

Cation Disorder in Three-Layer Aurivillius Phases: Structural Studies of $\text{Bi}_{2-x}\text{Sr}_{2+x}\text{Ti}_{1-x}\text{Nb}_{2+x}\text{O}_{12}$ ($0 < x < 0.8$) and $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ ($x = 1$ and 2)

C. H. Hervoches and P. Lightfoot¹*School of Chemistry, University of St. Andrews, St. Andrews, Fife, KY16 9ST, United Kingdom*

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The solid solutions $\text{Bi}_{2-x}\text{Sr}_{2+x}\text{Ti}_{1-x}\text{Nb}_{2+x}\text{O}_{12}$ ($0 < x < 0.6$) (1) and $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ ($x = 1$ and 2) (2) have been analyzed in detail by a combination of powder X-ray and neutron diffraction. Both solid solutions adopt a tetragonal variant of the archetypal three-layer Aurivillius phase structure of the parent phase $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The X-ray studies of (1) clearly show that, contrary to earlier assumptions, Sr^{2+} partially substitutes into the $[\text{Bi}_2\text{O}_2]$ layers, even at the stoichiometric composition $\text{Bi}_2\text{Sr}_2\text{TiNb}_2\text{O}_{12}$, the maximum amount of substitution being about 30% at $x = 0.6$. The neutron study demonstrates that the Sr^{2+} in this site adopts a significantly more isotropic coordination environment than Bi^{3+} , thus stabilizing this unexpected disorder. The disorder is shown to be driven by the requirement for size matching of the fluorite-like and perovskite-like layers. A similar level of disorder is found in $\text{Bi}_2\text{La}_2\text{Ti}_3\text{O}_{12}$, and this is shown to be due to the requirements for optimum local coordination environment at the $\text{La}^{3+}/\text{Bi}^{3+}$ sites. © 2000 Academic Press

materials of choice for these applications are currently $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BTO), representing $n = 2$ and $n = 3$ (“two-layer” and “three-layer”) Aurivillius phases, respectively (Fig. 1). Due to the dramatically increased importance of these materials recently, it now seems timely to further explore the solid state chemistry and structure of them, with the aim of understanding their properties from the crystallochemical point of view, and designing improved materials.

Consideration of the structural chemistry of the Aurivillius phases can offer useful guidelines toward the search for new materials, in particular compositional limitations. Typically (5), the perovskite A site (A being 12-coordinated) can be occupied by large cations such as Ca^{2+} , Sr^{2+} , Ba^{2+} , Bi^{3+} , and Ln^{3+} , and the B site by d^0 cations such as Ti^{4+} , Nb^{5+} , and W^{6+} . However, in early work at least, the $[\text{M}_2\text{O}_2]$ layers (M being 8-coordinated) were considered much less flexible, and were only thought to be occupied by Bi^{3+} , leading to constraints on the overall composition, and alternate layers of fixed ideal charge, $[\text{Bi}_2\text{O}_2]^{2+}$ and $[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]^{2-}$. More recent work has suggested that other lone-pair cations, such as Pb^{2+} and Tl^+ , could occupy the $[\text{M}_2\text{O}_2]$ layers, but that cations not possessing a stereochemically active lone pair could not (6, 7), the suggested reason for this being that lone-pair cations are favored in the square-antiprismatic M -site because an off-center displacement may occur to accommodate the lone pair. Our own work (8), which has subsequently been supported by others (9), has in fact suggested that cation disorder does occur in some of these systems (specifically the two-layer materials $\text{Bi}_2\text{ANb}_2\text{O}_9$; $A = \text{Ca}, \text{Sr}, \text{Ba}$). In this paper we present further conclusive evidence that cations of this type, specifically Sr^{2+} and La^{3+} , can indeed occupy the $[\text{M}_2\text{O}_2]$ units, and we suggest that the driving force for this behavior is based on tolerance factor arguments, i.e., the size matching of the fluorite- and perovskite-like blocks which, to some extent, competes with the preference of Bi^{3+} for an asymmetric coordination environment. The particular

INTRODUCTION

The Aurivillius phases are a class of complex bismuth-based oxides with layered intergrowth structures consisting of alternate stacking of fluorite-like and perovskite-like layers (1). Thus, the general formula of the family, $\text{M}_2\text{A}_{n-1}\text{B}_n\text{O}_{3n+3}$, may be broken down into fluorite-like $[\text{M}_2\text{O}_2]$ units and perovskite-like $[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$ blocks. The ferroelectric properties of these materials have been known since the pioneering work of Smolenski *et al.* (2) and Subbarao (3), but it is only recently that their potential for use in thin-film nonvolatile memory applications has been discovered (4). Their physical properties, in particular negligible polarization fatigue, make them competitive with existing commercial materials based on $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$. The

¹To whom correspondence should be addressed: E-mail pl@st-and.ac.uk.

