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## The Structure of the Fourteen-Layer Polytype of Barium Chromium Trioxide, $\text{BaCrO}_3$

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### Abstract

One of the products of the reaction between  $\text{CrO}_2$  and  $\text{Ba}_2\text{CrO}_4$  at 1573 K and 6.0–6.5 GPa is a fourteen-layer polytype of  $\text{BaCrO}_3$ . The compound crystallizes in space group  $P6_3/mmc$  with  $a = 5.650$  (2),  $c = 32.467$  (5) Å,  $Z = 14$ . The structure was determined from 346 independent reflections collected by counter methods and refined by least-squares methods to a conventional  $R$  value of 4.1%. It consists of a fourteen-layer stacking sequence of close-packed  $\text{BaO}_3$  layers, Zhdanov notation for the sequence  $12(3)212(3)21$ , with all the  $\text{O}_6$  octahedral sites occupied by Cr. In each cell there are strings of three pairs of face-sharing octahedra in which the pairs are linked to each other by corner sharing; the strings in turn are joined to each other by octahedra sharing only corners. The structure is thus closely related to the four-layer, six-layer, and twenty-seven-layer polytypes of  $\text{BaCrO}_3$ .

### Introduction

A number of barium chromium oxides have been prepared from high pressure/high-temperature reactions of BaO or  $\text{Ba}_2\text{CrO}_4$  with  $\text{CrO}_2$  (Chamberland, 1969). These compounds include several polytypes of  $\text{BaCrO}_3$  with layer structures. A discussion of structure relations in mixed metal oxides which can be described in terms of close-packed layers of composition  $\text{AO}_3$  has been given by Katz & Ward (1964). For hexagonal-close-packed structures, structure information may be conveyed by using a number to indicate the

number of layers per unit cell and the letter  $H$  or  $R$  to indicate the lattice type, e.g.  $12R$  to indicate a twelve-layer structure based on a rhombohedral lattice. We have recently reported on a  $27R$  polytype of  $\text{BaCrO}_3$  (Haradem, Chamberland & Katz, 1980). A  $14H$  polytype of  $\text{BaCrO}_3$  is the subject of the present paper.

### Experimental

The barium chromium oxide used in our study was from a sample prepared at 1573 K and 6.0–6.5 GPa in a tetrahedral-anvil press. In addition to large, black crystals of the  $14H$  compound, microcrystalline  $4H$   $\text{BaCrO}_3$ ,  $\text{BaCrO}_4$ , and a water-soluble product were formed. The crystal used for the structure determination, after an attempt to make it spherical in a sphere grinder, was shaped like an elliptical cylinder with one end rounded and had dimensions ranging from 0.167 to 0.242 mm.

X-ray precession photographs showed hexagonal symmetry, Laue group  $6/mmm$ . The only systematic absences were  $hhl$  reflections with  $l$  odd, so the probable space group is one of  $P6_3mc$ ,  $P6_2c$ , or  $P6_3/mmc$ .

Approximately 2200 reflections out to  $2\theta = 54^\circ$  were measured on a computer-controlled Picker single-crystal diffractometer using graphite-monochromatized  $\text{Mo } K\alpha$  radiation with the diffractometer operating in the  $\omega$ -scan mode. Three standard reflections were measured periodically and showed no tendency to drift. Their maximum intensity variation was  $\pm 3.5\%$ . Hexagonal cell dimensions,  $a = 5.650$  (2),  $c = 32.467$  (5) Å, were determined by least-squares

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refinement using the diffractometer angles for 24 reflections.

After correction for absorption, 335 reflections were considered unobserved since their intensities were  $< 3\sigma_f$ . Symmetry-related reflections were averaged and the structure was finally determined from a set of 346 independent, observed reflections.

### Structure determination and refinement

The cell dimensions are consistent with a fourteen-layer stacking of close-packed  $\text{BaO}_3$  layers. For the composition  $\text{BaCrO}_3$ , all of the  $O_6$  octahedral sites would be occupied by Cr. Structures based on close stacking of close-packed  $\text{AO}_3$  layers with smaller cations occupying  $O_6$  octahedral sites have been observed for a number of mixed metal oxides (Katz & Ward, 1964). For the  $27R$  polytype there were a total of 15 stacking sequences possible, so the various possibilities were tested to determine the correct sequence. For  $14H$ , however, there are 131 stacking sequences possible, so a final structure was deduced by considering the known stoichiometric polytypes:  $4H$ ,  $6H$ , and  $27R$ .

