

Structure of Sr₄IrO₆ by Time-of-Flight Neutron Powder Diffraction

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Abstract. Strontium iridium oxide, Sr₄IrO₆, $M_r = 638.7$, rhombohedral, $R\bar{3}c$, $a = 9.73439$ (9), $c = 11.8920$ (2) Å (hexagonal setting), $V = 975.9$ Å³, $Z = 6$, $D_x = 6.52$ g cm⁻³. Rietveld refinement of time-of-flight neutron powder diffraction data in the range 3000–19300 μs [collected at 298 K, $F(000) = 417.8$ fm, 1051 contributing reflections] resulted in $R_f = 3.7\%$, $R_p = 6.1\%$, $R_{wp} = 3.5\%$ and $\chi^2 = 0.99$. Sr₄IrO₆ is isostructural with Sr₄PtO₆.

Introduction. In recent years much of our research has focused on the electronic properties of cations of metals from the second transition series. In particular, a wide range of mixed ruthenium oxides with perovskite or perovskite-related structures have been investigated (Attfield *et al.*, 1992). Such systems provide interesting examples of the competition between itinerant and localized electron behaviour. This study has now been extended to include the mixed oxides of third row transition metals with particular emphasis on iridium. There has recently been a resurgence of interest in such mixed oxides with a number of research groups reporting results on ternary iridium oxides (Chamberland & Philpotts, 1992; Wiley & Poepelmeier, 1991). In order to complement a large body of magnetic susceptibility data collected by us on a wide range of mixed oxides of iridium, we have embarked on a program of neutron scattering. Collection of neutron powder diffraction data for iridium-containing compounds is hampered by the high absorption cross section of the metal ($\sigma_a = 425 \times 10^{-24}$ cm²) and consequently no iridium oxide has been the subject of a detailed structural study by neutron diffraction. This paper, in describing the refinement of the crystal structure of Sr₄IrO₆, demonstrates that this problem may be overcome in time-of-flight diffraction by the application of a wavelength-dependent absorption correction, thus permitting a more precise determination of iridium to oxygen distances than is possible using X-ray methods.

Experimental. A pure polycrystalline sample of Sr₄IrO₆ was synthesized by conventional solid state

methods. Stoichiometric quantities of dried IrO₂ and spectroscopic grade SrCO₃ were ground together in an agate mortar and pre-reacted at 973 K in an alumina crucible for 24 h in order to decompose the carbonate. The mixture was then reground, pelletized and fired successively for one week at 1273 and 1373 K. The sample was removed from the furnace at intervals and its X-ray powder diffraction pattern recorded, thus enabling the course of the reaction to be followed. Frequent regrinding and pelletizing helped to maintain sample homogeneity. The sample was quenched to room temperature by removal from the furnace after the final firing. X-ray powder diffraction data for the final product showed the material to be monophasic. Indexing of the pattern in the rhombohedral space group $R\bar{3}c$ resulted in lattice parameters which were in good agreement with those reported previously (Randall & Ward, 1959).

Time-of-flight neutron powder diffraction data were collected at room-temperature on the Polaris spectrometer, operating in its high-intensity, medium-resolution mode, at ISIS, Rutherford Appleton Laboratory, Oxon. A weighed amount of sample (*ca* 5 g) was loaded into a vanadium can and data were collected for about 6 h. Data from the highest resolution back-scattering bank of detectors (C-bank) were summed and normalized. Data in the range 3000–19300 μs were used in the refinement; the value of the lower limit was chosen to be well above the neutron absorption edge of iridium which was clearly visible at 1140 μs (0.66 eV). The background was fitted by a ten-term Chebyshev polynomial, the parameters being included as variables in the least-squares minimization. A complex peak-shape function was utilized which involved a convolution of Gaussian, Lorentzian and two exponential functions. The latter two peak-shape parameters were fixed by instrumental characteristics, whereas the former two included refinable terms. In addition, a scale factor, cell parameters, atomic and isotropic thermal parameters were refined. The final cycles of refinement involved 23 variables. Refinement was carried out on the Rutherford Laboratory VAX computer using the program *TF14LS* incorporating subroutines from the Cambridge Crystallographic

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Table 1. Atomic coordinates and isotropic temperature factors for Sr_4IrO_6

		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Sr(1)	6(a)	0.0	0.0	0.25000	0.52 (2)
Sr(2)	18(e)	0.36550 (9)	0.0	0.25000	0.39 (1)
Ir	6(b)	0.0	0.0	0.0	0.22 (1)
O	36(f)	0.18402 (9)	0.02677 (9)	0.09891 (6)	0.43 (1)

