CONTRIBUTION NO. 1479 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION,
E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE 19898

The Preparation and Crystallographic Properties of $BaCrO_3$ Polytypes

BY B. L. CHAMBERLAND

Received August 7, 1968

Several hexagonal $BaCrO_3$ polytypes were prepared at high pressures and high temperatures in a tetrahedral anvil apparatus. Two systems were studied: (a) the reaction of CrO_2 with BaO and (b) the reaction of CrO_2 with Ba_2CrO_4. The reaction temperature and the reactants utilized were influencing factors in the formation of the various polytypes. Single crystals of the 4-, 6-, 9-, 12-, 14-, and 27-layer modifications of hexagonal $BaCrO_3$ were isolated in various experiments. The space groups of the polytypic phases were determined from single-crystal X-ray studies, and refined cell dimensions for most of the phases were obtained using Guinier X-ray powder diffraction data. Reactions at pressures less than 3000 atm did not yield $BaCrO_3$.

Introduction

A. History.—Ternary oxides of the type $BaMO_3$, where M is a transition metal, have been extensively studied by Ward and coworkers[1-3] and by several other research groups.[4-6] All of the first-row transition metals capable of existing in a stable tetravalent state are known to form $BaMO_3$ derivatives except for vanadium and chromium. Previous attempts[7,8] to prepare a Cr^{4+} derivative with the $BaCrO_3$ composition have been unsuccessful. Ba_2CrO_4, Sr_2CrO_4, Ba_3CrO_5, and Na_4CrO_4 comprise the first tetravalent chromium derivatives reported[7-9] in the literature. Another sodium chromium(IV) oxide, Na_2CrO_3, has been reported[10] but the X-ray data are more consistent with the formulation $NaCrO_2$ having the hexagonal $NaFeO_2$ structure. A fluoride, K_2CrF_6, has been characterized[11] as a chromium(IV) derivative from magnetic studies. More recently, the preparation of $CaCrO_3$,[12] $SrCrO_3$,[13] and $PbCrO_3$[14] at high pressure has been reported.

This paper describes the preparation and certain crystallographic features of a variety of $BaCrO_3$ compositions prepared by the interaction of CrO_2 with BaO or Ba_2CrO_4 at high pressure.

B. Stacking Sequences.—Different $BaMO_3$ variants can be described on the basis of the stacking sequences of close-packed BaO_3 layers.[15] These sequences and the ordering of the transition metal ions in the octahedral sites can lead to several different structures. Cubic packing of the BaO_3 layers results in O_6 octahedra sharing corners with neighboring octahedra. Metal ions occupy the central positions of the octahedra. The perovskite structure results from such an arrangement and can be regarded as a 3-layer hexagonal cell [cubic (111) → hexagonal (110)].[15] At the other extreme, hexagonal packing of BaO_3 layers leads to the formation of face-sharing O_6 octahedra. Once again, the transition metal occupies the center of these octahedra. This packing generates a 2-layer hexagonal cell, as exemplified by $BaNiO_3$. Alternate cubic and hexagonal packing of BaO_3 layers results in a variety of layered structures discussed by Katz and Ward.[15] For example, a 4-layer arrangement, exemplified by the high-temperature form of $BaMnO_3$, is obtained with the layer sequence chch in which c and h represent cubic and hexagonal packing, respectively. Other stacking sequences are possible, and several are given in ref 15.

The unit cell of these layered structures is determined by the number of BaO_3 layers per cell. In this paper, the symbols nH or nR, where n represents the number of such layers, H indicates hexagonal symmetry, and R represents rhombohedral symmetry, are used to describe the structural variants. A pictorial representation of the 3H, 4H, 6H, and 9R structures has been given.[16]

