

## The Structure of the 27-Layer Polytype of BaCrO<sub>3</sub>

PAUL S. HARADEM, BERTRAND L. CHAMBERLAND,  
AND LEWIS KATZ

*Department of Chemistry and Institute of Materials Science,  
University of Connecticut, Storrs, Connecticut 06268*

Received March 15, 1979

Twenty-seven-layer barium chromium oxide, BaCrO<sub>3</sub>, was prepared at 1200°C and 60–65 kbar by reaction of CrO<sub>2</sub> and Ba<sub>2</sub>CrO<sub>4</sub>. The compound crystallizes in space group  $R\bar{3}m$  with hexagonal cell dimensions  $a = 5.652 \pm 0.002$ ,  $c = 62.75 \pm 0.02$  Å. The structure was determined from 1070 independent reflections, of which 811 were considered observed, collected by automated counter methods, and refined by least-squares methods to a conventional  $R$  value of 4.1%. The structure consists of a 27-layer stacking sequence of close-packed BaO<sub>3</sub> layers, Zhdanov notation for the sequence (3)2(2)2, with all of the O<sub>6</sub> octahedral sites occupied by Cr. Strings of four pairs of face-sharing octahedra in which the pairs are linked to each other by corner sharing are in turn joined to each other by octahedra sharing only corners. The structure is thus closely related to the four-layer and six-layer polytypes of BaCrO<sub>3</sub>. Bariums in two of the five crystallographic positions showed large thermal anisotropy and are better described in terms of half atom occupancy in split sites.

### Introduction

Several barium chromium oxides, including polytypes of BaCrO<sub>3</sub>, have been prepared from high-pressure, high-temperature reactions of BaO or Ba<sub>2</sub>CrO<sub>4</sub> with CrO<sub>2</sub> by Chamberland (1). On the basis of expected layer thicknesses for close-stacked BaO<sub>3</sub> layers (see, for example, Ref. (2)) one of these polytypes was assumed to have a 27-layer repeat structure. Since it was determined to have a rhombohedral lattice type, the polytype was labeled 27R. Our experience has shown that inorganic compounds do not always have their predicted compositions, even in the Ba–Cr–O system (3); in addition, the 27-layer repeat sequence was longer than any we had studied so far in our program on complex metal oxides. We therefore undertook a determination of the structure of 27R BaCrO<sub>3</sub>.

### Experimental

The barium chromium oxide used in our study was prepared at 1200°C and 60–65 kbar by reaction of CrO<sub>2</sub> and Ba<sub>2</sub>CrO<sub>4</sub> for 1 hr in a tetrahedral anvil press. This method of preparation is preferred over that utilizing BaO and CrO<sub>2</sub> since it minimizes the possibility of generating undesired side reactions which frequently occurred when hygroscopic or impure BaO was used as the reactant. The crystal was black and had a blocky shape of which the volume could be approximated by a sphere of radius 0.093 mm.

X-Ray precession photographs showed hexagonal (trigonal) symmetry, Laue group  $\bar{3}m$ . The only systematic absences were those of a rhombohedral lattice, so the probable space group is one of  $R32$ ,  $R3m$ , or  $R\bar{3}m$ . Intensities were measured on a Picker FACS-1 single-crystal diffractometer using

graphite monochromatized  $MoK\alpha$  radiation. The diffractometer was operated in the  $\theta-2\theta$  scan mode. Hexagonal cell dimensions,  $a = 5.652 \pm 0.002$ ,  $c = 62.75 \pm 0.02$  Å, were determined by least-squares refinement of the diffractometer angles for 12 reflections. The structure determination was based on 1070 independent reflections ( $2\theta$  to  $70^\circ$ ) of which 811 were considered observed. A spherical absorption correction was applied. Lorentz and polarization corrections, as well as other data treatment and computations, were carried out with the program package "The X-Ray System" (4).

