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X-Ray and Neutron Diffraction Study of $CaBi_2O_4$

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The crystal structure of the 1 : 1 $CaO–Bi_2O_3$ compound ($CaBi_2O_4$) has been determined by single crystal X-ray and neutron powder diffraction techniques. The compound crystallizes with the symmetry of the monoclinic space group *C*2/*c* and lattice parameters $a = 16.6130(5)$ Å, $b = 11.5900(4)$ Å, $c = 13.9939(4)$ Å, $\beta = 134.048(1)°$. The structure consists of sheets parallel to the *b*–*c* plane and connected by Ca–O bonds. There is a structural unit in each layer consisting of four Bi atoms, ten oxygen atoms, and two calcium atoms. The Bi atoms are fourfold coordinated and the coordination polyhedron may be described as a short distorted pyramid, open on one end to accommodate the lone-pair electrons of the bismuth atoms. Calcium is seven-coordinated and the coordination polyhedron may be described as a monocapped trigonal prism.

INTRODUCTION

The compound $CaBi_2O_4$ was first reported by Conflant *et al.* (1). In a subsequent work (2), this material was synthesized at 650°C and found to be stable up to a temperature of about 800°C, where it decomposes into $Ca_4Bi_6O_{13}$ and a face-centered cubic solid solution. Phase equilibria experiments (3) suggested that the 1 : 1 $CaO–Bi_2O_3$ composition is unstable above 778 ± 5°C, and X-ray powder diffraction measurements showed that this material crystallizes with the symmetry of space group *C*2/*c* and lattice parameters $a = 16.6295(8)$ Å, $b = 11.5966(5)$ Å, $c = 14.0055(6)$ Å, and $\beta = 134.036(3)°$. (It is worth pointing out that these lattice parameters do not define the conventional monoclinic cell because they do not define the unit cell based on the two shortest translations in the plane perpendicular to the unique axis *b*. The conventional cell has lattice parameters $a_c = 16.6295$, $b_c = 11.5966$, $c_c = 12.2027$, $\beta_c = 124.40°$, and is related to the one adopted in this paper by the axial transformation (100/0 -1 0/-1 0 -1).) No other structural results, however, were reported in the studies previously mentioned.

As a part of an ongoing study on the properties of the system alkali metal/bismuth oxide/copper oxide, the title compound was prepared and characterized crystallographically. Since Ca and Bi can substitute for each other, leading either to oxygen nonstoichiometry or to cation site vacancy, the structure of $CaBi_2O_4$ was elucidated by using two complementary techniques, single crystal X-ray and neutron powder diffraction methods, to precisely determine both the heavy atoms and the oxygen atoms in the unit cell. The results of this study are reported in the following sections.

EXPERIMENTAL RESULTS

(*a*) *Single Crystal X-Ray Diffraction*

Single crystals of $CaBi_2O_4$ were synthesized as described in Ref. (3). A sample of approximate size 0.08 × 0.05 × 0.05 mm^3 was selected for the X-ray measurements which were carried out using Mo*Kα* radiation ($\lambda = 0.71073$ Å) and a computer controlled kappa-axis diffractometer equipped with a graphite monochromator. Cell constants and the orientation matrix necessary for data collection were obtained by least squares refinement from the setting angles of 25 reflections in the range $10° < \theta < 18°$. These preliminary results confirmed the monoclinic symmetry of the crystal (space group *C*2/*c*).

The sample was stable during the entire data collection period, as monitored by three standard reflections. A total of 2093 reflections were measured, of which 1323 were

TABLE 1
Collection of Neutron Powder Diffraction Data

Monochromatic beam:	220 reflection of a Cu monochromator
Wavelength:	1.545(1) Å
Horizontal divergences:	10′, 20′, 10′ of arc for the in-pile, monochromatic beam and diffracted beam collimators, respectively
Sample container:	Vanadium can of about 10 mm diameter
2θ angular range:	5–120°, steps: 0.05°.
Peak shape:	Gaussian
Scattering amplitudes (10^{-12} cm):	$b(\text{Bi}) = 0.853$, $b(\text{Ca}) = 0.490$, $b(\text{O}) = 0.581$

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TABLE 2

Refined Structural Parameters of $CaBi_2O_4$ from Powder Neutron Diffraction and Single Crystal X-Ray Data[a]

Chemical unit cell:
Space group: C2/c, Z=16.

a=16.6130(5)Å, b=11.5900(4)Å, c=13.9939(4)Å, ß=134.048(1)°, V=1936.68(13)Å^3.
16.643(4)Å, 11.580(4)Å, 13.994(5)Å, 133.92(2)°, 1942.8(4)Å.^{3}.