It should be noted that a plot of the c axis or preferably the c/a ratio of a hexagonal $BaMO_3$ cell *vs.* the number n of repeat sequences gives a straight line. The relationship $c/a \simeq 0.4107n$ is derived from such a linear plot. A similar relationship also holds true for the various hexagonal CdI_2 polytypes (c *vs.* n), pseudotetragonal $(Bi_2O_2)^{2+}(M_{m-1}R_mO_{m-1})^{2-}$ compositions (c/a *vs.* m), and hexagonal or rhombohedral polymorphs of SiC (c *vs.* Z, where Z is the number of formula units in the hexagonal cell). Other polytypic layer structures probably show a similar relationship. From the slope of a c *vs.* n plot for the known $BaMO_3$ com-

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TABLE I

INDEXED POWDER DIFFRACTION PATTERNS OF VARIOUS BaCrO$_3$ POLYTYPES[a]

Hexagonal Four-Layer				Hexagonal Six-Layer				Rhombohedral Twelve-Layer				Hexagonal Fourteen-Layer				Rhombohedral Twenty-Seven-Layer			
I	h k l	d(obs)	d(calcd)	I	h k l	d(obs)	d(calcd)	I	h k l	d(obs)	d(calcd)	I	h k l	d(obs)	d(calcd)	I	h k l	d(obs)	d(calcd)
25	1 0 1	4.3394	4.3418	2	1 0 1	4.5889	4.5909	10	1 0 1	4.8295	4.8287	20	1 0 4	4.1927	4.1933	20	1 0 7	4.2923	4.2938
90	1 0 2	3.3839	3.3846	30	1 0 2	3.9647	3.9698	40	0 0 6	4.6261	4.6253	20	1 0 6	3.6314	3.6325	5	0 1 8	4.1499	4.1504
100	1 1 0	2.8293	2.8296	60	1 0 3	3.3286	3.3308	20	0 1 5	3.6752	3.6748	55	1 0 7	3.3691	3.3694	15	0 1 11	3.7105	3.7126
90	1 0 3	2.6316	2.6318	100	1 1 0	2.8122	2.8135	70	1 0 7	3.0825	3.0829	5	0 0 10	3.2462	3.2515	75	1 0 13	3.4350	3.4349
40	2 0 1	2.3705	2.3706	80	1 0 4	2.7993	2.8007	100	1 1 0	2.8316	2.8311	10	1 0 8	3.1276	3.1270	75	0 1 14	3.3035	3.3037
40	0 0 4	2.3397	2.3397	15	2 0 1	2.3976	2.3988	50	1 1 3	2.7072	2.7071	100	1 1 0	2.8264	2.8261	10	1 0 16	3.0584	3.0588
95	2 0 2	2.1712	2.1709	10	1 0 5	2.3862	2.3870	30	0 2 1	2.4437	2.4423	50	1 1 10	2.7086	2.7084	10	0 1 17	2.9439	2.9453
20	1 0 4	2.1115	2.1115	35	2 0 2	2.2947	2.2954	30	2 0 2	2.4146	2.4144	5	1 0 11	2.5316	2.5303	100	1 1 0	2.8249	2.8247
80	2 0 3	1.9274	1.9271	10	0 0 6	2.2804	2.2816	20	0 0 12	2.3131	2.3126	5	2 0 3	2.3863	2.3874	65	1 0 19	2.7359	2.7360
25	1 1 4	1.8032	1.8032	2	1 1 4	2.1731	2.1733	75	0 1 11	2.2435	2.2434	20	1 0 12	2.3703	2.3706	80	0 1 20	2.6398	2.6398
25	1 0 5	1.7489	1.7486	70	2 0 3	2.1488	2.1493	20	0 2 7	2.0851	2.0852	40	2 0 4	2.3429	2.3436	10	1 0 22	2.4623	2.4628
65	2 1 2	1.7227	1.7224	65	2 0 4	1.9848	1.9849	40	0 1 14	1.8382	1.8378	10	0 0 14	2.3236	2.3225	5	2 0 2	2.4411	2.4389
20	2 0 4	1.6925	1.6923	5	2 0 5	1.8192	1.8202	15	2 1 4	1.7901	1.7906	10	2 0 5	2.2955	2.2906	10	2 0 5	2.4008	2.4010
65	3 0 0	1.6339	1.6337	10	2 1 2	1.7784	1.7786	10	2 0 11	1.7585	1.7583	55	2 0 7	2.1648	2.1653	30	0 2 7	2.3594	2.3599
70	2 1 3	1.5928	1.5928	15	1 1 6	1.7721	1.7721	30	2 1 7	1.6795	1.6790	30	1 1 10	2.1293	2.1330	15	2 0 8	2.3349	2.3352
40	2 0 5	1.4871	1.4875	30	2 1 3	1.7081	1.7080	30	1 2 8	1.6349	1.6347	20	2 0 8	2.0968	2.0967	35	0 0 27	2.3217	2.3224
15	2 1 4	1.4523	1.4524	55	3 0 0	1.6241	1.6244	20	3 0 3	1.6081	1.6096	55	2 0 10	1.9553	1.9554	15	2 0 11	2.2475	2.2480
55	2 2 0	1.4149	1.4148	50	2 1 4	1.6224	1.6219	20	1 1 15	1.5479	1.5487	15	2 0 11	1.8858	1.8851	10	1 1 18	2.1947	2.1941
5	1 1 6	1.3658	1.3661	5	1 0 8	1.6147	1.6146	30	3 0 6	1.5414	1.5411	10	2 1 4	1.8046	1.8040	70	0 2 13	2.1817	2.1817
2	3 1 1	1.3457	1.3452	2	3 0 2	1.5814	1.5805	30	2 2 0	1.4156	1.4155	20	1 1 14	1.7938	1.7943	15	0 1 26	2.1631	2.1632
2	3 0 4	1.3394	1.3395	10	2 1 5	1.5281	1.5282	5	3 1 2	1.3530	1.3535	20	1 0 17	1.7817	1.7815	70	2 0 14	2.1466	2.1469
40	2 0 6	1.3161	1.3159	10	2 0 7	1.5253	1.5251	2	0 1 20	1.3353	1.3352	30	2 0 13	1.7501	1.7493	10	0 2 16	2.0749	2.0752
40	3 1 2	1.3052	1.3054	5	1 1 8	1.4626	1.4620	10	2 2 9	1.2868	1.2865	30	2 1 7	1.7186	1.7188	10	2 0 17	2.0395	2.0387
40	3 1 3	1.2461	1.2462	5	1 0 9	1.4516	1.4520					10	1 0 18	1.6941	1.6947	55	0 2 19	1.9649	1.9653
				2	2 0 8	1.4007	1.4004					5	2 1 8	1.6831	1.6839	60	2 0 20	1.9286	1.9287
				20	2 1 7	1.3409	1.3408					60	3 0 0	1.6309	1.6317				

