Cation Disorder in Pb-Doped $SrBi_2Nb_2O_9$

Brendan J. Kennedy*

Centre for Heavy Metals Research, School of Chemistry, F11, The University of Sydney,
Sydney NSW 2006, Australia

Brett A. Hunter

Australian Nuclear Science and Technology Organisation, Private Mail Bag 1,
Menai NSW 2234, Australia

Received April 12, 2001. Revised Manuscript Received September 4, 2001

Cation disorder in Pb_{1-x} $Sr_xBi_2Nb_2O_9$ has been studied using a combination of powder synchrotron X-ray and neutron diffraction methods. The oxides all adopt an orthorhombic structure, space group $A2_1am$ in which the A-type cations, Sr and Pb, are disordered over the Bi_2O_2 and perovskite layers. Although the Pb shows a marked preference for the Bi_2O_2 layers, relative to that of Sr, there are still appreciable amounts of Sr present in the Bi_2O_2 layers. This is discussed in terms of local bonding effects and bond valence sum analysis.

Introduction

$SrBi_2Ta_2O_9$-based ferroelectrics have superior fatigue and thin film conductivity properties to the commonly used lead−zirconium−titanium oxides; however, their fabrication requires higher temperatures and, the available data suggests, their electrical properties are very sensitive to the processing conditions.[1] They also have the significant advantage of not containing any lead. $SrBi_2Ta_2O_9$ (SBT) is an Aurivillius-type layered compound. Oxides of this type were first reported in 1949 when Aurivillius described the formation of a series of layered bismuth oxides of the general formula $Bi_2A_{m-1}B_mO_{3m+3}$ ($m = 1, 2, 3, 4$). These consist of α-PbO-type $[Bi_2O_2]^{2+}$ layers interwoven with ($m - 1$) perovskite-type layers having the composition $[A_{m-1}B_mO_{3m+1}]^{2-}$.[2] Shortly thereafter, Smolenski and Subbarao[3−5] identified these materials as promising ferroelectrics, prompting numerous studies during the 1960s and early 1970s on the preparation and electronic properties of these types of oxides. A large number of these early studies were the subject of the review by Subbarao[6] in 1973. In general Aurivillius-type oxides exhibit a great variability in the metal cation stoichiometry, thus presenting the potential for systematic control of their physical and electronic properties. The A-site cations include Ca, Sr, Ba, Pb, Bi, Na, rare-earth ions, or mixtures of these, while the octahedral B-site invariably contains small highly charged cations such as Ti^{4+}, Nb^{5+}, Ta^{5+}, $W^{6+,}$ or Mo^{6+}.

The $m = 2$ oxides, with the general formula $ABi_2M_2O_9$ (A = Sr or Pb; M = Nb or Ta), show small distortions from the archetypal tetragonal structure, resulting in orthorhombic symmetry.[7,8] The orthorhombic structures can described by space group $A2_1am$, with a and $b \approx 5$ Å and $c \approx 25$ Å.

In comparison with the ease of substitution into the perovskite layers, it was long believed that it was not possible to substitute other cations into the Bi_2O_2 layers without destroying the structure.[3,9] The Bi_2O_2 layers are comprised of a square planar net of oxygen anions with the Bi^{3+} cations alternatively above and below the plane and can be described as forming caps of BiO_4 square pyramids. The asymmetric coordination environment of the Bi cations is due to the stereochemical activity of the $6s^2$ lone pair electrons. It is this distorted environment that is thought to limit cation substitution into the Bi_2O_2 layers.[9] Recently, it has been established that other cations with sterochemically active lone pair electrons such as Sn^{2+}, Sb^{3+}, Pb^{2+}, or Te^{4+} can be introduced, at least in part, into the Bi_2O_2 layers.[10−15]

The first direct experimental evidence for thermally induced disorder in the distribution of the Pb^{2+} and Bi^{3+} ions over the two different sites in $PbBi_2Nb_2O_9$ was provided by Srikanth, Subbarao, and co-workers using powder neutron diffraction methods.[16] As noted by these authors, the small difference in the neutron scattering lengths of Pb and Bi limits the precision of their

---

* To whom correspondence should be addressed. Phone: 61-2-9351-2742. Fax: 61-2−9351 3329. E-mail: Kennedyb@chem.usyd.edu.au.

(1) Scott, J. F.; Paz de Araujo, C. A.; Scott, M. C.; Huffman, M. *Mater. Res. Soc. Bull.* **1996**, *21*, 33.

(2) Aurivilllius, B. *Ark. Kemi* **1949**, *1*, 463.

(3) Subbarao, E. C. *J. Phys. Chem. Solids* **1962**, *23*, 665.

(4) Subbarao, E. C. *J. Am. Ceram. Soc.* **1962**, *45*, 166.

(5) Smolenski, G. A.; Isupov, V. A.; Agranovskaya, A. I. *Sov. Phys. Solid State* **1959**, *3*, 651.