Table 2. Bond distances (Å) and selected angles (°) for Sr_4IrO_6

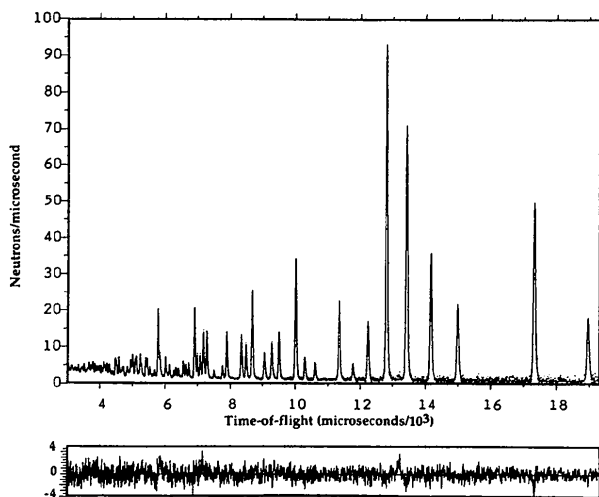
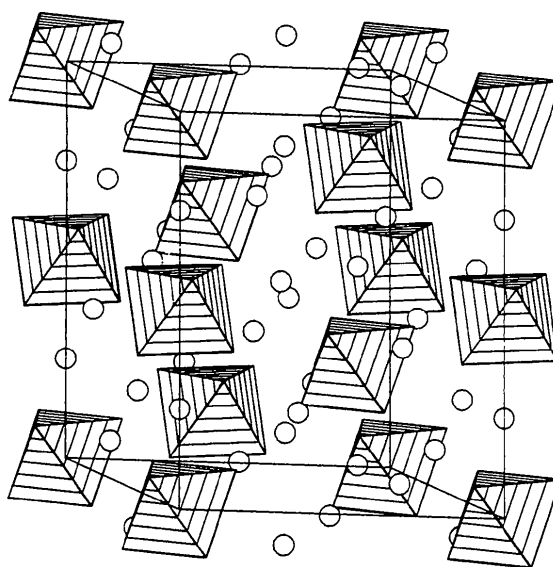
Sr(1)—O	2.457 (1) (6 ×)	Sr(2)—O	2.615 (2)
Sr(2)—O	2.623 (2) (2 ×)	Sr(2)—O	2.614 (2)
Sr(2)—O	2.595 (2) (2 ×)	Ir—O	2.047 (1) (6 ×)
Sr(2)—O	2.774 (2) (2 ×)		
O—Sr(1)—O	72.41 (1) (6 ×)	O—Ir—O	180.0 (3 ×)
O—Sr(1)—O	150.06 (2) (3 ×)	O—Ir—O	90.29 (1) (6 ×)
O—Sr(1)—O	130.64 (2) (3 ×)	O—Ir—O	89.71 (1) (6 ×)
O—Sr(1)—O	94.96 (1) (3 ×)		

Subroutines Library (Brown & Matthewman, 1987). All data manipulation and display was performed using Genie spectrum manipulation software (David *et al.*, 1986). The initial structural model was obtained from the single-crystal X-ray determination of the structure of Sr_4PtO_6 , space group $R\bar{3}c$ (Randall & Katz, 1959). Initial refinement resulted in high *R* factors ($R_I \approx 17\%$) which were only reduced at the expense of negative thermal parameters. These problems appeared to result from significant attenuation of the sample arising from the large absorption cross section of iridium. An absorption correction which has been described elsewhere (Hull & Mayers, 1989) was then applied to the normalized data. Subsequent refinement proceeded smoothly and convergence was achieved with final agreement factors of $R_I = 3.7\%$, $R_p = 6.1\%$, $R_{wp} = 3.5\%$ and a goodness-of-fit index $\chi^2 [(R_{wp}/R_E)^2]$ of 0.99. The *R* factors are defined in the original paper of Rietveld (1969).

Discussion. The final observed, calculated and difference profiles are shown in Fig. 1. The refined cell parameters for the hexagonal axes of the rhombohedral space group $R\bar{3}c$ are $a = 9.73439$ (9), $c = 11.8920$ (2) Å. Final atomic coordinates and isotropic temperature factors are given in Table 1* and bond distances and angles in Table 2. The material adopts the rhombohedral K_4CdCl_6 structure. A polyhedral representation obtained using the *STRUPLO* (Fischer, 1985) plotting program is given in Fig. 2. The structure may be viewed as chains constructed from IrO_6 octahedra linked by trigonal

* The numbered intensity of each measured point on the profile has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55835 (64 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1016]

prismatically coordinated Sr(1) ions such that the IrO_6 and $\text{Sr}(1)\text{O}_6$ polyhedra share faces. These chains run parallel to the *c* axis and project onto the *xy* plane at (0,0), (1/3, 2/3) and (2/3, 1/3). The chains are held together by additional strontium, Sr(2), ions of more complex coordination geometry. The bond lengths given in Table 2 agree well with the respective sums of ionic radii quoted by Shannon & Prewitt (1969). However, the ionic radius of Ir^{IV} was derived from X-ray diffraction measurements on Ca_2IrO_4 (Babel, Rudorff & Tschopp, 1966) and CaIrO_3 (Rodi & Babel, 1965). To the best of our knowledge the present work is the first neutron study reported for an oxide of iridium and the errors given

Fig. 1. Observed, calculated and difference profiles of Sr_4IrO_6 at room temperature.Fig. 2. Polyhedral representation of the structure of Sr_4IrO_6 ; open circles represent Sr^{2+} ions, IrO_6 octahedra are hatched.

in Tables 1 and 2 are more than an order of magnitude lower than those previously quoted for Ca₂IrO₄ and CaIrO₃. We therefore believe the Ir—O bond length reported here to be more reliable than that determined in the earlier X-ray studies.

