A Powder Neutron Diffraction Determination of the Structure of Sr₆Co₅O₁₅, Formerly Described as the Low-temperature Hexagonal Form of SrCoO₃ ₋ ₓ

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The structure of $Sr_6Co_5O_{15}$ is determined by Rietveld analysis of powder neutron diffraction data and identified as the low-temperature hexagonal form of $SrCoO_{3-x}$.

The precise identity of the strontium cobalt oxide phase usually described as the low-temperature hexagonal ('H-') form of $Sr_2Co_2O_5$ (or $SrCoO_{3-x}$) has been a puzzle for a number of years.[1-11] At high temperatures ($T > 900$ °C) $Sr_2Co_2O_5$ adopts the brownmillerite structure, and is well characterized.[1] On cooling, brownmillerite $Sr_2Co_2O_5$ undergoes an exothermic transition, with the formation of a hexagonal phase with a structure related to that of $2H\text{-}BaNiO_3$.[1] A more extensive study of the effects of temperature and oxygen partial pressure was carried out by Takeda et al.,[2] who proposed that the hexagonal phase is cobalt deficient $SrCo_{1-u}O_x$ ($u = ca.$ 0.1). Rodríguez and González-Calbert[3] reported that $H\text{-}Sr_2Co_2O_5$ had a rhombohedral unit cell with $a = 9.426$ and $c = 12.495$ Å but no atomic positions were determined. Battle et al.[4-6] used Co–K-edge EXAFS measurements on low-temperature $Sr_2Co_2O_5$ (or $SrCoO_{3-x}$) and found Co–Co distances of ca. 2.43 Å, indicative of face-sharing CoO_6 octahedra. Other studies[7-11] have examined the magnetic and other physical properties of low-temperature $SrCoO_{3-x}$, but until now, the crystal structure and exact composition of this phase have remained uncertain.

In this report, we describe the structure of rhombohedral $Sr_6Co_5O_{15}$ ($SrCo_{0.833}O_{2.5}$), which appears to be stoichiometric, and is related to the 2H-hexagonal-perovskite-type phase. As high-temperature brownmillerite $Sr_2Co_2O_5$ cools in air, phase separation into $Sr_6Co_5O_{15}$ and Co_3O_4 occurs.

$Sr_6Co_5O_{15}$ was prepared as follows: stoichiometric amounts of $SrCO_3$ and Co_3O_4 (both 99.995% pure) were ground together and placed in an alumina crucible to give a 1 : 1 Sr : Co ratio. The crucible was heated in a box furnace, in air, to 570 °C, at 5 °C min⁻¹, and annealed for 1 h. The temperature was then raised to 1060 °C at 2 °C min⁻¹, and held for 10 h. The furnace was turned off, and the sample allowed to cool to ambient temperature. The sample was removed, reground and heated at 2 °C min⁻¹ to 1060 °C (held for 10 h). The resulting black powder was annealed at 800 °C for four days and at 875 °C for 32 days.

The furnace was then turned off to cool. The final black product was gently ground in order to return the sintered solid to powder form. Initial X-ray powder investigations revealed a clean, highly-crystalline pattern. Some of the lines could be assigned to Co_3O_4, as suggested earlier.[1] The $Sr_6Co_5O_{15}$ structure was solved ab initio from powder neutron diffraction data, and optimized by the Rietveld method.† At the end of the refinement, it was apparent that $Sr_6Co_5O_{15}$ is isostructural with the recently reported $Ba_6Ni_5O_{15}$.[12]

$Sr_6Co_5O_{15}$ contains two strontium, three cobalt and three oxygen atom sites in the asymmetric unit. On the basis of the

Rietveld refinement, all of these sites are fully occupied, leading to a Sr : Co ratio of 6 : 5. Assuming the usual valences for Sr and O, then the average Co-atom valence is +3.6.

Both Sr atoms are eight-cordinated by O atoms $\{d_{av}[Sr(1)\text{–}O] = 2.649(2), d_{av}[Sr(2)\text{–}O] = 2.597(2)$ Å$\}$, in irregular coordination. The Sr(1) and Sr(2) species are segregated into separate c-direction columns. Two cobalt atoms, Co(2) and Co(3) (both site symmetry 3) are octahedrally coordinated by nearby oxygen atoms $\{d_{av}[Co(2)\text{–}O] = 1.866(5)$ Å; $d_{av}[Co(3)\text{–}O] = 1.918(5)$ Å$\}$ and the third, Co(1) (site symmetry 32), occupies a distorted trigonal prism $\{d[Co(1)\text{–}O] = 1.973(3)$ Å$\}$.

