JOURNAL OF SOLID STATE CHEMISTRY 43, 309–313 (1982)

Crystal Structure of the 4H $BaCrO_3$ Polytype

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Received February 9, 1982; in final form March 29, 1982

The structure of the four-layer hexagonal $BaCrO_3$ polytype, prepared at high temperature and high pressure, was determined utilizing a Picker FACS-I diffractometer. The hexagonal black crystal was found to crystallize with a four-layer stacking sequence in space group $P6_3/mmc$ having unit cell parameters $a = 5.660(1)$ and $c = 9.357(1)$ Å. The structure was determined from 668 independent reflections of which 605 were considered observed. Equivalent reflections were averaged and this operation yielded 130 unique, observed reflections. Refinement of the structure by least-squares methods gave a conventional R value of 3.0%. The structure consists of a four-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 β-$BaMnO_3$ and the recently reported $BaRhO_3$ and $SrMnO_3$.

Introduction

The $BaCrO_3$ system was reported (*1*) to form a variety of different $BaMO_3$ polytypes. The most stable and recurring forms were the 4H and 6H varieties. The structures of other $BaCrO_3$ polytypes have been reported, 14H (*2*) and 27R (*3*). The structure of a nonstoichiometric and nonperovskite-related Ba/Cr/O product was also determined (*4*).

In an effort to correlate the structure of the various $BaCrO_3$ polytypes with their magnetic and electrical properties, a study of the structure of the remaining polytype was originated.

Experimentation

Preparation. The preparation of $BaCrO_3$ was performed in a tetrahedral anvil apparatus under a variety of conditions and utilizing various reactants. The synthesis of this particular polytype was through the reaction of Ba_2CrO_4 and CrO_2 at 1000°C and 60–65 kbar for 1 hr. Powder diffraction studies and preliminary single-crystal studies indicated the presence of the four-layer analog of $BaCrO_3$. Several single crystals, isolated in the form of black hexagonal plates, showed the characteristic pattern of a four-layer structure. Indexation of the powder pattern was successfully carried out by the close analogy of the pattern with that of the isostructural high-temperature form of $BaMnO_3$ (4H). The high-pressure products were washed in dilute HCl to isolate a product free from acid-soluble reactants such as BaO, $BaCO_3$, and Ba_2CrO_4.

Crystallographic studies. Preliminary X-ray powder diffraction analysis of the product indicated a four-layer $BaMO_3$ polytype. Precession data taken on several single crystals showed the characteristic four-

0022-4596/82/090309-05$02.00/0

layer repeat sequence in the *hh0l* and *hk0l* precession photographs.

The hexagonal plates from individual high-pressure experiments were studied by the precession method and were all found to possess hexagonal symmetry with a four-layer stacking sequence. The space group was found to be $P6_3/mmc$, $P6_3mc$, or $P\bar{6}2c$ and the unit cell parameters from the precession data suggested $a = 5.659$ and $c = 9.321$ Å. The Guinier data on the powdered product yielded the parameters $a = 5.692(3)$ and $c = 9.3592(7)$ Å, where the figures in parentheses represent the standard deviations in the last reported figure.

Structure determination. The unit cell parameters for the crystal used in the single-crystal experiment were determined in the PICK-II least-squares refinement program using 28 reflections within the angular range $31° < 2\theta < 53°$; the reflections were automatically centered on a Picker FACS-I four-circle diffractometer using Mo$K\alpha_1$ radiation ($\lambda = 0.70930$ Å). The unit cell parameters were found to be $a = 5.660(1)$ and $c = 9.357(1)$ Å. The calculated volume is 259.63 Å^3, giving a calculated density, with $Z = 4$, of 6.07 g cm^{-3}.

A crystal with hexagonal bipyramid shape (0.20 × 0.20 × 0.29 mm) (vol. = 6.45×10^{-6} cm^3) was used for data collection. Precise dimensions of the crystal were determined with a microscope utilizing high magnification. These data were used in an absorption correction program written by N. W. Alcock and modified by B. Lee for a crystal of general shape.

