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Synthesis and structure of $Ba_6Co_6ClO_{16}$, a new cobalt oxychloride with a layered perovskite-related structure

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Abstract

Well-developed single crystals of the title compound were prepared using a $BaCl_2$ flux and investigated by X-ray diffraction methods using Mo($K\alpha$) radiation and a Charge Coupled Device (CCD) detector. The crystal structure was solved and refined in the hexagonal symmetry with $P\bar{6}m2$ space group, $a = 5.6698(2)$ Å and $c = 14.4654(5)$ Å to a final $R_1 = 0.022$ for 44 parameters with 1418 individual reflections. The structure of $Ba_6Co_6ClO_{16}$, which is related to the 6H-perovkite-type structure of $BaMnO_{2.88}$, is formed by the periodic stacking along [001] of five [BaO_3] layers separated by a [BaOCl] with a (*hhhchc*) stacking sequence. The [BaO_3] stacking creates tetranuclear face sharing octahedra units Co_4O_{15} containing Co(III) connected by dimers of corner-sharing CoO_4 tetrahedra. This new oxychloride belongs to the family of compounds formulated as $[BaOCl]M'_2[Ba_{n+1}M_nO_{3n+3}]$ where n represents the thickness of the octahedral string in hexagonal perovskite slabs.

Keywords: Barium cobalt oxychloride; Hexagonal perovskite; 6H perovskite-type structure; Crystal structure

1. Introduction

The ideal ABX_3 perovskite can be described from the cubic close-packing of AX_3 layers with the B cations occupying the octahedral holes resulting in a three-dimensional framework *ccc* of only corner-sharing octahedra. In opposite, in the ideal hexagonal perovskite ABX_3 the B cations occupy octahedra that are connected by face-sharing to form chains running down the *c*-axis of the hexagonal unit cell, the stacking sequence of the AX_3 layers is *hh*. Intermediate structures called hexagonal perovskite containing different proportions of cubic stacking (corner-sharing octahedra) and hexagonal stacking (face-sharing octahedra) are formed between the two ideal structures. Depending on the *h* and *c* layers stacking sequence, strings of two (*h*), three (*hh*) or four (*hhh*) face-sharing octahedra are corner shared (*c*) or separated by layers of one (*cc*), two (*ccc*), three (*cccc*), … corner-shared octahedra. Many $BaBO_3$ oxides are known corresponding to the different sequences. Furthermore, deficient layers such as BaO_2, BaOCl, BaCl, can be combined to BaO_3 layers to form numerous new compounds derived from hexagonal perovskite [1]. For example, the introduction of double Ba_2Cl_2 layers in an hexagonal perovskite-type arrangement of RuO_6 octahedra allows the formation of the series $[Ba_2Cl_2][Ba_{n+1}Ru_nO_{3n+3}]$ for $n = 2, 3$ [2] or 4 [3] where n represents the thickness of the octahedral string in hexagonal perovskite slabs. The replacement of the middle *h* or *c*-BaO_3 layer in a *chc* or a *ccc* block by a deficient BaO_2 layer results in the creation of two B-cation tetrahedra corner shared (to form a B_2O_7 dimer) or not, respectively. This type of structure is observed, for example, (1) in $Ba_5Fe_5O_{14}$ [4,5] where a *h*-BaO_3 layer is replaced by a BaO_2 layer in a *hhchc* sequence forming trimeric units of three face-shared octahedra cross linked by dimers of corner-shared tetrahedra and (2)

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in 12H-$BaCoO_{2.6}$ [6] where a c-BaO_3 layer is replaced by a BaO_2 layer in a *hhhccc* sequence forming isolated units of four face-shared octahedral flanked on both boundaries by non-connecting BO_4 tetrahedra to form isolated blocks. A BaOCl layer, deduced from a BaO_2 layer by the substitution of Cl to one O atom, can only replace a h-BaO_3 layer to form a B_2O_7 dimer of two corner-shared tetrahedra. For BaO_3 and BaOCl stacking, up today, only $Ba_5B_5ClO_{13}$ compounds have been evidenced in which units of three face-shared octahedra are connected by B_2O_7 units. In these compounds B is Co [7] or a combination of two [8,9] or three metals [10]. For B = Co, the $Ba_5Co_5ClO_{13}$ compound is obtained [7] and can be described as the term $n = 3$ of a series $Ba_{n+2}Co_nCo_2ClO_{3n+4}$.