The structural motif in $Sr_6Co_5O_{15}$ (Figs. 1 and 2) consists of isolated, infinite columns of face-sharing CoO_6 groups which propagate along the crystallographic c direction. Infinite columns of SrO_8 units separate the cobalt–oxygen stacks. The repeat unit for the Co–O species consists of four distorted octahedra sharing faces (a Co_4O_{15} unit), interspersed by prismatically-coordinated Co(1) atoms. The cobalt-atom chain configuration is $[\text{–Co(1)–Co(3)–Co(2)–}$ $\text{Co(2')–Co(3')–}]_\infty$, which results in extremely short inter-octahedral cobalt–cobalt distances: $d[Co(2)\text{–}Co(2')] = 2.36(4)$, $d[Co(2)\text{–}Co(3)] = 2.52(3)$ Å. The face-sharing prismatic/octahedral Co(1)–Co(3) distance is 2.50(2) Å. For comparison, the $Co^{III}\text{–}Co^{III}$ separations (via face-sharing octahedra) in the $12H\text{–}BaCoO_{2.6}$ phase[13]
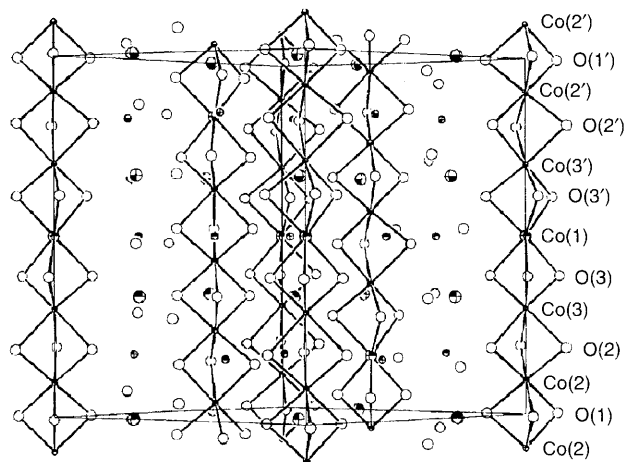
Fig. 1 ORTEP view approximately along [110] of the $Sr_6Co_5O_{15}$ structure, with selected atoms labelled (50% thermal ellipsoids). Sr and Co species represented by shaded circles, O by plain circles. Sr–O bonds omitted for clarity. Compare with Fig. 22 of ref. 14. Selected bond distances (Å) and angles (°): Co(1)–O(3ⁱ⁻ᵛⁱ) 1.973(3), Co(2)–O(1ⁱ⁻ⁱⁱⁱ) 1.87(2), Co(2)–O(2ᵛⁱⁱ⁻ⁱˣ) 1.90(2), Co(3)–O(2ᵛⁱⁱ⁻ⁱˣ) 2.04(1), Co(3)–O(3ⁱᵛ⁻ᵛⁱ) 1.80(1), Co(1)–Co(3ˣ,ˣⁱ) 2.50(2), Co(2)–Co(2ˣⁱⁱ) 2.36(4) Co(2)–Co(3ˣ) 2.52(3); O(3)ⁱ–Co(1)–O(3ⁱⁱ) 76.3(2), O(3ⁱ)–Co(1)–O(3ⁱᵛ) 128.3(2), O(3ⁱ)–Co(1)–O(3ᵛ) 148.6(2), O(3ⁱ)–Co(1)–O(3ᵛⁱ) 90.0(2), O(1ⁱ)–Co(2)–O(1ⁱⁱ) 84.7(7), O(1ⁱ)–Co(2)–O(2ᵛⁱⁱ) 95.46(9), O(1ⁱ)–Co(2)–O(2ᵛⁱⁱⁱ) 92.8(1), O(1ⁱ)–Co(2)–O(2ⁱˣ) 177.5(6), O(2ᵛⁱⁱ)–Co(2)–Co(2ᵛⁱⁱⁱ) 87.1(7), O(2ᵛⁱⁱ)–Co(3)–O(2ᵛⁱⁱⁱ) 79.7(5), O(2ᵛⁱⁱ)–Co(3)–O(3ⁱᵛ) 174.4(5), O(2ᵛⁱⁱ)–Co(3)–O(3ᵛ) 100.1(2), O(2ᵛⁱⁱ)–Co(3)–O(3ᵛⁱ) 94.8(2), O(3ⁱᵛ)–Co(3)–O(3v) 85.5(6), Co(2ˣⁱⁱⁱ)–O(1)–Co(2ˣⁱᵛ) 78.0(1), Co(2ᵛⁱⁱ)–O(2)–Co(3ᵛⁱⁱ) 79.6(7), Co(1ˣ)–O(3)–Co(3ˣᵛ) 82.9(4). Symmetry codes: i $-1 + x, y, z$; ii $-y, -1 + x - y, z$; iii $1 + y - x, 1 - x, z$; iv $y, -1 + x, 1 - z$; v $1 - x, 1 - y - x, 1 - z$; vi $-1 + x - y, -y, 1 - z$; vii $1/3 + y, -1/3 + x, 2/3 - z$; viii $1/3 - x, 2/3 + y - x, 2/3 - z$; ix $-2/3 + x - y, -1/3 - y, 2/3 - z$; x x, y, z; xi $y, x, 1 - z$; xii $y, x -z$; xiii $1 + x, y, z$; xiv $1 + y, x, -z$; xv $1 + y, x, 1 - z$.