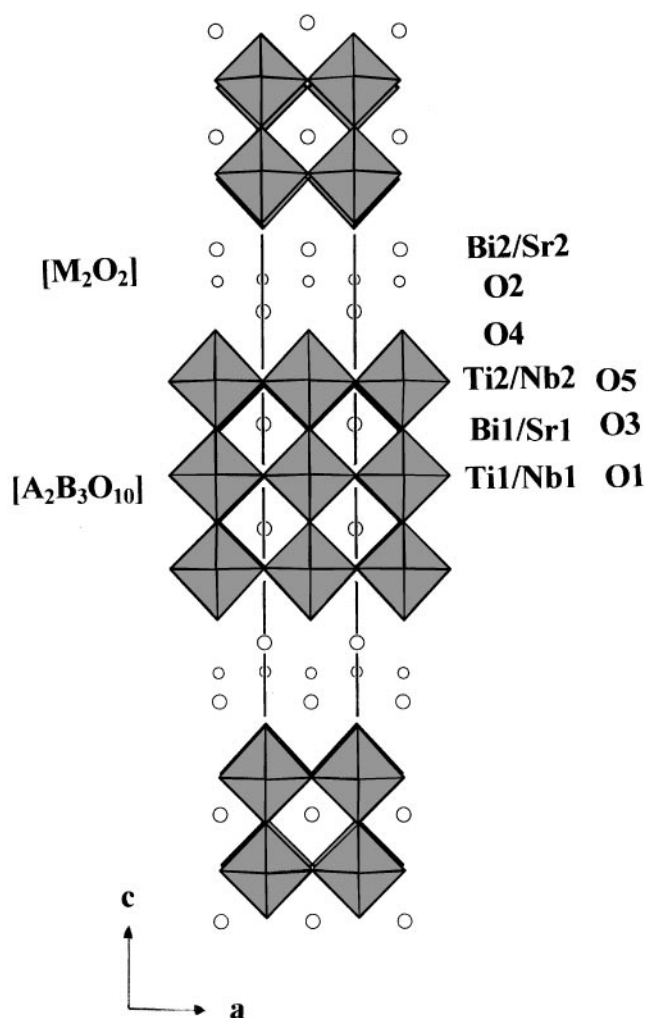


FIG. 1. Ideal tetragonal structure of the $n = 3$ Aurivillius phase $[M_2O_2][A_{n-1}B_nO_{3n+1}]$, showing the regular intergrowth of fluorite-like and perovskite-like layers.

materials studied here derive from the three-layer archetype $Bi_4Ti_3O_{12}$ (10, 11). First, we examine the solid solution $Bi_{2-x}Sr_{2+x}Ti_{1-x}Nb_{2+x}O_{12}$, the existence of which unambiguously suggests that substitution of Sr^{2+} into the $[M_2O_2]$ layers *must* occur and, second, the phases $Bi_3LaTi_3O_{12}$ and $Bi_2La_2Ti_3O_{12}$, selected from the solid solution $Bi_{4-x}La_xTi_3O_{12}$, which has recently been shown to possess physical properties in thin-film form superior to those of the parent BTO phase (12). Rietveld analysis of powder X-ray and neutron diffraction data is used.

EXPERIMENTAL

Polycrystalline samples of $Bi_{2-x}Sr_{2+x}Ti_{1-x}Nb_{2+x}O_{12}$ ($0 < x < 0.8$) and $Bi_{4-x}La_xTi_3O_{12}$ ($x = 1, 2$) were prepared by traditional solid state reaction. Stoichiometric quantities of Bi_2O_3 , La_2O_3 , $SrCO_3$, TiO_2 , and Nb_2O_5 (Aldrich,

>99%) were thoroughly mixed and ground, and heated at elevated temperature in air until phase purity was established. Typical reaction conditions were 24 hours at $850^\circ C$ followed by two firings of 24 hours at $1000^\circ C$, with intermediate regrindings.

X-ray powder diffraction data were recorded on a Stoe STADI/P transmission diffractometer using $CuK\alpha_1$ radiation, and equipped with a small linear PSD covering about $6^\circ 2\theta$. Data were collected over the range $4^\circ < 2\theta < 120^\circ$, the entire run lasting about 15 hours.

Neutron powder diffraction data were recorded at the CLRC ISIS spallation source, Chilton, UK, on the HRPD high-resolution diffractometer. Approximately 10 g of material was loaded in a cylindrical vanadium can of 11 mm diameter and data were collected for a period of about 5 hours. The ISIS source operates in energy-dispersive (time-of-flight) mode, with scattered neutrons being detected at fixed detector banks centered at 90° and 168° . Only the data from the 168° (high-resolution) banks were used for the Rietveld refinement. Corrections were made for incident neutron flux distribution and scattering from the vanadium sample holder.

STRUCTURE REFINEMENT

(i) $Bi_{2-x}Sr_{2+x}Ti_{1-x}Nb_{2+x}O_{12}$

Preliminary examination of the raw X-ray powder diffraction data for $Bi_2Sr_2TiNb_2O_{12}$ suggested that this phase could be indexed in the ideal $n = 3$ tetragonal cell, $a \sim 3.89 \text{ \AA}$, $c \sim 33.2 \text{ \AA}$, space group $I4/mmm$. Starting parameters for Rietveld refinement for this model were taken from the high-temperature study of BTO (11). Initially the M site was assigned as 100% Bi and the A site as 100% Sr. In order to produce the most accurate and reliable set of derived structural parameters, a systematic and self-consistent refinement strategy was applied to this phase, and this was then used for each of the subsequent phases to be analyzed. Data were analyzed using the GSAS program suite (13). Each refinement consisted of the same basic parameter set, *viz.* three parameters to model the background, four for the peak-shape (pseudo-Voigt), scale-factor, lattice parameters, and detector zero-point, atomic coordinates for all atoms, isotropic thermal parameters for the metal sites (which were constrained to be equivalent for the M and A sites and for the two crystallographically distinct B sites), and site occupancies for the Bi/Sr distribution over the M/A sites and the Nb/Ti distribution over the two B sites. Constraints were applied to these occupancy parameters such that the total stoichiometry remained fixed at the ideal value expected from the synthesis, and all sites remained 100% occupied. The total number of parameters in this model was therefore 21. As a further subtlety, it was thought that allowing the Bi/Sr to occupy slightly different positions at both the M and A sites was reasonable, given

