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Crystal Structure of the 6H $BaCrO_3$ Polytype

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A product from the reaction between CrO_2 and Ba_2CrO_4 at 900°C under 60–65 kbar was found to be the six-layer polytype of $BaCrO_3$ from powder diffraction studies. A hexagonal black crystal obtained from this reaction was isolated for single crystal studies and structure determination. The crystal was found to possess a six-layer stacking sequence of BaO_3 layers with space group $P6_3/mmc$ and had unit cell parameters $a = 5.629(2)$, $c = 13.698(6)$ Å, and $Z = 6$. The structure was determined from 936 independent reflections of which 693 were considered observed. Averaging equivalent reflections yielded 163 unique, observed reflections. Refinement of the structure by least-squares methods gave a conventional R value of 4.8% ($R_w = 6.2\%$). The structure consists of a six-layer stacking sequence of close-packed BaO_3 layers containing tetravalent chromium in all the octahedral oxygen interstices. The compound was found to be isostructural with previously reported $BaMO_3$ phases.

Introduction

Several different polytypes were obtained (*1*) in the $BaCrO_3$ system prepared under high pressure conditions in a tetrahedral anvil press. The most stable and recurring forms were the 4H and 6H varieties. Single crystal structure determinations of all the $BaCrO_3$ polytypes have been reported (*2, 4*) with the exception of the 6H variety. The purpose of this study was the investigation of the remaining, and quite common, polytype of $BaCrO_3$ in an effort to obtain the structural details required to interpret and correlate the magnetic and electrical properties of all phases in this system.

Experimentation

Preparation

The barium chromium(IV) oxide used in this study was obtained (*1*) from a reaction of Ba_2CrO_4 with CrO_2 at 900°C and 60 to 65 kbar in a tetrahedral anvil press. Several black hexagonal platelets were isolated in the product after treatment with dilute HCl to remove any trace of water-soluble byproducts. Powder diffraction studies and the single crystal studies on several of these platelets indicated the 6H $BaMO_3$ structure and it was assumed that the entire product of this particular experiment was single phase.

Crystallographic Studies

X-ray precession and rotation photographs on a crystalline plate showed hexagonal symmetry, Laue group $6/mmm$. The only systematic absences were hhl reflections with l odd, so that the probable space group is one of $P6_3mc$, $P\bar{6}2c$, or $P6_3/mmc$. The unit cell parameters from the precession data suggested $a = 5.58$ and $c = 13.62$ Å. A cone axis photograph, perpendicular

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to the ($hk0$) plane, confirmed the fact that the crystal was hexagonal and contained a six-layer stacking sequence along the c axis.

Structure Determination

The single crystal used for data collection was a hexagonal plate (0.22 × 0.27 × 0.12 mm) (volume = 4.74×10^{-6} cm^3). No attempt was made to grind the hexagonal plate into a sphere since all previous experiments on crystals of this shape yielded only circular disks. Precise dimensions of the crystal were determined with a microscope utilizing high magnification and a calibrated millimeter scale.

Unit cell parameters were determined in a PICK-II least-squares refinement program using 15 reflections within the angular range $31 < 2\theta < 55°$; the reflections were automatically centered on a computer-controlled Picker FACS-1 four-circle diffractometer and graphite monochromatized $MoK\alpha_1$ radiation ($\lambda = 0.70930$ Å). The unit cell parameters were found to be $a = 5.629(2)$ and $c = 13.698(6)$ Å, where the figures in parentheses represent the standard deviations in the last reported figure. The calculated volume is 375.88 $Å^3$, giving a calculated density of 6.29 g cm^{-3}, with $Z = 6$. The unit cell dimensions can be compared to Guinier data previously reported (*1*) for 6H $BaCrO_3$; $a = 5.6269(4)$ and $c = 13.690(2)$ Å.

Diffraction intensities were measured with the Picker unit using the ω scan mode and a radiation take off angle of 1.5°. Ten-second background counts were taken at both ends of a θ–2θ scan 1.4°, corrected for dispersion. A data set of 936 reflections was collected in the angular range $2\theta < 55°$; this represents $\frac{1}{4}$ of the sphere of reflection. Three standard reflections were systematically monitored during the experiment; the maximum variation in observed intensity was never greater than ±3.5% over the data collection period.

