JOURNAL OF SOLID STATE CHEMISTRY **102**, 132–139 (1993)

Synthesis and Structure of $Ca_6Bi_6O_{15}$: Its Relationship to $Ca_4Bi_6O_{13}$

J. B. PARISE

Center for High Pressure Research and Department of Earth and Space Sciences, State University of New York, Stony Brook, New York 11794–2100*

C. C. TORARDI

Du Pont Central Research and Development, Experimental Station, Wilmington, Delaware 19880–0356

AND C. J. RAWN, R. S. ROTH, B. P. BURTON, AND A. SANTORO

National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Received February 28, 1992; in revised form June 11, 1992; accepted June 24, 1992

Single crystals and powdered samples of the bismuth(III) calcium oxide $Ca_6Bi_6O_{15}$ have been synthesized and studied using both X-ray and neutron diffractometry. The compound crystallizes in the space group $P\bar{1}$ with $Z = 2$. Cell parameters, obtained with the single-crystal X-ray diffractometer, were $a = 10.101(3)$, $b = 10.130(2)$, $c = 10.466(2)$ Å, and $\alpha = 116.86(1)$, $\beta = 107.18(2)$, $\gamma = 92.90(2)°$. As with other materials in the series M–Bi–O (M = Ca, Sr) studied thus far, at least some Bi is found in threefold coordination with oxygen; the remaining Bi are fourfold coordinated. The structure is related to that of $Ca_4Bi_6O_{13}$, which has been studied using neutron powder diffraction. Both compounds are composed of layers containing alternating Bi- and Ca-rich segments. These layers stack to form Bi-rich slabs containing tunnels accommodating the Bi $6s^2$ lone pairs.

Introduction

In previous publications (*1–6*), we described the synthesis and structure of the compounds $Ca_4Bi_6O_{13}$ and $Sr_2Bi_2O_5$, which both contain Bi in threefold coordination. This bonding environment for Bi is unusual in oxides, as evidenced by the lack of an ionic radius for 3-coordinated Bi^{3+} in Shannon's compilation of ionic sizes (*7*). However, recent evidence (*8*) that the Bi in the superconducting compounds in the system Sr–Bi–Ca–Cu–O is 3-coordinated suggests that this coordination for Bi is favored in compounds containing alkaline earths. Studies of the compounds in the systems M–Bi–O (M = Ca, Sr) have been undertaken in our laboratories to better understand the phase relationships, conditions of formation, and bonding and crystal chemical relationships between these materials. This paper represents part of this work. Previously (*4*) we showed that the compound reported by others as "$Ca_7Bi_6O_{16}$" is in fact $Ca_6Bi_6O_{15}$.

---

* The Center for High Pressure Research is an NSF-funded Science and Technology Center.

0022-4596/93 $5.00

TABLE I

SUMMARY OF X-RAY DIFFRACTION DATA FOR $Ca_6Bi_6O_{15}$

Space group	$P\bar{1}$
a, Å	10.101(3)
b, Å	10.130(2)
c, Å	10.466(2)
α, deg	116.86(1)
β, deg	107.18(2)
γ, deg	92.90(2)
Temperature, °C	20
Volume, $Å^3$	891.2
Z	2
Formula weight	1734.35
Calculated density, g/cm^3	6.462
μ(Mo), cm^{-1}	606.21
Diffractometer	Enraf–Nonius CAD4[b]
Radiation	Mo$K\alpha$
Diffraction maxima collected	3229
Min and max 2θ, deg	4.7, 60.0
Max $\|h\|$, $\|k\|$, $\|l\|$	14, 14, 14
Data octants	$+++$, $-++$, $+-+$, $--+$
Scan method	ω
Absorption method	DIFABS[a]
Transmission factors, range	0.005–0.02
Number of unique data ($I > 3\sigma(I)$)	1721
Refinement method	Full-matrix least-squares on F
Anomalous dispersion	Bi and Ca
Weighting scheme	$\propto[\sigma^2(I) + 0.0008I^2]^{-1/2}$
Atoms refined	Anisotropic: Bi, Ca; isotropic: O
Parameters varied	170
Parameter/data ratio	10.12
R	0.044
R_w	0.043
Error of fit	0.98
Sec. extinction coefficient, mm	$0.071(3) \times 10^{-4}$

[a] CAD4 diffractometer, Enraf–Nonius Inc., The Netherlands. This equipment is identified by trade name in this article for complete specification of experimental procedures. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology.

