Misture [19] have recently discussed the origins of such BVS anomalies since they are commonly observed in Aurivillius type oxides. In general BVS anomalies are related to either rotation of the octahedra (see below) or stiochiometric variations including disorder and vacancies. The structural model developed here allows for rotation of the TiO_6 octahedra. Since the BVS sums for the remaining three oxides studied here do not show similar anomalies we believe CBT-5 is a unique problem. There is no evidence from the structural refinements to indicate any oxygen vacancies are present in this compound and we suspect the unusual BVS results for CBT-5 are an artifact of the problems experienced in fitting the diffraction profiles.

In general the displacement parameters for the oxygen atoms were all reasonanble and their was no reason to suspect any oxygen vacancies to be present. Nevertheless in light of the recent work of Haluska and Misture [19] we sought to confirm this by attempting to refine the site occupancies of the oxygen cations. Invariably this failed to improve the refinements and the final refined site occupancies were always with three esds of the nominal value. In the final refinements they were assumed to be fully occupied. We conclude there is no evidence for any oxygen vacancies.

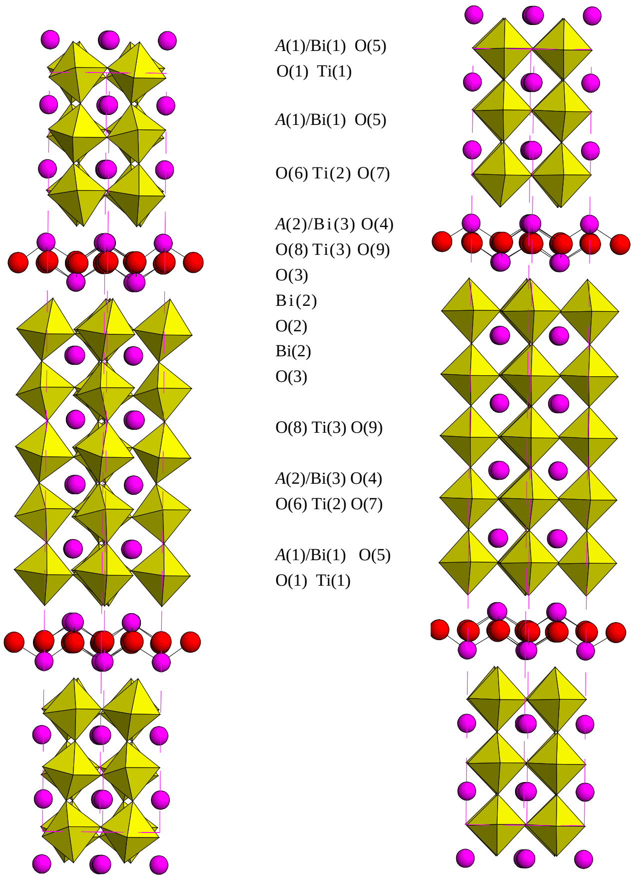

Fig. 2. Structure of $Ca_2Bi_4Ti_5O_{18}$ (left) and $Ba_2Bi_4Ti_5O_{18}$ (right). The Bi atoms are represented by the small shaded sphere. Note the difference in the rotations of the octahedra.

The most striking difference between the two structures shown in Fig. 2 is the reduction in the tilting of the TiO_6 octahedra resulting from the larger Ba cation. It is the rotation of the TiO_6 octahedra, which gives rise to the $\sqrt{2}a \times \sqrt{2}b$ superstructure seen in all four oxides. Considering just the perovskite-like units then the rotation of the octahedra can be thought to result from a compromise between the Ti–O and A–O bonding requirements. This is often expressed in terms of a tolerance factor, t, defined as $t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$ where r_A is the radius of the 12-coordintate A^{2+} cation, r_O, the radius of the 4-coordinate oxygen anion and r_B the radius of the six-coordinate Ti^{4+} cation. As the size of the A-type cation increases through the series Ca $(1.34) < Sr(1.44) \approx Pb(1.49) < Ba(1.61\,\text{Å})$ then t increases, from less then unity in CBT-5 to greater than 1 in BBT-5. This results in a reduction both of the tilting of the TiO_6 octahedron and in the degree of the orthorhombic splitting given by $2(a-b)/(a+b)$, Table 1. The TiO_6 octahedra rotations in $A = Ba$ are very minimal as can be seen from the tilting angle of TiO_6 both around a and c direction, Table 4. For the other three oxides, the tilting angle was found to increase in order of $Pb \approx Sr < Ca$, in accordance with the tolerance factor. The same trend was also observed for the interpolyhedral angle (Ti(1)–Ti(2)–Ti(3) and Ti(2)–Ti(1)–Ti(2)). Except for $A = Ca$, all the calculated BVS fall within the expected values.