(6) Subbarao, E. C. *Ferroelectrics* **1973**, *5*, 267.

(7) Rae, A. D.; Thompson, J. G.; Whithers, R. L. *Acta Crystallogr., Sect B* **1992**, *48*, 418.

(8) Shimakawa, Y.; Kubo, Y.; Nakagawa, Y.; Kamiyama, T.; Asano, H.; Izumi, F. *Appl. Phys. Lett.* **1999**, *74*, 1904.

(9) Newnham, R. E.; Wolfe, R. W.; Dorrian, J. F. *Mater. Res. Bull.* **1971**, *6*, 1029.

(10) Rentschler, T. *Mater. Res. Bull.* **1997**, *32*, 351.

(11) Rentschler, T.; Karus, M.; Wellm, A.; Reller, A. *Solid State Ionics* **1996**, *90*, 49.

(12) Millan, P.; Castro, A.; Torrance, J. B. *Mater. Res. Bull.* **1993**, *28*, 117.

(13) Millan, P.; Ramirez, A.; Castro, A. *J. Mater. Sci. Lett.* **1995**, *14*, 1657.

(14) Castro, A.; Millan, P.; Martinez-Lope, M. J.; Torrance, J. B. *Solid State Ionics* **1993**, 63−65, 897.

(15) Castro, A.; Millan, P.; Enjalbert, R. *Mater. Res. Bull.* **1995**, *30*, 871.

(16) Srikanth, V.; Idink, H.; White, W. B.; Subbarao, E. C.; Rajagopal, H.; Sequeira, A. *Acta Crystallogr., Sect. B* **1996**, *52*, 432.

10.1021/cm010327e CCC: $20.00 © 2001 American Chemical Society
Published on Web 11/21/2001

determination.[16] To overcome this limitation, we subsequently used anomalous dispersion X-ray diffraction methods to accurately quantify the extent of disorder.[17] A near statistical disorder of Pb and Bi over the two sites was observed.

Recent structural studies on $ABi_2Nb_2O_9$, (A = Sr, Ba) gave contradictory results.[18,19] In accordance with the argument that the presence of lone pair electrons is essential for the substitution into the $[Bi_2O_2]^{2+}$ layers, Ismunandar et al. reported that there was no cation disorder in these oxides.[18] Conversely, Blake and coworkers reported a slight disorder in these systems,[19] and they postulated that the differences observed between the two studies may have resulted from the differing annealing conditions used. Subsequently, Ismunandar confirmed the presence of Sr or Ba/Bi disorder and demonstrated that the extent of this is dependent on the thermal history of the sample.[20] The extent of Sr or Ba/Bi disorder was markedly less than the amount of Pb/Bi disorder found in $PbBi_2Nb_2O_9$, demonstrating the importance of the lone pair electrons.

In the present work we further examine the tendency for cation disorder in the types of Aurivillius-type oxides. In particular, we wish to investigate how important the lone pair is in promoting disorder in competition with other divalent cations. To do this, we have prepared and structurally characterized a series of oxides of the type $Pb_{1-x}Sr_xBi_2Nb_2O_9$ ($0 \leq x \leq 1$). Obviously, conventional X-ray methods cannot be used to study disorder between isoelectronic ions such as Pb^{2+} and Bi^{3+}; however, anomalous dispersion diffraction methods are capable of distinguishing between these two elements. To quantify the cation disorder in $Pb_{1-x}Sr_xBi_2Nb_2O_9$, we have carried out detailed structural studies of selected compositions using a combination of powder neutron and anomalous dispersion synchrotron X-ray diffraction methods. This allows for an unambiguous determination of site disorder in these complex oxides.

Experimental Section

Samples of $Pb_{1-x}Sr_xBi_2Nb_2O_9$ ($x = 0.875$, 0.750, 0.625, 0.5, 0.375, 0.250, and 0.125) were prepared by the solid-state reaction of $SrCO_3$ (Aldrich, 99.5%), PbO (Aldrich, 99.98%), Bi_2O_3 (Aldrich, 99.999%), and Nb_2O_5 (Aldrich, 99.9%), using a method similar to that employed for $PbBi_2Nb_2O_9$.[16] The intimately mixed materials were heated in air at 700 °C for 12 h, 800 °C for 24 h, 900 °C for 24 h, and finally 1000 °C for 24 h in a muffle furnace. The samples were slowly cooled (5 K/min) to 600 °C, at which time they were removed from the furnace. EDAX measurements showed no significant variation from the expected stiochiometries. Synchrotron powder X-ray diffraction data were collected using the Debye Scherrer camera at the Australian National Beamline Facility, Photon Factory, Japan.[21] Samples were loaded into 0.3-mm glass capillaries that were rotated during the measurements. All measurements were performed under vacuum to minimize air scatter. This diffractometer is equipped with an automatic sample changer capable of holding eight samples. The BAS2000 Fuji image plates are 20 × 40 cm and each covers 40° in 2θ. A thin strip ≈0.5-cm wide is used to record each diffraction pattern, and by translating the image plate behind a Weissenberg screen, it is possible to collect around 20 diffraction patterns on each image plate. In this work we placed eight samples in the sample changer and collected data at two wavelengths for each sample before replacing the image plates. By repeating this process, diffraction patterns were recorded at eight wavelengths ca. 0.800, 0.898, 0.917, 0.922, 0.927, 0.947, 0.952, and 0.957 Å, for each sample. These wavelengths were chosen to provide a maximum difference in the scattering factors for Bi^{3+} and Pb^{2+} as a result of the enhancement of the complex scattering factor near an appropriate absorption edge. The maximum variation in f' and f'' were for Bi 6.9 and 6.0 eV and for Pb 7.7 and 6.4 eV.