[a] Hexagonal indexing used for all polytypes. Refined lattice parameters are given in Table IV.

pounds, c is found to be approximated by $2.308n$. This parameter is in good agreement with the value given by Donohue, Katz, and Ward.[17]

C. Polytypism in BaMO$_3$ Compounds.—Polytypes consist of identical structural layers stacked on top of each other at constant intervals along the c axis, perpendicular to the layers. They differ only in stacking sequence. Polytypism is known in the BaMnO$_3$ system; Hardy[4] has reported a low-temperature 2H polytype and a high-temperature 4H phase. More recently a third polytype, 9R BaMnO$_3$, has been reported.[18] Precise analytical data have not been presented for any of these hexagonal variants.

Several forms of BaTiO$_3$ have been claimed,[6,19,20] but only two polytypic forms are known: the cubic phase (stable above 120°) and the hexagonal barium titanate phase (formed above 1000°). The structural relationship between these two polytypes has been described by Burbank and Evans.[6] The hexagonal BaTiO$_3$ phase is known to be slightly oxygen deficient, containing some trivalent titanium. Equilibrium between the two phases can be regulated by the oxygen partial pressure above the system

$$\mathrm{BaTiO_3(cubic)} \xrightleftharpoons{-\mathrm{O_2}} \mathrm{BaTiO_3(hexagonal)}$$

The structure of a particular polytype appears to be very dependent upon the stoichiometry. When the stoichiometry varies greatly, as in the BaFeO$_{3-x}$ example, several structure types are possible, giving rise to polymorphic phases[21–23] and not polytypic species.