### Structure Determination and Refinement

The cell dimensions are consistent with a 27-layer stacking of close-packed  $BaO_3$  layers. For the composition  $BaCrO_3$  all of the  $O_6$  octahedral sites would be occupied by Cr. Structures based on close stacking of close-packed  $BaO_3$  layers with smaller cations occupying  $O_6$  octahedral sites have been observed for a number of complex metal oxides (5). For a stacking of 27 layers there are 11 sequences in  $R\bar{3}m$  and four more in  $R3m$  (6). After testing the various possibilities the correct sequence was found to be, in Zhdanov notation, (3)2(2)2, space group  $R\bar{3}m$ . With the origin at a symmetry center lying in a sphere the layer sequence may be designated  $ABACABCBAABCACBCACBCABAC(A)$ , where  $A$  layers have spheres at  $00z$ ,  $B$  layers at  $\frac{2}{3}\frac{1}{3}z'$ ,  $C$  layers at  $\frac{1}{3}\frac{2}{3}z''$ . 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 oxygen atoms are placed so as to complete the  $BaO_3$  close-packed layers. The unrefined model placed Ba and O atoms in layers with spacing  $c/27$ , and Cr atoms halfway between the  $BaO_3$  layers. On three-dimensional least-squares refinement the Ba atoms shifted somewhat out of the O layers, and the Cr atoms in octahedra sharing faces moved

apart so that their interatom distance was greater than the layer spacing.

The anisotropic refinement showed large thermal vibration amplitudes for the Ba atoms originally at  $z = 0$  and  $z = 2/27$ . A converging refinement and a better fit to the data were obtained by splitting these sites and assuming random occupancy with population parameters of 0.5. The final refinement with all atoms anisotropic, correction for anomalous dispersion, and a weighting scheme similar to one previously described (7) converged (average shift/error, 0.02; maximum shift/error, 0.07) to a conventional  $R$  of 0.041. Neutral atom form factors were used. A refinement in  $R3m$  without split barium sites gave poorer agreement despite the larger number of parameters. A final  $\Delta F$  map showed maxima as high as 4 electrons/Å<sup>3</sup> in the vicinity of barium atoms and 2 electrons/Å<sup>3</sup> in the vicinity of chromium atoms, but was otherwise essentially flat.

Final atomic parameters are given in Table I, and an illustration of the structure is given in Fig. 1. The site splittings for Ba(1) and Ba(3)–Ba(6) are not shown in the figure since they are only 0.5 and 0.2 Å, respectively. The environment of the Cr atoms is shown in Fig. 2. Bond lengths and angles are given in Table II. The table of observed and calculated structure factors has been deposited with the National Auxiliary Publication Service (NAPS).<sup>1</sup> The figures were prepared using ORTEP (8).

<sup>1</sup> See NAPS document No. 03566 for 8 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance for each NAPS Accession number. Institutions and organizations may use purchase orders when ordering, however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are \$5.00. Microfiche are \$3.00. Outside of the U.S. and Canada, postage is \$3.00 for a photocopy or \$1.50 for a fiche.

TABLE I  
 ATOMIC PARAMETERS<sup>a</sup> FOR 27R BaCrO<sub>3</sub>, SPACE GROUP R $\bar{3}m$  (NO. 166)