The powder neutron diffraction patterns were recorded in 0.05° steps in the range $0° < 2\theta < 154°$ using neutrons of wavelength 1.883 Å on the high-resolution powder diffractometer (HRPD)[22] at the HIFAR reactor operated by the Australian Nuclear Science and Technology Organisation. In each case the lightly ground sample was contained in a thin-walled 12-mm-diameter vanadium can that was slowly rotated during the measurements to minimize the effects of preferred orientation.

The structural refinements were performed using the Rietveld method[23] with the PC version of the program LHPM.[24] The background was defined by a fourth-order polynomial in 2θ and was refined simultaneously with the profile parameters. A pseudo-Voigt function was chosen to generate the profiles. The values of f' and f'' used in the refinements were calculated using the program FPRIME.[25]

Structure Refinement

The powder X-ray diffraction patterns demonstrated that all samples were single-phase Aurivillius-type oxides. All the peaks could be indexed in space group $A2_1am$. We previously observed that insensitivity of the neutron data to cation disorder limits the precision of the refined site occupancies when using combined X-ray and neutron diffraction data sets.[17] Consequently, the structures were sequentially refined using the X-ray and neutron diffraction data sets rather than as a combined refinement. Initially, the structures were refined using powder neutron diffraction data to obtain accurate positions of the oxygen atoms. At the outset, it was assumed that the cations were fully ordered; that is, the Sr and Pb only occupy the perovskite A-type sites. The background, cell, profile, positional, and isotropic displacement parameters of all atoms were refined. It was assumed that the Sr and Pb cations occupy identical positions in the lattice and that the atomic displacements of the atoms on equivalent sites were equal. Once a satisfactory structural model was obtained from the powder neutron diffraction studies, it was used as a starting point to refine the cation disorder using the synchrotron X-ray diffraction data.

For the X-ray measurements the initial wavelength (0.79993 Å) was determined using a Si 640b standard. All other wavelengths were obtained by refinement. The

---

(17) Ismunandar; Kennedy, B. J.; Hunter, B. A. *Solid State Ionics.* **1998**, *112*, 281.

(18) Ismunandar; Kennedy, B. J.; Gunawan, Marsongkohadi *J. Solid State Chem.* **1996**, *126*, 135.

(19) Blake, S. M.; Falconer, M. J.; McCreedy, M.; Lightfoot, P. *J. Mater. Chem.* **1997**, *7*, 1609.

(20) Ismunandar; Kennedy, B. J. *J. Mater. Chem.* **1999**, *9*, 541.

(21) Sabine, T. M.; Kennedy, B. J.; Garrett, R. F.; Foran, G. J.; Cookson, D. J. *J. Appl. Crystallogr.* **1995**, *28*, 513.

(22) Howard, C. J.; Ball, C. J.; Davis, R. L.; Elcombe, M. M. *Aust. J. Phys.* **1983**, *36*, 507.

(23) Rietveld, H. M. *J. Appl. Crystallogr.* **1969**, *2*, 65.

(24) Hill, R. J.; Howard, C. J. *Australian Atomic Energy Commission Report No. M112*; AAEC(now ANSTO) Lucas Heights Research Laboratories, Sydney, Australia, 1986.

(25) Cromer, D. T.; Liberman, D. A. *Acta Crystallogr., Sect B* **1981**, *47*, 267.

Table 1. Cell Parameters, Cation Occupancies, and Measures of Fit for $Pb_{1-x}Sr_xBi_2Nb_2O_9$; the 4a Sites Are within the Perovskite-like Layers and the 8b Sites Form the Bi_2O_2 Layers