R_N=2.93, R_p=4.81, R_W=6.25, R_B=5.81, χ=1.08.
R_F=3.5, R_W=3.9.

Atom	Site	x	y	z	B(Å^2)	Occupancy
Bi(1)	8f 1	0.8715(4)	0.1570(4)	0.5597(4)	0.62(8)	1
		0.87206(5)	0.15711(8)	0.56083(6)	0.59(2)	1
Bi(2)	8f 1	0.8729(3)	0.3484(3)	0.2709(4)	1.01(8)	1
		0.87250(5)	0.34963(8)	0.27022(6)	0.69(2)	1
Bi(3)	8f 1	0.6546(3)	0.2145(3)	0.2151(4)	0.61(8)	1
		0.65495(5)	0.21447(8)	0.21573(6)	0.63(2)	1
Bi(4)	8f 1	0.6505(4)	0.0106(3)	0.4862(4)	0.90(9)	1
		0.65015(5)	0.01048(8)	0.48483(6)	0.66(2)	1
Ca(1)	8f 1	0.8749(6)	0.0353(6)	0.3350(7)	1.1(1)	1
		0.8761(3)	0.0363(3)	0.3317(3)	-0.5(3)*	
Ca(2)	8f 1	0.8767(7)	0.1492(6)	0.0808(8)	0.8(1)	1
		0.8772(3)	0.1504(4)	0.0799(3)	0.48(8)*	1
O(1)	8f 1	0.7030(5)	0.1107(6)	0.3927(6)	1.4(1)	1
		0.704(1)	0.109(2)	0.391(1)	1.4(3)*	1
O(2)	8f 1	0.6798(5)	0.9304(5)	0.6547(6)	0.8(1)	1
		0.682(1)	0.930(2)	0.659(1)	1.2(3)*	1
O(3)	8f 1	0.8279(5)	0.2414(5)	0.3792(6)	1.0(1)	1
		0.8295(9)	0.241(2)	0.382(1)	0.7(3)*	1
O(4)	8f 1	0.6986(5)	0.3364(5)	0.1377(6)	0.9(1)	1
		0.699(1)	0.338(2)	0.137(1)	1.3(3)*	1
O(5)	8f 1	0.8213(5)	0.0348(6)	0.6376(6)	1.2(1)	1
		0.824(1)	0.035(2)	0.640(1)	1.3(3)*	1
O(6)	8f 1	0.6659(5)	0.8570(6)	0.4206(6)	1.0(1)	1
		0.6685(9)	0.860(1)	0.422(1)	0.9(3)*	1
O(7)	8f 1	0.9437(5)	0.0242(5)	0.5502(6)	0.5(1)	1
		0.945(1)	0.026(1)	0.551(1)	0.8(3)*	1
O(8)	8f 1	0.9306(5)	0.1876(5)	0.2844(6)	0.8(1)	1
		0.9306(5)	0.189(1)	0.285(1)	0.4(3)*	1

[a] First line from neutron data, second line from X-ray data.

* Starred atoms were refined anisotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(\frac{4}{3}[a^2 * B(1, 1) + b^2 * B(2, 2) + C^2 * B(3, 3) + ac (\cos \beta) * B(1, 3)]$.