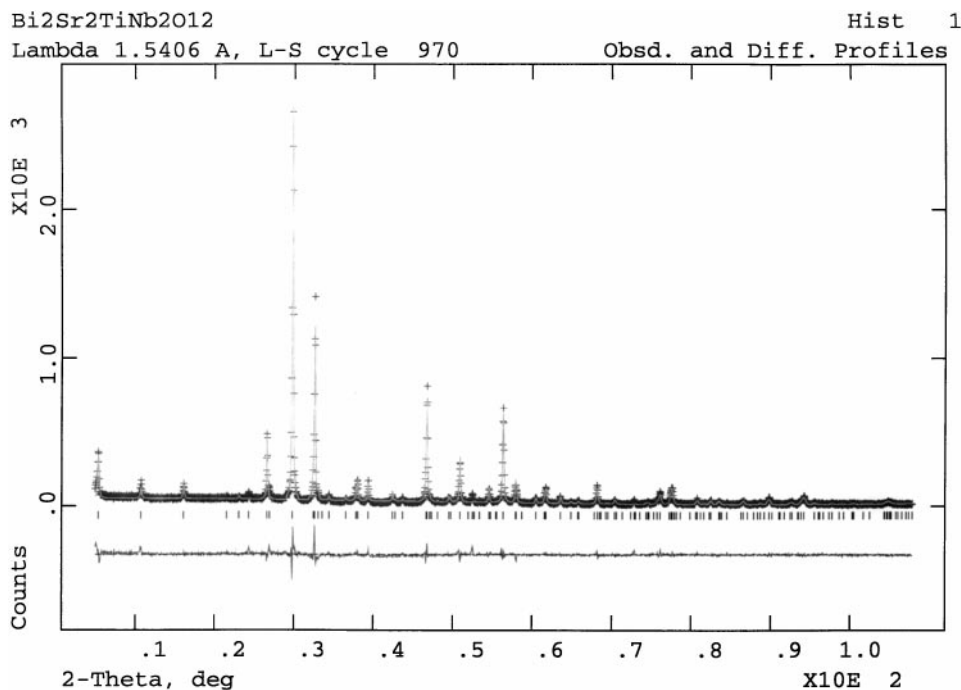


FIG. 2. Final Rietveld plot for the X-ray study of $\text{Bi}_2\text{Sr}_2\text{TiNb}_2\text{O}_{12}$. $R_{\text{wp}} = 0.157$ for 22 variables, 5800 data points, and 163 contributing reflections.

their differing coordination preferences. Addition of these two extra variables, while still imposing the thermal parameter and occupancy constraints, was therefore tested. It was found possible to split the M site into two successfully, but splitting of the A site made an insignificant difference in the refinement. Allowing the disordering of Bi/Sr over the two available sites led to marked improvements of the profile fit in all cases. For example, for $\text{Bi}_2\text{Sr}_2\text{TiNb}_2\text{O}_{12}$, the R_{wp} values obtained for the ordered and disordered models were 0.173 and 0.159, respectively. Splitting of the M sites lead to a much smaller improvement in fit (typically only about 0.1% in R_{wp}), but did lead to stable convergence and a sensible geometry at the split sites. A typical final Rietveld plot is shown in Fig. 2.

It is well known that precise determination of oxygen positional parameters in the presence of heavy atoms is not feasible from X-ray powder data. Hence, in order to obtain a more complete model of the behavior of this solid solution, we have used neutron powder diffraction (NPD). Rietveld refinement of NPD data for $\text{Bi}_{1.8}\text{Sr}_{2.2}\text{Ti}_{0.8}\text{Nb}_{2.2}\text{O}_{12}$ was carried out in GSAS using a strategy slightly modified from that described above. In this case, it proved feasible to refine isotropic temperature factors for all atoms and anisotropic temperature factors for O, but no attempt was made to vary the Bi/Sr distribution as the neutron scattering factor contrast for these elements is relatively much smaller than that for X-rays (neutron scattering lengths, b ($\times 10^{-12}$ m): Bi, 0.8533; Sr, 0.702; Ti,

−0.3438; Nb, 0.7054; O, 0.5805). This distribution was therefore fixed at the values obtained from the corresponding X-ray refinement. Note that the scattering contrast for Nb/Ti, conversely, is very high and neutron diffraction provides a better determination of this elemental distribution than X-rays. As in the case of the X-ray refinement, a “split-site” model was allowed for the Bi/Sr occupancy of the M sites, resulting in a much more pronounced improvement in fit this time (not split, $R_{\text{wp}} = 0.167$; split, $R_{\text{wp}} = 0.161$; representing a highly significant improvement for the addition of only one variable). The final Rietveld fit for this model is shown in Fig. 3, with final refined positional and thermal parameters in Table 1 and selected bond lengths in Table 2. Unfortunately, a small amount of unidentifiable impurity phase is present in the neutron refinement. This is not observable in the corresponding X-ray data, the sample for which was made in a different batch.

(ii) $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ ($x = 1, 2$)

A similar strategy was adopted in the refinement of XPD data for these two materials. Again both samples could be well indexed using the standard tetragonal model, space group $I4/mmm$. In this case, six background parameters were used, and the same constraints were imposed on the M/A site thermal parameters and occupancies. The M sites were once again allowed to “split”, leading to improved agreement factors. Final agreement factors for $\text{Bi}_3\text{LaTi}_3\text{O}_{12}$