x	0.125	0.250	0.375	0.500	0.625	0.750	0.875
a (Å)	5.5073(2)	5.5066(2)	5.5067(2)	5.5074(1)	5.5140(1)	5.5222(1)	5.5136(1)
b (Å)	5.4936(2)	5.4966(2)	5.4985(2)	5.5034(1)	5.5109(1)	5.5191(1)	5.5110(1)
c (Å)	25.5095(8)	25.4567(7)	25.3852(7)	25.3326(5)	25.28779(5)	25.24681(5)	25.1380(5)
V (Å^3)	771.78(4)	770.52(4)	768.64(4)	767.81(3)	768.43(3)	769.46(3)	763.84(3)
N Sr (4a)	0.14(1)	0.18(1)	0.28(1)	0.38(1)	0.55(1)	0.62(1)	0.76(1)
N Pb (4a)	0.26(2)	0.23(2)	0.16(3)	0.13(2)	0.12(2)	0.05(2)	−0.01(2)
N Bi (4a)	0.60(2)	0.59(2)	0.57(3)	0.48(2)	0.33(2)	0.33(2)	0.25(2)
N Sr (8b)	−0.01(1)	0.03(1)	0.05(1)	0.06(1)	0.04(1)	0.07(1)	0.05(1)
N Pb (8b)	0.28(2)	0.26(2)	0.23(3)	0.18(2)	0.13(2)	0.10(2)	0.08(2)
N Bi (8b)	0.73(2)	0.71(2)	0.72(3)	0.76(2)	0.84(2)	0.83(2)	0.87(2)
R_p (%)	5.02	5.62	6.04	5.44	5.81	6.87	6.06
R_{wp} (%)	6.85	7.80	8.01	8.03	8.03	9.38	8.02

Table 2. Positional and Isotropic Atomic Displacements Parameters (Å^3) for $Pb_{1-x}Sr_xBi_2Nb_2O_9$ in Space Group $A2_1am$[a]

x	0.125	0.250	0.375	0.500	0.625	0.750	0.875
Pb/Sr y	0.2390(9)	0.2400(10)	0.2391(12)	0.2369(11)	0.2367(8)	0.2368(8)	0.2379(7)
Pb/Sr B_{iso}	0.40(3)	1.22(6)	1.52(6)	1.09(4)	1.69(5)	2.62(6)	0.12(4)
Bi x	0.4764(4)	0.4806(9)	0.4963(10)	0.4978(7)	0.4992(6)	0.5007(7)	0.5055(6)
y	0.7410(5)	0.7401(5)	0.7400(6)	0.7400(5)	0.7379(3)	0.7357(3)	0.7343(3)
z	0.2013(3)	0.2011(1)	0.2010(1)	0.2010(1)	0.2011(1)	0.2013(1)	0.2012(1)
Bi B_{iso}	0.23(2)	0.39(3)	0.45(3)	0.52(2)	1.63(3)	1.95(3)	0.41(2)
Nb x	0.4697(4)	0.4717(7)	0.4732(8)	0.4708(6)	0.4732(7)	0.4686(7)	0.4767(6)
y	0.7544(7)	0.7567(9)	0.7575(10)	0.7558(7)	0.7522(6)	0.7511(6)	0.7503(5)
z	0.4121(4)	0.4128(1)	0.4133(1)	0.4134(1)	0.4132(1)	0.4136(1)	0.4136(1)
Nb U_{iso}	−0.37(3)	0.16(3)	0.16(4)	−0.01(3)	0.78(3)	1.14(3)	0.62(2)
O(1) x	0.444(3)	0.437(3)	0.443(3)	0.459(4)	0.458(3)	0.459(3)	0.4580(3)
y	0.207(3)	0.203(3)	0.201(2)	0.202(3)	0.199(3)	0.200(2)	0.202(2)
B_{iso}	2.3(2)	2.0(2)	1.0(2)	1.8(2)	1.7(2)	2.0(2)	1.7(2)
O(2) x	0.446(2)	0.443(2)	0.457(2)	0.459(3)	0.456(2)	0.463(3)	0.464(3)
y	0.787(2)	0.783(2)	0.786(2)	0.792(2)	0.791(2)	0.792(1)	0.798(2)
z	0.3411 (2)	0.3406(2)	0.3404(2)	0.3407(2)	0.3411(2)	0.3411(2)	0.3147(2)
B_{iso}	1.2(1)	1.6(1)	2.2(2)	1.7(1)	1.5(2)	1.6(1)	1.3(1)
O(3) x	0.713(3)	0.718(3)	0.731(3)	0.727(3)	0.722(3)	0.733(2)	0.734(2)
y	−0.001(1)	−0.002(1)	−0.06(1)	−0.005(1)	−0.004(1)	−0.02(1)	−0.001(1)
B_{iso}	1.0(1)	0.9(1)	1.2(2)	1.0(1)	0.9(1)	0.8(1)	0.9(1)
O(4) x	0.664(2)	0.663(2)	0.672(2)	0.679(3)	0.676(3)	0.676(2)	0.673(2)
y	0.961(2)	0.961(2)	0.960(2)	0.957(2)	0.963(2)	0.962(1)	0.964(2)
z	0.0826(3)	0.0829(3)	0.0832(2)	0.0833(1)	0.0830(1)	0.0833(2)	0.0835(2)
B_{iso}	1.7(2)	2.1(2)	1.7(2)	1.5(2)	1.4(2)	1.6(2)	1.0(2)
O(5) x	0.727(2)	0.729(2)	0.736(3)	0.739(3)	0.738(3)	0.737(3)	0.735(3)
y	0.972(1)	0.971(1)	0.970(1)	0.971(2)	0.972(2)	0.976(1)	0.974(1)
z	0.5720(2)	0.5715(2)	0.5713(2)	0.5704(3)	0.5699(3)	0.5701(2)	0.5704(2)
B_{iso}	1.4(1)	1.3(1)	1.3(1)	1.6(2)	1.3(2)	1.2(1)	0.91(1)