Majority of the prepared compounds contains mixed valence transition metals and exhibits unusual electronic properties correlated to the crystal structure. In the present paper we report the powder synthesis, the crystal growth and the crystal structure determination of a new oxychloride $Ba_6Co_6ClO_{16}$ that contains tetrameric units of face-shared CoO_6 octahedra connected by dimeric units of corner shared CoO_4 octahedra and is the term $n = 4$ of the predicted series.

2. Experimental

$Ba_6Co_6ClO_{16}$ single crystals were grown by a flux method using a procedure similar to that described by Yamaura et al. [7] for the synthesis of $Ba_5Co_5ClO_{13}$ single crystals. Typically, a 2 g mixture of $BaCO_3$ (Fisher, 99%), Co_3O_4 (Fluka, Assay >71% (KT) Co) and $BaCl_2 \cdot 2H_2O$ (Prolabo, Rectapur) with the 3:1:6 ratio was well ground in an agate mortar and heated in air at 1000 °C in an alumina crucible for 48 h. The crucible was then slowly cooled to 850 °C at 0.5 °C/min and finally quenched to room temperature. The excess of $BaCl_2$ was dissolved in hot water and two types of black shiny crystals were extracted from the preparation. Several single crystals were tested on a Bruker Smart CCD X-ray diffractometer. The needle-shaped crystals correspond to the previously reported $Ba_5Co_5ClO_{13}$ compound. The plate-like crystals also give an hexagonal cell with the same a parameter, $a \approx 5.67$ Å, but with lower c parameter, $c \approx 14.45$ Å and correspond to the new $Ba_6Co_6ClO_{16}$ compound.

Pure powder of $Ba_6Co_6ClO_{16}$ was synthesized by solid state reaction between the same reactants in stoechiometric ratio 11:4:1, at 900 °C during 24 h. Several intermediate regrindings were realized in order to homogenize the mixture. The resulting dark powder was examined by X-ray diffraction using a Huber G670 diffractometer with Guinier geometry, equipped with front-monochromator using Cu$K\alpha_1$ radiation ($\lambda = 1.54056$ Å).

Energy dispersive spectroscopy realized on several crystals revealed the presence of all elements introduced in the preparation: Ba, Co, Cl and O. Measurements were performed on a JEOL JSM-5300 scanning microscope equipped with an IMIX system of Princeton Gamma Technology, at 15 kV. Quantitative analysis realized on several points lead to the following ratio: Ba/Cl = 6.58(13) and Co/Cl = 6.62(12).

Redox chemical analysis was realized on the powder compound. A precise amount of $Ba_6Co_6ClO_{16}$ powder sample (≈ 0.08 g) was dissolved into a mixture of 100 mL of 2 N hydrochloric acid and 50 mL of 1 N phosphoric acid, with an excess of $FeCl_2$ solution (20 mL, 0.0974 N). Chemical reactions were:

$$Co^{3+} + Fe^{2+} \rightarrow Co^{2+} + Fe^{3+}$$

and $$Co^{4+} + Fe^{2+} \rightarrow Co^{2+} + Fe^{3+}$$

leading to the global reaction: $Co^{x+} + (x-2)\,Fe^{2+} \rightarrow Co^{2+} + (x-2)\,Fe^{3+}$.

The proportioning of the excess of Fe^{2+} was realized with a $K_2Cr_2O_7$ solution (0.0167 N) in presence of a redox indicator according to

$$6\,Fe^{2+} + Cr_2O_7^{2-} + 14\,H^+ \rightarrow 6Fe^{3+} + 2\,Cr^{3+} + 7\,H_2O.$$

The oxidation state of cobalt was deduced from the difference between initial Fe^{2+} ions and Fe^{2+} ions titrated after the previous reaction. The results lead to a mean oxidation degree for cobalt of +3.33 (Table 1). So, the formula of the studied compound can be written $Ba_6Co_6ClO_{15.5}$ showing a weak deficiency in oxygen atoms. This hypothesis will be confirmed by structural considerations in the last part of this paper.

2.1. Crystal structure determination

A black plate-like crystal of $Ba_6Co_6ClO_{16}$ was selected, mounted on a glass fiber and aligned on a Bruker X8 CCD 4 K diffractometer. The X-ray intensity data were measured at room temperature using a Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) selected by a graphite monochromator. A strategy based on phi and omega scans has been chosen. According to the cell parameters of the compound and the high quality of the selected crystal, the scan angle and the Dx parameter were adjusted to limit the overlapping of reflections, i.e. in our case, the

Table 1
Mean oxidation state for cobalt (x) in $Ba_6Co_6ClO_{16}$

Experiment	m (g)	V (mL)	x
1	0.0746	15.90	3.328
2	0.0894	15.10	3.327
3	0.0998	14.50	3.336
4	0.0852	15.30	3.335