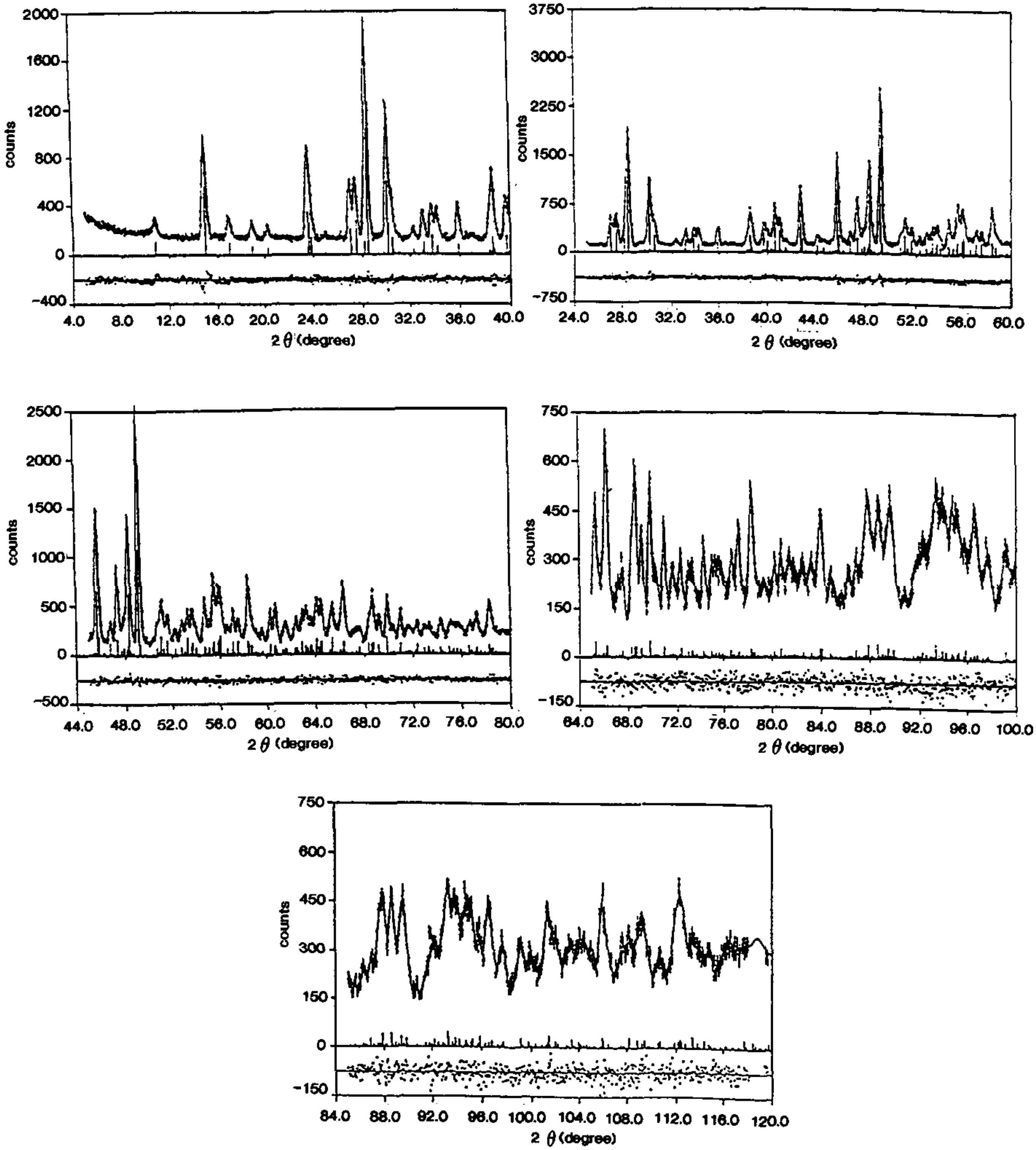

FIG. 1. Calculated (continuous line) and observed (circles) neutron profiles for each of the five counters of the diffractometer. The differences between calculated and observed intensities are plotted at the bottom of each diagram.

TABLE 3

Selected Bond Distances (Å) and Bond Angles (°) in $CaBi_2O_4$ from Neutron Data

Ca(1)–O(2)	2.379(9)	Bi(2)–O(3)	2.442(8)
Ca(1)–O(3)	2.71(1)	Bi(2)–O(4)	2.090(7)
Ca(1)–O(4)	2.757(9)	Bi(2)–O(6)	2.282(7)
Ca(1)–O(5)	2.38(1)	Bi(2)–O(8)	2.044(7)
Ca(1)–O(7)^{1}	2.325(9)	Average:	2.215
Ca(1)–O(7)	2.368(10)		
Ca(1)–O(8)	2.319(9)	Bi(3)–O(1)	2.343(8)
Average:	2.46	Bi(3)–O(2)	2.050(7)
		Bi(3)–O(3)	2.113(7)
Ca(2)–O(4)	2.371(10)	Bi(3)–O(4)	2.193(7)
Ca(2)–O(5)	2.654(10)	Average:	2.175
Ca(2)–O(6)	2.507(9)		
Ca(2)–O(6)	2.526(10)	Bi(4)–O(1)	2.325(8)
Ca(2)–O(7)	2.474(9)	Bi(4)–O(2)	2.251(7)
Ca(2)–O(8)	2.361(9)	Bi(4)–O(5)	2.063(8)
Ca(2)–O(8)^{1}	2.367(10)	Bi(4)–O(6)	2.098(8)
Average:	2.466	Average:	2.184
Bi(1)–O(1)	2.118(8)		
Bi(1)–O(3)	2.307(7)		
Bi(1)–O(5)	2.270(8)		
Bi(1)–O(7)	2.012(7)		
Average:	2.177		
O(1)–Bi(1)–O(3)	74.40(27)	O(1)–Bi(3)–O(3)	73.72(25)
O(1)–Bi(1)–O(5)	74.17(29)	O(1)–Bi(3)–O(4)	150.27(28)
O(1)–Bi(1)–O(7)	97.16(27)	O(1)–Bi(3)–O(2)	89.93(29)
O(3)–Bi(1)–O(5)	148.23(28)	O(3)–Bi(3)–O(4)	76.77(24)
O(3)–Bi(1)–O(7)	89.96(28)	O(3)–Bi(3)–O(2)	93.09(28)
O(5)–Bi(1)–O(7)	89.39(27)	O(4)–Bi(3)–O(2)	95.16(27)
O(3)–Bi(2)–O(4)	71.86(26)	O(1)–Bi(4)–O(5)	73.98(27)
O(3)–Bi(2)–O(6)	142.43(27)	O(1)–Bi(4)–O(2)	154.59(31)
O(3)–Bi(2)–O(8)	78.81(26)	O(1)–Bi(4)–O(6)	88.28(27)
O(4)–Bi(2)–O(6)	82.54(28)	O(5)–Bi(4)–O(2)	80.74(28)
O(4)–Bi(2)–O(8)	106.97(30)	O(5)–Bi(4)–O(6)	93.78(28)
O(6)–Bi(2)–O(8)	83.10(27)	O(2)–Bi(4)–O(6)	96.01(26)