An absorption correction program written by N. W. Alcock and B. Lee for a crystal of general shape was applied to the hexagonal plate prior to data treatment. Of the 936 data collected, 693 were considered observable according to the criterion $|F_0| > 3.0\,\sigma_F$, where

$$\sigma_F \text{ is defined as } 0.02|F_0| + [B + k^2C]^{1/2}/2|F_0|L_p$$

where C is the total scan count, k is the ratio of scanning time to the total background time, B is the total background count, and L_p is the Lorentzian and polarization corrections.

The corrected data were then averaged with a computer program written by L. Finger and using the hexagonal transformation for determining equivalent reflections. This operation generated 163 independent reflections which were assigned all positive hkl values prior to refinement.

Structure Refinement

Powder diffraction studies and single crystal precession data suggested a six-layer polytype of $BaCrO_3$ composition. Since this structure was previously investigated (*5*) for the case of hexagonal $BaTiO_3$ formed at high temperature, it was decided to attempt the structure refinement based on this particular compound. The most probable space group for this structure was taken to be $P6_3/mmc$ (#194).

A full-matrix least-squares refinement (*6*) using the positional parameter for six atoms, a $1/\sigma^2$ weighting scheme, zero-valent scattering factor (*7*) for Ba, Cr, and O, isotropic temperature factors, and corrections for secondary extinction and anomalous dispersion yielded a residual $R = 0.095$ and a weighted residual $R_w = 0.12$. The final anisotropic refinement, based on a data : parameter ratio of 11.6 with 14 independently varied parameters, yielded $R = 0.048$ and $R_w = 0.062$ for the observed data.

TABLE I

ATOMIC PARAMETERS FOR $BaCrO_3$ (6H)

Atom	Position	x	y	z	$B_{11}{}^{a}$	$B_{33}{}^{a}$	B_0
Ba(1)	$2b$	0	0	$\frac{1}{4}$	0.23(11)	0.13(1)	—
Ba(2)	$4f$	$\frac{1}{3}$	$\frac{2}{3}$	0.0925(1)	0.18(9)	0.18(1)	—
Cr(1)	$2a$	0	0	0	0.16(25)	0.14(3)	—
Cr(2)	$4f$	$\frac{1}{3}$	$\frac{2}{3}$	0.8465(3)	0.05(16)	0.16(2)	—
O(1)	$6h$	0.5205(29)	−0.5221	$\frac{1}{4}$	—	—	0.93(26)
O(2)	$12k$	0.8320(20)	−0.8339	0.0803(7)	—	—	1.73(20)

[a] Thermal parameters are multiplied by 100.

The B_{ij}'s are defined by the general temperature factor $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Note: For Ba and Cr atoms, B_{22} and B_{12} were not refined since $B_{11} = B_{22}$, and $B_{12} = \frac{1}{2}B_{11}$. For oxygen, only the overall temperature factor B_0 was refined.

Table I presents the positional and temperature parameters from the final refinement cycle (anisotropic for the metal atoms and isotropic for the oxygen atoms). Except for two ripples at the periphery of the Ba atoms, the difference Fourier map was essentially flat and equivalent to 0.2 of an oxygen atom or less.

An illustration of the structure, which is a projection of the unit cell on the (110) plane, is given in Fig. 1. The figure was prepared using ORTEP (*8*). Bond lengths and angles calculated in the ORFFE program are given in Table II. A listing of observed and calculated structure factors comprises Table III.

Results and Discussion

As previously mentioned (*1*), the most common products in the $BaCrO_3$ synthesis are the 4H and 6H polytypes. These two modifications are believed to be stoichiometric and more stable from a structural point of view. The 4H polytype contains pairs of face-shared octahedra which are vertex shared. The 6H polytype, shown in Fig. 1, also contains pairs of face-shared octahedra but these units are vertex shared to individual CrO_6 octahedra. The packing sequence for $BaCrO_3$ (6H) is cchcch or AB CACB(A) where A layers have Ba atoms at $00z$, B layers at $\frac{2}{3}\frac{1}{3}z'$, C layers at $\frac{1}{3}\frac{2}{3}z''$. The Zhdanov notation for this sequence is

