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THE FORMATION OF HEXAGONAL $BaCrO_{2.90}$ WITH A 5-LAYER STACKING SEQUENCE

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The compound $BaCrO_{2.90}$ was synthesized with a 5-layer hexagonal perovskite-like structure by firing in argon. The lattice parameters were a= 5.732 Å and c= 11.920 Å. The atomic coordinates of each atom in $BaCrO_{2.90}$ were determined by means of trial and error method. This compound was found to be of the $Ba_5Ta_4O_{15}$ type.

It is well known that mixed oxides of the $BaB^{4+}O_3$ type, where B is a first-row transition metal, exist in the hexagonal form with several different structures. $BaNiO_3$ has a 2-layer hexagonal structure[1] and $BaMnO_3$ has 2-, 4-, and 9-layer hexagonal structures.[2,3] $BaCrO_3$ obtained by high pressure technique has 4-, 6-, 9-, 12-, 14-, and 27-layer modifications.[4] These hexagonal layered structures are closely related to the cubic perovskite structure, and have stacking sequences of BaO_3 layers having complete hexagonal close-packing or both hexagonal and cubic close-packing.[5] The smaller cation B seems to play an important role in the formation of hexagonal layered structures. In the previous study,[6] the compounds Ba_2CrNbO_6 and Ba_2CrTaO_6 have been prepared with the perovskite-like structure with two polytypes (6-, and 8-layer) and were found to transform to the cubic perovskite structure at high pressure. As a result of further examination of the barium-chromium oxide system, a new hexagonal phase of approximate composition $BaCrO_{2.90}$ was obtained by firing in argon. The present paper describes the preparation and crystallographic feature of $BaCrO_{2.90}$.

This hexagonal phase was prepared by firing a powdered mixture of $BaCO_3$ and Cr_2O_3 (2:1) at 1300°C in argon. The color of the product was dark brown. The X-ray diffraction powder pattern could be completely indexed on the basis of a hexagonal unit cell with the dimensions a= 5.732 Å, c= 11.920 Å as shown in Table 1. This powder pattern differs from any of a variety of $BaCrO_3$ polytypes reported, but is well similar to that of $Ba_5Ta_4O_{15}$.[7,8] This new compound also seems to have a 5-layer close-packing of oxygen and barium ions. The chemical formula of new hexagonal compound, however, corresponds to that of oxygen-deficient perovskite and does not to that of $Ba_5Ta_4O_{15}$. When two mixtures of $BaCO_3$ and Cr_2O_3 with mole ratios of 5:2 and 3:2 respectively were fired, the reacted products gave the same powder pattern as new hexagonal phase previously mentioned, except the low values of peak intensities and any other phases were not observed. The best preparation

Table 1 Observed and Calculated Interplanar Spacings and Intensities for the Compound $BaCrO_{2.90}$.

H K L	d(obsd.)	d(calcd.)	I(obsd.)	I(calcd.)
1 0 1	4.593	4.586	5.9	6.0
1 0 2	3.820	3.817	16.7	13.7
1 0 3	3.107	3.104	89.2	89.2
0 0 4	2.987	2.982	4.3	3.3
1 1 0	2.871	2.868	100.0	100.0
1 0 4	2.558	2.557	14.0	6.1
2 0 0	2.484	2.484	2.2	0.9
2 0 1	2.432	2.431	3.8	5.5
0 0 5	2.386	2.386	8.6	4.1
2 0 2	2.294	2.293	14.0	14.2
1 0 5	2.152	2.151	6.5	6.6
2 0 3	2.108	2.107	45.7	41.0
1 1 4	2.068	2.067	12.9	12.6
2 0 4	1.9092	1.9086	5.4	6.1
1 0 6	1.8456	1.8459	17.7	17.7
1 1 5	1.8348	1.8343	4.3	4.0
2 1 2	1.7910	1.7910	2.2	6.2
2 0 5	1.7214	1.7207	5.9	3.3
2 1 3	1.6981	1.6979	27.4	27.3
3 0 0	1.6562	1.6560	16.1	18.8
1 1 6	1.6343	1.6340	2.2	1.0
2 1 4	1.5889	1.5890	4.8	1.8
2 0 6	1.5521	1.5522	12.4	12.4
2 1 5	1.4756	1.4755	4.3	4.6
1 1 7	1.4648	1.4651	3.8	1.5
2 2 0	1.4343	1.4341	17.2	16.3
1 0 8	1.4281	1.4282	5.4	5.0
2 1 6	1.3650	1.3651	14.5	16.3
3 1 3	1.3017	1.3019	11.8	13.7

Hexagonal; a= 5.732 Å, c= 11.920 Å, V= 339.16 $Å^3$

of this new compound resulted from the mixture of $BaCO_3$ and Cr_2O_3 with the mole ratio of 2:1. Then no reacted products were observed when fired in hydrogen.

