

Crystal Structure and Possible Charge Ordering in One-Dimensional $\text{Ca}_3\text{Co}_2\text{O}_6$

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The crystal structure of the one-dimensional oxide $\text{Ca}_3\text{Co}_2\text{O}_6$ has been solved by *ab initio* methods from powder X-ray diffraction data and refined from powder neutron diffraction data. The structure is closely related to that for $\text{Sr}_3\text{NiIrO}_6$. $\text{Ca}_3\text{Co}_2\text{O}_6$ crystallizes in space group $R\bar{3}c$, $Z = 6$ (hexagonal setting) and $a = 907.93(7)$ and $c = 1038.1(1)$ pm. The Co atoms form alternating, face-sharing coordination polyhedra of trigonal prisms and octahedra. In this way one-dimensional Co–O chains are formed that run along the trigonal axis. The chains are separated by eight coordinated calcium atoms. The separation between Co atoms within the chains are 259.5 pm which suggest metal–metal interactions. Based on interatomic Co–O distances and bond strength considerations, it is proposed that either charge or spin ordering of the different Co species occurs within the chains. © 1996 Academic Press, Inc.

INTRODUCTION

Low-dimensional materials have attracted interest among chemist and physicists owing to their highly anisotropic and rather unique physical properties. Among metal oxides, low-dimensionality usually refers to systems where metal–metal separations are short within a plane or along a chain. The latter situation is not frequent among oxides. However, in the class of $A_4\text{PtO}_6$ related oxides ($A = \text{Ca}, \text{Sr}, \text{Ba}$), the AO_6 trigonal prisms and PtO_6 octahedra share common faces along the chain direction giving a material with $-A\text{--Pt--A--Pt--}$ chains (1–3). This structure type has recently been described for other oxides, like Sr_3MIR_6 with $M = \text{Ni}, \text{Cu},$ and Zn , where the one-dimensional chains consists of alternating face-sharing MO_6 and IrO_6 polyhedra (4).

In the Ca–Co–O system, the compound $\text{Ca}_3\text{Co}_2\text{O}_6$ has been known for a long time (5, 6). However, only its diffraction pattern has been described in the literature. As part of a broader study of perovskite related phases in the La–Ca–Co–O system, it was considered important to obtain detailed structure data for $\text{Ca}_3\text{Co}_2\text{O}_6$. The structure was therefore solved *ab initio* on the basis of powder X-

ray diffraction (PXD) data, and the oxygen (light atom) positions were subsequently confirmed by powder neutron diffraction (PND) data. The resulting structure proved to be of the type described above which implies that the entire one-dimensional chains are built by face-sharing CoO_6 polyhedra. The present study reports on the crystal structure of $\text{Ca}_3\text{Co}_2\text{O}_6$ between 40 and 298 K.

EXPERIMENTAL

Starting materials for the syntheses were CaCO_3 (Merck, p.a.), $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (>99%, Fluka), and citric acid monohydrate $\text{C}_3\text{H}_4(\text{OH})(\text{COOH})_3 \cdot \text{H}_2\text{O}$ (reagent grade, Sturge biochemicals). The Co content of the acetate was determined gravimetrically. The citric acid was dissolved in distilled water at 100°C, whereafter CaCO_3 and Co–acetate were added under stirring. The clear citrate solution was dehydrated at 450 K forming first a polymer gel and finally a porous, X-ray amorphous xerogel. Most of the carbonaceous species were thereafter removed by incineration at 720 K for a few hours. The sample was then ground in an agate mortar and pressed into pellets, which were placed in alumina crucibles and heated at 1273 K for 1 week with one intermittant grinding.

The reaction products were from room temperature powder X-ray diffraction (Guinier–Hägg camera, $\text{CuK}\alpha_1$ and $\text{CrK}\alpha_1$ radiation, Si as internal standard) assured to be phase pure. In experiments with off-stoichiometric compositions or with annealing temperature higher than ascribed by phase diagram data, impurities of CaO , Co_3O_4 , CoO , or $\text{Ca}_3\text{Co}_4\text{O}_9$ were observed. High temperature powder X-ray diffraction data were collected with a Guinier Simon camera (Enraf Nonius) between 300 and 800 K. The samples were kept in a rotating, silica glass capillary, and the temperature change was synchronized with the movement of the film cassette. The linear volume thermal expansion coefficient for the temperature interval 300–800 K is $\alpha_V = 4.7 \times 10^{-5} \text{ K}^{-1}$.