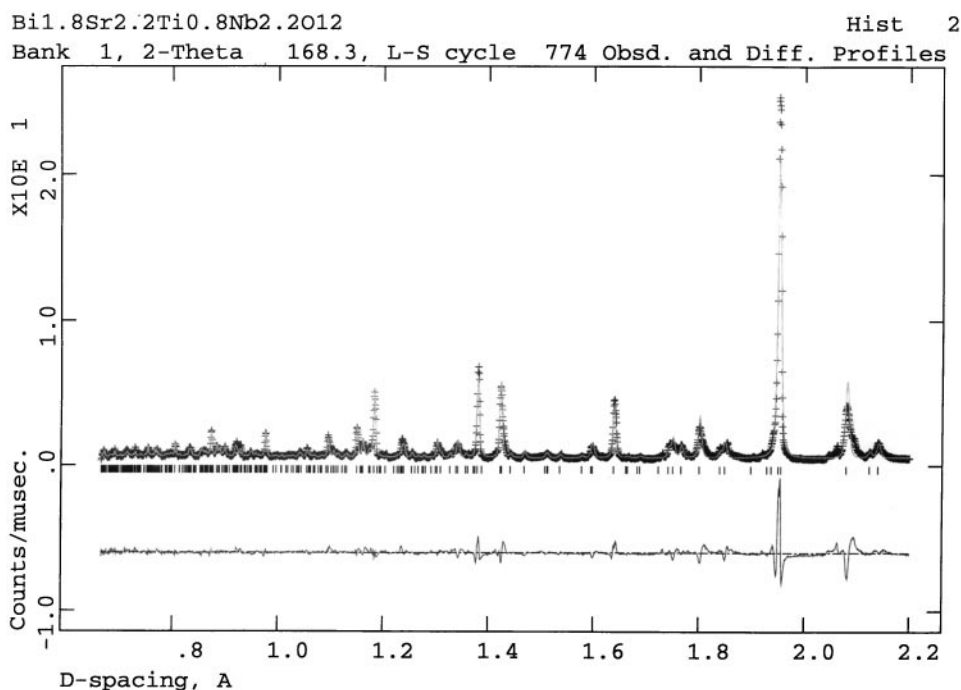


FIG. 3. Final Rietveld plot for the neutron study of Bi_{1.8}Sr_{2.2}Ti_{0.8}Nb_{2.2}O₁₂. $R_{wp} = 0.161$ for 32 variables, 4405 data points, and 1363 contributing reflections.

and Bi₂La₂Ti₃O₁₂ were $R_{wp} = 0.104$ and 0.133 for 25 variables in each case. The final Rietveld plot for Bi₂La₂Ti₃O₁₂ is shown in Fig. 4.

TABLE 1

Final Parameters from the Neutron Rietveld Refinement of Bi_{1.8}Sr_{2.2}Ti_{0.8}Nb_{2.2}O₁₂, Group *I4/mmm*, $a = 3.9012(1)$ Å, $c = 33.292(1)$ Å

Name	X	Y	Z	U_{iso} ($\times 100 \text{ \AA}^2$)	Occ.
Bi1	0.5	0.5	0.0637(2)	2.56(14)	0.11 ^a
Sr1	0.5	0.5	0.0637(2)	2.56(14)	0.89 ^a
Bi2	0.5	0.5	0.2150(2)	2.07(16)	0.79 ^a
Sr2	0.5	0.5	0.1913(10)	2.07(16)	0.21 ^a
Ti1	0.5	0.5	0.5	1.12(13)	0.36(1)
Nb1	0.5	0.5	0.5	1.12(13)	0.64(1)
Ti2	0.5	0.5	0.3720(2)	1.12(13)	0.22(1)
Nb2	0.5	0.5	0.3720(2)	1.12(13)	0.78(1)
O1	0.5	0.5	0	7.6 ^b	1
O2	0.5	0	0.25	2.8 ^b	1
O3	0.5	0.5	0.4417(2)	3.0 ^b	1
O4	0.5	0.5	0.3204(2)	4.0 ^b	1
O5	0.5	0	0.1193(2)	1.9 ^b	1
Name	$U_{11}(\times 100)$	$U_{22}(\times 100)$	$U_{33}(\times 100)$		
O1	0.3(5)	17(1)	4.5(7)		
O2	0.3(3)	0.3(3)	7.6(7)		
O3	2.9(3)	2.9(3)	3.3(5)		
O4	4.8(4)	4.8(4)	2.2(6)		
O5	0.3(3)	1.2(3)	4.3(4)		

^aValue fixed according to X-ray refinement.

^bEquivalent isotropic temperature factor.

RESULTS AND DISCUSSION

(i) Bi_{2-x}Sr_{2+x}Ti_{1-x}Nb_{2+x}O₁₂

The most basic result to arise from this work concerns the confirmation of the existence of a solid solution within the range of composition studied. As early as 1972, Armstrong and Newnham (14) had examined the feasibility of preparing various solid solutions based on BTO, and had suggested a solubility limit of $x = 0.6$ in the formula Bi_{2-x}Sr_{2+x}Ti_{1-x}Nb_{2+x}O₁₂. In other words, the implication was that

TABLE 2

Selected Bond Lengths (Å) for Bi_{1.8}Sr_{2.2}Ti_{0.8}Nb_{2.2}O₁₂ from the Neutron Refinement

Bi1/Sr1-O1($\times 4$)	2.881(4)
Bi1/Sr1-O3($\times 4$)	2.7643(5)
Bi1/Sr1-O5($\times 4$)	2.688(5)
Bi2-O2($\times 4$)	2.271(4)
Bi2-O4($\times 4$)	3.001(5)
Sr2-O2($\times 4$)	2.76(2)
Sr2-O4($\times 4$)	2.786(5)
Sr2-O5($\times 4$)	3.09(3)
Bi2-Sr2	0.79(3) ^a
Ti1/Nb1-O1($\times 4$)	1.95061(3)
Ti1/Nb1-O3($\times 2$)	1.942(8)
Ti2/Nb2-O3	2.32(1)
Ti2/Nb2-O4	1.72(1)
Ti2/Nb2-O5($\times 4$)	1.973(1)

^aBi-Sr distance in the split *M* site.