A thermal analysis was carried out in order to determine the chemical formula of this hexagonal compound. The result is shown in Fig. 1. The DTA curve showed an exothermic peak at 645°C at a heating rate of 10°C/min. The weight gain of 7.44% was observed in the TG curve, corresponding to this exothermic reaction. The X-ray diffraction analysis showed the formation of barium chromate and it supported that the oxidation of Cr ion in the sample took place during the heating in air. From this result, new hexagonal compound is estimated to have the chemical composition of $BaCrO_{2.90}$. The density of sample measured with a pycnometer was 5.74 g/cm^3, which corresponds to 5 formula weights of $BaCrO_{2.90}$ per unit cell (theoretical density, 5.77 g/cm^3). The Cr ion in this compound is close to tetravalent state although the solid-state reaction was carried out in argon. The highly oxidizing states of transition metals have often been found in alkali and alkaline-earth oxides.[9,10,11] These phenomena are characteristic in the compounds which contain the ions with ability to form peroxide, i.e. Na, K, Sr and Ba. Hence, it is considered that the Ba ion plays an important role to stabilize a high oxidation state of Cr ion.

The cell dimension of $BaCrO_{2.90}$ suggests that this compound has a $Ba_5Ta_4O_{15}$ like structure, since $Ba_5Ta_4O_{15}$ has a hexagonal unit cell with a= 5.776 Å, c= 11.82

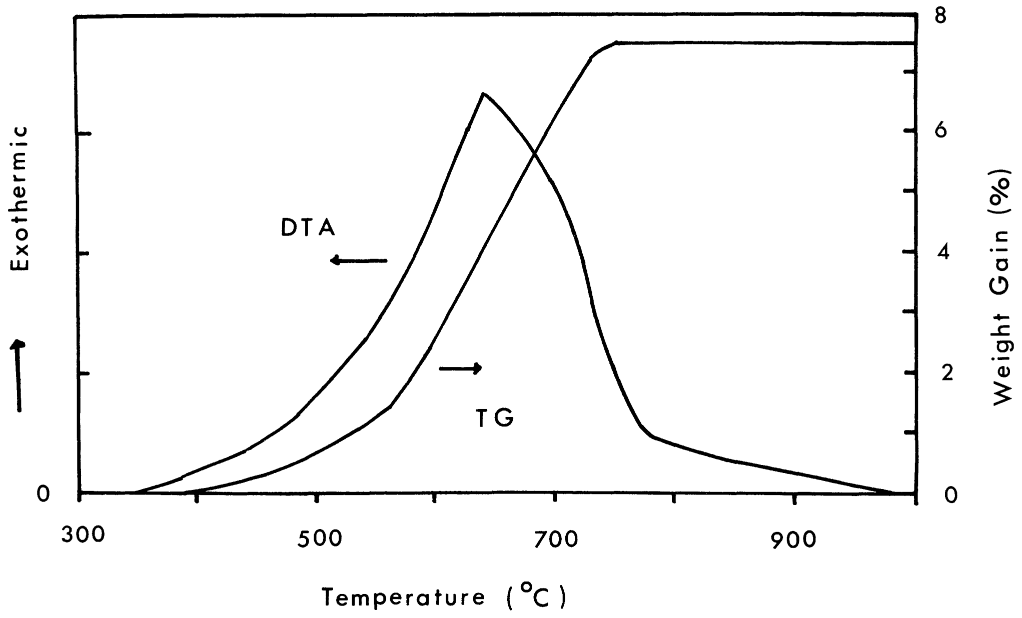

Fig. 1 DTA and TG curves of new hexagonal compound.

Å.8) The structure of this type is not a common one among oxides. The only other oxides reported to have this structure are $Ba_5Nb_4O_{15}$, $Sr_5Ta_4O_{15}$ and these oxygen deficient compounds. Assuming that $BaCrO_{2.90}$ is a compound of the $Ba_5Ta_4O_{15}$ type, the following questions are raised.

a) the chemical formula of both compounds is not identical.

b) the lattice parameter of c axis of $BaCrO_{2.90}$ is larger than that of $Ba_5Ta_4O_{15}$ although the ionic size of Cr ion is smaller than that of Ta ion.

