Oxygen-deficient strontium cobaltate, SrCoO$_{2.64}$

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Single crystals of strontium cobaltate, SrCoO$_{3-x}$, have been grown by the floating-zone method in an oxygen flow. The compound crystallizes with the cubic perovskite structure, with $Pm\bar{3}m$ symmetry, as determined by X-ray diffraction. Refinement of the O-atom site occupancy yields the chemical composition SrCoO$_{2.64}$ [x = 0.36 (3)]. The anisotropic displacement ellipsoids of the O atoms suggest that their positional disorder occurs in a direction perpendicular to that of the Co—O bonds.

Comment

Strontium cobaltate, SrCoO$_{3-x}$, exists over a wide range of oxygen non-stoichiometry, and several phases with different oxygen contents have been reported (Watanabe & Takeda, 1970). The cubic perovskite-type structure, with $Pm\bar{3}m$ symmetry, is stable over the composition range x = 0.0–0.4 (Takeda *et al.*, 1986). SrCoO$_3$ cubic perovskite contains low-spin Co^{4+} ions and is a ferromagnetic oxide, with a Curie temperature of 222 K (Taguchi *et al.*, 1979), and a metallic conductor (Taguchi *et al.*, 1980; Bezdicka *et al.*, 1993). Co^{3+} and Co^{4+} ions co-exist in the oxygen-deficient SrCoO$_{3-x}$ cubic perovskite. The magnetic and electric properties of this phase are sensitive to the oxygen deficiency (x), and the Curie temperature and the electric resistance both decrease with increasing x (Taguchi *et al.*, 1979, 1980). Hence, investigating the structural variation of SrCoO$_{3-x}$ cubic perovskite as a function of x is important for an understanding of its physical properties. To date, only lattice parameters determined using powder samples have been reported in this phase, and a full structure refinement, including displacement parameters, has not been published. The determination of these displacement parameters is important for understanding the behavior of oxygen vacancies in the structure.

The present structure refinement of SrCoO$_{3-x}$ cubic perovskite converged to an occupancy of 0.88 (1) for the O-atom site, yielding the chemical composition Sr(Co$^{4+}_{0.28}$-
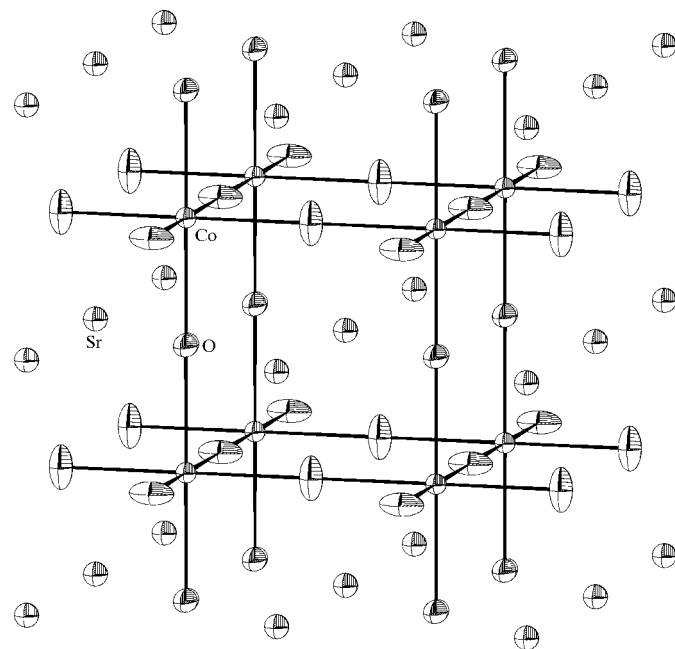
Figure 1
Displacement ellipsoids in SrCoO$_{2.64}$ cubic perovskite, drawn at the 50% probability level.