Experimental Section

Reagents.—Three types of barium oxide were used, and different products were obtained depending upon the particular oxide employed. Technical grade Baker and Adamson BaO was used directly in one series of experiments. This oxide, dried at 1000° *in vacuo*, and BaO, prepared by the thermal decomposition of BaCO$_3$ at 1100° *in vacuo*, were alternatively used in other experiments. BaCO$_3$ (99.9999%) was obtained from Spex Industries, and the BaO derived from it was handled in a nitrogen-filled drybox. Chromium dioxide was obtained by the hydrothermal reaction[24] of Cr$_2$O$_3$ and CrO$_3$. Ba$_2$CrO$_4$ was prepared according to literature procedures.[7]

Apparatus.—The tetrahedral anvil apparatus was of the National Bureau of Standards design.[25] The calibration of this apparatus has been presented.[26] Temperatures were measured as described by Hall[27] utilizing a Pt—Pt–10%Rh thermocouple, spot-welded on the platinum reaction capsule. No correction was made for the effect of pressure on the emf of the thermocouple. Single-crystal X-ray precession photographs were obtained using molybdenum radiation. Powder diffraction patterns were obtained by the Debye–Scherrer method and with a Hägg–Guinier camera. The Guinier data were obtained using monochromatic Cu Kα radiation (λ 1.54051 Å) and an internal standard of KCl (a = 6.2931 Å). The films were read on a Mann film reader, and the cell dimensions were obtained from a least-squares refinement of the powder data. The Guinier powder data of the polytypic BaCrO$_3$ phases identified in this study are given in Table I.

Results

Various BaCrO$_3$ modifications were prepared at 60–65 kbars pressure and at several different temperatures. The reactions studied at high pressure were

$$\mathrm{BaO} + \mathrm{CrO_2} \longrightarrow \mathrm{BaCrO_3} \tag{1}$$

$$\mathrm{Ba_2CrO_4} + \mathrm{CrO_2} \longrightarrow 2\mathrm{BaCrO_3} \tag{2}$$

Reaction 1 yielded a variety of products depending upon the barium oxide used and the reaction temperature (Table II).

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TABLE II

RESULTS OF REACTIONS BETWEEN BaO AND CrO_2 AT 60–65 KBARS UNDER VARIOUS CONDITIONS

	Conditions		Gradient,[a]	
BaO source	Temp, °C	Time, hr	°C (approx)	Acid-insol products[b]
Commercial, undried	250	1	200	CrO_2, CrOOH
	500	1	300	CrOOH
	750	1	400	o-rh
	800	1	100	o-rh
	900	1	100	o-rh, 4H
	1000	1	200	4H, M
	1000	1	500	9R, 4H, T, C
	1000	4	300	9R, 4H
	1100	1	150	4H, X
	1200	1	200	4H, X
Commercial, dried	1000	1	500	4H, T
	1000	2	400	4H, T
	1000	4	300	6H, CrO_2
$BaCO_3$ decompn	800	2	100	o-rh
	900	2	100	4H, o-rh
	1000	2	100	9R, T, 12R
	1100	1	150	9R, 6H, X
	1200	1	200	4H
	1200	2	200	4H

[a] Temperature gradient across platinum reaction vessel. Large gradients resulted when the platinum cylinder was used as a resistance heater. Smaller gradients were obtained when a graphite resistance heater was utilized to heat the platinum reaction vessel encapsulated in a BN sleeve. [b] Abbreviations: o-rh, orthorhombic; T, tetragonal; C, cubic; M, monoclinic; X, unknown phase; the number before H or R refers to the number of layers in the unit cell; H, hexagonal; R, rhombohedral symmetry.