Diffraction intensities were measured using Zr-filtered Mo$K\alpha_1$ radiation at a takeoff angle of 1.5° with the diffractometer operating in the ω scan mode. Ten-second background counts were taken at both ends of a 1.4° θ–2θ offset corrected for dispersion. Of the 668 data collected in the angular range $2\theta < 54°$, 605 were considered observable according to the criterion $|F_0| > 3.0\ \sigma_F$, where σ_F is defined as $0.02\ |F_0| + [C + k^2 B]^{1/2}/2\ |F_0|\ Lp$; the total scan count is C, k is the ratio of scanning time to the total background time, and B is the total background count. Three reflections were systematically monitored as standards during the experiment; the maximum variation in intensity observed was never greater than ±3% over the data collection period.

Intensity data were corrected for Lorentzian and polarization effects, and absorption corrections were carried out using the computer program already cited. The corrected data were then averaged using a program written by L. Finger (*5*) using the hexagonal transformation for determining equivalent reflections. This generated 130 independent reflections and these were assigned positive *hkl* values prior to refinement.

Structure refinement. The study of the precession photographs indicated a four-layer stacking sequence of BaO_3 layers with Cr located in octahedral interstices. Since this system was previously observed for (high-temperature form) $BaMnO_3$ (*6*), $BaRhO_3$ (*7*), and $SrMnO_3$ (*8*) systems, it was decided to attempt the refinement based on this particular ABO_3 structure. The most probable space group for these hexagonal polytypes is taken as $P6_3/mmc$ (No. 194).

A full-matrix refinement (*9*) using the positional parameter for five atoms, a $1/\sigma^2$ weighting scheme, zero-valent scattering factors for Ba, Cr, and O (*10*), isotropic temperature factors, and corrections for secondary extinction and anomalous dispersion yielded a residual $R = 0.12$ and a weighted residual $R_w = 0.22$. The final anisotropic refinement, based on a data : parameter ratio of 8.7 with the 15 independently varied parameters, yielded $R = 0.030$ and $R_w = 0.042$ for the observed data.

Table I presents the positional and anisotropic temperature parameters from the final anisotropic refinement. Except for the two ripples at the periphery of the Ba at-

TABLE I

ATOMIC PARAMETERS FOR $BaCrO_3$ (4H)

Atom	Position	x	y	z	B_{11}[a]	B_{22}[a]	B_{33}[a]
Ba(1)	2*a*	0	0	0	0.77(7)	[b]	1.63(3)
Ba(2)	2*c*	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	1.09(7)	[b]	0.18(2)
Cr	4*f*	$\frac{1}{3}$	$\frac{2}{3}$	0.6105(2)	0.73(10)	[b]	0.20(2)
O(1)	6*g*	$\frac{1}{2}$	0	0	1.17(32)	1.78(36)	0.20(8)
O(2)	6*h*	0.3705(13)	0.1852	$\frac{1}{4}$	0.97(32)	2.20(32)	0.27(8)

[a] Thermal parameters are multiplied by 100. The B's are defined by the general temperature factor exp $[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

[b] 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 O(2), the y parameter was not refined since $y = \frac{1}{2}x$; and $B_{12} = \frac{1}{2}B_{22}$.

oms, the difference Fourier map was essentially flat and equivalent to 0.2 of an oxygen atom or less.

An illustration of the structure is given in Fig. 1. The figure was prepared using ORTEP (*11*). Bond lengths and angles calculated in the ORFFE program are given in Table II. The table of observed and calculated structure factors comprises Table III.

Results and Discussion

Of the first-row transition metals, $BaMnO_3$ was first observed (*6*) to form a variety of different $BaMO_3$ polytypes based on the perovskite structure. The relationship between the cubic perovskite structure and hexagonal layer structures was established by Katz and Ward (*12*) in 1964.