The X-ray diffraction pattern at 298 K was indexed with the help of the TREOR program (7). Unit cell dimensions

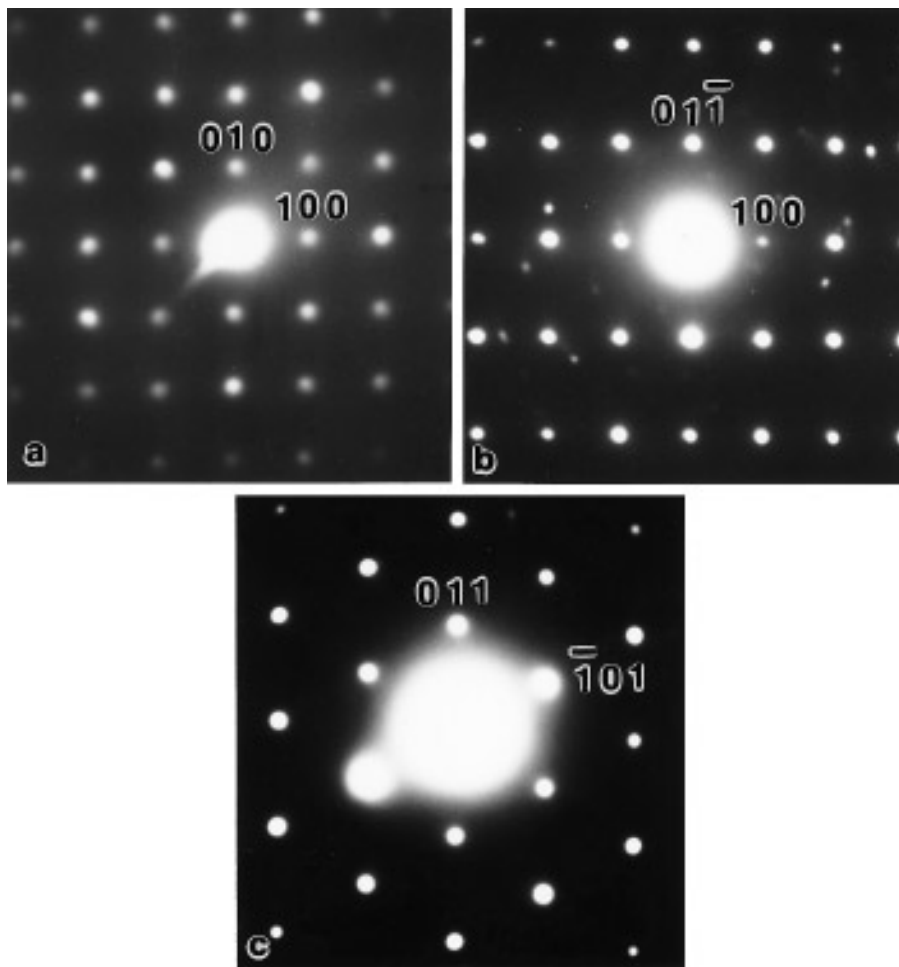


FIG. 1. SAD patterns of (a) [001], (b) [011], and (c) [1-11] projections. The indices refer to the rhombohedral setting.

were obtained from least-squares refinements using the CELLKANT program (8). Thermogravimetric analysis (TGA) was performed with a Perkin—Elmer, TGA7 system between 300 and 1400 K at a heating rate of 10 K min^{-1} . Differential scanning calorimetry (DSC) measurements were performed with a Mettler TA 3000 system between 100 and 800 K without revealing any anomalies.

The samples were investigated in a JEOL 2000FX transmission electron microscope (TEM). The powder of $\text{Ca}_3\text{Co}_2\text{O}_6$ was crushed in ethanol in an agate mortar and thin crystallites were placed on holey carbon films. By careful tilting of the specimens, selected area electron diffraction (SAD) patterns were recorded. The three-dimensional space and the Bravais lattice were then determined.

Powder X-ray diffraction data for the crystal structure determination were collected with a Siemens D500 diffractometer, using monochromatic $\text{CuK}\alpha_1$ radiation. The data were recorded in steps of 0.02° in 2θ between 10° , and 100° (Bragg Brentano geometry) and the counting time for each setting was 20 s. The fine powders were pressed

into a standard sample holder. Powder neutron diffraction data were collected with the OPUS III two-axis diffractometer at the JEEP II reactor, Kjeller. Cylindrical sample holders were used. Monochromatized neutrons of wavelength 182.5 pm were obtained by reflection from Ge(111). The scattered intensities were measured by five ^3He detectors, positioned 10° apart. Intensity data were collected from $2\theta = 5^\circ$ to 100° in steps of $\Delta 2\theta = 0.05^\circ$. Temperatures between 40 and 298 K were obtained by means of a Displex cooling system. A Lake Shore DRC 82C controller was used, and the temperature was measured and controlled by means of a silicon diode. Data corrections, deconvolution, structure determination, and profile refinements were performed with the ALLHKL (9), SIRPOW (10), and DBW3.2S (11) programs.