5. Variable temperature studies

As stated above peak splitting indicative of orthorhombic symmetry were observed in the room temperature synchrotron diffraction patterns only for CBT-5 and PBT-5. The temperature dependence of the structure for these two oxides was investigated between 300 and 1000 K, and the variation in the lattice parameters is illustrated in Fig. 3. In both cases the orthorhombic splitting is most conveniently monitored by inspection of the 2 0 0/0 2 0 orthorhombic pair. In the case of CBT-5 these overlap with the 2 0 2/0 2 2 and 0 1 8 reflections however the relative intensities of these are ca. 10% and 5%, respectively, of the 2 0 0/0 2 0 reflections and this overlap was not problematic in the analysis.

For both oxides there is an apparently continuous variation in the orthorhombic lattice parameters with

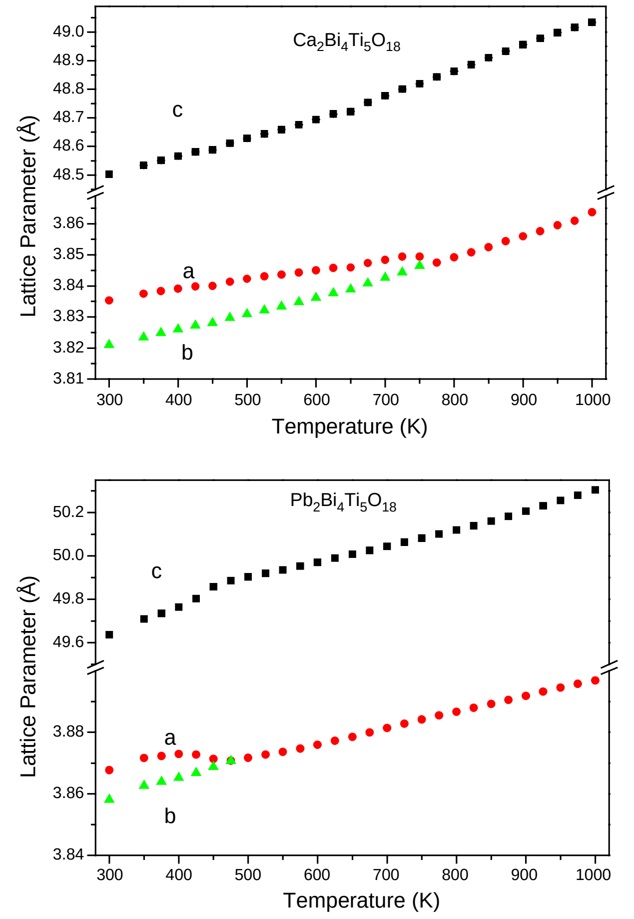

Fig. 3. Cell parameters of $Ca_2Bi_4Ti_5O_{18}$ and $Pb_2Bi_4Ti_5O_{18}$ as a function of temperature.

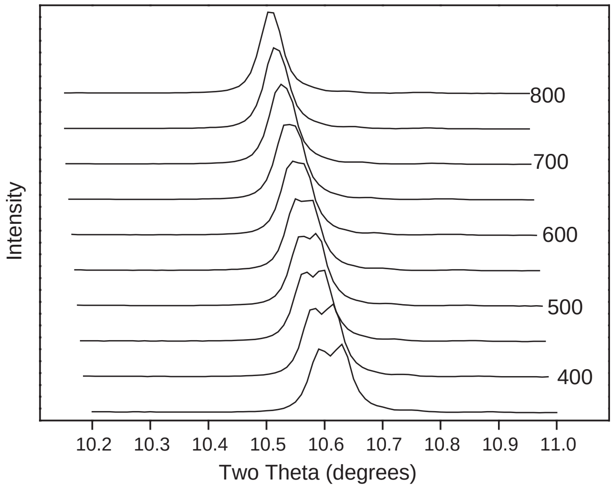

Fig. 4. Portion of variable temperature XRD plots of $Ca_2Bi_4Ti_5O_{18}$. The pattern positions have been adjusted to make an easy viewing.

the splitting of the 2 0 0/0 2 0 doublet, and the difference in the refined *a*- and *b*-parameters regularly decreasing as the temperature is increased. For CBT-5 the orthorhombic splitting persisted to ca. 675 K and for PBT-5 until 475 K (Fig. 4). Above these temperatures attempts to refine the structures in space group *B2eb* resulted in unacceptably large esds for the lattice parameters and the structures were refined in the tetragonal *I*4/*mmm* structure.