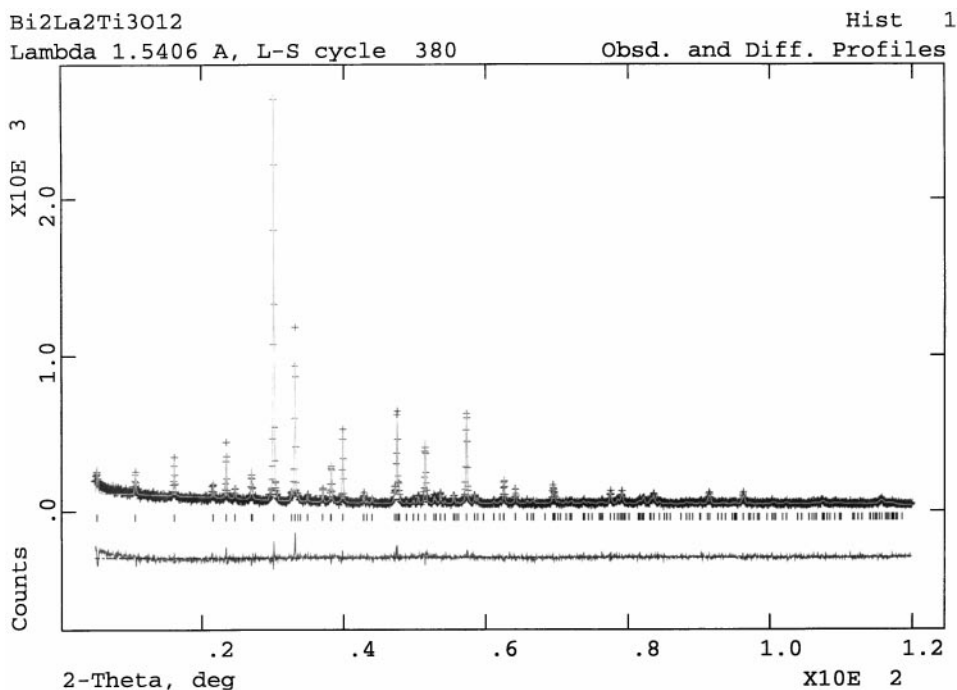


FIG. 4. Final Rietveld plot for the X-ray study of $\text{Bi}_2\text{La}_2\text{Ti}_3\text{O}_{12}$. $R_{\text{wp}} = 0.133$ for 25 variables, 5800 data points, and 157 contributing reflections.

Sr^{2+} must indeed substitute, at least partially, into the $[\text{M}_2\text{O}_2]$ layers. No detailed structure refinements were carried out, though the authors suggested a perfectly ordered structure to be most likely for $\text{Bi}_2\text{Sr}_2\text{TiNb}_2\text{O}_{12}$ on the basis of the intensities of several strong reflections.

Our work first confirms the ideal tetragonal structure (Fig. 1) to be adopted throughout the composition range studied. The variation of lattice parameter with x is shown in Fig. 5. For x in the range 0.6 to 0.8 a second phase appears in the powder pattern, suggesting a solid solubility limit at about $x = 0.6$ (see below). The second phase was identified as $\text{Sr}_5\text{Nb}_4\text{O}_{15}$ (PDF No. 28-1248). More detailed information on the nature of this solid solution can be obtained by analysis of the distribution of Bi/Sr over the M/A sites. This distribution, or “degree of disorder”, between the two sites is represented in Fig. 6. Three major features are apparent from these plots: (i) The occupancy of the M/A sites is not “ideal” (i.e., Bi/Sr) even at $x = 0$; there is approximately 20% mixing over the two sites at this composition. (ii) On substituting additional Sr ($x > 0$) the most significant change is that the Bi in the A site is preferentially substituted, rather than the additional Sr going into the M site; the A site becomes fully occupied by Sr at $x = 0.5$. (iii) In the range $0.5 < x < 0.8$ there appears to be further substitution of Sr into the M site; this correlates with the increasing c -axis throughout this range, although the secondary “ $\text{Sr}_5\text{Nb}_4\text{O}_{15}$ ” phase has appeared. We therefore cannot fully define the solid solution limit from our data, and cannot rule out the possibility of an Sr content above

2.6 in the Aurivillius phase, with a consequent partial substitution of Bi/Ti into the $\text{Sr}_5\text{Nb}_4\text{O}_{15}$ phase. The overall conclusion is clear, however, that there is unambiguously a significant occupancy of the $[\text{M}_2\text{O}_2]$ units by Sr^{2+} even at the stoichiometric $\text{Bi}_2\text{Sr}_2\text{TiNb}_2\text{O}_{12}$ composition,

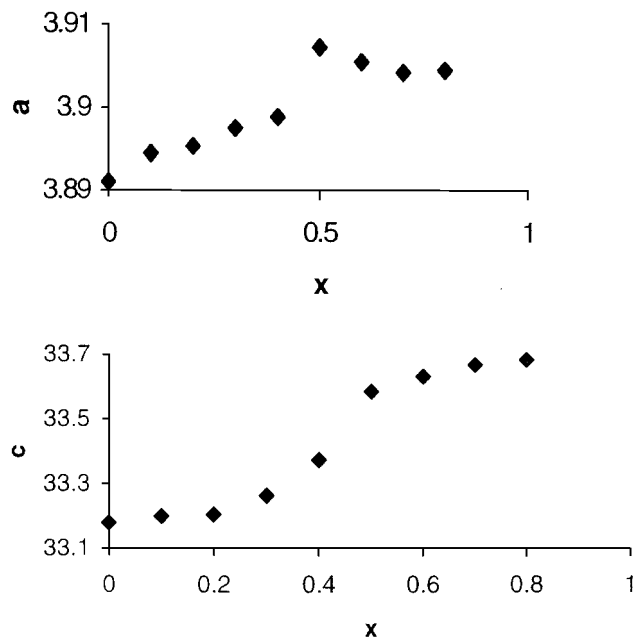


FIG. 5. Variation of tetragonal lattice parameters from the X-ray study of $\text{Bi}_{2-x}\text{Sr}_{2+x}\text{Ti}_{1-x}\text{Nb}_{2+x}\text{O}_{12}$.

