

distances $r(\text{VI}M^{3+}) + r(\text{IV}O^{2-}) = 2.02 \text{ \AA}$ (SrV₆O₁₁ and NaV₆O₁₁), 2.025 \AA (BaTi₂Fe₄O₁₁) and $r(\text{VI}M^{4+}) + r(\text{IV}O^{2-}) = 1.96 \text{ \AA}$ (SrV₆O₁₁ and NaV₆O₁₁), 1.985 \AA (BaTi₂Fe₄O₁₁) (Shannon, 1976). In SrT_xV_{6-x}O₁₁ (T = Ti, Cr and Fe) compounds, the distribution of trivalent and tetravalent cations among the M(1), M(2) and M(3) sites does not always conform to the results of the Madelung energy calculations (Kanke, Izumi, Takayama-Muromachi, Kato, Kamiyama & Asano, 1990). A localized *d*-electron model cannot explain the spontaneous magnetization of magnetically ordered NaV₆O₁₁ (Uchida, Kanke, Takayama-Muromachi & Kato, 1991); besides, NaV₆O₁₁ is a good metallic conductor independent of its magnetic transition (Kanke, Takayama-Muromachi, Kato & Matsui, 1990; Uchida *et al.*, 1991). Further study is needed to reveal the electronic and magnetic structures of the AT₆O₁₁-type compounds.

References

- B. A. FRENZ & ASSOCIATES, INC. (1985). *SDP Structure Determination Package*, 4th edition. College Station, Texas, USA, and Enraf-Nonius, Delft, The Netherlands.
- BROWN, I. D. & ALTERMATT, D. (1985). *Acta Cryst.* **B41**, 244–247.
- CADÉE, M. C. & IJDO, D. J. W. (1984). *J. Solid State Chem.* **52**, 302–312.
- DEROY, M. E., BESSE, J. P., CHEVALIER, R. & GASPERIN, M. (1987). *J. Solid State Chem.* **67**, 185–187.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- KANKE, Y., IZUMI, F., TAKAYAMA-MUROMACHI, E., KATO, K., KAMIYAMA, T. & ASANO, H. (1990). *J. Solid State Chem.* **92**, 261–272.
- KANKE, Y., TAKAYAMA-MUROMACHI, E., KATO, K. & MATSUI, Y. (1990). *J. Solid State Chem.* **89**, 130–137.
- SHANNON, R. D. (1976). *Acta Cryst.* **A32**, 751–767.
- TOWNES, W. D., FANG, J. H. & PERROTTA, A. J. (1967). *Z. Kristallogr.* **125**, S437–S449.
- UCHIDA, Y., KANKE, Y., TAKAYAMA-MUROMACHI, E. & KATO, K. (1991). *J. Phys. Soc. Jpn.* **60**, 2530–2533.

Acta Cryst. (1992). **C48**, 1380–1382

Structure of Sr₂Bi₂O₅ from X-ray and Neutron Powder Diffraction Data

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(Received 16 June 1991; accepted 13 January 1992)

Abstract. Bismuth strontium oxide, Sr₂Bi₂O₅, $M_r = 673.20$, orthorhombic, *Cmcm*, $T = 295 \text{ K}$, $a = 3.8268 (2)$, $b = 14.3142 (6)$, $c = 6.1724 (4) \text{ \AA}$, $V = 338.11 (2) \text{ \AA}^3$, $Z = 2$, $D_x = 6.612 (1) \text{ Mg m}^{-3}$. Rietveld refinement using neutron powder diffraction data [$\lambda = 2.57171 (7) \text{ \AA}$, $F(000) = 120.26 \text{ fm}$, 55 contributing reflections] resulted in $R_{wp} = 4.31\%$. Around Bi lie four O atoms at short distances, forming a tetrahedron, approximately. However, the occupation of two of these positions is mutually exclusive, *i.e.* the effective coordination is threefold. The resulting umbrella-like BiO₃ groups are, on average, linked in pairs. The SrO₆ prisms share edges along [001] giving sheets perpendicular to [010]. Bond distances and angles are consistent with related materials containing stereochemically active lone pairs.