Whilst both CBT-5 and PBT-5 are undoubtedly tetragonal and paraelectric at high temperatures it is probable that the transition to the paraelectric *I*4/*mmm* structure from the ferroelectric *B2eb* one occurs via an intermediate phase as was also observed for $SrBi_2Ta_2O_9$ [20].

In order to identify the space group of the intermediate phase we undertook a group theoretical analysis using the program ISOTROPY [31]. This confirmed that a direct *B2eb* to *I*4/*mmm* transition could not be continuous. The two modes responsible for the transition were identified as Γ_5^- describing the cation displacement and X_3^+ associated with the tilting of the TiO_6 octahedra [31]. Whichever of these modes condenses first, an intermediate orthorhombic structure based on a $\sqrt{2} \times \sqrt{2} \times 1$ superstructure of the parent *I*4/*mmm* structure is involved and the successive phase transitions through either of these intermediates are allowed to be continuous. If the initial distortion is cation displacement via the Γ_5^- mode then a ferroelectric orthorhombic structure that lacks any tilting of the TiO_6 octahedra is expected. The resulting structure in *Fmm*2 can continuously transform to the observed room temperature orthorhombic *B2eb* phase through tilting of the TiO_6 octahedra via the X_3^+ mode.[1] Alternatively the initial distortion may be the introduction of tilting of the TiO_6 octahedra resulting in a *Cmca* phase followed by cation displacement. The available synchrotron diffraction data does not allow us to unequivocally distinguish between these two possibilities however by analogy with $SrBi_2Ta_2O_9$ we favor the latter possibility [20]. The confirmation of this requires a high resolution neutron diffraction study.

6. Raman studies

Examples of the Raman spectra are given in Fig. 5. Despite repeated attempts under a variety of experimental conditions we failed to observe any signal from $Ca_2Bi_4Ti_5O_{18}$ in the Raman measurements. Four main peaks were observed in the Raman spectra for each of the three compounds $A_2Bi_4Ti_5O_{18}$ $A =$ Sr, Ba and Pb. Following the work of Kojima et al. [32] it is possible to identify the origins of each of these. The best resolved low wavelength feature is near $60\,cm^{-1}$ and this can be ascribed to a rigid body mode of the Bi_2O_2 layer. The small variation in the frequency of this is a consequence of the effective change in mass of the perovskite-type layers. The positions of the peaks at $\sim 280\,cm^{-1}$ are essentially independent of the *A*-cation and are ascribed in torsional bending of the TiO_6 octahedra. The observed frequency of these bands is similar to that seen in the related $n = 3$ and 4 Aurivillius titanates. The peak near $560\,cm^{-1}$ is a stretching mode of the pseudo perovskite layer $[TiO_6]_5$ layers. The position of this peak is only weakly dependent on the *A*-cation. The broadness of this peak, relative to the other modes, reflects the variety of environments within the perovskite layer. The position of the third peak near $880\,cm^{-1}$ varies strongly with the *A*-type cation, moving to higher frequency as the mass of the *A*-type cation increases. This trend is also observed in the $n = 3$ and 4 Aurivillius titanates. We did not observe any well defined modes below

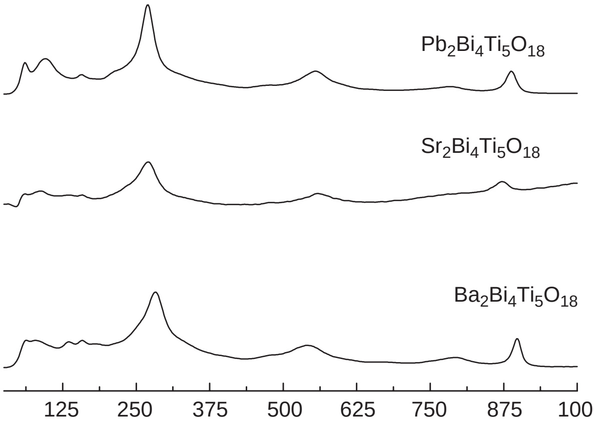

Fig. 5. Raman spectra of $A_2Bi_4Ti_5O_{18}$ ($A =$ Sr, Ba and Pb) at room temperature.

---

[1] This description refers still to the parent structure in *I*4/*mmm*.

$50\,\mathrm{cm}^{-1}$ that could be associated with rotation of the TiO_6 groups.

Acknowledgments

Ismu thanks HB X and TWAS for supporting the work and High Energy Accelerator Research Organization for the visiting scientist fellowship. We thank Dr E. Carter for assistance with the Raman measurements. BJK's work was partially supported by the Australian Research Council and the Access to Major Research Facilities program. The experiment at SPring-8 was carried out under proposal 2002B0001.