[b] Reference (9).

Experimental

Synthesis and Characterization

The compounds were synthesized in a manner similar to that described earlier (*1*). The crystal growth experiments were carried out in a 1 : 1 KCl/NaCl flux which was slowly cooled at controlled rates. Pale yellow single crystals of $Ca_6Bi_6O_{15}$ were obtained with starting Ca : Bi ratios of both 1 : 1 and 7 : 6. The flux-to-charge ratios used were 80 : 20, 50 : 50, and 20 : 80. The batch from which a crystal was chosen for the single-crystal X-ray diffraction study was obtained from a charge with a Ca : Bi ratio of 7 : 6 and a flux-to-charge ratio of 80 : 20; this charge was cooled from 750 to 645°C at 1°C/hr and annealed at 645°C for 64 hr. The experiments were performed in sealed Pt tubes with an inside diameter of 4.6 mm and a wall thickness of 0.2 mm. Irregularly shaped fragments were obtained from this process and were examined using optical microscopy and precession photography. There was no evidence of twinning and the crystals were found to be triclinic, space group $P1$ or $P\bar{1}$. Subsequent refinement confirmed the adequacy of the choice of the centric space group and a ratio of 1 : 1 for Bi : Ca rather than the 7 : 6 reported previously (*4*). The X-ray powder diffraction pattern from a homogeneous powder sample of $Ca_6Bi_6O_{15}$ was completely indexed on the basis of a triclinic unit cell with a = 10.1222(7), b = 10.1466(6), c = 10.4833(7) Å, α = 116.912(5), β = 107.135(6), and γ = 92.939(6)°. Unlike the $Ca_4Bi_6O_{13}$ compound (*5*), single-phase powders of $Ca_6Bi_6O_{15}$ showed no evidence of second harmonic signal generation.

For the neutron diffractometry, 40-g specimens were synthesized by mixing reagent-grade $CaCO_3$ and Bi_2O_3 in an agate mortar and pestle with acetone and then pelletized by cold isostatic pressing. The $Ca_6Bi_6O_{15}$ compound was synthesized by mixing together $CaCO_3$ and $\frac{1}{2}Bi_2O_3$ in the stoichiometric molar ratio 1 : 1 and given successive overnight heat treatments in air on Au foil with intermediate grindings and repelletizing at 700°C, 800°C, 900°C twice, and 750°C. For the 750°C heat treatment, a loose pellet was pressed in a stainless-steel die. The $Ca_4Bi_6O_{13}$ compound was synthesized according to procedures given in Ref. (*5*).

Structure Determination and Refinement

$Ca_6Bi_6O_{15}$. Single-crystal X-ray diffraction data were collected on an Enraf–

TABLE II

FRACTIONAL COORDINATES[a] ($\times 10^4$) AND ISOTROPIC THERMAL[b] Parameters for $Ca_6Bi_6O_{15}$