Introduction. The binary compound Sr₂Bi₂O₅ is of interest because of its relationship to the superconducting compounds Sr₂Bi₂Ca_{n-1}Cu_nO_{2n+4+ δ} , studied by the Solid State Group of Leiden University (Groen, 1990). The T_c of Sr₂Bi₂Ca_{n-1}Cu_nO_{2n+4+ δ} is strongly related to the O content (Groen & De Leeuw, 1989). The structure of Sr₂Bi₂O₅ is reported here. Guillermo, Conflant, Boivin & Thomas (1978) described the system SrO–Bi₂O₃, Conflant & Boivin (1979) and recently Abbattista, Brisi, Mazza & Valini (1991) studied the SrO–Bi₂O₃–O₂ system, but no crystal structures were determined. Moreover, bismuth oxide materials are of interest for their high ionic conduction properties.

Experimental. Sr₂Bi₂O₅ was prepared from AR Sr(NO₃)₂ and Bi₂O₃ by heating appropriate mixtures

Table 1. Fractional atomic coordinates, thermal parameters (\AA^2) and occupation for O2 of $\text{Sr}_2\text{Bi}_2\text{O}_5$ at 295 K

	x	y	z	B	n
Sr	0	0.1897 (1)	0.25	0.90 (7)	
Bi	0	0.4378 (1)	0.25	0.81 (5)	
O1	0	0.3405 (1)	0.4882 (3)	0.95 (6)	
O2	0	0.9898 (4)	0.25	1.56 (11)	0.5

$$R_p = 3.15\%; R_{wp} = 4.31\%; DW-d = 0.63; \chi^2_{\text{red}} = 2.08.$$

Table 2. Atomic distances (\AA) in $\text{Sr}_2\text{Bi}_2\text{O}_5$ at 295 K

Sr—O1 ⁱ	2.612 (1) × 2	Bi—O1 ⁱ	2.025 (2) × 2
Sr—O1 ⁱⁱ	2.542 (1) × 4	Bi—O2 ^v	2.053 (2)
Sr—O2 ⁱⁱⁱ	2.861 (6)		

Symmetry code: (i) 0, y, z; 0, y, $\frac{1}{2} - z$; (ii) $\pm \frac{1}{2}, \frac{1}{2} - y, -z$; $\pm \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) 0, y, $\frac{1}{4}$; (iv) $\frac{1}{2}, \frac{1}{2} + y, \frac{1}{4}$.

in a gold crucible in air at 873 K overnight and subsequently for 3 d at 1023 K with repeated grindings, and then air cooled. The X-ray powder diffraction pattern, obtained with a Philips PW1050 diffractometer, was in agreement with the data of JCPDS File No. 39-1472 (Wong-Ng, McMurdie, Paretzkin, Hubbard & Dragoo, 1988). Electron diffraction patterns (Siemens, Elmiscop 102 electron microscope, double tilt, lift cartridge, 100 kV) did not show the doubling of the a axis as reported by Conflant & Boivin (1979) from Weissenberg data; their unit-cell determination was found to be inaccurate because of incorrect indexing of the X-ray powder pattern. The absent reflections in the X-ray diffraction, as well as in electron diffraction patterns, indicate the space group $Cmcm$ or a lower one. The experimental density of 6.52 Mg m^{-3} (Conflant & Boivin, 1979) led to $Z = 2$.

Because no single crystals could be prepared the crystal structure was derived from X-ray powder diffraction data. From the intensity distribution of the X-ray powder diffraction data and the requirements of the space group $Cmcm$, a starting model could be constructed with Bi at 4(c) (0, y, $\frac{1}{4}$) with $y \approx \frac{7}{16}$; Sr at 4(c), $y \approx \frac{3}{16}$; O1 at 8(f) (0, y, z), $y \approx \frac{5}{16}$, $z \approx \frac{1}{2}$ and O2 at 4(c) with $y \approx 0$, and site occupancy $n = 0.5$. Rietveld's (1969) method was used for refinement of neutron powder diffraction data on the powder diffractometer at the Petten High-Flux Reactor: $5 < 2\theta < 154^\circ$ in steps of 0.1° ; neutrons at 295 K from (111) planes of a Cu crystal; pyrolytic graphite with a total thickness of 120 mm as a second-order filter; Soller slits, horizontal divergence 0.5° , placed between the reactor and the monochromator and in front of each of the four ^3He counters; sample holder ($\varnothing 10.0 \text{ mm}$) consisted of a V tube, closed with Cu plugs fitted with O rings. No precautions to avoid preferred orientation were taken. The neutron diffraction pattern was analyzed with the program *DBW* 3.2 version 8804 (Wiles & Young, 1982).