unique, and, of these, 1137 were observed. Lorentz-polarization and absorption corrections were applied as described in Ref. (4).

The structure was determined by using direct methods (MULTAN) and difference Fourier syntheses, and it was refined using full-matrix least-squares techniques and the non-Poisson weighting scheme with $p = 0.4$. The atomic scattering factors used in these calculations were those given by Cromer and Waber (5). In the first stages of the refinement, the stoichiometric formula $CaBi_2O_4$ was assumed, and the Ca and Bi atoms were considered to be completely ordered in their sites. With this model, the temperature factor of one of the Ca atoms (Ca(1)) became negative. This anomalous behavior of B (Ca1) could be a consequence of a small substitution of Ca by Bi or, more likely, could be due to insufficient correction for the effects of absorption on the observed intensities. The linear absorption coefficient of $CaBi_2O_4$ is in fact large (733 cm^{-1}) and the average value of μR may certainly be outside the range of applicability of the φ scan method of correction for certain reflections. In the final refinement we therefore assumed the formula $CaBi_2O_4$ for the compound and in Table 2 are shown the results of the X-ray diffraction experiment obtained for the ordered model.

(*b*) *Powder Neutron Diffraction*

The neutron powder diffraction data were collected at room temperature, using the high-resolution five-counter diffractometer at the Reactor of the National Institute of Standards and Technology, with the experimental conditions shown in Table 1. The refinement was carried out with the Rietveld method (6), adapted to the multicounter diffractometer and modified to include background parameters (7).

The initial refinement of $CaBi_2O_4$ was made using as starting parameters those measured by X-ray diffraction and assuming the symmetry of space group $C2/c$. In addition, the Ca and Bi atoms were considered to be completely ordered on their sites and their occupancies were not allowed to vary. The results of these calculations definitely confirm the $C2/c$ symmetry and give very good agreement between observed and calculated intensities (Table 2). Refinements with anisotropic thermal factors showed that none of the atoms has pronounced anisotropic character, and did not improve significantly the values of the R-factors. In addition, attempts to refine models in which Ca may be substituted by Bi invariably converged towards an ordered distribution of these cations. In agreement with the X-ray results, no evidence of extra oxygen in the structure was found in the neutron experiment. The final refinement was therefore carried out with the initial ordered model corresponding to the formula $CaBi_2O_4$. Figure 1 shows the experimental and calculated profiles for the five counters of the diffractometer. The final structural parameters are given in Table 2 and in Table 3 the relevant bond distances and angles are shown.

DISCUSSION

As shown in Tables 2 and 3, the X-ray and neutron results for the structure of $CaBi_2O_4$ are generally in good agreement. Most of the corresponding positional parameters are within 3σ from each other, with only a few differing as much as 5σ. Differences in the corresponding bond distances and angles are less than 0.3%. Since the positions of the oxygen atoms are determined more precisely from neutron diffraction patterns than from X-ray data, in the following discussion of the structure of $CaBi_2O_4$ we will use the values of bond lengths and angles obtained in the neutron refinement.