Co$^{3+}_{0.72}$)O$_{2.64}$ [x = 0.36 (3)]. This result agrees well with the composition Sr(Co$^{4+}_{0.34}$Co$^{3+}_{0.66}$)O$_{2.67}$ obtained by chemical analysis and also with the composition estimated from the correlation between lattice parameter and oxygen deficiency proposed by Takeda *et al.* (1986). The presence of oxygen vacancies is reflected in the larger displacement parameter of the O-atom site [U_{eq} = 0.025 (2) Å^2]. The same observation has also been reported for other non-stoichiometric perovskites (*e.g.* Harrison *et al.*, 1995). The strong anisotropy of the displacement ellipsoid in a direction perpendicular to that of the Co—O bonds (Fig. 1) suggests that positional disorder of the O atoms occurs in the same direction. Selected interatomic distances are given in Table 1.

Experimental

Single crystals of the title compound were grown by the floating-zone method. Stoichiometric amounts of the starting materials, *viz.* powders of SrCO$_3$ and CoO (99.9%), were mixed well and the mixture was placed in a platinum crucible and heated at 1300 K for 10 h under a flow of oxygen. The reaction product was reground and pressed hydrostatically into a rod of 8 mm in diameter and 40 mm in length, which was then sintered at 1500 K for 1 h in an oxygen atmosphere. For the crystal growth, the sintered rod was placed in an image-type floating-zone furnace, with a halogen lamp as a heat source. The crystal growth was carried out under oxygen at a flow rate of 1 l min^{-1}. Upper and lower shafts were counter-rotated at a rate of 25 r.p.m. and the growth rate was 2 mm h^{-1}. The composition of the grown crystals was analyzed by an electron microprobe analyzer, EDTA titration and iodometric oxidation–reduction titration. The analytical results gave a chemical composition of 54.8 wt% SrO, 16.1 wt% CoO$_2$ and 29.2 wt% Co$_2$O$_3$, with a total of 100.1 wt%, corresponding to the composition Sr(Co$^{4+}_{0.34}$Co$^{3+}_{0.66}$)O$_{2.67}$.

inorganic compounds

Crystal data

$SrCoO_{2.64}$
$M_r = 188.79$
Cubic, $Pm\bar{3}m$
$a = 3.8530 (4)$ Å
$V = 57.20 (2)$ Å^3
$Z = 1$
$D_x = 5.483$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25
   reflections
$\theta = 20.0$–$22.5°$
$\mu = 30.22$ mm^{-1}
$T = 296$ K
Sphere, black
0.08 mm (radius)

Data collection

Rigaku AFC-7R diffractometer
ω–2θ scans
Absorption correction: spherical
   (Sasaki, 1987)
   $T_{min} = 0.008$, $T_{max} = 0.011$
539 measured reflections
120 independent reflections
96 reflections with $F > 3\sigma(F)$
$R_{int} = 0.011$

$\theta_{max} = 60.0°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 9$
3 standard reflections
   every 100 reflections
   intensity decay: none

Refinement

Refinement on F
$R = 0.021$
$wR = 0.011$
$S = 1.88$
96 reflections
7 parameters
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max} < 0.0001$
$\Delta\rho_{max} = 2.80$ e Å^{-3}
$\Delta\rho_{min} = -2.64$ e Å^{-3}
Extinction correction: isotropic
   Type I (Becker & Coppens,
   1974a,b)
Extinction coefficient:
   0.054 (2) × 10^{-4}

The maximum and minimum residual electron densities are located at (0, 0, 0) and (0.46, 0.46, 0.46), respectively.

Data collection: *WinAFC* (Rigaku, 1999); cell refinement: *WinAFC*; data reduction: *RADY* (Sasaki, 1987); program(s) used to refine structure: *RADY*; molecular graphics: *ATOMS for Windows* (Dowty, 2000).

Table 1
Selected interatomic distances (Å).

Sr—O	2.7245 (2)	O—O^i	2.7245 (2)
Co—O	1.9265 (2)		

Symmetry code: (i) z, x, y.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1039). Services for accessing these data are described at the back of the journal.

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