RESULTS AND DISCUSSION

The PXD pattern collected by the Guinier–Hägg film technique was indexed by means of the TREOR (7) pro-

TABLE 1
Crystal Data for $\text{Ca}_3\text{Co}_2\text{O}_6$ at 40 and 298 K

Formula	$\text{Ca}_3\text{Co}_2\text{O}_6$		
Formula weight	334.10		
Color	black		
Space group	$R\text{-}3c$		
Z	2 (RH-setting), 6 (HEX-setting)		
λ (pm)	182.5 (neutron), 154.0598 (X-ray)		
2θ range	5–100° (neutrons and X-ray)		
Number of reflections	57 (neutron), 89 (X-ray)		
Number of parameters	15		
Profile function	Gaussian (neutron), pseudo-Voigt (X-ray)		
	40 K	298 K (PND)	298 K (PXD) ^a
a_{H} (pm)	906.1(1)	908.7(1)	907.93(7)
c_{H} (pm)	1036.7(1)	1038.91(6)	1038.1(1)
V_{H} (10^6 pm^3)	737.12	742.93	743.37
R_{wp}	3.77	3.02	1.31
R_{p}	4.95	4.06	2.25

^a Guinier–Hägg data.

gram on a rhombohedral lattice with dimensions $a_{\text{R}} = 628.1 \text{ pm}$, $\alpha = 92.56^\circ$ ($a_{\text{H}} = 907.93 \text{ pm}$, $c_{\text{H}} = 1038.1 \text{ pm}$ in hexagonal setting), figure of merit $M(20) = 16$ (12). A smaller orthorhombic unit cell was also suggested, however, as judged from the cell content and as proved by electron microscopy (TEM) it was incorrect. SAD patterns showing simultaneously both the zero and first order zones were exposed. From all such patterns the approximate size of the unit cell was obtained. All other single crystal SAD patterns recorded in TEM could be indexed on the rhombohedral unit cell. Figure 1 shows SAD patterns in the [001], [011], and [1-11] projections.

Structure factors were extracted from the recorded diffractometer PXD profile with the ALLHKL program (9). The PXD data indicate probable systematic extinctions for hhl , $l = 2n + 1$ (and hhh , $h = 2n + 1$; rhombohedral setting). The presence of reflections of the type hhl , like (010) and (100) in Fig. 1a and the (11-1) and (-11-1) in Fig. 1b, may appear due to multiple diffraction effects and the TEM data are probably consistent with the condition hhI , $I = 2n$. Therefore, convergent beam electron diffraction (CBED) was used in order to get further information on the space group symmetry, but a unique solution was not achieved. The direct method program SIRPOW (10) was applied for space group setting $R\text{-}3$, and a solution, which subsequently was proven to be consistent with space group $R\text{-}3c$, was found. The solution was verified by Rietveld type refinements using the DBW3.2S program (11), and improved coordinates for the oxygen atoms were deduced from PND data. No improvements in the R factors were gained on reducing the symmetry from $R\text{-}3c$. Crystal data and information on the data collection are given in Table 1 and refined atomic coordinates are listed in Table

2. The observed and difference PND patterns at 298 K are shown in Fig. 2.

The crystal structure of $\text{Ca}_3\text{Co}_2\text{O}_6$ is closely related to those for $\text{Sr}_3\text{M}(\text{IrO}_6)$ (4). A projection of the structure on the hexagonal ab plane is shown in Fig. 3. The Co–O atoms are part of chains of face sharing polyhedra running parallel to c . These chains are separated by eight coordinated Ca atoms. The one-dimensional chains are illustrated in Fig. 4. The chains consist of alternating face-sharing trigonal prisms (containing Co2) and octahedra (with Co1). As a result of the face sharing, the Co atoms become close in separation, $d(\text{Co1}–\text{Co2}) = 259.5 \text{ pm}$, see Table 3. The trigonal prismatic coordination is rather untypical for cobalt. Each chain is surrounded by six other chains at a distance of $a/\sqrt{3} = 524 \text{ pm}$ (Fig. 3). Each Co atom has $2 + (6 + 6)$ Co neighbors, two at 259.5 pm, six at 531 pm, and six at 552 pm. The distance ratio between nearest and next nearest Co neighboring atoms is 2.05.