Atom	x	y	z	B_{iso}
Bi(1)	586(2)	7923(2)	146(2)	1.0(1)′
Bi(2)	4308(2)	9805(2)	3068(2)	0.9(1)′
Bi(3)	9239(1)	8484(2)	6492(2)	0.9(1)′
Bi(4)	3130(1)	5725(2)	5332(2)	0.9(1)′
Bi(5)	5734(2)	6891(2)	3329(2)	1.1(1)′
Bi(6)	6650(2)	7474(2)	8173(2)	0.9(1)′
Ca(1)	3439(9)	9022(10)	8520(11)	1.6(3)′
Ca(2)	7892(8)	7996(9)	1869(9)	1.3(3)′
Ca(3)	1525(8)	8930(9)	4835(10)	1.1(3)′
Ca(4)	9379(8)	5221(10)	3369(10)	0.9(3)′
Ca(5)	5878(9)	3466(9)	250(11)	1.4(3)′
Ca(6)	8255(9)	4312(10)	8395(11)	1.3(3)′
O(1)	9254(25)	6220(28)	5772(30)	1.3(4)
O(2)	8395(27)	6871(30)	9615(33)	1.6(5)
O(3)	981(28)	8202(31)	2276(34)	1.9(5)
O(4)	1718(25)	6551(27)	4070(29)	1.1(4)
O(5)	9127(25)	8290(27)	4399(29)	1.2(4)
O(6)	6270(24)	6032(27)	1398(29)	1.0(4)
O(7)	1368(27)	9428(30)	7255(32)	1.6(5)
O(8)	3845(28)	7259(31)	2217(33)	1.8(5)
O(9)	5924(27)	8351(30)	9974(32)	1.8(5)
O(10)	887(28)	5741(31)	9195(32)	1.7(5)
O(11)	3420(26)	8996(29)	742(30)	1.3(4)
O(12)	4559(26)	7986(29)	6682(31)	1.4(4)
O(13)	2682(27)	6342(30)	7353(31)	1.6(5)
O(14)	6358(26)	9284(30)	3417(32)	1.7(5)
O(15)	5615(30)	5310(33)	7363(36)	2.5(6)

[a] Space group $P\bar{1}$.

[b] Metal atom sites (′) were refined with anisotropic thermal parameters; B_{eq} is given for these atoms.

TABLE III

ANISOTROPIC THERMAL PARAMETERS FOR $Ca_6Bi_6O_{15}$ ($Å^2 \times 10^3$), $\exp[-19.739(U_{11}h^2a^*a^* \ . \ . \ . \ +2(U_{12}hka^*b^* \ . \ . \ .))]$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi(1)	11.5(7)	15.0(8)	12.5(9)	4.2(6)	3.6(7)	6.6(7)
Bi(2)	10.7(7)	13.9(8)	11.6(8)	5.3(6)	4.4(7)	6.5(7)
Bi(3)	10.9(7)	11.4(7)	13.2(8)	1.7(5)	4.9(6)	6.1(7)
Bi(4)	10.2(7)	12.8(8)	12.1(9)	2.9(6)	3.9(7)	6.4(7)
Bi(5)	12.4(7)	15.0(8)	12.6(8)	5.3(6)	3.5(7)	6.9(7)
Bi(6)	11.5(8)	11.6(8)	13.0(9)	2.6(6)	4.9(7)	6.2(7)
Ca(1)	28(5)	15(4)	17(5)	11(4)	7(4)	7(4)
Ca(2)	20(4)	13(4)	7(4)	−2(3)	−2(3)	1(3)
Ca(3)	7(4)	8(4)	24(5)	−2(3)	0(3)	7(4)
Ca(4)	5(3)	16(4)	13(4)	−2(3)	0(3)	9(4)
Ca(5)	16(4)	6(4)	24(5)	2(2)	1(4)	5(4)
Ca(6)	17(4)	13(4)	19(4)	1(3)	5(4)	8(4)

TABLE IV

Selected Interatomic Distances (Å) and Bond Valence Sums[a] for $Ca_6Bi_6O_{15}$.