[a] The atoms have the following sites: Pb/Sr on 4a (0,y,0), Bi on 8b (x,y,z), Nb on 8b (x,y,z), O(1) on 4a (x,y,0), O(2) on 8b (x,y,z), O(3) on 8b (x,y,0.2500), O(4) on 8b (x,y,z), and O(5) on 8b (x,y,z).

structures were refined using data sets collected at eight wavelengths. At this stage of the refinements the anions were placed according to the results from the neutron diffraction studies and the positions of these were not further refined. The atomic displacement parameters of the oxygen atoms were refined to model any small differences between the nuclear and atomic (electron cloud) distributions. In modeling of the disorder of Pb, Bi, and Sr, the occupancies of both sites were constrained so that both were fully occupied and that the stoichiometry of the compound was maintained. After several cycles the validity of the model was confirmed using the neutron diffraction data. The oxygen positional parameters were then updated before the structural refinements were completed using the X-ray diffraction data. Values of the cell parameters and various measures of fit from the refinements are listed in Table 1. The positional and atomic displacement parameters are listed in Table 2. A view of the orthorhombic structure is given in Figure 1 and an example of a refinement is shown in Figure 2.

Discussion

The lattice parameters for the series of compounds $Pb_{1-x}Sr_xBi_2Nb_2O_9$ obtained in the present work are shown in Figure 3, together with values obtained previously for the two end members $PbBi_2Nb_2O_9$[16] and $SrBi_2Nb_2O_9$.[19] Considering the c axis, we observe that replacement of Pb^{2+} (ionic radii 1.43 Å) with the smaller Sr^{2+} ion (1.40 Å) results in the expected progressive reduction in the value of the c axis. However, examination of the variation in the a and b axes reveals that these are approximately independent of the Pb:Sr ratio at low Sr contents, $x < 0.4$, and at higher Pb contents the a and b parameters actually increase. Given the similarity of the size of the Pb^{2+} and Sr^{2+} cations, the insensitivity of the a and b parameters at low substitution levels is not surprising; however, their increase at higher Sr^{2+} is unexpected. Although we have quoted illustrative ionic radii for Pb^{2+} and Sr^{2+}, those for eight-coordinate metal oxides,[26] it is reasonable to assume that the size of Pb^{2+} will always be larger that that of

---

(26) Shannon, R. D. *Acta Crystallogr., Sect A* **1976**, *32*, 751.

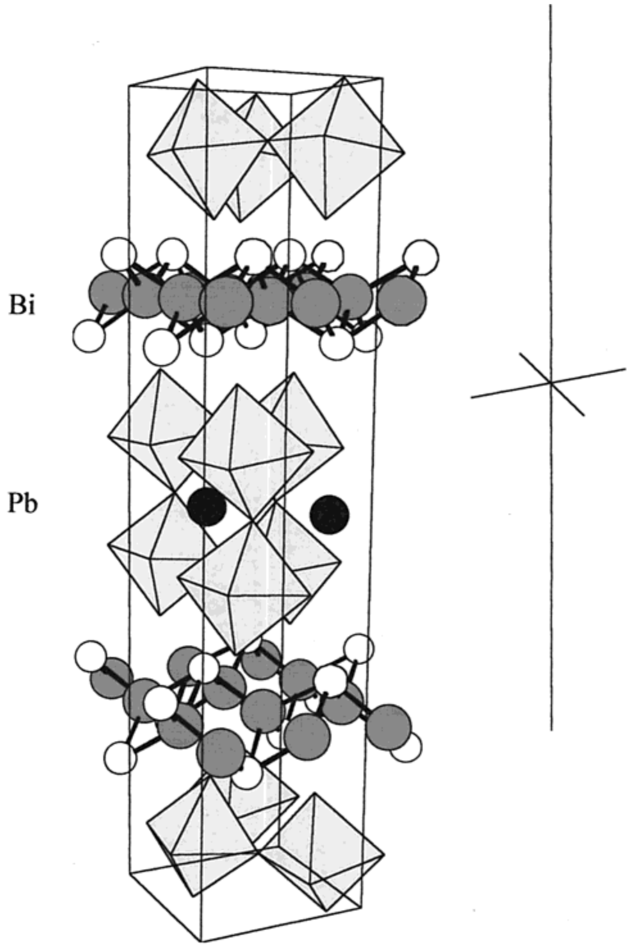

Figure 1. Representation of the orthorhombic cell for $Pb_{1-x}Sr_xBi_2Nb_2O_9$. The Nb atoms are at the center of the octahedra.