Table 1 Atomic Positional Parameters for $Sr_6Co_5O_{15}$

Atom	W^a	x	y	z	$U_{iso}/Å^2$
Sr(1)	9d	0.3206(4)	0	0	0.019(2)
Sr(2)	9e	0.6447(4)	0	0.5	0.007(2)
Co(1)	3b	0	0	0.5	0.017(7)
Co(2)	6c	0	0	0.095(2)	0.006(3)
Co(3)	6c	0	0	0.299(2)	0.005(4)
O(1)	9d	0.8466(5)	0	0	0.0134(4)
O(2)	18f	0.4959(4)	−0.3254(4)	0.4789(2)	0.0134(4)
O(3)	18f	0.8419(4)	−0.0229(4)	0.6116(3)	0.0134(4)

a Wyckoff letter

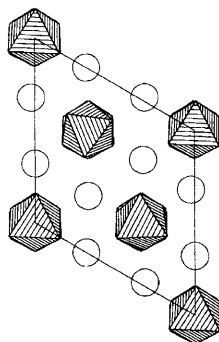**Fig. 2** Polyhedral (STRUPLO) plot of the $Sr_6Co_5O_{15}$ structure viewed down [001], showing the isolated columns of Co/O atoms interspersed by Sr atoms (plain circles)

are 2.41(3) and 2.45(2) Å. Similar short Ni–Ni contacts to the Co–Co distances in $Sr_6Co_5O_{15}$ were seen in $Ba_6Ni_5O_{15}$.[12]

The structural relationship of the $Sr_6Co_5O_{15}$ and $Ba_6Ni_5O_{15}$ structures to other hexagonal perovskite phases including the 2H-polytype, and the Sr_4PtO_6 and $Sr_4Ru_2O_9$ phases, has been described very recently by Darriet and Subramanian.[14]

The nickel valence distribution in $Ba_6Ni_5O_{15}$ was first postulated as random occupancy of the three nickel-atom sites by Ni^{2+}, Ni^{3+} and Ni^{4+}.[12] However, a completely ordered distribution of one Ni^{2+} cation at the prismatic site (multiplicity three) and two Ni^{4+} cations at the two octahedral sites (both with multiplicity six) also satisfies the charge-balancing criterion.[14] The cobalt valence distribution in $Sr_6Co_5O_{15}$ requires further study. Previous work, which assumed a different atomic composition for this phase, or which neglected the presence of Co_3O_4, will need to be re-evaluated.

Footnote

† *Crystal data* for $Sr_6Co_5O_{15}$: M_r = 1060.37, trigonal, space group $R32$ (no. 155), a = 9.5035(2), c = 12.3966(4) Å, V = 969.62(6) Å³, Z = 3, $F(000)$

= 1449, T = 298(2) K. The trigonal powder pattern of $Sr_6Co_5O_{15}$ was indexed using TREOR90 (X-ray data), and possible rhombohedral space groups were determined by inspection. Starting positions for the Sr and O atoms (space group $R32$) were determined from intensities extracted from powder neutron data by using the direct methods program SIRPOW92. These atomic positions were optimized by Rietveld refinement against powder neutron data (high resolution neutron powder diffractometer at Brookhaven National Laboratory, λ = 1.8861 Å, program GSAS). The cobalt atoms were easily found from difference Fourier syntheses and added to the model. Refinement of the Co and O site occupancies did not indicate significant deviation from full occupancy. A second phase of Co_3O_4 (spinel structure; a = 8.0862(4) Å, V = 528.72(7) Å³, space group $Fd\bar{3}m$) was also included in the profile refinement. Refinement of 37 profile and atomic parameters resulted in final residuals of R_p = 8.64% and R_{wp} = 11.24%.

Atomic coordinates and thermal parameters have been deposited at the Fachinformationszentrum Karlsrühe, z.H. Dr P. Luksch, D-76344 Eggenstein Leopoldshafen 2, Germany. See Information for Authors, Issue No. 1.

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