Bi(1)–O(2)a[b]	2.201(24)	Bi(4)–O(1)e	2.615(23)
Bi(1)–O(3)	2.025(29)	Bi(4)–O(4)	2.118(26)
Bi(1)–O(10)f	2.056(28)	Bi(4)–O(12)	2.205(25)
Bi(1)–O(11)	2.789(23)	Bi(4)–O(13)	2.114(25)
s(Bi1)[a]	2.69	Bi(4)–O(15)e	3.199(28)
		Bi(4)–O(15)	2.960(32)
Bi(2)–O(3)	3.347(25)	s(Bi4)[a]	2.69
Bi(2)–O(8)	2.285(27)		
Bi(2)–O(11)	2.058(27)	Bi(5)–O(5)	3.289(22)
Bi(2)–O(12)b	2.328(24)	Bi(5)–O(6)	2.059(24)
Bi(2)–O(14)	2.130(25)	Bi(5)–O(8)	2.070(28)
s(Bi2)[a]	2.72	Bi(5)–O(14)	2.427(26)
		Bi(5)–O(15)e	2.237(28)
		s(Bi5)[a]	2.81
Bi(3)–O(1)	2.067(25)		
Bi(3)–O(3)b	3.052(27)	Bi(6)–O(2)	2.265(29)
Bi(3)–O(5)	2.077(25)	Bi(6)–O(9)	2.061(25)
Bi(3)–O(7)h	2.064(25)	Bi(6)–O(11)b	3.238(26)
s(Bi3)[a]	2.71	Bi(6)–O(12)	2.462(27)
		Bi(6)–O(15)	2.045(28)
		s(Bi6)[a]	2.80
Ca(1)–O(7)	2.290(29)		
Ca(1)–O(9)j	2.328(28)	Ca(4)–O(1)	2.294(26)
Ca(1)–O(9)	2.815(30)	Ca(4)–O(1)m	2.346(27)
Ca(1)–O(11)k	2.343(28)	Ca(4)–O(4)h	2.386(23)
Ca(1)–O(11)b	3.348(24)	Ca(4)–O(5)	2.847(26)
Ca(1)–O(12)	2.380(25)	Ca(4)–O(10)e	2.326(28)
Ca(1)–O(13)	2.385(27)	Ca(4)–O(13)e	2.251(25)
Ca(1)–O(14)b	3.233(28)		
		Ca(5)–O(6)	2.270(26)
Ca(2)–O(2)f	2.336(28)	Ca(5)–O(6)d	2.576(27)
Ca(2)–O(3)h	3.004(27)	Ca(5)–O(8)d	2.454(28)
Ca(2)–O(5)	2.440(28)	Ca(5)–O(9)e	2.403(26)
Ca(2)–O(6)	2.279(23)	Ca(5)–O(10)e	3.139(26)
Ca(2)–O(7)b	2.334(27)	Ca(5)–O(11)d	2.465(27)
Ca(2)–O(9)f	2.531(30)	Ca(5)–O(13)e	2.413(30)
Ca(2)–O(14)	2.551(26)	Ca(5)–O(14)d	3.489(29)
		Ca(5)–O(15)e	3.109(29)
Ca(3)–O(3)	2.307(30)		
Ca(3)–O(4)	2.210(26)	Ca(6)–O(2)	2.288(29)
Ca(3)–O(5)b	2.733(26)	Ca(6)–O(3)e	2.545(29)
Ca(3)–O(5)c	2.328(23)	Ca(6)–O(4)e	2.330(26)
Ca(3)–O(7)	2.406(27)	Ca(6)–O(8)e	2.319(26)
Ca(3)–O(12)	3.537(28)	Ca(6)–O(10)o	2.439(30)
Ca(3)–O(14)b	2.345(27)	Ca(6)–O(10)h	2.658(26)
		Ca(6)–O(15)	2.976(32)

---

[a] Bond valence sums calculated using the expression $s = (R/2.01)^{-5}$ for Bi^{3+} [see Ref. (*16*)].

[b] Symmetry operation codes: (a) $-1 + X, Y, -1 + Z$; (b) $1 - X, 2 - Y, 1 - Z$; (c) $-1 + X, Y, Z$; (d) $1 - X, 1 - Y, -Z$; (e) $1 - X, 1 - Y, 1 - Z$; (f) $X, Y, -1 + Z$; (g) $2 - X, 2 - Y, 1 - Z$; (h) $1 + X, Y, Z$; (i) $1 + X, Y, 1 + Z$; (j) $1 - X, 2 - Y, 2 - Z$; (k) $X, Y, 1 + Z$; (l) $-X, 2 - Y, 1 - Z$; (m) $2 - X, 1 - Y, 1 - Z$; (n) $2 - X, 1 - Y, 2 - Z$; (o) $1 - X, 1 - Y, 2 - Z$.