Coherent scattering lengths: Bi 8.533, Sr 7.02, O 5.805 fm (Koester, Rauch, Herkens & Schroeder, 1981). 24 parameters were present in the refinement: a scale factor, three half-width parameters defining the Gaussian-like shape of the reflections, six background parameters, the counter zero error, the unit-cell parameters, the atomic positional parameters, isotropic thermal parameters and an asymmetry parameter. The largest correlation matrix element for structural parameters is 0.60.

Discussion. Atomic parameters are given in Table 1 and selected distances in Table 2.* The agreement between the observed and calculated profiles of the data is shown in Fig. 1. Fig. 2(a) shows a projection of the structure. The structure consists of rows of trigonal prisms, SrO_6 , running parallel to [100], connected by common edges parallel to [001], with Sr at $z = \frac{1}{4}$, combined with identical prisms with Sr at $z = \frac{3}{4}$, sharing edges parallel to (001). In this way sheets of SrO_6 prisms are found at $y = \frac{1}{4}$ and $\frac{3}{4}$ respectively. Between the sheets the Bi is in three coordination because only one half of the O2-atom sites are occupied. As a result, umbrella-like BiO_3 groups with a common O2 atom are formed. The lone pair could be present at the missing O-atom position. The Bi—O distances agree with values for Bi in three coordination in sillenites such as $\text{Bi}_{12}\text{Bi}_{0.5}\text{Fe}_{0.5}\text{O}_{19.5}$ where the Bi—O bond length is 2.018 (8) \AA (Radaev, Muradyan & Simonov, 1991). The structure might be a high-temperature modifi-

* Lists of primary diffraction data and details of the Rietveld analysis, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55053 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0273]

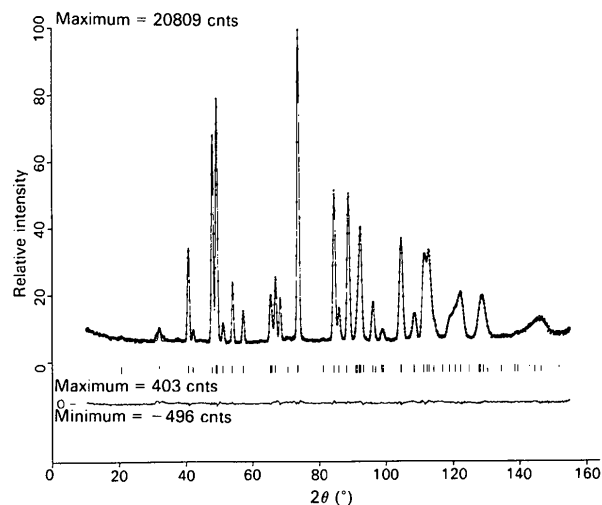


Fig. 1. Observed (dots) and calculated (full line) neutron diffraction profile of $\text{Sr}_2\text{Bi}_2\text{O}_5$ at 295 K, position of nuclear lines and $I(\text{obs.}) - I(\text{calc.})$ is indicated.

cation, owing to the lack of ordering of the O2 atoms. Sr₂Bi₂O₅ is a potential oxide ion conductor. The results of the conductivity measurements will be published elsewhere in the near future.

Recently, after this paper's first submission, Torardi, Parise, Santoro, Rawn, Roth & Burton (1991) reported the structure of the low-temperature form of Sr₂Bi₂O₅. In this phase the O-atom vacancies are ordered along [100] with consequent doubling of the *a* axis. The Bi atoms along the chain are not

evenly spaced, thereby contributing to the superstructure effect. In consecutive Bi layers, at a distance of $\frac{1}{2}b$, there are two equally likely ways of vacancy ordering, depending on the position of the *b* glide mirror plane [Fig. 2 (b)]. The glide mirror plane may be situated at $x = \frac{1}{4}$ or at $x = \frac{3}{4}$ of the small cell. In both cases the space group is *Pbmm*. If ordering of vacancies occurs only in the (010) planes, and not between these planes, the overall symmetry is as given in this paper. The ordering described by Torardi, Parise, Santoro, Rawn, Roth & Burton (1991) results in superstructure reflections that are not present in our experiment.