TABLE III

RESULTS OF HIGH-PRESSURE (60–65 KBARS) REACTIONS OF CrO_2 AND Ba_2CrO_4 AT VARIOUS TEMPERATURES

Conditions		
Temp, °C	Time, hr	Acid-insol products[a]
500	2	CrOOH
750	2	4H
750	2	6H
800	1	4H
800	2	4H
900	2	6H
900	2	4H
1000	2	6H
1000	1	4H
1200	1	27R
1300	2	4H
1300	2	4H, 6H, 14H
1400	1	4H, (C)[b] and 6H (E)[b]

[a] Same legend as Table II. [b] C = center; E = ends.

The experiments utilizing Ba_2CrO_4 and CrO_2 as reactants (reaction 2) yielded single-phase products at a particular reaction temperature in the high-pressure apparatus. High temperatures, however, led to the formation of a mixture of polytypes (Table III).

Two additional high-pressure experiments gave significant results. First, no reaction occurred between $BaCO_3$ and CrO_2 at 1000° and 60–65 kbars for 2 hr, and, second, Ba_2CrO_4 at 1000° and 60–65 kbars for 2 hr yielded 4H $BaCrO_3$ as an acid-insoluble product.

Several experiments at pressures below 3000 atm did not yield the desired $BaCrO_3$.

Crystallographic Properties

1. **4-Layer Hexagonal Polytype.**—The reaction of BaO and CrO_2 or Ba_2CrO_4 and CrO_2 at 750–1300° often yields a 4-layer hexagonal $BaCrO_3$ polytype. The powder pattern of this black, crystalline product had spacings and intensities similar to those reported for the "high-temperature" or 4H $BaMnO_3$ phase. Single-crystal precession data indicated $P\bar{6}2c$, $P6_3mc$, and $P6_3/mmc$ as possible space groups for the hexagonal structure. The Guinier data were refined and gave the cell dimensions $a = 5.6592 \pm 0.0003$ and $c = 9.3592 \pm 0.0007$ Å. The c/a ratio indicates a 4-layer sequence according to the general equation $c/a = 0.4107n$. Elemental and thermogravimetric analyses could be performed only on the 4H polytype since it was the only compound obtained in sufficient quantity and purity (free of other polytypes). *Anal.* Calcd for $BaCrO_3$: Ba, 57.9; Cr, 21.9; O, 20.2. Found: Ba, 56.0; Cr, 21.1; O, 21.3, 21.65. Calcd weight gain on oxidation to $BaCrO_4$: 6.74%. Found: 6.72%.

2. **6-Layer Hexagonal Polytype.**—A black, crystalline hexagonal variant, isotypic with hexagonal $BaTiO_3$, was obtained between 750 and 1100° in the tetrahedral anvil reaction of Ba_2CrO_4 and CrO_2. Since the X-ray diffraction pattern of this phase so closely resembled that of the 6-layer $BaTiO_3$, a single-crystal analysis was not considered necessary. The Guinier data were indexed and refined to obtain the hexagonal cell dimensions $a = 5.6269 \pm 0.0004$ and $c = 13.690 \pm 0.002$ Å. The c/a ratio of 2.433 is consistent with a 6-layer stacking sequence.

3. **9-Layer Rhombohedral Polytype.**—In the relatively few experiments where commercial BaO was used and a larger thermal gradient was applied, the product contained several large, black crystals which formed on the cooler ends of the reaction cylinder. These crystals were isolated and studied crystallographically. The single-crystal precession data indicated rhombohedral symmetry with the possible space groups R32, R3m, and $R\bar{3}m$. Cell dimensions were calculated from precession photographs: $a = 5.62$ and $c = 22.95$ Å. The c/a ratio approximates a 9- or a 10-layer stacking sequence, but the space group is more consistent with a 9-layer structure. Insufficient product was isolated to obtain elemental analyses or a good diffraction pattern for a more accurate determination of the cell dimensions.