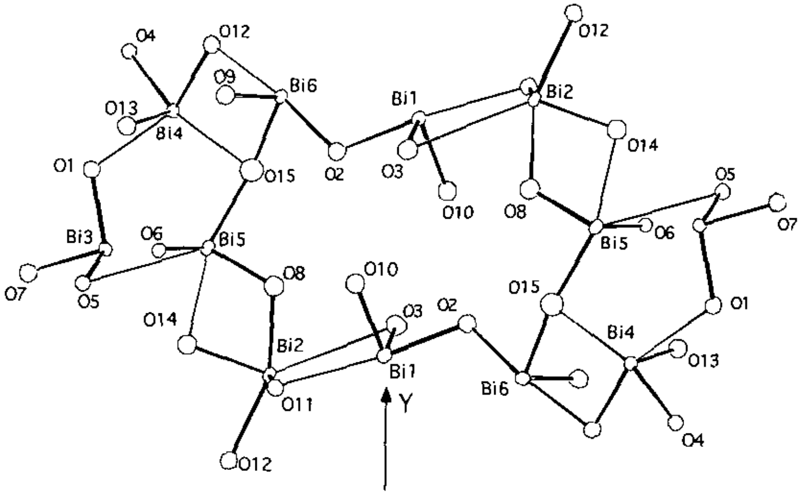

FIG. 1. An ORTEP (*15*) representation of the coordination environments for the six unique atoms of Bi found in the structure of $Ca_6Bi_6O_{15}$. Those interatomic distances greater than 2.7 Å are represented as thinner lines (see Table IV). Atoms of Ca, omitted for clarity, are coordinated to oxygen atoms extending into the cavity shown (see Figs. 2 and 3). The *b*-axial direction is oriented vertically; the horizontal direction is as for that in Figs. 2 and 3.

Nonius CAD-4 diffractometer using the experimental parameters given in Table I. The cell parameters were determined from 25 reflections with $6° < \theta \leq 23°$. Data were corrected for Lorentz and polarization effects; an absorption correction was performed using the program DIFABS following the solution of the structure (*9*). Structure solution was initiated using a Patterson-function peak-search/solution algorithm developed by J. C. Calabrese (*10*), which located the positions of all Bi atoms. All other atoms were located in subsequent Fourier and Fourier difference syntheses. The final refinement employed an anisotropic model and an isotropic model for the thermal motion of the metal and oxygen atoms, respectively; the final discrepancy indices reported in Table I were obtained. The refined atomic parameters are given in Tables II and III, respectively. Note that the thermal parameters of the metal atoms are similar to those of the other ordered alkali-metal bismuthates (*5, 6*).

Given the penchant for other compounds in this system to form superstructures involving oxygen ordering (*5, 6*), we thought it prudent to collect neutron diffraction data on a powdered sample to confirm the correctness of the model derived from X-ray data.

Neutron powder diffraction data were collected at the BT1 station of the reactor at the National Institute of Standards and Technology, Gaithersburg, Maryland. Fifteen grams of powder were placed in a vanadium can. A data set was collected in the range $5° < 2\theta < 100°$ in steps of 0.05° in 2θ at a neutron wavelength of 1.553 Å, obtained from the (220) reflection of a Cu monochromator. The divergences were 10, 20, and 10 arcmin for the in-pile, monochromatic and diffracted beams, respectively. The pattern was scrutinized; all peaks could be indexed on the basis of the primitive unit cell found from the single-crystal study and reported in Table I. Using the atomic parameters from the single-crystal X-ray study, Riet-

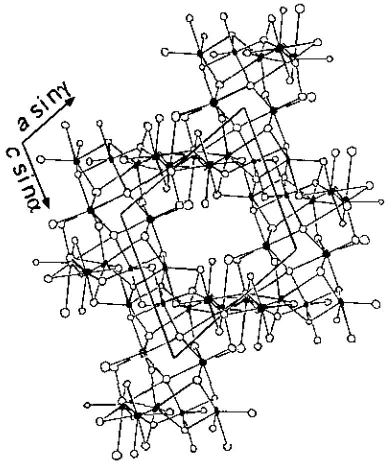

FIG. 2. View down [010] of $Ca_6Bi_6O_{15}$ showing only the interconnected Ca–O polyhedral framework. Bi atoms occupy the channels which are parallel with the b axis. Ca atoms are shaded.