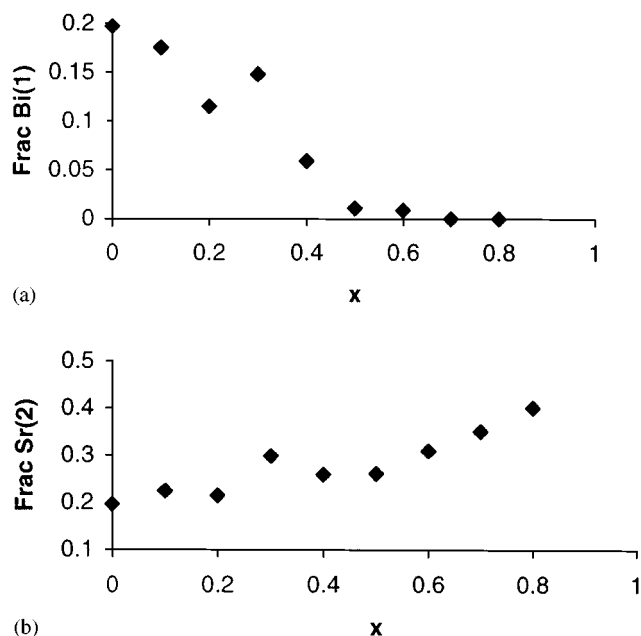


FIG. 6. Distribution of Bi/Sr over the M/A sites in the solid solution $\text{Bi}_{2-x}\text{Sr}_{2+x}\text{Ti}_{1-x}\text{Nb}_{2+x}\text{O}_{12}$ obtained from X-ray Rietveld refinement. (a) Occupancy of Bi in the A site; (b) occupancy of Sr in the M site.

and that this occupancy increases up to the solid solubility limit.

Earlier suppositions that cations without lone pair, such as Sr^{2+} , would not be able to occupy the $[M_2O_2]$ units are shown to be invalid. This is not necessarily surprising, as our refinements show that there is no requirement for the two cations within the $[M_2O_2]$ sites to occupy exactly the same “off-center” coordination environment; indeed the difference in position between the Bi and Sr sites in this block is significant, at about 0.8 \AA , leading to much more regular coordination around the Sr site, as shown in Tables 1 and 2 and Fig. 7. Our previous studies of the Sillén phases

SrBiO_2Cl and CaBiO_2Cl (15), which also adopt layered intergrowth structures containing analogous $[M_2O_2]$ units, show clearly that both Sr/Bi and Ca/Bi combinations can occupy the $[M_2O_2]$ sites, though in those cases the differing coordination preferences even lead to perfect ordering of the two cations, leading to a long-range crystallographic superstructure. Although our attempts to allow splitting of the Bi/Sr occupancy of the A site were unsuccessful, we suspect that the environment around the Bi^{3+} cation in this site is indeed different from that of Sr^{2+} , on the local scale, and this is manifested in the large thermal parameters around O(1), which represents a “twisting” of the $\text{Ti}(1)\text{O}_6$ octahedron around the $[001]$ axis to optimize bonding at the Bi site.

Simple geometrical (“tolerance-factor”) arguments can be used to rationalize the observation of partial disordering of the M/A sites, by considering the size matching of the “fluorite” and “perovskite” blocks in the ab plane. Armstrong and Newnham (14) suggested this approach to explain solid solution formation limits in BTO derivatives, but did not consider the possibility of cation disorder. These authors suggested an “ideal” a -parameter for a $[\text{Bi}_2\text{O}_2]$ block to be 3.80 \AA , by analogy with the known parent structure of $\alpha\text{-PbO}$. They also derived an empirical formula for the a -parameter of an idealized perovskite block $[\text{A}_2\text{B}_3\text{O}_{12}]$,

$$a = 1.33r_B + 0.60r_A + 2.36 \text{ \AA} \quad [1]$$

where r_B represents the six-coordinate cation radius and r_A an eight-coordinate cation radius, taken from Shannon (16). Ionic radii (\AA) used in the following discussion are Bi^{3+} , 1.17; Ca^{2+} , 1.12; Sr^{2+} , 1.26; Ba^{2+} , 1.42; La^{3+} , 1.16; Ti^{4+} , 0.61; Nb^{5+} , 0.64; and mean $[\text{Nb}_2\text{Ti}]$ 0.63. From [1], the idealized a -parameter for an ideal $[\text{Sr}_2\text{TiNb}_2\text{O}_{10}]$ block is calculated to be 3.96 \AA , a severe mismatch of the ideal

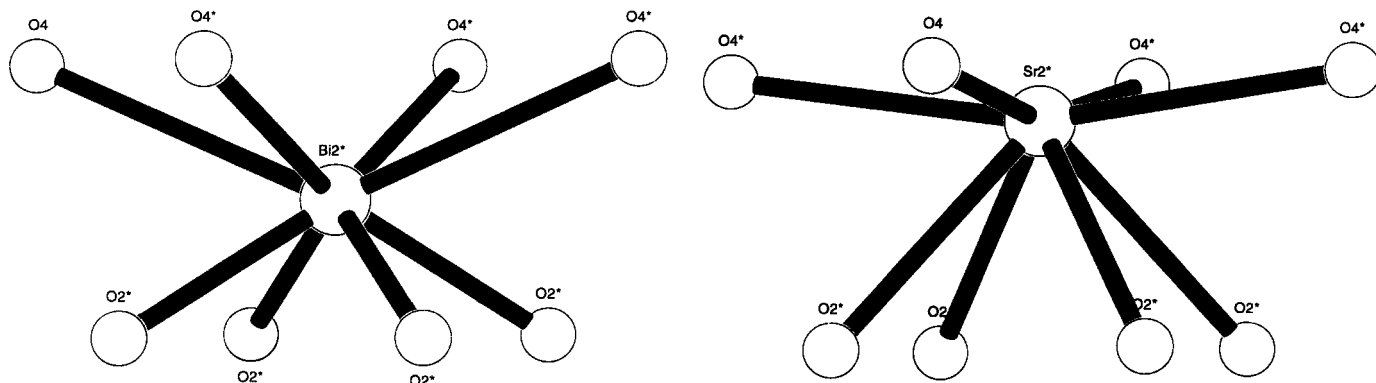


FIG. 7. Local environments of cations occupying the square-antiprismatic M sites in $\text{Bi}_{1.8}\text{Sr}_{2.2}\text{Ti}_{0.8}\text{Nb}_{2.2}\text{O}_{12}$ obtained from neutron Rietveld refinement. The two sites are offset from each other by about 0.8 \AA along the c -axis (see Table 1). This displacement causes the local geometry around Sr2 to be much more regular than that around Bi2, with eight approximately equal bond lengths (see Table 2).