Atom	Position	x	y	z	Population	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
Ba(1)	6c	0	0	0.00437(2)	0.5	0.77	0.77	1.60(11)	0.38(1)	0	0
Ba(2)	6c	$\frac{2}{3}$	$\frac{1}{3}$	0.03767(1)	1.0	1.30	1.30	0.79(4)	0.65(1)	0	0
Ba(3)	6c	0	0	0.07477(20)	0.5	0.74	0.74	5.23(68)	0.37(5)	0	0
Ba(6)	6c	0	0	0.07792(20)	0.5	0.56	0.56	2.13(13)	0.28(4)	0	0
Ba(4)	6c	$\frac{1}{3}$	$\frac{2}{3}$	0.11224(1)	1.0	0.75	0.75	0.95(4)	0.37(1)	0	0
Ba(5)	6c	0	0	0.14645(1)	1.0	0.64	0.64	1.41(4)	0.32(1)	0	0
Cr(1)	6c	$\frac{1}{3}$	$\frac{2}{3}$	0.01635(3)	1.0	0.89	0.89	1.00(10)	0.45(3)	0	0
Cr(2)	6c	$\frac{1}{3}$	$\frac{2}{3}$	0.05861(3)	1.0	0.95	0.95	0.91(10)	0.48(3)	0	0
Cr(3)	6c	$\frac{2}{3}$	$\frac{1}{3}$	0.09167(3)	1.0	0.75	0.75	0.77(10)	0.37(3)	0	0
Cr(4)	6c	$\frac{2}{3}$	$\frac{1}{3}$	0.13322(3)	1.0	0.62	0.62	1.08(10)	0.31(3)	0	0
Cr(5)	3b	0	0	$\frac{1}{2}$	1.0	0.62	0.62	0.84(13)	0.31(4)	0	0
O(1)	9e	$\frac{1}{2}$	0	0	1.0	1.31(23)	1.61	0.94(30)	0.81(17)	0.78	0.39(23)
O(2)	18h	0.1834(6)	0.3668	0.03735(9)	1.0	2.40(31)	2.40	1.30(23)	1.95(44)	0.02(17)	-0.02
O(3)	18h	0.4999(5)	0.9998	0.07435(8)	1.0	1.47(26)	1.47	0.94(21)	1.15(37)	0.11(15)	-0.11
O(4)	18h	0.3711	0.1855(6)	0.11170(8)	1.0	1.52(26)	1.52	0.97(21)	1.09(38)	0.02(16)	-0.02
O(5)	18h	0.5008(5)	0.0015	0.14875(9)	1.0	1.12(25)	1.12	1.55(24)	0.51(38)	-0.14(18)	0.14

<sup>a</sup> Thermal parameters are multiplied by 100.

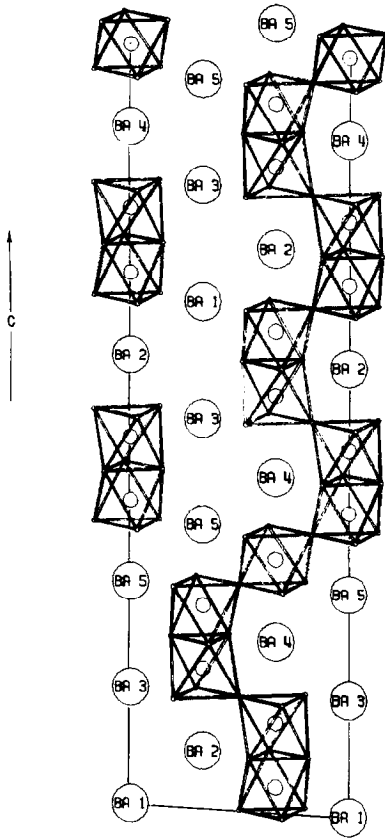


FIG. 1. A portion of the structure of 27R BaCrO<sub>3</sub>.

### Discussion

Although the 27-layer polytype was obtained by reaction of CrO<sub>2</sub> and Ba<sub>2</sub>CrO<sub>4</sub> at 60–65 kbar and 1200°C, the usual stoichiometric products over the temperature range 750 to 1400°C were the four-layer and six-layer (hexagonal BaTiO<sub>3</sub> structure) polytypes. At first glance it might appear that the 27-layer polytype is appreciably different from the others; however, it is very closely related. This may be seen readily by describing the structures in terms of hexagonal (h) layers, for which the two neighboring layers are alike, and cubic (c) layers, for which the two neighboring layers are of different types. With this layer description, the four-layer polytype has the sequence hchc, i.e., a