veld refinement of only the diffractometer-dependent parameters, for example, zero-point, unit-cell constants and peak half-widths, led to convergence and confirmed the structure reported in Table II. The lattice parameters obtained were a = 10.109(2), b = 10.130(2), c = 10.460(2)Å, α = 116.87(2), β = 107.137(7), and γ = 92.994(7)°. The final discrepancy factors for the powder neutron Rietveld refinement were $R_{wp} = 9.49$, $R = 9.77$, and $\chi^2 = 2.54$.

$Ca_4Bi_6O_{13}$. An anonymous referee's concern with the choice of space group for this compound (*5*) prompted us to carry out a neutron powder diffraction study on this material as well. Using the instrumental settings described above, data were collected in the range $5° < 2\theta < 100°$ in steps of 0.05° 2θ. The pattern was consistent with the published unit cell and space group (*5*). Refinement of the model, based on the X-ray single-crystal result, confirms the published structure. In particular, the oxygen coordinated solely to two atoms of Bi was modeled as a split site, suggestive of the type of site disorder discussed in Ref. (*5*); no evidence of a superstructure was discernible from the neutron powder data.

Results and Discussion

As has now been observed in all of the well-ordered alkaline-metal bismuth oxides, the coordination of the bismuth shows a tendency toward 3-coordination, though in the case of $Ca_6Bi_6O_{15}$ the coordination is better described as 3 + 1. All six unique Bi atoms are coordinated by three atoms of oxygen at a distance less than 2.3 Å (Table IV). All sites, except Bi(3), also have at least one additional oxygen atom at a distance less than 2.8 Å. The calculated valence sums (Table IV) for Bi are in the range 2.7–2.8 when contributions from oxygen atoms up to 3.4 Å distant are included. The relationship between the Bi sites is depicted in Fig. 1, where a fragment of the Bi–O network is shown.

The coordination geometry about the Ca sites is distorted octahedral. All six Ca have six oxygen atoms at a distance less than 2.9 Å, with Ca(2) and Ca(6) possessing an additional oxygen at approximately 3 Å (Table IV). A complex three-dimensional framework is formed by corner, edge, and face sharing of Ca polyhedra (Fig. 2). This framework contains channels oriented parallel to the b-axial direction. Bismuth ions occupy the channels in such a manner as to form narrow tunnels, also parallel to b, accommodating the Bi lone-pair electrons. Although the structure of $Ca_6Bi_6O_{15}$ can be described in this manner, it does not highlight the fundamental similarities that it has in common with the structure of $Ca_4Bi_6O_{13}$ (*5*). However, simple structural principles, which may also apply to other members of the alkaline earth bismuthates, relate the structures of $Ca_4Bi_6O_{13}$ and $Ca_6Bi_6O_{15}$. These are described below.

The structures of both compounds consist of stacked layers of metal atoms, each layer having the composition of 6Ca:6Bi in