Sr^{2+} in a similar geometry. Likewise, Bi^{3+} (ionic radii = 1.31 Å) will always be smaller than either Pb^{2+} or Sr^{2+}. The observed expansion in the *a* and *b* parameters upon replacing Pb^{2+} with Sr^{2+} in $Pb_{1-x}Sr_xBi_2Nb_2O_9$ suggests the site of replacement—that is, the extent of disorder—is structurally important.

The variations in site occupancies are illustrated in Figure 4. This clearly illustrates the Bi^{3+} is found in both the perovskite-type A sites and the Bi_2O_2 layers. Conversely, Pb^{2+} and/or Sr^{2+} are also found in these two sites. The presence of Pb^{2+} in the oxide inhibits the uptake of Sr^{2+} into the Bi_2O_2 layers but only at the lowest Sr content studies does it totally inhibit it. The amount of Sr in the Bi_2O_2 layers increases as the total amount of Sr present in the oxides is increased, although this is not a linear effect, the largest effect being at low Sr contents. In $Pb_{0.125}Sr_{0.875}Bi_2Nb_2O_9$ we do not find any Pb^{2+} in the perovskite-type A sites; the small amount of Pb present is preferentially present in the Bi_2O_2 layer. At higher levels both Pb and Sr are found in both sites. This is contrary to the simple expectation that the $6s^2$ lone pair electrons in Pb^{2+} are the only contributing factor in the observed cation disorder. While this result demonstrates that the presence of lone pair electrons are not the dominating factor as suggested,[10-15] the occupancy of Pb^{2+} and Bi^{3+} in the Bi_2O_2 layers are clearly mirror images of each other at high Pb contents and demonstrates the competition between Pb^{2+} and Bi^{3+} for these sites.

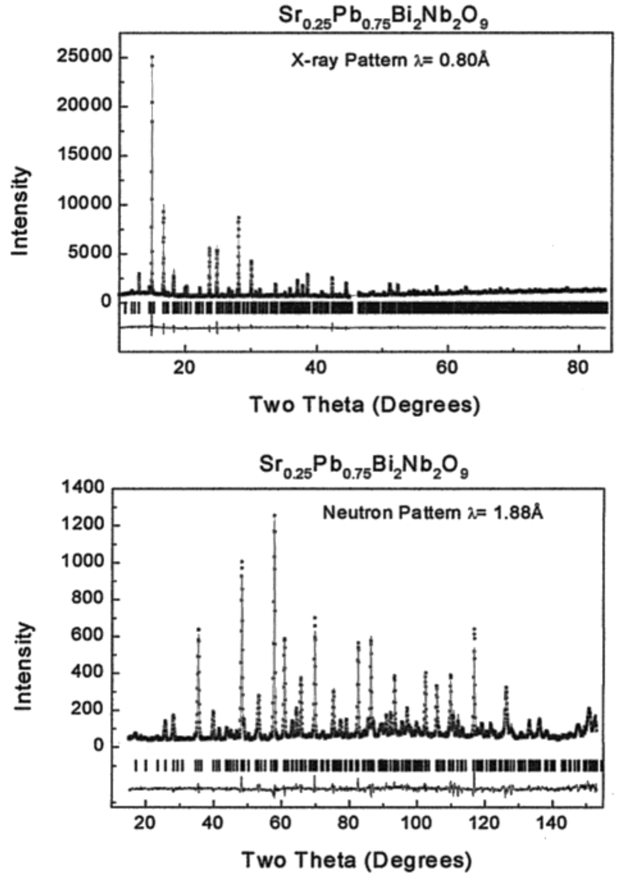

Figure 2. Rietveld fit for synchrotron X-ray and neutron powder diffraction data of $Sr_{0.25}Pb_{0.75}Bi_2Nb_2O_9$.

Reconsidering now the lattice parameters then, we observe that the variation in the amount of Bi^{3+} in the Bi_2O_2 sites mirrors that of the *a*- and *b*-lattice parameters. It appears that while the *c* parameter is dependent on the bulk composition it is insensitive to the site occupancies, whereas the *a* and *b* parameters are sensitive to the amount of Bi^{3+} in the perovskite-type A sites. The formation of the orthorhombic cell in these compounds is a result of the A-type cation being too small for the holes in the perovskite layers and this causes a tilting of the MO_6 octahedra. When large amounts of Bi^{3+} are present in the perovskite layer, the lattice is contracted in the *ab* plane, and as the amount of Bi^{3+} in these sites decreases, the contracting force is removed, resulting in the observed expansion of the *a* and *b* parameters. At the same time the contraction in the *c* axis is assisted by the reduction in the attractive electrostatic forces between the $[Bi_2O_2]^{2+}$ and $[ANb_2O_7]^{2-}$ layers due to the lower net charge in these resulting from cation disorder. Hervoches and Lightfoot[29] have suggested that the tilting in the Aurivillius-type compounds is also driven by a mismatch in the relative sizes of the $[Bi_2O_2]^{2+}$ and $[ANb_2O_7]^{2-}$ layers; the tilting effectively reduces the width of the perovskite blocks in the *ab* plane. The tilts increase as the amount of the smaller Bi^{3+} ions in the perovskite layers increases;

---

(27) Garnier, P.; Moreau, J.; Gavari, J. R. *Mater. Res. Bull.* **1990**, *25*, 979.