References

[1] B. Aurivillius, Ark. Kemi 1 (1949) 499.
[2] G.A. Smolenskii, V.A. Isupov, A.I. Agranovskaya, Sov. Phys. Solid State (Engl. Transl.) 3 (1959) 651.
[3] E.C. Subbarao, J. Phys. Chem. Solids 23 (1962) 665.
[4] N. Yasuda, M. Miyayama, T. Kudo, Solid State Ionics 133 (2000) 273.
[5] D.J. Buttrey, T. Vogt, U. Wildgruber, W.R. Robinson, J. Solid State Chem. 111 (1994) 118.
[6] C.A.P. de Araujo, J.D. Cuchlaro, L.D. McMillan, M. Scott, J.F. Scott, Nature (London) 374 (1995) 627.
[7] Ismunandar, B.J. Kennedy, Gunawan, Marsongkohadi, J. Solid State Chem. 126 (1996) 135.
[8] S.M. Blake, M.J. Falconer, M. McCreedy, P. Lightfoot, J. Mater. Chem. 7 (1997) 1609.
[9] Y. Shimakawa, Y. Kubo, Y. Nakagawa, T. Kamiyama, H. Asano, F. Izumi, App. Phys. Lett. 74 (1999) 1904.
[10] C.H. Hervoches, A. Snedden, R. Riggs, S.H. Kilcoyne, P. Manuel, P. Lightfoot, J. Solid State Chem. 164 (2002) 280.
[11] V. Srikanth, H. Idink, W.B. White, E.C. Subbarao, H. Rajapogal, A. Sequeria, Acta Crystallogr. B 52 (1996) 432.
[12] Ismunandar, B.A. Hunter, B.J. Kennedy, Solid State Ionics 112 (1998) 281.
[13] Ismunandar, B.J. Kennedy, J. Mater. Chem. 9 (1999) 541.
[14] N.C. Hyatt, J.A. Hriljac, T.P. Comyn, Mater. Res. Bull. 38 (2003) 837–846.
[15] E.C. Subbarao, J. Am. Ceram. Soc. 45 (1962) 564.
[16] E.C. Subbarao, J. Am. Ceram. Soc. 45 (1962) 166.
[17] B. Aurivillius, P.H. Fang, Phys. Rev. 126 (1962) 893.
[18] H. Irie, M. Miyayama, T. Kudo, J. Appl. Phys 90 (2001) 4089.
[19] M.S. Haluska, S.T. Misture, J. Solid State Chem. 177 (2004) 1965.
[20] R. Macquart, B.J. Kennedy, B.A. Hunter, C.J. Howard, Y. Shimakawa, Intergr. Ferroelectr. 44 (2002) 101.
[21] C.H. Hervoches, J.T.S. Irvine, P. Lightfoot, Phys. Rev. B 64 (2002) 100102(R).
[22] R. Macquart, B.J. Kennedy, B.A. Hunter, C.J. Howard, J. Phys. Condens. Matter 14 (2002) 7955.
[23] Q. Zhou, B.J. Kennedy, C.J. Howard, Chem. Mater. 15 (2003) 5025.
[24] Ismunandar, T. Kamiyama, A. Hishikawa, Q. Zhou, B.J. Kennedy, Y. Kubota, K. Kato, J. Neutron Res., 2004, in press.
[25] E. Nishibori, M. Takata, K. Kato, M. Sakata, Y. Kubota, S. Aoyagi, Y. Kuroiwa, M. Yamakata, N. Ikeda, Nucl. Instrum. Methods A 467–468 (2001) 1045.
[26] T. Kamiyama, K. Oikawa, N. Tsuchiya, M. Osawa, H. Asano, N. Watanabe, M. Furusaka, S. Satoh, I. Fujikawa, T. Ishigaki, F. Izumi, Physica B 213/214 (1995) 875.
[27] T. Ohta, F. Izumi, K. Oikawa, T. Kamiyama, Physica B 234–236 (1997) 1093.
[28] C.J. Howard, B.A. Hunter, A Computer Program for Rietveld Analysis of X-ray and Neutron Powder Diffraction Patterns, Lucas Heights Research Laboratories, NSW, Australia 1998, pp. 1–27.
[29] A.D. Rae, J.G. Thompson, R.L. Withers, Acta Crystallogr. B 46 (1990) 474.
[30] B.J. Kennedy, C.J. Howard, B.C. Chakoumakos, J. Phys. C: Condens. Matter 11 (1999) 1479–1488.
[31] H.T. Stokes, D.M. Hatch, ISOTROPY Software Package for Group Analysis of Phase Transitions in Crystalline Solids, Brigham Young University, Utah, 2001.
[32] S. Kojima, R. Imaizumi, S. Hamazaki, M. Takashige, Jpn. J. Appl. Phys. 33 (1994) 5559.