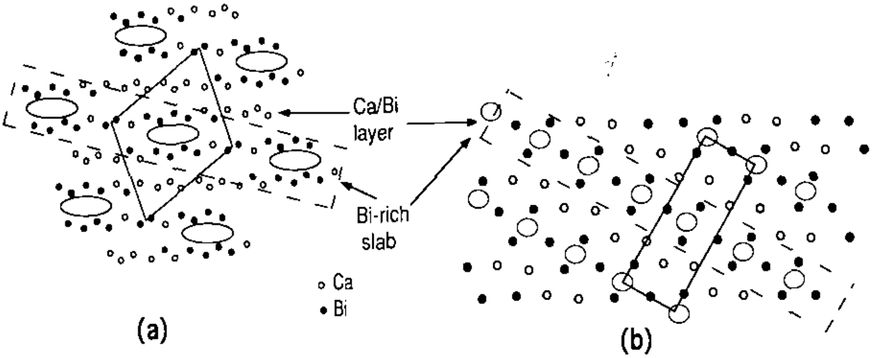

FIG. 3. View (a) down [010] for $Ca_6Bi_6O_{15}$ and (b) down [001] for orthorhombic $Ca_4Bi_6O_{13}$ emphasizing the mixed Ca/Bi layers, detailed in Fig. 4. These layers stack so as to form Bi- and Ca-rich three-dimensional slabs, the former probably containing the Bi $6s^2$ lone pair in tunnels within the structure, illustrated by the open ellipses and large open circles in (a) and (b), respectively. Oxygen atoms are excluded for the sake of clarity.

$Ca_6Bi_6O_{15}$ and 4Ca : 6Bi in $Ca_4Bi_6O_{13}$. The layers stack in a manner that brings together the Bi atoms from adjacent layers. This arrangement creates tunnels between the layers that are occupied by bismuth lone-pair electrons. This is shown schematically in Fig. 3, where the two calcium bismuthates are shown to be composed of sheets oriented horizontally. The metal-atom sheets are interconnected by oxygen atoms, which have been omitted from Fig. 3 for the sake of clarity. These sheets stack to produce slabs of alternating Bi- and Ca-rich regions, indicated by the dotted line in Fig. 3. In the Ca-rich regions of $Ca_6Bi_6O_{15}$, the Ca is 6- and 7-coordinated in distorted and capped octahedra that share corners, edges, and faces with one another.

Within the sheets, shown end-on in Fig. 3, metal atoms are approximately closest packed (Fig. 4). In the case of $Ca_6Bi_6O_{15}$ the successive layers stack with approximate *ABAB*. . . packing; there are small displacements from the ideal packing sequence. The corresponding structural unit in $Ca_4Bi_6O_{13}$ can be derived from a hypothetical closest-packed layer, consisting of alternating triple chains of Ca and Bi, by the uniform removal of one-third of the Ca chains. The position of such regular line defects is illustrated schematically in Fig. 4b.

The compounds $Ca_6Bi_6O_{15}$ and $Ca_4Bi_6O_{13}$, in common with other low-temperature forms of alkaline earth bismuthates (*6*, *11*), contain an ordered arrangement of alkaline earth and Bi atoms. This contrasts with most of the Sr–Bi–O and Ca–Sr–O phases reported to date which are of the rhombohedral sillenite type (*12*, *13*). In these materials, the alkaline-earth metal and the bismuth are disordered and occupy the same crystallographic sites in high-symmetry crystal structures. The body-centered tetragonal phase, $Sr_4(Bi_{5-x}Sr_x)O_{11.5-(x/2)}$ ($x \approx 0.3$), has BiO_3 and SrO_6 units, each with a disordered oxygen atom, and a site containing both bismuth and strontium (*14*), while the lower-temperature phase of $Sr_2Bi_2O_5$ possesses an ordered cation arrangement and resulting lower symmetry (*6*). The low-temperature ordering of Ca and Bi in both $Ca_6Bi_6O_{15}$ and $Ca_4Bi_6O_{13}$ leads to the segregation of Bi and Ca into symmetrically distinct structural sites.

Conclusion

The structure of $Ca_6Bi_6O_{15}$ is related to that of $Ca_4Bi_6O_{13}$. In both compounds, the