4. **12-Layer Rhombohedral Polytype.**—Small amounts of a 12-layer, hexagonal variant were obtained in the high-temperature reactions of CrO_2 with BaO or with Ba_2CrO_4. This product was difficult to isolate, but a suitable powder pattern was obtained by dividing longitudinally into five parts a tetrahedral anvil product. The black, crystalline 12R polytype was found in the center portion, indicating that it formed at the highest temperature (1000°). Single-crystal data were obtained (possible rhombohedral space groups: R32,

R3m, and R$\bar{3}$m), and refinement of the Guinier data yielded the hexagonal cell dimensions $a = 5.6621 \pm 0.0006$ and $c = 27.752 \pm 0.006$ Å. The c/a ratio of 4.901 is consistent with a 12-layer stacking sequence.

5. **14-Layer Hexagonal Polytype.**—In a high-temperature reaction (1300°), disproportionation occurred with the formation of large crystals of a new BaCrO$_3$ modification, microcrystalline 4H BaCrO$_3$, BaCrO$_4$, and a water-soluble product. The BaCrO$_3$ variant obtained as large, black crystals was studied with a precession camera and was found to have hexagonal symmetry with the possible space groups P6_3mc, P$\bar{6}$2c, and P6_3/mmc. Refinement of the Guinier data gave cell dimensions $a = 5.6522 \pm 0.0006$ and $c = 32.515 \pm 0.005$ Å. The c/a ratio indicates a 14-layer polytype and the space group is consistent with an even-numbered repeat unit.

6. **27-Layer Rhombohedral Polytype.**—At 1200°, the reaction of CrO$_2$ with Ba$_2$CrO$_4$ yielded hexagonal black crystals which were studied on a single-crystal precession camera. This polytype was found to have the possible rhombohedral space groups R32, R3m, and R$\bar{3}$m and a 62-Å c axis. The Guinier powder data were refined to give the hexagonal cell dimensions $a = 5.6494 \pm 0.0003$ and $c = 62.705 \pm 0.003$ Å. The c/a ratio and space group suggest a 27-layer BaCrO$_3$ variant.

7. **Orthorhombic Phase.**—The reaction of BaO and CrO$_2$ at relatively low temperatures normally yields lustrous black flakes. Single-crystal studies indicated orthorhombic symmetry with the possible space groups Pna2$_1$ or Pnam. Refinement of the powder data gave the cell dimensions $a = 5.710 \pm 0.001$, $b = 20.045 \pm 0.005$, and $c = 4.014 \pm 0.001$ Å. The composition of this product is unknown, but it is not believed to contain tetravalent chromium. A tga oxidation of the orthorhombic phase indicated a 2.46% weight gain to 1100°. The oxidation products were BaCrO$_4$ and Cr$_2$O$_3$.

8. **Cubic Phase.**—A small octahedral crystal was isolated in the tetrahedral anvil product from the reaction of commercial BaO and CrO$_2$ at 1000°. Precession studies on this crystal indicated cubic symmetry with a cell constant of 10.68 Å and the space group Fd3m. This product perhaps has the pyrochlore structure and can be formulated as Ba$_2$Cr$_2$O$_7$, containing pentavalent chromium. Attempts to synthesize this composition directly at high pressure have been unsuccessful.

9. **Monoclinic Phase.**—A reaction of commercial grade BaO with CrO$_2$ at 1000° and high pressures yielded large, black crystals which were found to have monoclinic symmetry from single-crystal precession studies. The complex diffraction pattern was suitably indexed and refined from the single-crystal monoclinic cell dimensions. The unit cell is given by: $a = 14.721 \pm 0.003$, $b = 3.985 \pm 0.001$, $c = 5.792 \pm 0.002$ Å, and $\beta = 100.89 \pm 0.02°$; the space group is C2, Cm, or C2/m.

10. **Other Phases.**—As shown in Table II, BaO and CrO$_2$ did not react below 250°, and CrO$_2$ was recovered as the principal insoluble product from acid solution. At slightly higher temperatures (500–600°) CrOOH, the orthorhombic variety, is formed, presumably by the reaction of CrO$_2$ with traces of water in the untreated basic oxide. A tetragonal phase has also been observed in certain reaction products of the BaO–CrO$_2$ system. Single crystals of this phase could not be obtained, but the powder pattern was indexed on a tetragonal basis with the cell dimensions $a = 11.81$ and $c = 8.39$ Å. The composition and formulation are unknown.