The four-layer stacking sequence *ABAC*, or the packing sequence $(hc)_2$, has the Zhdanov notation $|(1)(1)|$. The structure consists of pairs of face-shared octahedra which are further linked by vertices along the *c* axis of the unit cell. The polyhedral representation of the structure is shown in Fig. 1. This structural type has been reported for β-$BaMnO_3$, $SrMnO_3$, the high-pressure forms of $BaRuO_3$ (*13*) and $BaRhO_3$ (*7*), and the solid solutions of $BaRuO_3/SrRuO_3$ and $BaMnO_3/SrMnO_3$. Lattice images of 4H $BaCrO_3$ were studied by Gai *et al.* (*14*) and their results were interpreted as showing the $(ch)_2$ stacking sequence.

This stable structure represents a midpoint between the perovskite structure (100% cubic packing of AO_3 layers) and the $BaNiO_3$ structure (100% hexagonal packing of AO_3 layers). The consequence of the alternating of cubic and hexagonal packing leads to face-shared octahedral units which allow a short metal-to-metal distance for the transition metal ions. For the four-layer

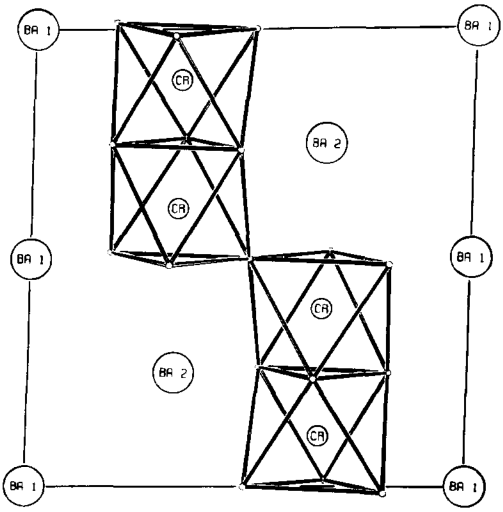

FIG. 1. The projection of the hexagonal (110) plane for $BaCrO_3$ (4H).

TABLE II

BOND LENGTHS AND ANGLES IN $BaCrO_3$ (4H)

Distances (Å)						Angles (°)		
Ba(1)–O(1)	6@	2.830(1)	O(1)–O(1)	4@	2.830(1)	O(1)–Cr–O(1)	3@	94.08(7)
–O(2)	6@	2.962(4)	–O(2)	4@	2.807(2)	–O(2)	3@	170.35(17)
						–O(2)	6@	92.49(10)
						O(2)–Cr–O(2)	3@	80.16(20)
Ba(2) –O(1)	6@	2.836(4)						
–O(2)	6@	2.854(1)	O(2)–O(2)	2@	2.514(11)			
			–O(1)	4@	2.807(2)			
			–O(2)	2@	3.146(11)			
Cr –O(1)	3@	1.934(1)				Cr–O(2)–Cr		83.94(27)
–O(2)	3@	1.952(5)				Cr–O(1)–Cr		180.0
Cr –Cr		2.611(4)						
Cr–O (1)–Cr		3.867(2)						

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS (5x)