In Zhdanov notation (*International Tables for X-ray Crystallography*, 1959) the  $4H$  polytype has the stacking sequence 22, the  $6H$  polytype has the stacking sequence 33, and the  $27R$  polytype has the stacking sequence 3222. In terms of coordination polyhedra, each of these known  $\text{BaCrO}_3$  polytypes has pairs of face-sharing octahedra linked directly to each other either by sharing corners ( $4H$ ) or through octahedra sharing only corners ( $6H$ ) or both ( $27R$ ). These structural features suggest a sequence containing only 2's and 3's. For fourteen layers one would need an even

Table 1. Atomic parameters for  $14H$   $\text{BaCrO}_3$

Space group  $P6_3/mmc$  (No. 194). Errors in the last place are given in parentheses. The anisotropic temperature factor takes the form:  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ . Values of  $\beta$  are  $\times 10^2$ .

	Position	$x$	$y$	$z$	$\beta_{11}^*$	$\beta_{33}$
Ba(1)	2(d)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	1.02 (9)	0.010 (2)
Ba(2)	4(e)	0	0	0.10499 (3)	0.43 (6)	0.007 (1)
Ba(3)	4(f)	$\frac{1}{3}$	$\frac{2}{3}$	0.03904 (3)	0.41 (6)	0.011 (1)
Ba(4)	4(f)	$\frac{1}{3}$	$\frac{2}{3}$	0.17328 (5)	0.41 (7)	0.080 (2)
Cr(1)	2(a)	0	0	0	0.08 (18)	0.016 (5)
Cr(2)	4(e)	0	0	0.20886 (9)	0.50 (16)	0.006 (3)
Cr(3)	4(f)	$\frac{1}{3}$	$\frac{2}{3}$	0.56492 (9)	0.37 (12)	0.001 (3)
Cr(4)	4(f)	$\frac{1}{3}$	$\frac{2}{3}$	0.64506 (9)	0.43 (14)	0.008 (3)

		$x$	$y$	$z$	$B$ ( $\text{\AA}^2$ )
O(1)	12(k)	0.1676	0.3352 (22)	0.5344 (2)	0.50 (13)
O(2)	12(k)	0.5179	0.0359 (19)	0.1061 (2)	0.51 (13)
O(3)	12(k)	0.1644	0.3327 (22)	0.6799 (2)	0.63 (13)
O(4)	6(h)	0.1511	0.3203 (31)	$\frac{1}{4}$	1.09 (21)

$$*\beta_{11} = \beta_{22} = 2\beta_{12}; \beta_{23} = \beta_{13} = 0.$$

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) in  $14H$   $\text{BaCrO}_3$