Discussion

In this investigation several BaCrO$_3$ polytypic phases have been isolated. These include the 4-, 6-, 9-, 12-, 14-, and 27-layer, close-packed, hexagonal structures. The lattice parameters and space groups for the different polytypes are summarized in Table IV.

Table IV

Crystallographic Data of BaCrO$_3$ Polytypes

Layer type	Probable space group	Cell dimensions, Å	
		a	c
4H	P6_3/mmc	5.659	9.359
6H	P6_3/mmc	5.627	13.690
9R	R$\bar{3}$m	5.62[a]	22.95[a]
12R	R$\bar{3}$m	5.662	27.752
14H	P6_3/mmc	5.652	32.515
27R	R$\bar{3}$m	5.649	62.705

[a] Data obtained only from single-crystal precession photographs.

The critical parameters in the formation of any specific hexagonal variant are not known. Nucleation and crystal growth of a single BaCrO$_3$ variant occurred most readily in the Ba$_2$CrO$_4$–CrO$_2$ reaction in which impurities such as H$_2$O, CO$_3{}^{2-}$, and OH$^-$ were minimized.

The various reactions with CrO$_2$ were carried out in a tetrahedral anvil press since the stability of the oxide above 750° requires pressures of 30 kbars or greater.[28–30] The use of high pressure would favor the formation of stoichiometric phases; however, the reactions utilizing commercial BaO, which probably contained traces of moisture and carbonate, yielded a variety of products. It was noted previously that BaCO$_3$ in commerical BaO might lead to a chromium-rich, nonstoichiometric product, while traces of moisture in the reactant might produce lower or mixed-valency states of chromium in the product.

Chromium is probably tetravalent in barium metachromate and can be represented by the formulation BaCr^{IV}O$_3$. Alternate formulations involving mixed oxidation states, *e.g.*, Ba$_2$Cr^{II}Cr^{VI}O$_6$, Ba$_2$Cr^{III}Cr^{V}O$_6$, or Ba$_3$Cr$^{III}{}_2$Cr^{VI}O$_9$, are much less reasonable. This conclusion is based on the comparison of cell dimensions with those of other isotypic, BaMO$_3$-layered compounds

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(28) B. L. Chamberland, *Mater. Res. Bull.*, **2**, 827 (1967).

(29) N. Kawai, A. Sawaoka, S. Kikuchi, and N. Tamagawa, *Jap. J. Appl. Phys.*, **6**, 1397 (1967).

(30) R. C. DeVries, *Mater. Res. Bull.*, **2**, 999 (1967).

TABLE V

CRYSTALLOGRAPHIC PROPERTIES OF ISOTYPIC $BaMO_3$ COMPOSITIONS

Composition	Stacking sequence[a]	Layer type	Cell dimensions, Å			
			a	*c*	*c/a*	Ref
$BaCrO_3$	ch	4H	5.659	9.359	1.654	This work
$BaMnO_3$	ch	4H	5.669	9.375	1.654	4
$BaTiO_3$	cch	6H	5.735	14.05	2.450	6
$BaCrO_3$	cch	6H	5.627	13.690	2.433	This work
$BaFeO_{3-x}$ ($x = 0.05$)	cch	6H	5.674	13.74	2.422	21
$BaCrO_3$	chh	9R	5.62	22.95	4.08[b]	This work
$BaMnO_3$	chh	9R	5.662	20.915	3.693	18
$BaRuO_3$	chh	9R	5.75	21.60	3.757	3
$BaCrO_3$	chhc	12R	5.662	27.752	4.901	This work
$Ba_4Re_2CoO_{12}$	chhc	12R	5.71	27.7	4.85	*c*