(28) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr., Sect B* **1991**, *47*, 192.

(29) Hercoches, C. H.; Lightfoot, P. *J. Solid State Chem.* **2000**, *153*, 66.

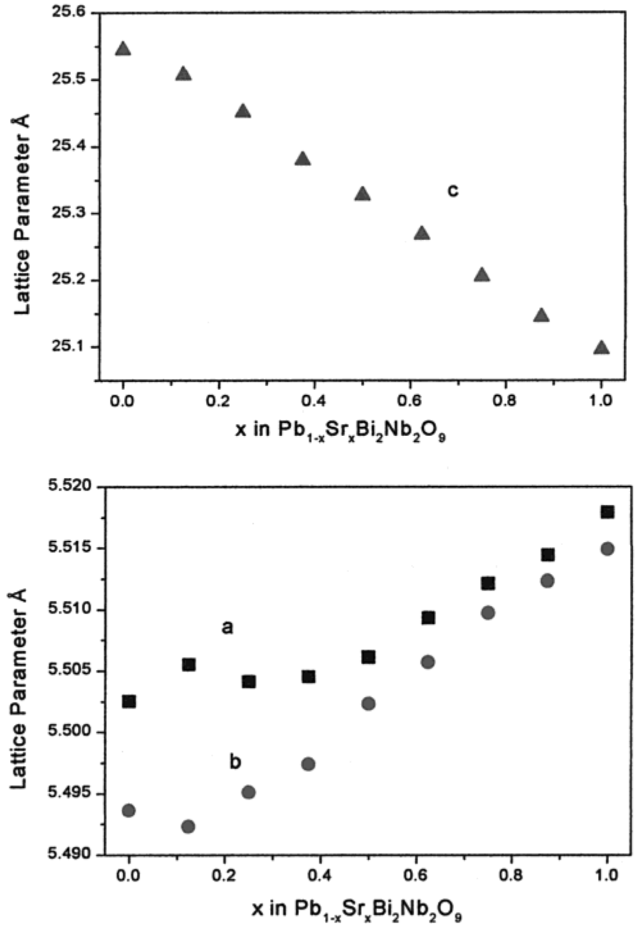

Figure 3. Variations in the lattice parameters for the series of oxides $Pb_{1-x}Sr_xBi_2Nb_2O_9$. The estimated standard deviations are smaller than the size of the symbols.

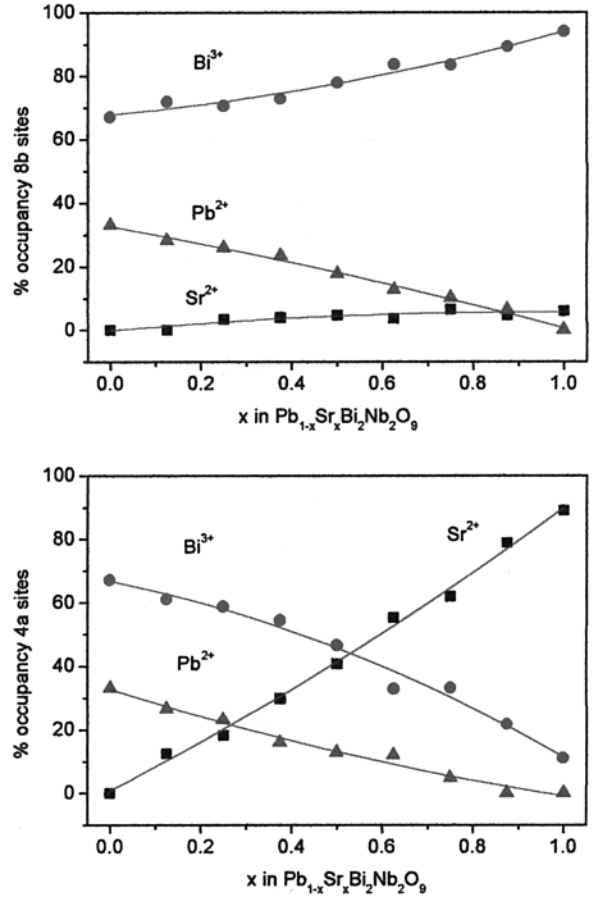

Figure 4. Variations in the site occupancies in the series of oxides $Pb_{1-x}Sr_xBi_2Nb_2O_9$, obtained from refinements using anomalous dispersion diffraction methods for (a) the 8b or Bi_2O_2 sites and (b) the 4a or perovskite-like ANb_2O_7 layers.