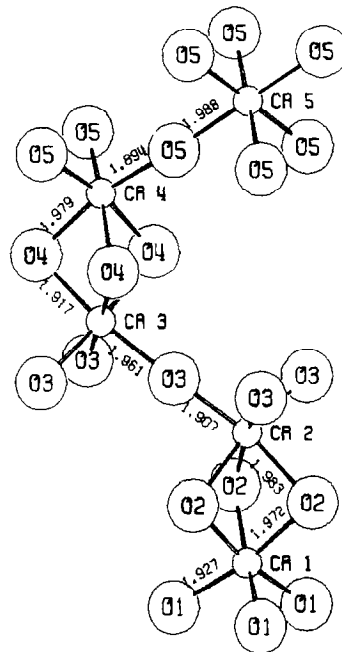


FIG. 2. The coordination of the five crystallographic types of chromium.

repetition of hc pairs; the six-layer polytype has the sequence hcchcc, i.e., a repetition of hcc triples; and the 27-layer has the sequence hchchchcc, i.e., sets of four hc pairs separated by c layers. (Only nine layers need be described, since the R-lattice hexagonal cell is triply primitive; the full cell repeats the nine-layer sequence three times before the unit cell is completed.) There are various ways of emphasizing the relationship between the 27-layer cell on the one hand, and the four- and six-layer cells on the other. One way is to say that after two repetitions of the four-layer structure a c layer is introduced; thus 8/9 of the structure is the same as the four-layer structure. Since the introduction of the c layer creates an hcc sequence, one can also say that 5/9 of the structure is the same as the six-layer structure. And without reference to other structures one can say that there are strings of four pairs of face-sharing octahedra in which the pairs are linked to each other by corner

TABLE II  
INTERATOMIC DISTANCES AND ANGLES

Distances (Å)				
Ba(1)-O(1)	2.839(1)	6x	Cr(3)-O(3)	1.961(4) 3x
-O(2)	2.740(5)	3x	-O(4)	1.916(4) 3x
	3.174(5)	3x	Cr(4)-O(4)	1.979(4) 3x
Ba(2)-O(1)	2.872(1)	3x	-O(5)	1.894(4) 3x
-O(2)	2.831(4)	6x	Cr(5)-O(5)	1.987(4) 6x
-O(3)	2.822(4)	3x		
Ba(3)-O(2)	2.956(11)	3x	Cr(1)-Cr(2)	2.652(3)
-O(3)	2.826(3)	6x	Cr(3)-Cr(4)	2.607(3)
-O(4)	2.944(11)	3x		
Ba(6)-O(2)	3.115(11)	3x	O(1)-O(1)	2.825 4x
-O(3)	2.835(3)	6x	-O(2)	2.813(5) 4x
-O(4)	2.791(10)	3x	O(2)-O(1)	2.813(5) 2x
Ba(4)-O(3)	2.883(4)	3x	-O(2)	2.542(3) 2x
-O(4)	2.832(4)	6x		3.108(3) 2x
-O(5)	2.817(5)	3x	-O(3)	2.795(7) 2x
Ba(5)-O(4)	2.838(4)	3x	O(3)-O(2)	2.795(7) 2x
-O(5)	2.829(3)	6x	-O(3)	2.823(3) 2x
	2.892(5)	3x		2.827(3) 2x
Ba(1)-Ba(1)	0.548(2) <sup>a</sup>		-O(4)	2.809(7) 2x
Ba(3)-Ba(6)	0.198(18) <sup>a</sup>		O(4)-O(3)	2.809(7) 2x
			-O(4)	2.506(5) 2x
Cr(1)-O(1)	1.927(3)	3x		3.145(5) 2x
-O(2)	1.972(5)	3x	-O(5)	2.790(7) 2x
Cr(2)-O(2)	1.983(5)	3x	O(5)-O(4)	2.790(7) 2x
-O(3)	1.906(3)	3x	-O(5)	2.811(3) 2x
				2.838(2) 2x
				2.782(7) 2x
Angles (°)				
O(1)-Cr(1)-O(1)	94.3(1)			
O(1)-Cr(1)-O(2)	92.3(1)			
O(2)-Cr(1)-O(2)	80.2(2)			
O(1)-Cr(1)-O(2)	170.3(2)			
O(2)-Cr(2)-O(2)	79.7(2)			
O(2)-Cr(2)-O(3)	91.8(2)			
O(3)-Cr(2)-O(3)	95.6(2)			
O(2)-Cr(2)-O(3)	168.9(2)			
O(3)-Cr(3)-O(3)	92.2(1)			
O(3)-Cr(3)-O(4)	92.8(2)			
O(4)-Cr(3)-O(4)	81.7(2)			
O(3)-Cr(3)-O(4)	172.7(2)			
O(4)-Cr(4)-O(4)	78.6(2)			
O(4)-Cr(4)-O(5)	92.2(2)			
O(5)-Cr(4)-O(5)	95.9(2)			
O(4)-Cr(4)-O(5)	167.9(2)			
O(5)-Cr(5)-O(5)	91.1(2)			
O(5)-Cr(5)-O(5)	88.9(2)			
O(5)-Cr(5)-O(5)	180(5)			