3.80 Å for $[\text{Bi}_2\text{O}_2]$. The observed a -parameter of about 3.89 Å represents a compromise, causing relief of strain in the intergrowth. There is, of course, an alternative mechanism for relief of strain in structures of this type—that of octahedral tilting, as occurs in the parent BTO phase itself (11). Newnham's corresponding a -parameter for an ideal perovskitic $[\text{Bi}_2\text{Ti}_3\text{O}_{10}]$ block is 3.89 Å. The size mismatch in that case is relieved by octahedral tilting in the room temperature structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, effectively reducing the width of the perovskite blocks, and causing a lowering of symmetry from tetragonal to orthorhombic or monoclinic. In our case, the structure retains tetragonal symmetry, signifying no octahedral tilting but, instead, adopts the M/A site disorder mechanism as the preferred method of matching the two blocks, and thus relieving strain. A similar rationalization may be obtained by considering bond-valence-sum (BVS) analysis at the A site, as was suggested by us in earlier work on the two-layer systems (8).

It is interesting to pursue this reasoning further, by application to the hypothetical $\text{Bi}_2\text{Ca}_2\text{TiNb}_2\text{O}_{12}$ and $\text{Bi}_2\text{Ba}_2\text{TiNb}_2\text{O}_{12}$ analogues. Equation [1] gives ideal a -parameters of 3.86 Å and 4.04 Å, respectively, for the perovskite blocks in these compounds. It may be expected that the Ca^{2+} compound would therefore be *more* stable than the Sr^{2+} , and involve *less* cation disorder, whereas the Ba^{2+} compound would be under much more strain and therefore require *increased* cation disorder. In fact, according to Ref. (14), the solid solubility limit for Ca^{2+} is $x = 0.1$, and for Ba^{2+} it is $x = 1.3$. The Ba^{2+} result is understandable in terms of the above argument but the Ca^{2+} result seems anomalous. In support of this argument, however, are our earlier results on the two-layer system $\text{Bi}_2\text{ANb}_2\text{O}_9$ ($A = \text{Ca}, \text{Sr}, \text{Ba}$), where cation disorder increases in the expected order, $\text{Ca} < \text{Sr} < \text{Ba}$ (8).

The possibility of disorder of Nb/Ti over the two available B sites (Fig. 1) must also be considered. This is unlikely to be influenced by ionic size arguments since the two are very similar. The X-ray refinements were found to be relatively insensitive to this distribution, but the enhanced contrast with neutrons made it possible to ascertain that a slight preference of Ti for the central site in the block occurs (Table 1). This site has a more symmetrical oxygen coordination, which is often more associated with $4d^0$ rather than $3d^0$ elements in perovskite B sites (17), due to the second-order Jahn–Teller effect. However, ionic charge effects may also play a role.

(ii) $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$

The most important parameters to be obtained from this study are the refined occupancies of the M/A sites, obtained using the split-atom model described earlier. These are for M , 94(1)% Bi/6(1)% La and 79(1)% Bi/21(1)% La, and

for A , 56(1)% Bi/44(1)% La and 21(1)% Bi/79(1)% La, for $\text{Bi}_3\text{LaTi}_3\text{O}_{12}$ and $\text{Bi}_2\text{La}_2\text{Ti}_3\text{O}_{12}$, respectively. In order to understand the cation disorder in this system, an alternative argument needs to be applied. Since the ionic radii of Bi^{3+} and La^{3+} are very similar, it is more reasonable to ask why the perfectly *disordered* model $[\text{BiLaO}_2][\text{BiLaTi}_3\text{O}_{10}]$ is not observed. From [1] the ideal a -parameter for the $[\text{BiLaTi}_3\text{O}_{10}]$ block is 3.89 Å, again causing strain in the “smaller” fluorite block. However, La^{3+} in the $[\text{BiLaO}_2]$ unit would inevitably prefer to be more central than the Bi^{3+} position, by analogy with the Sr^{2+} case presented above (see also, for example the preference for La^{3+} to adopt the symmetrical *inner* cation site in the triple-fluorite-layer Sillen phase $\text{Bi}_2\text{LaO}_4\text{Cl}$ (18)). Bond valence arguments (19) suggest that the centralization would inevitably decrease the BVS of La^{3+} , thus resulting in an additional need for contraction of the ideal a -parameter of the $[\text{BiLaO}_2]$ unit, in order to satisfy the bonding requirements of La^{3+} . This acts to destabilize the $[\text{BiLaO}_2]$ disorder, resulting in a marked, but not complete, preference of La^{3+} for the A site of the perovskite block instead.

Interestingly, the inherent strain present in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_2\text{La}_2\text{Ti}_3\text{O}_{12}$ is relieved in different ways in the two systems—by octahedral tilting and lowering of symmetry in the case of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, and by cation disorder in the case of $\text{Bi}_2\text{La}_2\text{Ti}_3\text{O}_{12}$. We reason that the lowering of symmetry mechanism is preferable in BTO since this gives natural rise to a more unsymmetrical coordination environment for Bi^{3+} in the A site, whereas lowering of symmetry in a hypothetical ordered $[\text{Bi}_2\text{O}_2][\text{La}_2\text{Ti}_3\text{O}_{10}]$ is less preferred, and La^{3+} chooses to optimize its more regular environment via partial disorder, simultaneously allowing off-centering of Bi^{3+} in the perovskite block, with consequent relief of strain.