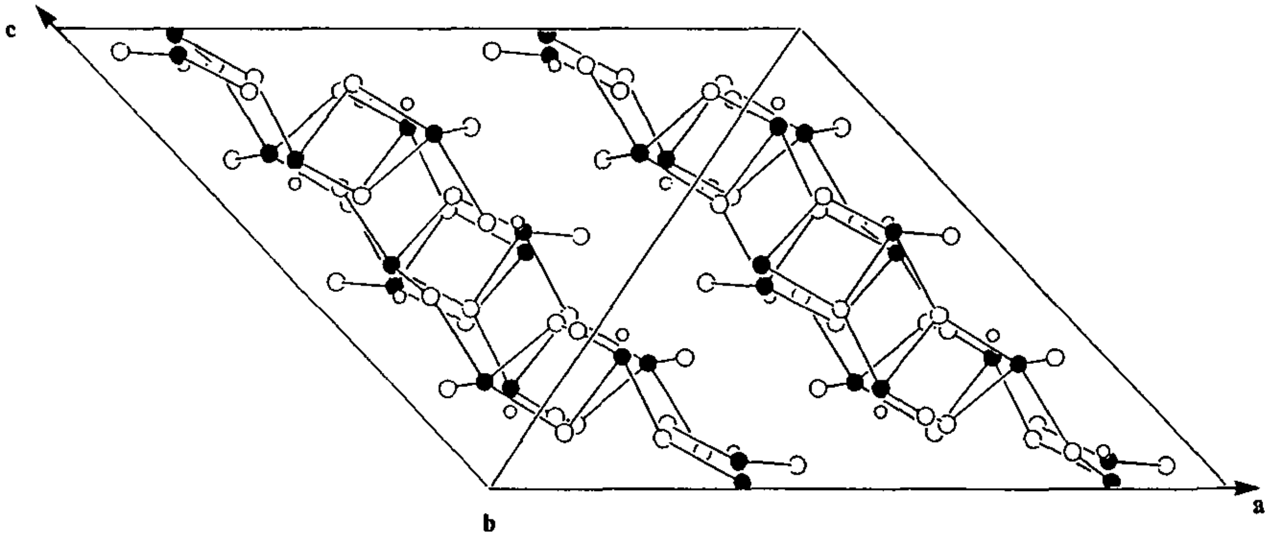

FIG. 2. Projection on the (010) plane of the unit cell of the $CaBi_2O_4$. Large and small open circles represent oxygen and calcium sites respectively. The full circles represent the bismuth sites. For simplicity only the Bi–O bonds are drawn in the figure.