Oxides of the type *A*₂*M*₂O₅ with *A* an alkaline earth and *M* a trivalent ion are relatively rare and are of the perovskite-related brown millerite type, such as Ca₂Fe₂O₅, Sr₂In₂O₅ and Ba₂Tl₂O₅, in which the trivalent ions are half in octahedral and half in tetrahedral coordination. The structure of Sr₂Bi₂O₅ is of a new type.

The authors are indebted to Mr G. H. Renes for the collection of the electron diffraction patterns.

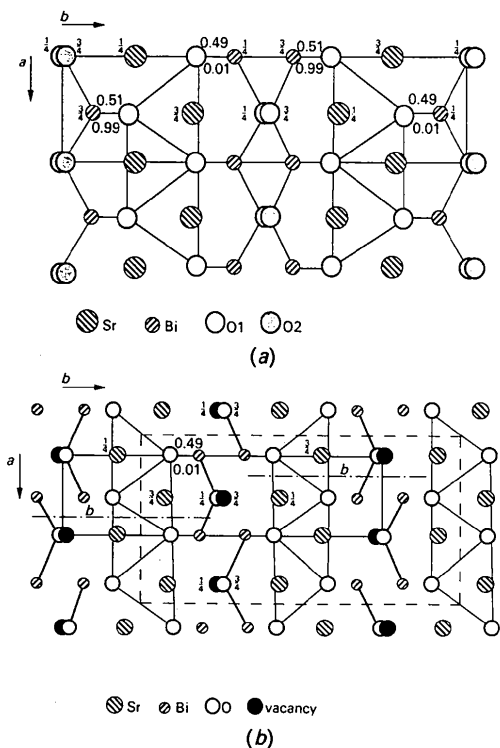


Fig. 2. (a) The structure of Sr₂Bi₂O₅ with space group *Cmc*₂₁. (b) The two possible ways of vacancy ordering in the structure of Sr₂Bi₂O₅. Indicated are the two positions of the *b*-glide mirror plane and the doubled unit cell.

References

- ABBATISTA, F., BRISI, C., MAZZA, D. & VALLINI, M. (1991). *Mater. Res. Bull.* **26**, 107–117.
- CONFLANT, P. & BOIVIN, J.-C. (1979). *Acad. Sci. Paris*, **288C**, 161–163.
- GROEN, W. A. (1990). PhD Thesis. Leiden Univ., The Netherlands.
- GROEN, W. A. & DE LEEUW, D. M. (1989). *Physica C*, **159**, 417–421.
- GUILLERMO, R., CONFLANT, P., BOIVIN, J.-C. & THOMAS, D. (1978). *Rev. Chim. Minér.* **15**, 153–159.
- KOESTER, L., RAUCH, H., HERKENS, M. & SCHROEDER, K. (1981). Report 1755. Kernforschungsanlage Jülich, Germany.
- RADAEV, S. F., MURADYAN, L. A. & SIMONOV, V. I. (1991). *Acta Cryst.* **B47**, 1–6.
- RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
- TORARDI, C. C., PARISE, J. B., SANTORO, A., RAWN, C. J., ROTH, R. S. & BURTON, B. P. (1991). *J. Solid State Chem.* **93**, 228–235.
- WILES, D. B. & YOUNG, R. A. (1982). *J. Appl. Cryst.* **15**, 149–151.
- WONG-NG, W., MCMURDIE, H., PARETZKIN, B., HUBBARD, C. & DRAGOO, A. (1988). *Powder Diffr.* **3**, 186.

Acta Cryst. (1992). **C48**, 1382–1386

Structure of Sr₅(BO₃)₃Cl

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(Received 12 July 1991; accepted 13 January 1992)

Abstract. Pentastrontium chloride trisorthoborate, Sr₅(BO₃)₃Cl, *M*_r = 649.98, orthorhombic, *C*222₁, *a* = 10.000 (2), *b* = 14.202 (2), *c* = 7.421 (1) Å, *V* =

1053.9 (3) Å³, *Z* = 4, *D*_x = 4.096 Mg m⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 24.7 mm⁻¹, *F*(000) = 1176, *T* = 295 K, *R* = 0.045 for 911 independent reflections

0108-2701/92/081382-05\$06.00

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