(iii) Summary of Related Work

The possibility of cation disorder between the M and A sites of the Aurivillius phases was first suggested by Smolenski (2) purely on the basis of the observation of a broader ferroelectric transition in $\text{Bi}_2\text{BaNb}_2\text{O}_9$ vs $\text{Bi}_2\text{SrNb}_2\text{O}_9$. The first direct experimental observation of this disordering was presented by Blake *et al.* (8). This was followed up by a detailed study by Ismunandar and Kennedy (9), who showed that although cation ordering of this type appears to be inherent in these systems, the precise degree of disorder may depend on the actual synthetic conditions employed. In none of these studies, involving cations without stereochemically active lone-pair effects, does the amount of substitution into the $[\text{M}_2\text{O}_2]$ layer rise above about 14%. However, in lone-pair systems, especially Pb^{2+} substitution, much higher occupancies of the $[\text{M}_2\text{O}_2]$ units have been reported. For example, Ismunandar *et al.*

have suggested (20), from anomalous X-ray powder diffraction studies, that quenched samples of $\text{Bi}_2\text{PbNb}_2\text{O}_9$ display almost statistical disorder of Bi/Pb over the M/A sites, and Millan *et al.* (6) have even suggested the existence of a complete solution $\text{Bi}_{2-x}\text{Pb}_x\text{SrNb}_2\text{O}_{9-x/2}$ ($0 < x < 2$). These authors have also explored the substitution of other lone-pair cations into the $[M_2O_2]$ units, and report solid solubility limits of $x = 1$ in $\text{Bi}_{2-x}\text{Sn}_x\text{Nb}_2\text{O}_9$ and $\text{Bi}_{2-x}\text{Sr}_x\text{Nb}_2\text{O}_{9-x/2}$ (7), and $x = 0.5$ in $\text{Bi}_{2-x}\text{Te}_x\text{Sr}_{1-x}\text{Na}_x\text{Nb}_2\text{O}_9$ (21). Rentschler has studied several Pb-doped two-layer and three-layer systems, and has suggested the possibility of La^{3+} occupation of the $[M_2O_2]$ units in the solid solution $\text{Bi}_{2-x}\text{Pb}_x\text{La}_2\text{Ti}_{3-x}\text{Nb}_x\text{O}_{12}$ (22); however, he did not consider the possibility of Sr^{2+} disorder in the corresponding system $\text{Bi}_2\text{Sr}_{2-x}\text{Pb}_x\text{TiNb}_2\text{O}_{12}$. In the two-layer system $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_{1-x}\text{Nd}_x\text{Nb}_2\text{O}_9$ (23) he suggested mixed occupancy of the M sites by Bi/Pb and of the A sites by Nd/Sr, based on a combination of X-ray powder diffraction and Nd L-III edge EXAFS.

CONCLUSIONS

In conclusion, the present work provides the most definitive evidence so far of the substitution of non-lone-pair cations into the $[M_2O_2]$ layers of the Aurivillius phases. This is shown to be a natural consequence of the requirements for size-matching of the fluorite-like $[M_2O_2]$ layers and the perovskite-like $[A_{n-1}B_nO_{3n+1}]$ layers. Rietveld analysis of X-ray powder diffraction data allows quantification of the degree of disorder in the system $\text{Bi}_{2-x}\text{Sr}_{2+x}\text{Ti}_{1-x}\text{Nb}_{2+x}\text{O}_{12}$, while the neutron diffraction results show clearly that splitting of the M sites in the $[M_2O_2]$ units occurs, leading to much more satisfactory (i.e., more “symmetrical”) bonding around Sr^{2+} in this site. Further studies by local structural techniques such as EXAFS may be useful in exploring the nature of this disorder in more detail.

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REFERENCES

1. B. Aurivillius, *Ark. Kemi* **1**, 499 (1949).
2. G. A. Smolenski, V. A. Isupov, and A. I. Agranovskaya, *Sov. Phys. Solid State (Engl. Transl.)* **3**, 651 (1953).
3. E. C. Subbarao, *J. Phys. Chem. Solids* **23**, 665 (1962).
4. C. A. Paz de Araujo, J. D. Cuchlaro, L. D. McMillan, M. C. Scott, and J. F. Scott, *Nature (London)* **374**, 627 (1995).
5. B. Frit and J. P. Mercurio, *J. Alloys Compd.* **188**, 27 (1992).
6. P. Millan, A. Castro, and J. B. Torrance, *Mater. Res. Bull.* **28**, 117 (1993).
7. P. Millan, A. Ramirez, and A. Castro, *J. Mater. Sci. Let.* **14**, 1657 (1995).
8. S. M. Blake, M. J. Falconer, M. McCreedy, and P. Lightfoot, *J. Mater. Chem.* **7**, 1609 (1997).
9. Ismunandar and B. J. Kennedy, *J. Mater. Chem.* **9**, 541 (1999).
10. A. D. Rae, J. G. Thompson, R. L. Withers, and A. C. Willis, *Acta Crystallogr., Sect. B* **47**, 174 (1991).
11. C. H. Hervoches and P. Lightfoot, *Chem. Mater.* **11**, 3359 (1999).
12. B. H. Park, B. S. Kang, S. D. Bu, T. W. Noh, J. Lee, and W. Jo, *Nature (London)* **401**, 682 (1999).
13. A. C. Larson and R. B. Von Dreele, Los Alamos National Laboratory Report No. LA-UR-86-748, 1987.
14. R. A. Armstrong and R. E. Newnham, *Mater. Res. Bull.* **7**, 1025 (1972).
15. S. M. Fray, C. J. Milne, and P. Lightfoot, *J. Solid State Chem.* **128**, 115 (1997).
16. R. D. Shannon, *Acta Crystallogr., Sect. A* **32**, 751 (1976).
17. N. S. P. Bhuvanesh and J. Gopalakrishnan, *J. Mater. Chem.* **7**, 2297 (1997).
18. C. J. Milne, P. Lightfoot, J. D. Jorgensen, and S. Short, *J. Mater. Chem.* **5**, 1419 (1995).
19. I. D. Brown, *Acta Crystallogr., Sect. B* **48**, 553 (1992).
20. Ismunandar, B. A. Hunter, and B. J. Kennedy, *Solid State Ionics* **112**, 281 (1998).
21. P. Duran-Martin, A. Castro, P. Millan, and B. Jimenez, *J. Mater. Res.* **13**, 2565 (1998).
22. T. Rentschler, *Mater. Res. Bull.* **32**, 351 (1997).
23. T. Rentschler, M. Karus, A. Wellm, and A. Reller, *Solid State Ionics* **90**, 49 (1996).