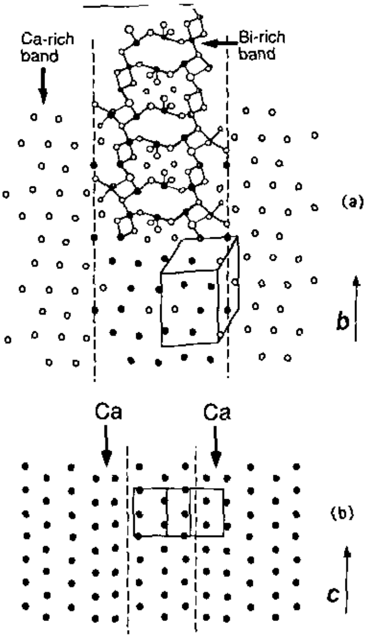

FIG. 4. Approximately closest-packed arrangement of metal atoms in a single layer of (a) $Ca_6Bi_6O_{15}$ and (b) $Ca_4Bi_6O_{13}$, shown to consist of Ca- and Bi-rich bands. (*a*) An ORTEP (*15*) representation has been included at the top to emphasize the distortion from ideal close packing within this layer due to the accommodation of the Bi lone pair. Only Bi–O bonds less than 3.0 Å are shown. (b) For $Ca_4Bi_6O_{13}$, all lone pairs presumably point between the planes, thereby leading to a more regular packing. The closest packing is disrupted by the removal of a line of Ca from a closest-packed layer of ideal composition Ca_3Bi_3 which consists of regularly spaced triple lines of Bi and Ca; the positions of the removed chains of Ca are indicated by the vertical arrows in (b).

Bi and Ca atoms are ordered, a feature common to all the low-temperature forms of the alkaline-earth bismuthates studied thus far (*5*, *6*, *11*). These materials are related structurally by the stacking of layers, which are at least partially closest packed with respect to the metal atoms. The layers stack to produce alternating Bi- and Ca-rich slabs, with the Bi lone pairs concentrated into tunnels. Metal–oxygen bonding interconnects these layers to produce three-dimensional structures.

Acknowledgments

We thank William Marshall for collecting the single-crystal X-ray data set for $Ca_6Bi_6O_{15}$. J.B.P. thanks the DuPont Company and the NSF, through Grant DMR 9024249, for financial support.

References

1. R. S. Roth, C. J. Rawn, B. P. Burton, and F. Beech, *J. Res. NIST* **95,** 291 (1990).
2. N. M. Hwang, R. S. Roth, and C. J. Rawn, *J. Am. Ceram. Soc.* **73,** 2531 (1990).
3. B. P. Burton, C. J. Rawn, R. S. Roth, and N. M. Hwang, *J. Res. NIST,* to be published (1992).
4. R. S. Roth, N. M. Hwang, C. J. Rawn, B. P. Burton, and J. J. Ritter, *J. Am. Ceram. Soc.* **74,** 2148 (1991).
5. J. B. Parise, C. C. Torardi, M.-H. Whangbo, C. J. Rawn, R. S. Roth, and B. P. Burton, *Chem. Mater.* **2,** 454 (1990).
6. C. C. Torardi, J. B. Parise, A. Santoro, C. J. Rawn, R. S. Roth, and B. P. Burton, *J. Solid State Chem.* **93,** 228 (1991).
7. R. D. Shannon, *Acta Crystallogr. A* **32,** 751 (1976).
8. C. C. Torardi, J. B. Parise, M. A. Subramanian, J. Gopalakrishnan, and A. W. Sleight, *Physica C* **157,** 115 (1989); C. C. Torardi, E. M. McCarron, P. L. Gai, J. B. Parise, J. Ghoroghchian, M.-H. Whangbo, and J. C. Barry, *Physica C* **176,** 347 (1991).
9. N. Walker and D. Stuart, *Acta Crystallogr. A* **39,** 158 (1983).
10. J. C. Calabrese, personal communication.
11. P. Lightfoot, J. A. Hriljac, S. Pei, Y. Zheng, A. W. Mitchell, D. R. Richards, B. Dabrowski, J. D. Jorgensen, and D. G. Hinks, *J. Solid State Chem.* **92,** 473 (1991).
12. L. G. Sillen and B. Aurivillius, *Z. Kristallogr.* **101,** 483 (1939).
13. B. Aurivillius, *Ark. Kemi Mineral. Geol.* **16A,** 1 (1943).
14. C. C. Torardi, R. S. Roth, C. J. Rawn, J. B. Parise, and B. P. Burton, to be published.
15. C. K. Johnson, "ORTEP: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustration," Oak Ridge National Laboratory Report 5138 (1976).
16. I. D. Brown and K. K. Wu, *Acta Crystallogr. B* **32,** 1957 (1976).