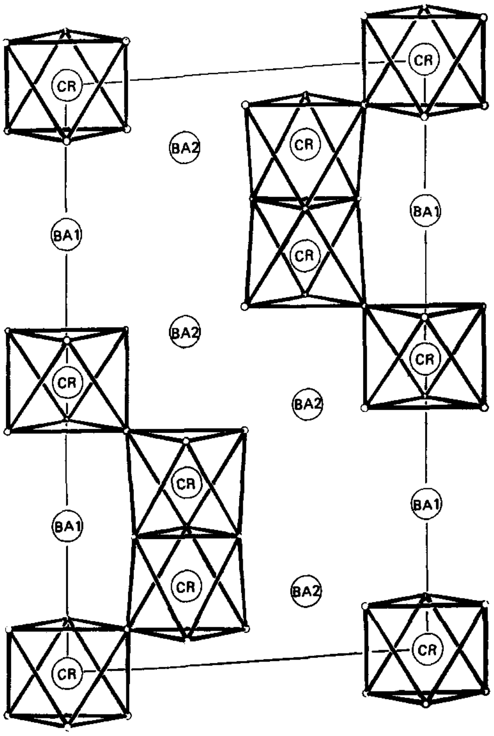

FIG. 1. Projection of the hexagonal (110) plane in $BaCrO_3$ (6H).

TABLE II

BOND LENGTHS AND ANGLES IN $BaCrO_3$ (6H)

Distances (Å)						Angles (°)		
Ba(1)-O(1)	6@	2.821(1)	O(1)-O(1)	2@	2.459(1)	O(2)-Cr(1)-O(2)	6@	91.90(3)
-O(2)	6@	2.844(1)	-O(1)	2@	3.168(1)	-O(2)	3@	180(12)
			-O(2)	4@	2.785(1)	-O(2)	6@	88.10(3)
Ba(2)-O(1)	3@	2.830(1)						
-O(2)	6@	2.819(1)	O(2)-O(2)	2@	2.736(1)	O(2)-Cr(2)-O(2)	3@	94.66(14)
-O(2)	3@	2.864(2)	-O(1)	2@	2.785(1)	-O(1)	3@	168.9(2)
			-O(2)	2@	2.799(2)	-O(1)	6@	92.84(3)
Cr(1)-O(2)	6@	1.967(1)	-O(2)	2@	2.828(1)	O(1)-Cr(2)-O(1)	3@	78.63(14)
Cr(2)-O(1)	3@	1.941(3)				Cr(2)-O(1)-Cr(2)		85.96(18)
-O(2)	3@	1.904(2)						
						Cr(1)-O(2)-Cr(2)		177.98(23)
Cr(2)-Cr(2)		2.646(8)						
Cr(1)-O(2)-Cr(2)		3.870(5)						

\|(3)(3)\|. The Cr atoms occupy all the O_6 octahedral sites and the Ba atoms occupy cuboctahedral and "twinned" cuboctahedral sites.

This particular structure has been reported for several $BaMO_3$ compounds and the high pressure form of $SrMnO_3$ (*9, 10*). A few ternary fluorides are also known to exist with this six-layer structure and these include $CsMnF_3$ (*11*), $RbNiF_3$ (*12, 13*), and the high pressure form of $CsNiF_3$ (*14*). Compound with the $Ba_2MM'O_6$ or

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS (5×)