h	k	l	F_{OBS}	F_{CALC}	h	k	l	F_{OBS}	F_{CALC}	h	k	l	F_{OBS}	F_{CALC}	h	k	l	F_{OBS}	F_{CALC}	h	k	l	F_{OBS}	F_{CALC}
0	0	2	50	51	0	3	10	47	41	1	3	0	19	16	2	0	1	295	289	2	4	2	363	354
0	0	4	755	736	0	5	0	54	62	1	3	1	106	106	2	0	2	791	764	2	4	3	312	310
0	0	6	263	280	0	5	1	97	98	1	3	2	381	392	2	0	3	686	673	2	4	4	174	166
0	0	8	699	699	0	5	2	256	260	1	3	3	392	397	2	0	4	308	304	2	4	5	224	219
0	0	10	43	48	0	5	3	296	306	1	3	4	171	165	2	0	5	437	439	2	4	6	302	283
0	1	0	37	33	0	5	4	165	163	1	3	5	260	263	2	0	6	535	521	2	5	0	461	455
0	1	1	117	111	0	5	5	208	214	1	3	6	303	303	2	0	7	121	121	2	5	1	30	25
0	1	2	593	567	0	5	6	213	204	1	3	7	44	43	2	0	8	65	62	3	3	0	565	593
0	1	3	605	595	0	5	7	41	37	1	3	8	95	90	2	0	9	253	252	3	3	2	20	26
0	1	4	242	230	1	1	0	1128	1157	1	3	9	167	162	2	0	10	154	168	3	3	4	207	213
0	1	5	354	356	1	1	2	46	41	1	4	0	633	664	2	0	11	326	315	3	3	6	136	141
0	1	6	397	398	1	1	4	324	306	1	4	1	23	23	2	2	0	998	1046	3	4	0	49	50
0	1	7	37	39	1	1	6	245	256	1	4	2	33	30	2	2	2	54	51	3	4	1	80	77
0	1	8	119	126	1	1	8	477	475	1	4	3	22	23	2	2	4	439	437	3	4	2	216	215
0	1	9	202	203	1	1	10	61	49	1	4	4	232	228	2	2	6	175	182	4	0	0	72	86
0	1	10	73	87	1	2	0	49	48	1	4	5	20	18	2	2	8	515	505	4	0	1	165	166
0	1	11	292	286	1	2	1	129	134	1	4	6	152	158	2	3	1	77	75	4	0	2	461	478
0	3	0	832	902	1	2	2	411	408	1	4	7	27	18	2	3	2	345	356	4	0	3	413	425
0	3	1	43	46	1	2	3	488	491	1	4	8	332	332	2	3	3	314	322	4	0	4	211	211
0	3	2	42	39	1	2	4	232	227	1	5	0	35	41	2	3	4	134	127	4	0	5	287	296
0	3	3	33	43	1	2	5	316	320	1	5	1	91	87	2	3	5	215	212	4	0	6	366	368
0	3	4	266	269	1	2	6	326	314	1	5	2	262	260	2	3	6	284	278	4	0	7	83	81
0	3	5	34	31	1	2	7	56	53	1	5	3	279	273	2	3	7	27	26	4	0	8	42	44
0	3	6	191	211	1	2	8	88	85	1	5	4	130	132	2	3	8	93	92	4	0	9	193	188
0	3	7	38	28	1	2	9	193	193	1	5	5	190	190	2	4	0	73	72	6	0	0	569	562
0	3	8	412	412	1	2	10	59	62	2	0	0	116	119	2	4	1	116	114	6	0	2	50	50

$BaMO_3$ analogs these distances are 2.61 Å in $BaCrO_3$, 2.63 Å in $BaMnO_3$, and 2.63 Å in $BaRhO_3$. These short distances result from some *d* orbital overlap between neighboring metal atoms. The Cr–Cr distance observed in other $BaCrO_3$ polytypes varies slightly (average distances are given): 4H (2.61 Å), 6H (2.65 Å), 14H (2.64 Å), and 27R (2.63 Å). The observed metal-to-metal distance in the 4H polytype of $BaCrO_3$ was found to be the shortest and this particular polytype possesses the largest amount of hexagonal packing character. A strong correlation between these two factors was developed from these structural investigations.

All the other features of the structure for the four-layer polytype of $BaCrO_3$ are consistent with the model. The average Cr–O bond distance of 1.94 Å is in agreement with the predicted (*15*) value of 1.95 Å. The twelve-coordinated sites for each Ba atom are well behaved and no unusual features were encountered in the structural determination.

Acknowledgments

The author wishes to acknowledge the financial support from the University of Connecticut Research Foundation and the assistance of Dr. J. B. Anderson. Computations were carried out at the University of Connecticut Computer Center.

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