Ba(1)—O(4) $\times 6$	2.829 (9)	Cr(1)—O(1) $\times 6$	1.985 (4)
—O(3) $\times 6$	2.852 (6)	Cr(2)—O(3) $\times 3$	1.912 (4)
Ba(2)—O(1) $\times 3$	2.817 (6)	—O(4) $\times 3$	1.993 (2)
—O(2) $\times 6$	2.831 (1)	Cr(3)—O(1) $\times 3$	1.900 (4)
—O(3) $\times 3$	2.875 (6)	—O(2) $\times 3$	1.976 (5)
Ba(3)—O(2) $\times 3$	2.828 (1)	Cr(4)—O(2) $\times 3$	1.928 (5)
—O(1) $\times 6$	2.830 (3)	—O(3) $\times 3$	1.953 (4)
—O(1) $\times 3$	2.885 (6)	Cr(2)—Cr(2)	2.671 (6)
Ba(4)—O(3) $\times 6$	2.829 (1)	Cr(3)—Cr(4)	2.602 (4)
—O(2) $\times 3$	2.833 (6)	Cr(1)—O(1)—Cr(3)	3.885 (8)
—O(4) $\times 3$	3.063 (1)	Cr(2)—O(3)—Cr(4)	3.865 (8)
O(1)—O(1) $\times 2$	2.774 (11)	O(3)—O(2) $\times 2$	2.803 (8)
—O(2) $\times 2$	2.793 (8)	—O(4) $\times 2$	2.810 (6)
—O(1) $\times 2$	2.809 (1)	—O(3) $\times 2$	2.820 (9)
—O(1) $\times 2$	2.841 (1)	—O(3) $\times 2$	2.829 (1)
O(2)—O(2) $\times 2$	2.520 (1)	O(4)—O(4) $\times 2$	2.562 (1)
—O(1) $\times 2$	2.792 (9)	—O(3) $\times 4$	2.810 (6)
—O(3) $\times 2$	2.803 (8)	—O(4) $\times 2$	3.088 (1)
—O(2) $\times 2$	3.129 (1)		
O(1)—Cr(1)—O(1) $\times 6$	91.37 (23)	O(2)—Cr(4)—O(2) $\times 3$	81.63 (26)
$\times 3$	180.00 (0)	—O(3) $\times 3$	172.20 (35)
$\times 6$	88.63 (23)	$\times 9$	92.50 (17)
O(3)—Cr(2)—O(3) $\times 3$	95.03 (26)	Cr(1)—O(1)—Cr(3)	177.09 (43)
—O(4) $\times 3$	169.53 (22)	Cr(2)—O(3)—Cr(4)	178.42 (36)
$\times 6$	92.03 (14)	Cr(2)—O(4)—Cr(2)	84.17 (13)
O(4)—Cr(2)—O(4) $\times 3$	79.99 (10)	Cr(3)—O(2)—Cr(4)	83.57 (10)
O(1)—Cr(3)—O(1) $\times 3$	95.35 (26)		
—O(2) $\times 3$	168.81 (26)		
$\times 6$	92.18 (18)		
O(2)—Cr(3)—O(2) $\times 3$	79.26 (26)		
O(4)—Ba(1)—O(4) $\times 3$	173.84 (1)	O(2)—Ba(3)—O(1) $\times 6$	92.44 (11)
$\times 3$	66.16 (1)	$\times 6$	126.28 (16)
$\times 6$	120.00 (2)	$\times 6$	59.15 (15)
$\times 3$	53.84 (2)	$\times 3$	174.52 (41)
O(4)—Ba(1)—O(3) $\times 12$	91.76 (1)	$\times 6$	117.20 (9)
$\times 12$	59.29 (7)	$\times 3$	174.52 (41)
$\times 12$	118.68 (6)	O(1)—Ba(3)—O(1) $\times 3$	59.15 (15)
O(3)—Ba(1)—O(3) $\times 6$	59.29 (7)	$\times 6$	119.72 (3)
$\times 6$	146.71 (7)	$\times 3$	60.28 (3)
$\times 3$	110.11 (15)	$\times 6$	87.37 (12)
O(1)—Ba(2)—O(1) $\times 3$	60.56 (14)	$\times 6$	58.09 (20)
—O(2) $\times 6$	92.68 (12)	$\times 6$	116.34 (8)
$\times 6$	60.56 (14)	$\times 3$	58.06 (20)
$\times 6$	119.68 (15)	O(3)—Ba(4)—O(3) $\times 3$	173.81 (31)
—O(3) $\times 3$	109.90 (12)	$\times 3$	60.02 (3)
$\times 6$	146.60 (5)	$\times 6$	119.71 (4)
O(2)—Ba(2)—O(2) $\times 6$	119.98 (2)	$\times 3$	59.78 (1)
$\times 3$	172.74 (7)	$\times 6$	92.35 (12)
$\times 3$	67.11 (1)	$\times 6$	126.40 (16)
$\times 3$	52.88 (2)	$\times 6$	59.35 (15)
—O(3) $\times 6$	91.42 (12)	O(2)—Ba(4)—O(2) $\times 3$	67.06 (16)
$\times 6$	58.84 (15)	—O(4) $\times 3$	175.97 (14)
$\times 6$	117.48 (16)	$\times 6$	116.14 (8)
O(3)—Ba(2)—O(3) $\times 3$	58.73 (13)	O(4)—Ba(4)—O(4) $\times 3$	60.54 (4)
O(2)—Ba(3)—O(2) $\times 3$	67.16 (15)	O(3)—Ba(4)—O(4) $\times 6$	87.52 (12)
		$\times 6$	56.80 (14)
		$\times 6$	117.33 (15)

number of 3's, either two or four. However, four 3's (33332) would not repeat in fourteen layers, so we are left with sequences containing two 3's and four 2's. There are only two of these which repeat in fourteen layers: 332222 and 322322. The first of these corresponds to strings of five pairs of face-sharing octahedra linked to single pairs of face-sharing octahedra by octahedra sharing only corners; the second corresponds to strings of three pairs of face-sharing octahedra linked to other such strings by octahedra sharing only corners. This latter, more regular, model was adopted as a trial structure and found to be consistent with the observed data. Adapted to the *International Tables'* listings for space group  $P6_3/mmc$ , the sequence is  $|2(3)2|2(3)2|$ . With the origin at