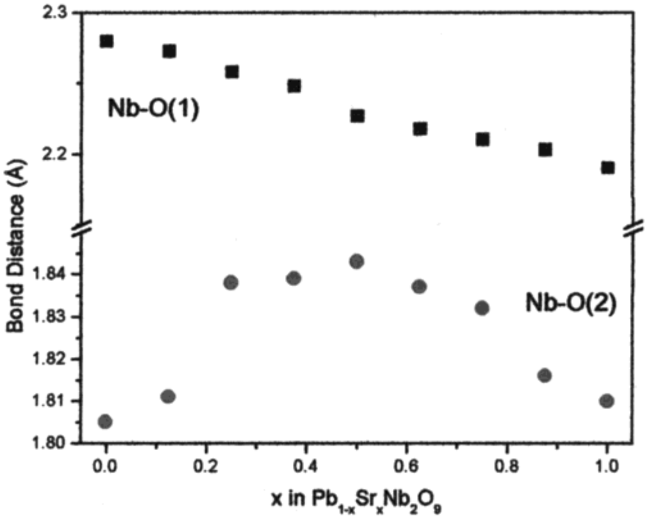

Figure 5. Variation of the Nb−O(1) and Nb−O(2) bond distance in the series of oxides. O(1) is the oxygen joining the two NbO_6 octahedra along the *c* axis while O(2) caps these octahedra and interacts with the Bi_2O_2 layers.

although the magnitude of this is small, the Nb−O−Nb angle changes by <1° over the series.

Considering now the influence of Pb doping has on the local geometries, we find that the average Nb−O distance is effectively constant across the series, increasing from 1.996(11) Å in $x = 0.125$ to 2.007(9) Å in $x = 0.875$. The Nb cation does not sit in the center of the NbO_6 polyhedra; rather, it is displaced ≈0.12 Å toward the $[Bi_2O_2]^{2+}$ layers. That is, it has one long Nb−O^1 bond, ≈2.20 Å, and one short Nb−O^2 bond, ≈1.82 Å. This long bond shows a small increase as the Sr content is increased, whereas the short Nb−O^2 bond length is approximately constant across the series; these are illustrated in Figure 5. There is no discernible change in the Bi−O^2 distances across the series.

The Bi is bonded to four oxygen atoms in a square pyramidal geometry similar to that found in α-PbO_2.[27] Here, the four strongly bonded oxygen atoms (Bi−O distance < 2.45 Å) can be viewed as forming the base and the Bi cation the apex of a pyramid. In addition to these short bonds there are four longer contacts, >2.65 Å, from oxygen atoms in the perovskite layers. Considering both short and long distances, the Bi coordination can be viewed as a distorted square antiprism. The $6s^2$ lone pair electrons (E) are directed toward the perovskite layers and can be considered to form the fifth vertex of a BiO_4E pyramid. There is a small contraction in the average of the four short Bi−O distances as the amount of Pb is decreased from $x = 0.125$ (2.317 Å) to $x = 0.500$ (2.307 Å). At still lower Pb contents the average distance increases slightly to 2.309 Å in $x = 0.875$. The decreasing amount of the larger divalent cations in these sites initially offsets the effect of the contraction in the *c* axis over the series.

One is now left to ponder the question why should Sr^{2+} be able to successfully compete with Pb^{2+} in occupying the Bi_2O_2 layers? It is clear that the presence of lone pair electrons on the A-type cation is a contributing factor but this is not the only factor. A second contributing factor is the overbonding of the A-type cations.[18,19] Valence bond sum[28] calculations give values of $\approx$2.5 for this site. This suggests the site is too small for the A-type cation and this strain is relieved by both distortion of the NbO_6 octahedra and partially replacing the larger A^{2+} cations with Bi^{3+}. At the same time the Bi^{3+} site is underbonded (VBS $\sim$ 2.7) and substitution of Pb/Sr into the Bi_2O_2 layer reduces this. Given the size difference between Pb^{2+} and Sr^{2+} is minimal, these two cations are equally capable of correcting these local valence inequalities. The suggestion that the relative size of the cations is critical in determining disorder is supported by the work of Blake et al.[19] where they reported disorder in the series $ABi_2Nb_2O_9$ (A = Ca, Sr, Ba) to increase down the group, that is, as the cation becomes larger. This change in size also acts to change the tilt of the NbO_6 octahedra, further influencing the degree of disorder. It remains to be seen if it is possible to alter the relative nature of the disorder in the Pb-containing systems by using a different cation. That is, will the larger cation, Ba^{2+}, more effectively compete with Pb to occupy the Bi_2O_2 layers so that no lead is found in the Bi_2O_2 layers or conversely will using a smaller cation such as Ca^{2+} ensure all the Pb occupies the Bi_2O_2 layers.

Acknowledgment. This work has been supported by the Australian Research Council, The Australian Institute of Nuclear Science and Engineering, and the Australian Synchrotron Research Program. We acknowledge the assistance of Dr. Hester in the synchrotron diffraction experiments.

CM010327E