The chemical composition $\text{Ca}_3\text{Co}_2\text{O}_6$ was confirmed by TGA and refinements on the occupation number for oxygen (PND data), which implies that cobalt formally is trivalent. TGA gave the composition $\text{Ca}_3\text{Co}_2\text{O}_{5.97}$ deduced from the decomposition reaction $\text{Ca}_3\text{Co}_2\text{O}_6 \rightarrow 3\text{CaO} + 2\text{CoO} + \frac{1}{2}\text{O}_2$ (g) occurring at 1309 K [1299 K according to literature (5, 6)]. The PND refinements gave the composition $\text{Ca}_3\text{Co}_2\text{O}_6$ within one calculated standard deviation, however, the occupation number for oxygen is strongly correlated to the value for the isotropic displacement factors. The Co–Co separation in $\text{Ca}_3\text{Co}_2\text{O}_6$ is close to that in metallic cobalt, 251 pm (13). In $\text{Sr}_3\text{NiIrO}_6$ direct metal–metal bonding was considered not to be active (4). However, for $\text{Ca}_3\text{Co}_2\text{O}_6$ metal bonding within the one-dimensional chains is probable. The arrangement of the chains in $\text{Ca}_3\text{Co}_2\text{O}_6$ and $\text{Sr}_3\text{NiIrO}_6$ are compared in Fig. 4. The only significant difference is ordering of the Ir and Ni atoms for the latter.

The Co–O distances for Co1 and Co2, respectively, in octahedral and trigonal prismatic coordination are signifi-

TABLE 2
Atomic Coordinates Refined from Powder X-Ray and Neutron Diffraction (in italics) Data

Atom	Site	x	y	z
Ca (298 K)	18e	<i>0.3690(2)</i>	0	1/4
(40 K)		<i>0.3691(4)</i>		
		<i>0.3690(4)</i>		
Co1	6b	0	0	0
Co2	6a	0	0	1/4
O (298 K)	36f	<i>0.1767(2)</i>	<i>0.0238(2)</i>	<i>0.1138(1)</i>
		<i>0.1820(7)</i>	<i>0.0241(11)</i>	<i>0.1151(6)</i>
(40 K)		<i>0.1764(2)</i>	<i>0.0227(3)</i>	<i>0.1140(2)</i>

Note. Space group $R\text{-}3c$. Calculated standard deviations in parentheses.

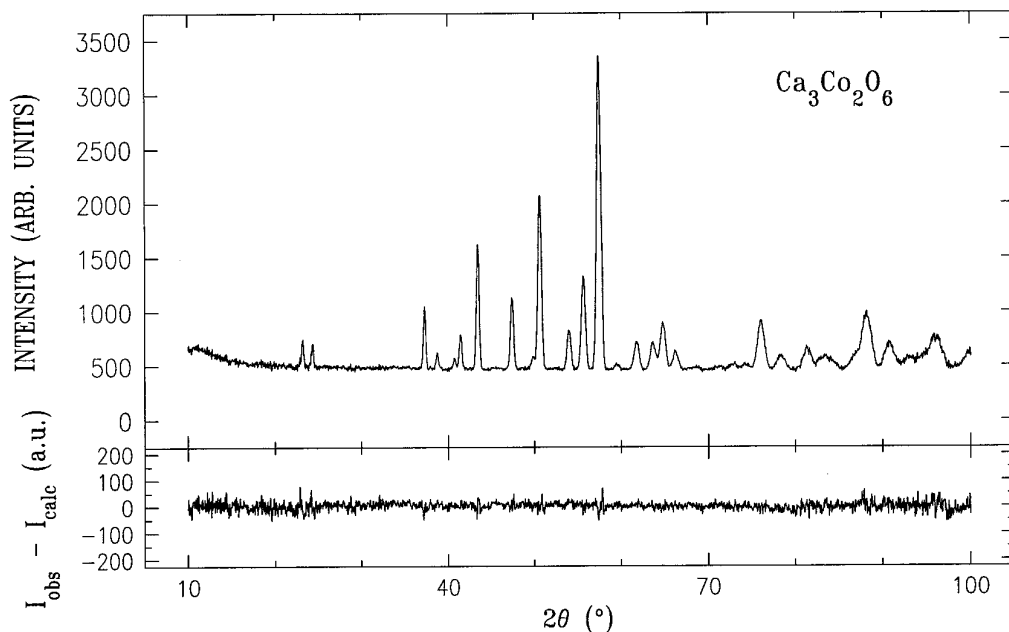


FIG. 2. Observed and difference PND pattern ($\lambda = 182.5$ pm) for $\text{Ca}_3\text{Co}_2\text{O}_6$ at 298 K.