[a] The $BaCrO_3$ stacking sequences are assumed to be the same as those reported for the isotypic analogs since the relative intensities and cell dimensions are similar. [b] The large *c/a* value for this variant was obtained from single-crystal precession data which may be inaccurate. [c] J. M. Longo, L. Katz, and R. Ward, *Inorg. Chem.*, **4**, 235 (1965).

which possess stable tetravalent states (Table V). Furthermore, octahedral coordination of Cr is only found for the 2+, 3+, 4+, and occasionally the 5+ ions. Since the hexagonal, layered structures give rise to predominantly octahedral sites, it would be difficult to substitute a large number of Cr^{6+} ions in the structure since this ion is always found in tetrahedral coordination. The formulations $Ba_2Cr^{II}Cr^{VI}O_6$ and $Ba_3Cr^{III}{}_2Cr^{VI}O_9$ are rejected since they would require 50 and 33% tetrahedral sites, respectively. In addition, when chromium is trivalent as in mixed perovskite-type compounds, a cubic structure is normally formed because of ordering of the B atoms on two different sites, *e.g.*, Ba_2CrBiO_6 cubic perovskite or the 3H system. Such a cubic system was not observed in this investigation, and the $Ba_2Cr^{III}Cr^{V}O_6$ possibility can also be rejected.

The various forms of $BaCrO_3$ can possibly arise from slight departures from stoichiometry by (a) cation deficiency, *e.g.*, $Ba_{1-x}CrO_3$ as in "bronze" compositions, (b) anion deficiency represented by $BaCrO_{3-x}$ as observed in $BaTiO_{3-x}$, (c) transition metal vacancies in the B site, *e.g.*, $BaCr_{1-x}O_3$ as in $Ba_5Ta_4O_{15}$ or $Ba_4Re_2CoO_{12}$, and, finally, (d) variable metal valencies on the B site mentioned above. The lack of complete and accurate elemental analyses on these $BaCrO_3$ polytypes precludes any definitive conclusions as to the exact stoichiometry and their relationship to any specific layer type or stacking sequence.

It can be noted that in Table III the predominant hexagonal products have the 4-layer or the 6-layer structure. These two variants are believed to be stoichiometric and can be represented by the formula $BaCr^{IV}O_3$. The 12-layer hexagonal variant may possibly contain vacancies in the B site as found for the 5-layered $Ba_5Ta_4O_{15}$ and the 12-layered $Ba_4Re_2CoO_{12}$. Its formulation could be represented by $BaCr_{1-x}O_3$ and may possibly be $Ba_4Cr_3O_{12}$ since the space group and lattice parameters are similar to those of $Ba_4Re_2CoO_{12}$.

The isolation of orthorhombic, tetragonal, and monoclinic phases possibly represents large deviations in the $BaCrO_3$ stoichiometry and the presence of chromium in mixed or lower oxidation states.

The electrical properties of a few hexagonal $BaCrO_3$ products have been determined (Table VI). The low activation energies and the resistivity values for the hexagonal $BaCrO_3$ variants are markedly different from those of tri- and pentavalent chromium derivatives.

TABLE VI

FOUR-PROBE ELECTRICAL RESISTIVITY DATA ON $BaCrO_3$ AND OTHER COMPOSITIONS

Composition	Layer type or structure	Resistivity at 298°K, ohm cm	Activation energy, eV
$BaCrO_3$	4H	4×10^{-1}	0.11
$BaCrO_3$	9R	2.8	0.09
$BaCrO_x$	o-rh	6×10^{9}	1.2
$Ba_3(CrO_4)_2$	H	7×10^{5}	0.28
CrOOH	o-rh	3×10^{8}	0.9

Acknowledgments.—The author wishes to thank Dr. P. C. Donohue and Professor R. Ward for helpful discussions on this system and Mr. K. R. Babcock, Miss M. S. Licis, and Dr. J. F. Whitney for space group determination. The Guinier data were obtained and refined by Miss M. S. Licis, and the electrical resistivity data were obtained by Mr. J. L. Gillson.