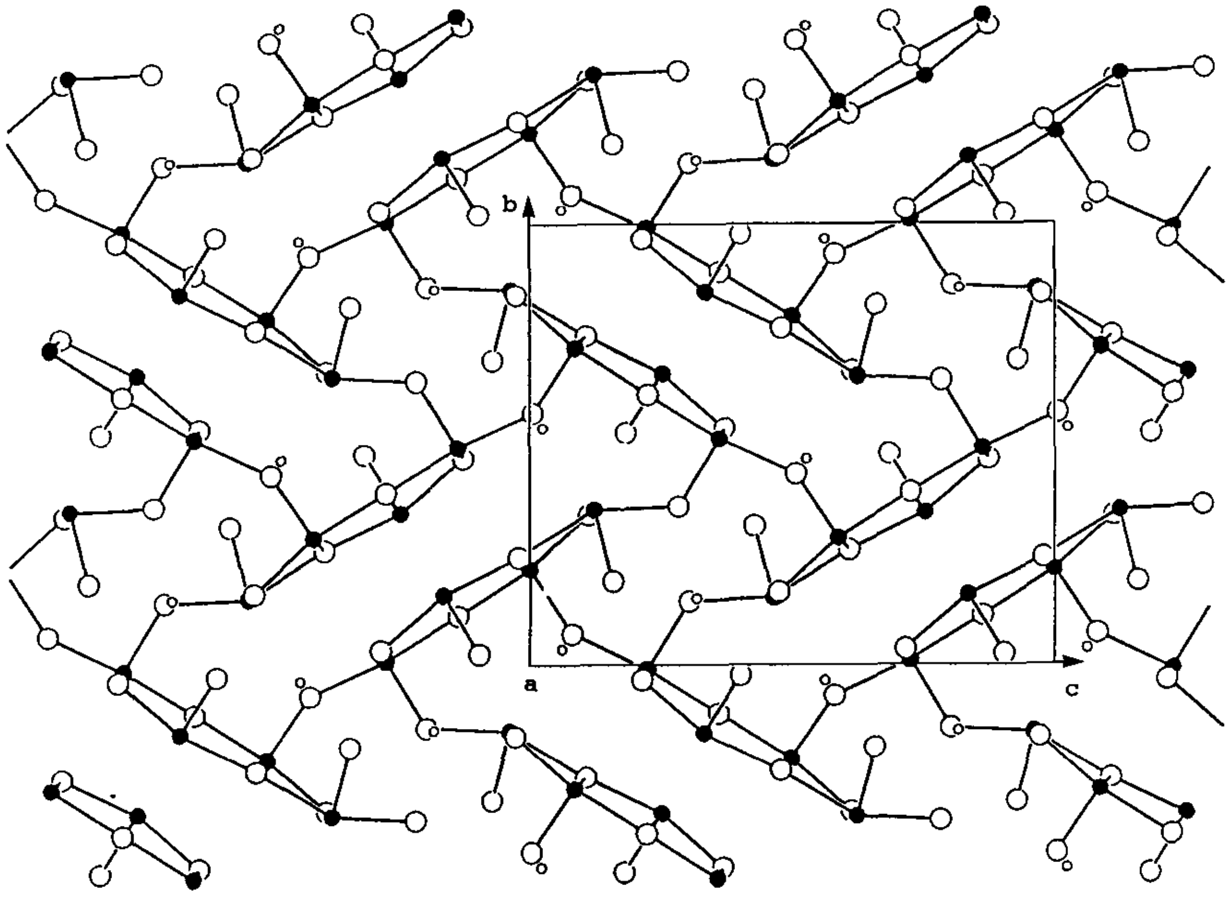

FIG. 3. Orthogonal projection on the (100) plane of the structure of $CaBi_2O_4$. Large and small open circles represent oxygen and calcium sites respectively. The full circles represent the bismuth sites. Only the Bi–O bonds are shown. Only the slab $0 < x < \frac{1}{2}$ is projected in the figure.

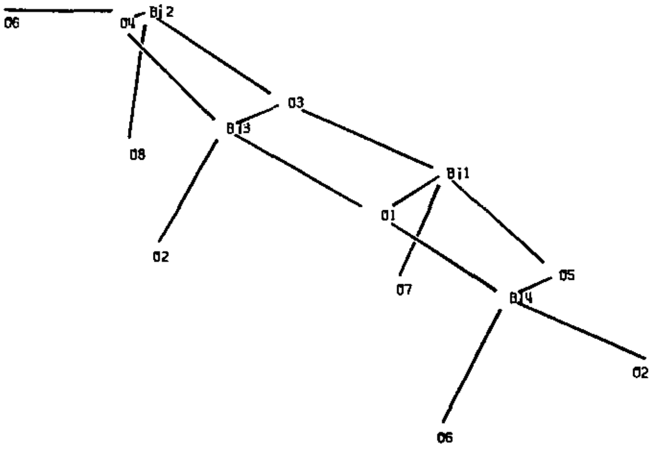

FIG. 4. The repeat structural unit of the $CaBi_2O_4$ structure. Only the Bi–O bonds are shown in the figure.

The projection along the unique axis *b* of the unit cell of $CaBi_2O_4$ is represented in Fig. 2. The structure consists of sheets parallel to the *c* axis and connected by Ca–O bonds. A projection on the *b–c* plane of one of these sheets is shown in Fig. 3. It is important to note that there is a repeat structural unit in the layer, consisting of four bismuth atoms, ten oxygen atoms, and one calcium atom located at both ends of each unit (Fig. 4). These units are elongated along directions approximately parallel to the [1, 2, 3] axis and are joined together by Bi–O–Bi and O–Ca–O bridges.

There are four symmetrically independent atoms of bismuth in the structure. The Bi–O distances range from 2.012(7) to 2.442(8) Å (Table 3). More specifically, the atoms Bi(1) and Bi(3), positioned in the center of the structural unit mentioned above, have average Bi–O distances of 2.177 and 2.175 Å, respectively, while the corresponding values for Bi(2) and Bi(4) are 2.215 and 2.184 Å. These values of the bismuth-oxygen bonding show that in $CaBi_2O_4$ the coordination number of the bismuth atoms