H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL
0	0	2	25	24	0	3	9	54	35	1	2	12	105	102	2	0	1	322	277	2	4	0	39	17
0	0	4	205	237	0	3	10	101	109	1	2	13	344	350	2	0	2	615	572	2	4	1	163	144
0	0	6	954	1138	0	3	12	668	680	1	2	14	99	99	2	0	3	912	867	2	4	2	294	285
0	0	8	396	469	0	3	14	157	150	1	2	15	72	60	2	0	4	1131	1132	2	4	3	504	467
0	0	10	61	68	0	3	15	25	20	1	3	1	108	99	2	0	5	539	535	2	4	4	650	623
0	0	12	993	1018	0	5	1	139	146	1	3	2	284	265	2	0	7	610	624	2	4	5	317	285
0	0	14	141	158	0	5	2	193	214	1	3	3	507	472	2	0	8	568	583	2	4	7	420	397
0	0	16	211	168	0	5	3	328	357	1	3	4	761	726	2	0	9	677	693	2	4	8	375	343
0	1	1	88	69	0	5	4	536	578	1	3	5	310	292	2	0	10	389	404	2	4	9	486	449
0	1	2	303	290	0	5	5	272	287	1	3	7	449	448	2	0	11	129	133	3	3	0	1012	1074
0	1	3	614	631	0	5	7	399	420	1	3	8	358	354	2	0	12	111	116	3	3	2	42	43
0	1	4	910	993	0	5	8	274	286	1	3	9	461	467	2	0	13	377	372	3	3	4	131	131
0	1	5	367	390	0	5	9	356	368	1	3	10	260	270	2	0	14	201	198	3	3	6	429	435
0	1	7	502	567	0	5	10	214	222	1	3	11	197	192	2	0	15	153	147	3	3	8	318	312
0	1	8	396	426	1	1	0	1867	1772	1	3	12	106	98	2	0	16	535	500	3	4	1	116	120
0	1	9	524	577	1	1	2	53	45	1	3	13	299	304	2	2	0	1764	1678	3	4	2	172	195
0	1	10	270	294	1	1	4	237	236	1	3	14	106	101	2	2	4	207	180	3	4	3	296	321
0	1	11	237	249	1	1	6	513	534	1	4	0	1141	1157	2	2	6	805	735	4	0	1	207	188
0	1	12	113	110	1	1	8	429	460	1	4	1	35	24	2	2	8	362	353	4	0	2	367	366
0	1	13	340	352	1	1	10	106	110	1	4	2	46	33	2	2	10	91	78	4	0	3	605	580
0	1	14	110	104	1	1	12	725	745	1	4	3	42	27	2	2	12	829	801	4	0	4	774	779
0	1	15	86	84	1	1	14	170	167	1	4	4	158	155	2	2	14	134	135	4	0	5	379	365
0	1	16	502	458	1	1	16	212	200	1	4	6	457	451	2	3	1	73	71	4	0	7	487	481
0	1	17	91	72	1	2	1	172	152	1	4	8	345	327	2	3	2	243	234	4	0	8	439	424
0	3	0	1492	1447	1	2	2	301	265	1	4	10	85	86	2	3	3	480	460	4	0	9	558	532
0	3	1	61	52	1	2	3	529	474	1	5	0	21	8	2	3	4	669	638	4	0	10	322	319
0	3	2	34	25	1	2	4	865	815	1	5	1	109	112	2	3	5	259	237	4	0	11	112	120
0	3	3	54	54	1	2	5	405	381	1	5	2	208	224	2	3	7	402	386	4	0	12	88	90
0	3	4	201	208	1	2	7	537	538	1	5	3	344	357	2	3	8	333	314	4	0	13	327	318
0	3	5	47	43	1	2	8	385	378	1	5	4	553	556	2	3	9	462	452	6	0	0	987	1053
0	3	6	484	494	1	2	9	470	480	1	5	5	242	243	2	3	10	242	242	6	0	4	132	138
0	3	7	48	37	1	2	10	268	279	1	5	6	37	18	2	3	11	208	195					
0	3	8	385	391	1	2	11	199	186	1	5	7	372	369	2	3	12	90	80					

$Ba_3MM'_2O_9$ composition predominantly crystallize with the six-layer, hexagonal $BaTiO_3$ structure. This structural preference was originally noted by Dickinson and Ward (*15*) in 1959. In these latter compositions the *M* and *M'* atoms have a random distribution in the octahedral sites. Recently the single crystal structure for a platinum-doped $BaTiO_3$ phase was reported by Fischer and Tillmanns (*16*). An ordered cationic distribution of octahedral ions has been noted (*17*) in a more complex compound, $Ba_3(YPtRu)O_9$.

Some important features determined in the $BaCrO_3$ (6H) compound are found in the Cr–Cr and Cr–O distances. The Cr–Cr distance in the face-shared octahedral pairs compare well with that distance observed in the other $BaCrO_3$ polytypes: 2.646(8) Å in $BaCrO_3$ (6H), 2.611(4) Å in $BaCrO_3$ (4H), 2.637(5) Å averaged in $BaCrO_3$ (14H), and 2.630(3) Å averaged in $BaCrO_3$(27*R*). This distance is slightly greater than that reported in the metal with the body-centered cubic structure (Cr–Cr = 2.50 Å).

The average Cr–O bond length of 1.945(2) Å is in good agreement with that found in other $(CrO_6)^{8-}$ systems: 1.943(3) Å in $BaCrO_3$ (4H), 1.954(4) Å in $BaCrO_3$ (14H), and 1.951(4) Å in $BaCrO_3$(27*R*). These data suggest a $^{VI}Cr^{4+}$ radius of 0.548 Å, which is in excellent agreement with 0.55 Å suggested by Shannon and Prewitt (*18*).

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