The Structure of $BaCoO_{2\cdot6}$ by a Combination of High-resolution Electron Microscopy and Neutron Powder Diffraction

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Summary The structure of perovskite-related 12 layer $BaCoO_{2\cdot6}$ has been determined by powder methods using direct lattice imaging and neutron diffraction.

THE perovskite-related compounds $BaMO_{3-x}$ (M = Mn, Fe, Co, Ni; $0\cdot0 < x < 0\cdot5$) have structures based on close-packed BaO_3 layers with M cations in octahedral interstices.[1] For $BaCoO_{3-x}$ two phases are known; 2H with all hexagonal BaO_3 stacking and 12H with an unknown sequence.[2]

We have shown previously that electron microscope lattice images may directly reveal the Ba stacking.[3] They show sheets of Ba atoms projected edge on along $<10\bar{1}0>$ as dark lines. The slope of these dark lines distinguishes cubic (c) from hexagonal (h) close-packed BaO_3 layers. Oxygen atoms do not contribute significant contrast in the image and consequently we cannot obtain information concerning the O vacancy distribution. The lattice image gives, therefore, a trial structure based only on cation positions. Profile analysis of powder neutron diffraction[4] data enables the positions of all atoms including oxygens to be determined but the method requires a reasonable trial model. Here we describe the combined use of these techniques in the structure analysis of 12H $BaCoO_{2\cdot6}$.

A powder sample (*ca.* 25 g) of 12H $BaCoO_{2\cdot6}$ was prepared by annealing the 12H phase for 90 days at 905 °C in a Pt crucible and quenching. The composition was found by chemical analysis to be $BaCoO_{2\cdot61(4)}$.

Lattice images were obtained with a Siemens Elmsikop 102 electron microscope at an accelerating voltage of 100 keV. Thin crystals on carbon-coated Cu grids were oriented with the electron beam along $<10\bar{1}0>$ and images were obtained at magnifications of 500,000 × with a 40μ objective aperture which included beams out to $0\cdot3$ Å^{-1}. Of the 42 possibilities for 12 layer stacking, the hitherto unknown sequence $(ccchhh)_2$ was found to correlate best with the image and an idealised $<10\bar{1}0>$ projection of this sequence is shown inset into the lattice image in the Figure.

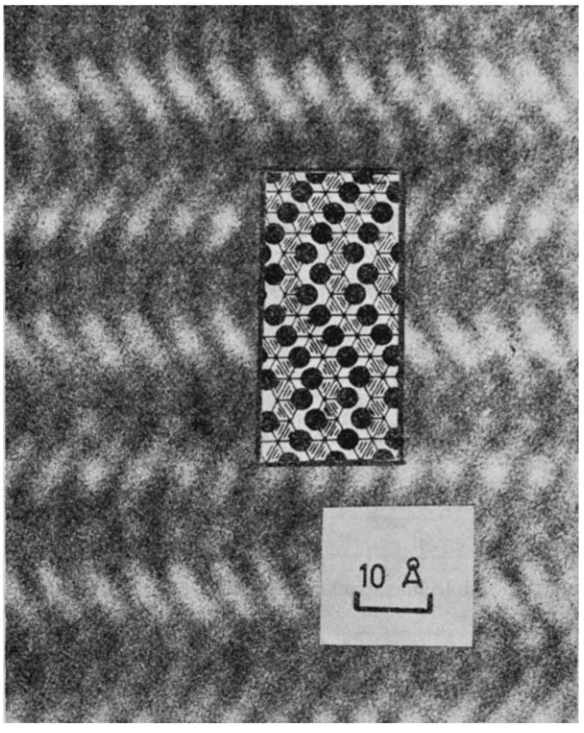

FIGURE. Lattice image of $BaCoO_{2.6}$ with electron beam along $<10\bar{1}0>$. Dark lines in the image correspond to sheets of Ba atoms viewed end on. Inset: idealised projection of the structure showing Ba atoms as filled circles and 'CoO_6' octahedra as cross-hatched parallelograms.

Neutron diffraction data were collected on a powder diffractometer at U.K.A.E.A. Harwell at 4·2 K with a wavelength of 1·5423 Å from the (511) planes of a Ge monochromator with a take-off angle of 90°. Data in the range $7° < 2\theta < 85°$ were refined by the profile analysis method[5] in space group $P6_3/mmc$ [$a = 5·671(1)$, $c = 28·55(1)$ Å] with starting parameters obtained from the lattice image. Preliminary refinement confirmed that the ccchhh stacking of Ba deduced from the lattice image was correct but indicated that the central cubic layer has composition BaO_2. With this model the 22 structural parameters including the oxygen occupation numbers were refined until the parameter shifts were less than 0·3 standard deviations. The final R factor based on integrated intensities is 0·07 and the composition from the occupation numbers is $BaCoO_{2·60(7)}$ in agreement with the chemical analysis.

The structure consists of CoO_4 tetrahedra corner-linked to the terminal oxygens of a string of four face-shared CoO_6 octahedra. The mean Co–O distances (tet., 1·78 Å and oct., 1·91 Å; *cf.* 1·78 Å in $Ba_2Co^{IV}O_4$[6] and 1·88 Å for $Co^{III}O_6$ from ionic radii[7]) indicate that the tetrahedra contain Co^{IV} and the octahedra Co^{III}.

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