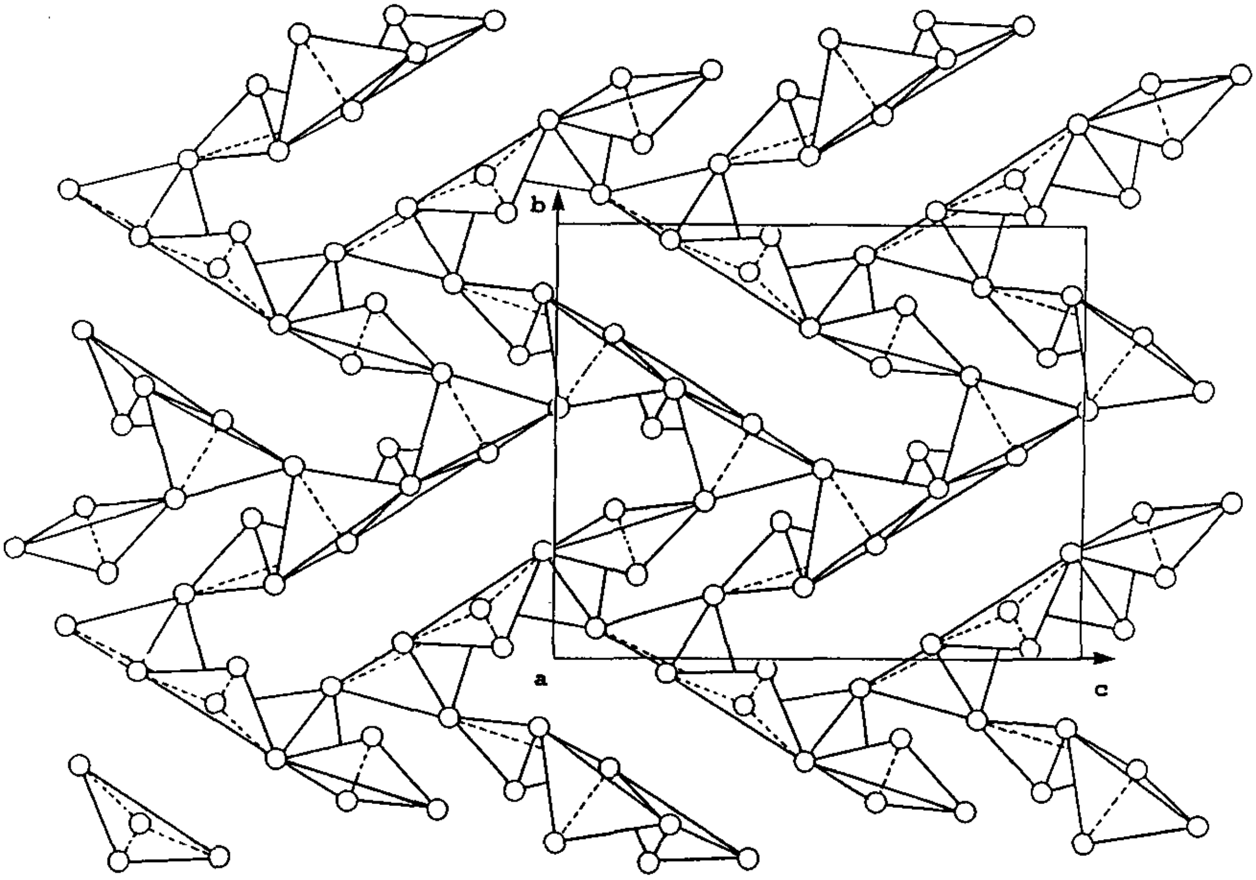

FIG. 5. Projection on the (100) plane of the structure of $CaBi_2O_4$ showing the pyramidal coordination polyhedra of the Bi atoms.