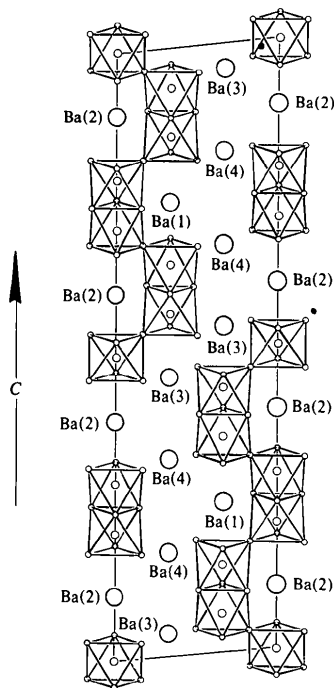


Fig. 1. Structure of  $14H$   $\text{BaCrO}_3$  showing the cations in the  $(110)$  plane and the  $\text{CrO}_6$  octahedra.

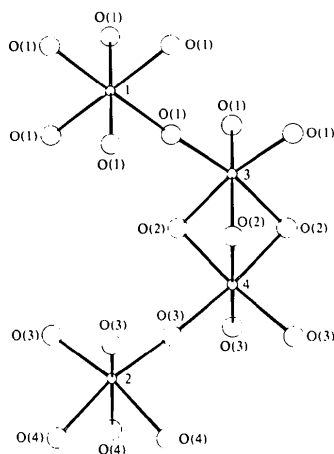


Fig. 2. The coordination of the four crystallographic types of chromium.

a symmetry center in a void between two layers, the layer sequence may be designated  $CACBCACBABC(B)C$ , where  $A$  layers have spheres at  $00z$ ,  $B$  layers at  $\frac{2}{3}\frac{1}{2}z'$ , and  $C$  layers at  $\frac{1}{3}\frac{2}{3}z''$ . The first layer,  $C$ , is at  $z \approx \frac{1}{8}$ . The structure has Ba atoms at the sites identifying the layers as  $A$ ,  $B$ , or  $C$  and Cr atoms at all the  $O_6$  octahedral sites. The unrefined model placed Ba and O atoms in layers with spacing  $c/14$  and Cr atoms halfway between the  $\text{BaO}_3$

layers. On three-dimensional least-squares refinement the Cr atoms in octahedra sharing faces moved apart so that their interatomic distance was greater than the layer spacing.

The final refinement, using analytic neutral-atom form factors including the real part of the anomalous-dispersion correction (*International Tables for X-ray Crystallography*, 1974) and all atoms anisotropic, was based on  $F$  and used a weighting function  $w = 1/\sigma_F^2$  where  $\sigma_F = 0.02|F_o| + (C + k^2 B)^{1/2}/2|F_o|$  Lp;  $C$  is the total scan count,  $k$  is the ratio of scanning time to total background time, and  $B$  is the total background count. An extinction correction was applied and the refinement converged (maximum shift/error = 0.02 for positional coordinates and 0.5 for an oxygen thermal parameter; average shift/error = 0.04) to a conventional  $R$  of 0.041 and weighted  $R$  of 0.047. A final  $\Delta F$  map showed maxima of about  $\frac{1}{4}$  of an oxygen peak in the vicinity of Ba atoms and about  $\frac{1}{10}$  of an oxygen peak in the vicinity of Cr atoms, but was otherwise essentially flat.

Final atomic parameters are given in Table 1. Bond lengths and angles are given in Table 2.\* An illustration of the structure is given in Fig. 1, and the environment of the Cr atoms is shown in Fig. 2. Calculations were performed using *ORFLS* and *ORFFE* (Busing, Martin & Levy, 1962, 1964). Drawings were prepared with Johnson's (1965) program *ORTEP*.

## Discussion

The stoichiometric polytypes of  $\text{BaCrO}_3$  whose structures are now well established are  $4H$ ,  $6H$ ,  $27R$ , and  $14H$ . The 'unit' of structure is the binuclear  $\text{Cr}_2\text{O}_9$  face-sharing pair of  $\text{CrO}_6$  octahedra. These octahedral pairs are corner linked to each other in  $4H$  and linked only through corner-sharing octahedra in  $6H$ . The  $27R$  and  $14H$  polytypes have mixtures of  $4H$  and  $6H$  features. In the  $27R$  structure there are strings of four pairs of face-sharing octahedra in which the pairs are linked to each other by corner sharing; the strings in turn are linked to each other by octahedra sharing only corners. In the  $14H$  structure there are strings of three pairs of face-sharing octahedra in which the pairs are linked to each other by corner sharing, and again the strings are linked to each other by octahedra sharing only corners.