$Ba_5Ta_4O_{15}$ belongs to space group D_{3d}^3-$P\bar{3}m1$ and has a vacant face-sharing octahedron, the central position of which is (0,0,1/2). Consequently the questions might be answered by the assumption that a fifth Cr ion lies at the position of (0,0,1/2) as shown in Fig. 2. In order to confirm the proposed structure, the reflection intensities for $BaCrO_{2.90}$ were calculated with a Facom 270-30 computer on the basis of the following atomic coordinates and were compared with those observed. In this case, the oxygen deficiency in the unit cell of $BaCrO_{2.90}$ was assumed to derive from the O(3) group as in the example of $Ba_5Ta_4O_{13}$.7) The trial and error method on about 100,000 combinations was carried out for eight atomic parameters. The atomic coordinates of each atom in $BaCrO_{2.90}$ were determined as follows:

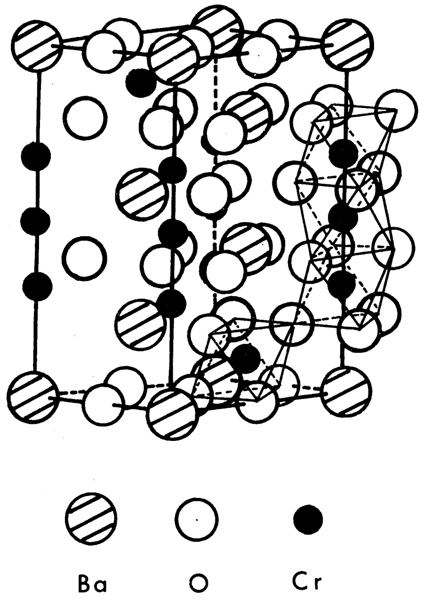

Fig. 2 Crystal structure of $BaCrO_{2.90}$.

Ba(1)	(a)	0,0,0	
Ba(2)	(d)	1/3,2/3,z; 2/3,1/3,$\bar{z}$	z=0.773
Ba(3)	(d)		z=0.428
Cr(1)	(d)		z=0.109
Cr(2)	(c)	0,0,z; 0,0,$\bar{z}$	z=0.280
Cr(3)	(b)	0,0,1/2	
O(1)	(e)	1/2,0,0; 0,1/2,0; 1/2,1/2,0	
O(2)	(i)	x,$\bar{x}$,z; x,2x,z; 2$\bar{x}$,$\bar{x}$,z	x=0.257
		$\bar{x}$,x,$\bar{z}$; $\bar{x}$,2$\bar{x}$,$\bar{z}$; 2x,x,$\bar{z}$	z=0.153
O(3)	(i)		x=0.154
			z=0.606

Good agreement between observed and calculated intensities was obtained as shown in the right side of Table 1. The reliability factor for observed intensities of the twenty-nine peaks was 0.0982. Consequently it seems reasonable to conclude that $BaCrO_{2.90}$ has a $Ba_5Ta_4O_{15}$ type structure.

As shown in Fig. 2, five chromium ions are in octahedral site with six oxygens. Among them three fifth of Cr ions form triple octahedra sharing common faces, and two fifth of Cr ions share common octahedral corners as in the perovskite structure. The cross section of the hexagonal (110) plane is shown in Fig. 3(a). It is found that $BaCrO_{2.90}$ has a 5-layer hexagonal structure with a stacking sequence a-b-c-b-c of BaO_3 layers. All of the cations lie in the (110) plane. The chromium ions sharing octahedral face are in contact with Cr-Cr=2.62 Å. In the case of $Ba_5Ta_4O_{15}$, the tantalum ion vacancies are where the hexagonal stacking occurs. This might be due to the high repulsive force between the highly charged Ta^{5+} ions. In the case of $BaCrO_{2.90}$, the vacancies are occupied with the fifth Cr ions. A structural difference between $BaCrO_{2.90}$ and $Ba_5Ta_4O_{15}$ is recognized in this respect. This is because the ionic size and charge of chromium ion are a little smaller than those of tantalum ion. It supports the result that the perovskite type compounds including Cr ion tend to have hexagonal layered structures with the octahedra sharing faces. It seems reasonable that the lattice parameter of c axis of $BaCrO_{2.90}$ is a little larger than that of $Ba_5Ta_4O_{15}$, concluding that the hexagonal cell extends along c direction