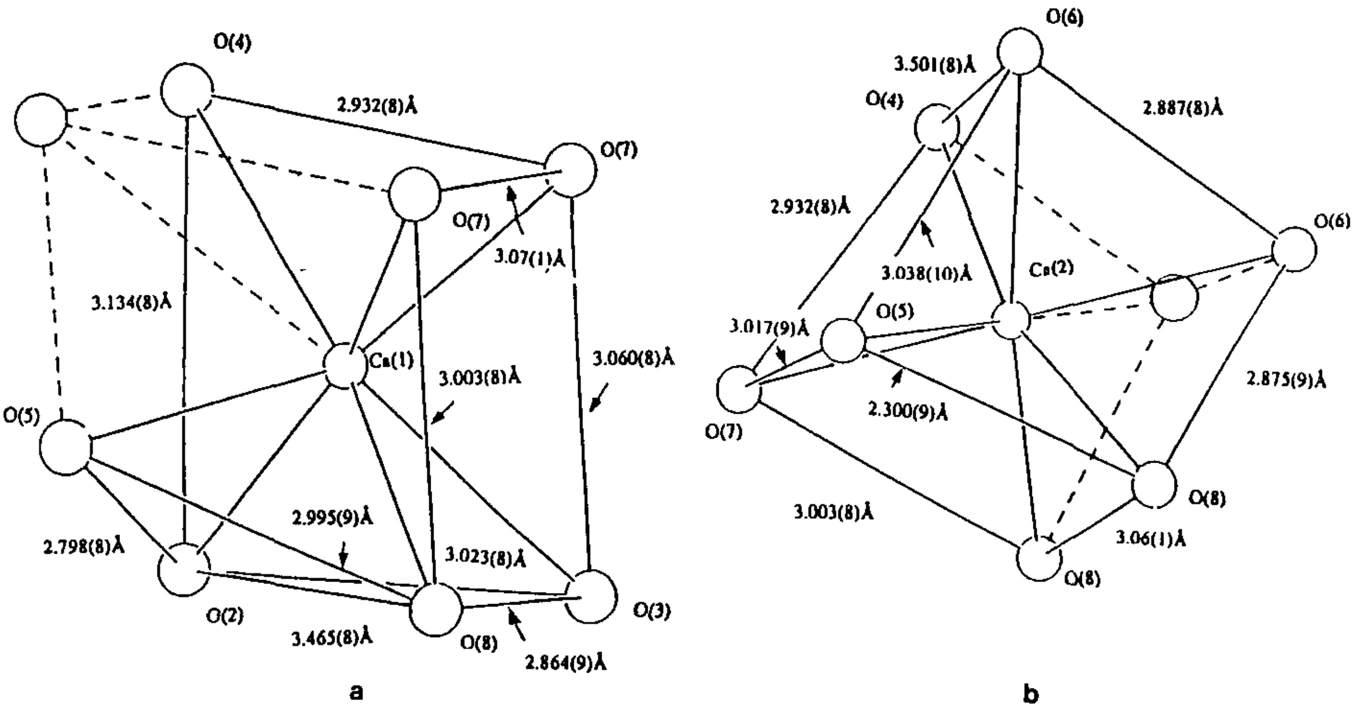

FIG. 6. Coordination polyhedra around (a) Ca(1) and (b) Ca(2). The relevant bond distances are indicated. The primed oxygen O′(7) and O′(8) are located on the adjacent layer of Ca(1) and Ca(2), respectively.

is four, in contrast with the results found for $Ca_4Bi_6O_{13}$ (8) and $Ca_6Bi_6O_{15}$ (9) in which bismuth is three- and fourfold coordinated. The BiO_4 coordination polyhedra may roughly be described as pyramids having a large triangular base and a short distance between the apex and the basal plane. All the Bi atoms are displaced out of the basal plane of the pyramids and are therefore located outside their first-coordination polyhedron. This apparently unusual location of the Bi atoms is similar to that found in the compounds $Ca_4Bi_6O_{13}$ (8) and $Ca_6Bi_6O_{15}$ (9), and can be similarly interpreted as being due to the presence of lone pair electrons pointing in a direction approximately opposite to the apex of the pyramids. With this configuration, the pairs would be located in the voids created by stacking of the structural units, as illustrated in Fig. 2. Since the oxidation states of the oxygen and calcium are 2− and 2+, respectively, the average oxidation state of Bi in the title compound is 3+. If however, the formal valences of the Bi atoms are calculated from the Bi–O interatomic distances using the Brown–Altermatt equation (10) with the Brese and O'Keeffe constants (11), one obtains values which are all significantly higher than the expected 3 valence units. These oxidation states of the Bi atoms, if real, would require the presence of a large number of Ca vacancies, and/or the incorporation of excess oxygen in the structure and are therefore inconsistent with the results of our refinements which do not show any significant departures from the stoichiometry corresponding to the formula $CaBi_2O_4$. More likely, the high values of the Bi valences reported above reflect the fact that the Brown–Altermatt equation cannot be applied to "lone pair" cations such as Bi^{3+} (12). In Fig. 5 the projection on the *b–c* plane of the frame of the oxygen pyramids is shown. The pyramids share one or two edges with the other pyramids within the same structural unit and corners with those of the other units.

The calcium atoms are seven-coordinated, with the oxygen atoms placed at the corners of a monocapped trigonal prism (Fig. 6). Of these atoms six are located on the same layer of the calcium and the seventh (O′(7) and O′(8) for Ca(1) and Ca(2) respectively) is placed on the adjacent layer (Fig. 2). For the two Ca atoms the average Ca–O bond lengths are nearly the same, but the individual interatomic distances present a large scatter (from 2.319(9) to 2.757(9) Å for Ca(1) and from 2.361(9) to 2.654(10) Å for Ca(2)).

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