<sup>a</sup> Site splitting.

sharing; the strings in turn are linked to each other by octahedra sharing only corners.

The split-site barium atoms are those which are least constrained in the  $z$  direction in that the nearest cations above and below are barium. For the other barium atoms there are the more highly charged chromium ions above and/or below. As previously indicated, the split-site random occupancy description fits the data better than the single-site with large thermal anisotropy description. Indeed the splitting was large enough to permit converging anisotropic refinement.

A description can also be offered in terms of the barium coordination polyhedra. Each barium is surrounded by 12 oxygens. The polyhedra formed about the Ba(2) and Ba(4) atoms are "twinned cuboctahedra" and the cations reside at their centers exhibiting relatively little thermal motion. The other barium cations, however, are in cuboctahedral sites which are stacked in linear chains of five units. Each of these polyhedra shares one or more of its triangular faces with other units in the chain. Ba(1), in the central polyhedra, shows random occupancy of sites above and below the oxygen layer, with a relatively large "site splitting" of 0.5 Å, because of its position in the chain and the minimal charge repulsion constraints from neighboring high-charged transition metal ions. Ba(3) and Ba(6) also represent barium distributed between two sites; this site splitting is consistent with their location in the chain of cuboctahedral groups. The Ba(5)

atoms, in the terminal cuboctahedra, are the most constrained and are "well behaved."

The electrical and magnetic properties of 27R BaCrO<sub>3</sub> are very similar to those of the 4H and 6H polytypes and quite different from those of the nonstoichiometric 12R phase. All the stoichiometric polytypes are semiconducting ferrimagnets, whereas the 12R product (Ba<sub>2</sub>Cr<sub>6.5</sub>O<sub>14</sub>) is a paramagnetic (mostly Cr<sup>3+</sup>) semiconductor.

### Acknowledgments

The authors are grateful to the National Science Foundation for support under Grants DMR 74-11818 and DMR 73-02616. Computations were carried out in the Computer Center of the University of Connecticut. Photographs of the figures were prepared by the University of Connecticut Photographic Laboratory.

### References

1. B. L. CHAMBERLAND, *Inorg. Chem.* **8**, 286 (1969).
2. P. C. DONOHUE, L. KATZ, AND R. WARD, *Inorg. Chem.* **4**, 306 (1965).
3. D. M. EVANS AND L. KATZ, *Acta Crystallogr. Sect. B* **28**, 1219 (1972).
4. J. M. STEWART, F. A. KUNDELL, AND J. C. BALDWIN (eds.), "The X-Ray System," Computer Science Center, University of Maryland, College Park, Md. (1970).
5. L. KATZ AND R. WARD, *J. Amer. Chem. Soc.* **3**, 205 (1964).
6. "International Tables for X-Ray Crystallography," Vol. II, p. 348, Kynoch Press, Birmingham (1959).
7. D. M. EVANS AND L. KATZ, *J. Solid State Chem.* **6**, 459 (1973).
8. C. K. JOHNSON, "ORTEP," ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn. (1965).