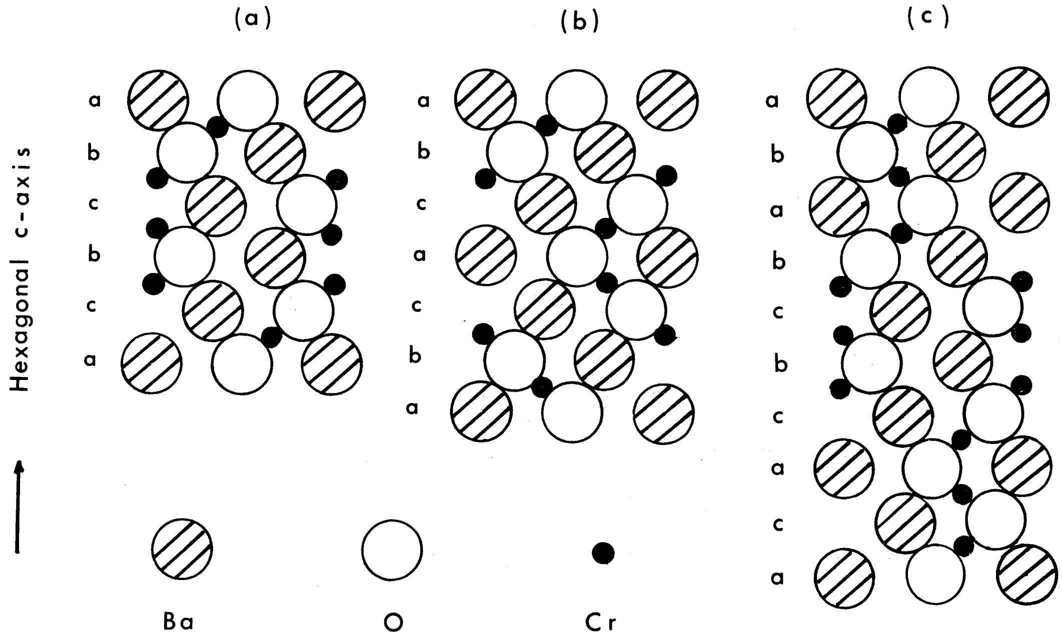

Fig. 3 The repetition of barium-oxygen layers in three hexagonal layered structures; (a) 5-layer structure, (b) 6-layer structure, and (c) 9-layer structure. All ions lie in the (110) plane.

for the Coulomb repulsive force between Cr ions in the face-shared octahedra.

In Fig. 3(b) and 3(c) 6-layer and 9-layer hexagonal structures, which are well encountered among the hexagonal perovskite-like compounds, are given for comparison. These structures are analogous to the 5-layer hexagonal structure. In particular, the stacking sequence between third and eighth layers in the 9-layer structure is the same as that of the 5-layer structure since the 9-layer structure has a stacking sequence a-b-a-b-c-b-c-a-c. A compound reported to have the 5-layer structure, however, has not been found in the hexagonal perovskite-like compounds. It is a rare case that the compound $BaCrO_{2.90}$ with the chemical composition of perovskite type has a $Ba_5Ta_4O_{15}$ type structure.

In the case of the barium-chromium oxide, the volume per molecule is 67.83 Å^3 for the 5-layer structure and is 62.56 and 69.75 Å^3, respectively, for 6-layer and 9-layer structures obtained by high pressure technique.$^{4)}$ The volume per molecule of the 5-layer structure is larger than that of the 6-layer structure and smaller than that of the 9-layer structure. This is reasonable, comparing the average number of Cr ions including in an octahedron chain. Because the strong repulsive force is acting between Cr ions in the face-shared octahedra in these unit cells.

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References

1) J.J. Lander, Acta Cryst., 4, 148 (1951).
2) A. Hardy, Acta Cryst., 15, 179 (1962).
3) Y. Syono and S. Akimoto, J. Phys. Soc. Japan, 26, 993 (1969).
4) B.L. Chamberland, Inorg. Chem., 8, 286 (1969).
5) L. Katz and R. Ward, Inorg. Chem., 3, 205 (1964).
6) Y. Torii and H. Matsumoto, J. Ceram. Soc. Japan, in press.
7) F. Galasso and L. Katz, Acta Cryst., 14, 647 (1961).
8) J. Shannon and L. Katz, Acta Cryst., B26, 102 (1970).
9) R. Scholder and G. Sperka, Z. Anorg. Allgem. Chem., 285, 49 (1956).
10) B.E. Gushee, L. Katz, and R. Ward, J. Am. Chem. Soc., 79, 5601 (1957).
11) C.C. Addison and M.G. Barker, J. Chem. Soc., 5534 (1965).

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