cantly different; see Table 3. An estimate of the valencies can be made according to the bond strength concept (14). The bond length parameter 1.70 was chosen for cobalt (14). For Co1 the valence of 3.35 is calculated, and for Co2 the valence is drastically lower, 2.25. The average bond valency is probably significantly less than expected which is a further indication of metal-metal interactions within the chains. The Co atoms in the one-dimensional chains exhibit ordering of alternating octahedral and trigonal prismatic Co species. In $\text{Sr}_3\text{NiIrO}_6$ this correspond to ordering of Ir^{IV} and Ni^{II} atoms (4). From comparisons between $\text{Ca}_3\text{Co}_2\text{O}_6$ and Sr_3MIrO_6 ($M = \text{Ni}, \text{Cu}, \text{Zn}$), it appears that

the atom with the larger size (covalent radius) prefers the trigonal prismatic coordination. The ordering in $\text{Ca}_3\text{Co}_2\text{O}_6$ may either represent charge ordering (say Co^{IV} and Co^{II} , or intermediate oxidation states if additional metallic bonding is present) or ordering of low and high spin species. The $\text{Ca}_3\text{Co}_2\text{O}_6$ phase appears to represent a unique system with charge/spin ordering in a quasi-one-dimensional oxide.

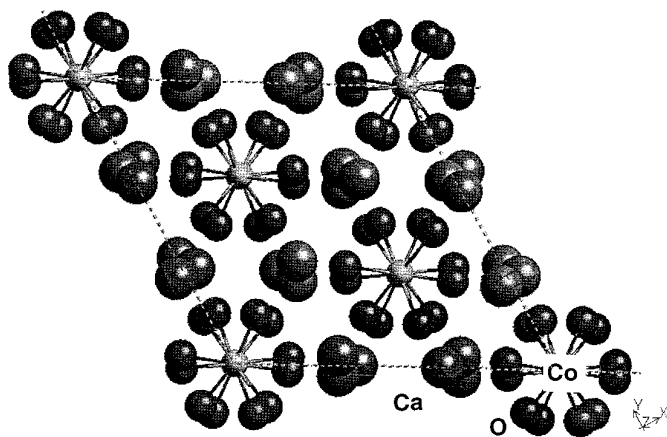


FIG. 3. Crystal structure of $\text{Ca}_3\text{Co}_2\text{O}_6$ projected on the hexagonal ab plane.

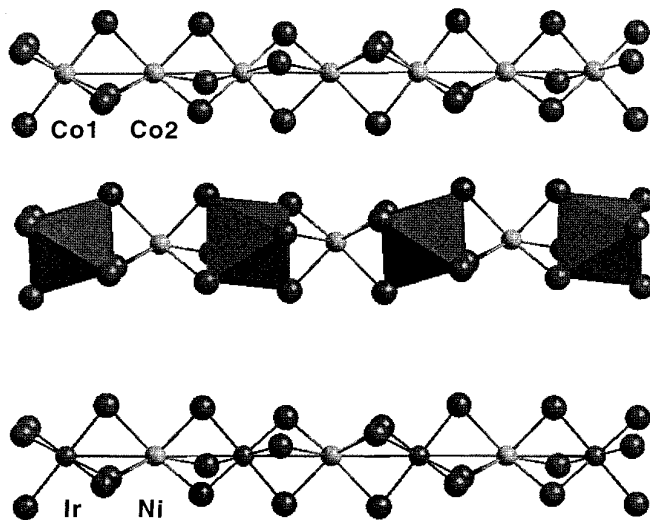


FIG. 4. One-dimensional Co-O chain in $\text{Ca}_3\text{Co}_2\text{O}_6$ (upper) compared with related chain in $\text{Sr}_3\text{NiIrO}_6$ (lower). Octahedra for Co (and Ir) are shown in the middle part.

TABLE 3
Interatomic Distances (in pm) for $\text{Ca}_3\text{Co}_2\text{O}_6$ at 298 K

Co1–O	(×6) 191.6
Co1–Co2	(×2) 259.5
Bond strength (valence): 3.35	
Co2–O	(×6) 206.2
Co2–Co1	(×2) 259.5
Bond strength (valence): 2.23	
Ca–O	(×2) 233.9
	(×2) 246.0
	(×2) 247.1
	(×2) 255.6

ACKNOWLEDGMENT

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