The polytypes may conveniently be described in terms of hexagonal ( $h$ ) layers, for which the two

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36274 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

neighboring layers are alike, and cubic (*c*) layers, for which the two neighboring layers are of different types. With this layer description, the *4H* polytype has the sequence *hchc*, i.e. a repetition of *hc* pairs; the *6H* polytype has the sequence *hcchcc*, i.e. a repetition of *hcc* triples or *hc* pairs separated by *c* layers; the *27R* polytype has the sequence *hchchchcc*, i.e. sets of four *hc* pairs separated by *c* layers. The *14H* polytype is *hcchcchchchcc*, i.e. sets of three *hc* pairs separated by *c* layers. (A 'missing' polytype which would have two *hc* pairs separated by *c* layers would repeat in fifteen layers and be designated *15R*.) Thus we are able to say that  $\frac{8}{3}$  of the *27R* polytype is the same as *4H* (and  $\frac{4}{3}$  is the same as *6H*). For the *14H* polytype we can say that  $\frac{6}{5}$  is the same as *4H* (and  $\frac{3}{5}$  is the same as *6H*). In both *27R* and *14H* one can pick out *6H* cells as well as the more obvious *4H* cells. The Cr—Cr distances in the face-sharing pairs are 2.60 and 2.67 Å in *14H*, 2.61 and 2.65 Å in *27R*. These polytypes are clearly closely related.

A twelve-layer barium chromium oxide (*12R*) has also been reported (Evans & Katz, 1972). However, this compound is not stoichiometric. Its composition is  $\text{Ba}_2\text{Cr}_{7-x}\text{O}_{14}$  ( $x \approx 0.5$ ), and its structure has both  $\text{BaO}_3$  and  $\text{O}_4$  layers and Cr atoms in both octahedral and tetrahedral sites. There are no close Cr—Cr distances, and the electrical and magnetic properties

are quite different from those of the stoichiometric compounds studied.

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## Die Kristallstruktur des Bleisilicats $\text{Pb}_{11}\text{Si}_3\text{O}_{17}$

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#### Abstract

The lead silicate  $\text{Pb}_{11}\text{Si}_3\text{O}_{17}$  crystallizes in space group  $P\bar{1}$  with  $a = 22.502$  (5),  $b = 12.982$  (2),  $c = 7.313$  (2) Å,  $\alpha = 92.52$  (2),  $\beta = 99.17$  (3),  $\gamma = 100.29$  (2)° and  $V = 2069.2$  (7) Å<sup>3</sup>;  $Z = 4$ ,  $D_x = 8.46$  Mg m<sup>-3</sup>. The structure was determined with 6903 X-ray diffraction intensities and refined to an  $R$  value of 0.087. The Si atoms form  $[\text{SiO}_4]^{4-}$  and  $[\text{Si}_2\text{O}_7]^{6-}$  groups to give a structural formula  $\text{Pb}_{11}[\text{SiO}_4][\text{Si}_2\text{O}_7]\text{O}_6$ . The unit-cell dimensions of the related compound  $\text{Pb}_{11}\text{Ge}_3\text{O}_{17}$  are  $a = 22.258$  (5),  $b =$

$19.900$  (5),  $c = 7.366$  (2) Å,  $\alpha = 97.56$  (2),  $\beta = 95.12$  (2),  $\gamma = 92.32$  (2)° and  $V = 3217$  (1) Å<sup>3</sup>.

#### Einleitung

Nach dem Ergebnis der neuesten Untersuchungen über die Phasengleichgewichte im System  $\text{PbO-PbSiO}_3$  (Hirota & Hasegawa, 1981) existieren nebst den in der Literatur übereinstimmend festgestellten Verbindungen,  $\text{PbSiO}_3$  und  $\text{Pb}_2\text{SiO}_4$ , zwei Bleisilicate  $\text{Pb}_{11}\text{Si}_3\text{O}_{17}$  und  $\text{Pb}_5\text{SiO}_7$ , die in den bereits veröffentlichten Phasendiagrammen nicht auftreten. Bei den zwei Letzgenannten handelt es sich nach Hirota & Hasegawa (1981) um die Phasen, die in der früheren Literatur fälschlich als die Modifikationen von 'Pb<sub>4</sub>SiO<sub>6</sub>' be-

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