This work demonstrates that although absorption of neutrons is a significant problem when working with iridium compounds, the application of an absorption correction makes data refinement to a high standard possible.

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References

- ATTFIELD, M. P., BATTLE, P. D., BOLLEN, S. K., KIM, S. H., POWELL, A. V. & WORKMAN, M. (1992). *J. Solid State Chem.* **96**, 344–359.
- BABEL, D., RUDORFF, W. & TSCHOPP, R. (1966). *Z. Anorg. Allg. Chem.* **347**, 282–288.
- BROWN, P. J. & MATTHEWMAN, J. C. (1987). Rutherford-Appleton Laboratory Report RAL-87-010.
- CHAMBERLAND, B. L. & PHILPOTTS, A. R. (1992). *J. Alloys Compd.* **82**, 355–363.
- DAVID, W. I. F., JOHNSON, M. W., KNOWLES, K. J., MORETON-SMITH, C. M., CROSBIE, G. D., CAMPBELL, E. P., GRAHAM, S. P. & LYALL, J. S. (1986). Rutherford-Appleton Laboratory Report RAL-86-102.
- FISCHER, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.
- HULL, S. & MAYERS, J. (1989). Rutherford-Appleton Laboratory Report RAL-89-118.
- RANDALL, J. J. & KATZ, L. (1959). *Acta Cryst.* **12**, 519–521.
- RANDALL, J. J. & WARD, R. (1959). *J. Am. Chem. Soc.* **81**, 2629–2631.
- RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
- RODI, F. & BABEL, D. (1965). *Z. Anorg. Allg. Chem.* **336**, 17–23.
- SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 925–945.
- WILEY, J. B. & POEPELMEIER, K. R. (1991). *Mater. Res. Bull.* **26**, 1201–1210.

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Structure of a Synthetic Double-Layer Silicate, Rb₂Cu₂Si₈O₁₉

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Abstract. Rb₂Cu₂Si₈O₁₉, $M_r = 826.7$, monoclinic, $P2_1/m$, $a = 11.450(2)$, $b = 8.409(2)$, $c = 9.847(1)$ Å, $\beta = 95.28(1)^\circ$, $V = 944.1(3)$ Å³, $Z = 2$, $D_x = 2.91$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 8.35$ mm⁻¹, $F(000) = 792$, $T = 298$ K, final $R = 0.045$ for 1411 independent reflections. The structure consists of staggered double sheets of SiO₄ tetrahedra. The sheets consist of six-membered rings. The doubling of sheets forms ten-membered rings viewed parallel to the c axis. These double sheets are linked by pairs of Cu atoms in four coordination sites. Rb atoms are located in the cavities of these ten-membered rings and have eight and ten nearest neighbours. The structure of this silicate is classified as Rb₂Cu₂{ $uB, 2_\infty$ }[⁴Si₈O₁₉] after the classification symbol of Liebau [*Structural Chemistry of Silicates* (1985), pp. 69–75, 121–126, 232, 250, 267. Berlin: Springer].

Introduction. This study was initiated with the purposes of exploring new phases of silicates and contri-

buting to the crystal chemistry of alkali copper silicates. Until now, two sodium copper silicates (Kawamura & Kawahara, 1976, 1977), a lithium copper silicate (Kawamura, Kawahara & Iiyama, 1978), a potassium copper silicate (Kawamura & Iiyama, 1981) and a caesium copper silicate (Heinrich & Gramlich, 1982) have been investigated. The hydrothermal synthesis of a series of rubidium copper silicates, Rb_xCu_ySi_pO_q, was attempted and several new phases were obtained. The present paper reports the structure of one of the newly synthesized phases.

Experimental. Hydrothermal synthesis of the title compound was carried out with a test-tube-type apparatus (723–873 K, 700–2500 kg cm⁻², 3 d) with reagent mixtures of CuSO₄·5H₂O, SiO₂ and Rb₂CO₃. Crystals of Rb₂Cu₂Si₈O₁₉ were deep bluish and less than 0.1 mm in size. The size of the crystal is approximately proportional to the pressure value. The chemical composition of the product was determined by X-ray microprobe analysis. A crystal with dimensions 0.02 × 0.03 × 0.01 mm was used for

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