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CATION ORDERING IN 8-LAYER $Ba_2(CrTa)O_6$

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The structure of the title compound has been determined from powder X-ray diffraction data and found to be much the same as in 8-layer $Ba_4(LiNb_3)O_{12}$. Only the Cr^{3+} ions occupy the face-shared octahedra, while the Ta^{5+} ions occupy the corner-shared octahedra.

In a previous work$^{1)}$, it was shown that the compounds $Ba_2(CrTa)O_6$ and $Ba_2(CrNb)O_6$ crystallize in hexagonal 6- and 8-layer forms, and are converted to a cubic perovskite phase at high pressure. The 8-layer stacking polytype is uncommon among hexagonal layer compounds. Cation ordering in these 8-layer compounds has not been determined, although six possible configurations are listed for a 8-layer repeat sequence.$^{2)}$ On the other hand, the compounds $Ba_2(FeTa)O_6$ and $Ba_2(MnTa)O_6$ are known to adopt the cubic perovskite structure.$^{3)}$ Consequently it is thought that the Cr^{3+} ion plays an important role in the formation of 8-layer structure. The unique stacking sequence may be related with cation ordering through such effects as cation-cation repulsion and metal-metal bonding. The purpose of the present study was to examine the cation distribution in 8-layer $Ba_2(CrTa)O_6$ and to interpret the origin of the superstructure. The tantalum compound was chosen because the large difference between Cr and Ta scattering powers makes X-ray diffraction experiments sensitive to the B cation distribution.

The title compound was newly prepared from reagents of $BaCO_3$, Cr_2O_3 and Ta_2O_5. The components were mixed in the stoichiometric molar ratio and then fired twice for 5 hrs at 1300°C in unpurified nitrogen. The oxygen partial pressure in this atmosphere was determined to be about 10^{-14} atm using a stabilized zirconia cell. The resulting product was dark green in color, and the oxidation of Cr^{3+} ion in the sample did not seem to occur during firings. The X-ray diffraction patterns were taken with a Philips diffractometer using Ni-filtered CuKα radiation and a proportional counter. The reflections were measured at a scanning speed of $(1/4)°\ 2\theta/\text{min}$ and the Bragg angles were corrected with a silicon standard. The lattice constants were refined by a least-squares computer program. The observed intensities were measured by cutting out and weighing tracings of the peaks. The powder-pattern intensity was calculated by the method previously reported.$^{4)}$

Analysis of the X-ray diffraction of the product showed that $Ba_2(CrTa)O_6$ crystallized well and that it did not contain any additional compound. All the reflections could be satisfactorily indexed on the basis of a hexagonal cell with the dimensions a=5.7369(2) and c=18.782(1) Å, as given in Table 1. The cell dimensions are consistent with a 8-layer repeat sequence of close-packed BaO_3 layers. The pycnometrically measured density of 7.62 g/cm^3 was in agreement with the calculated value of 7.49 g/cm^3 for four formula units of $Ba_2(CrTa)O_6$ per cell. From these results the product is regarded as a single phase of 8-layer $Ba_2(CrTa)O_6$.

The reflections show no systematic absences for general reflections of HKL type and the hexagonal cell is therefore primitive. However, the reflections of HHL type are systematically absent when L=2n+1. Additionally, structural absences H-K=3n for L=2n+1 are observed. So the possible space group is $P6_3mc$ (No. 186), $P\bar{6}2c$ (No. 188), or $P6_3/mmc$ (No. 194). On the basis of this absence rule, two possible 8-layer configurations can be selected from "International Tables"[2]: 25% and 75% cubic stacking sequences with $P6_3/mmc$ symmetry. The former consists of strings of four face-shared octahedra linked by corner sharing, and has been found only in 8-layer $BaMnO_{3-x}$ with oxygen deficiencies[5]. The latter consists of two face-shared octa-

Table 1. X-ray diffraction data for 8-layer $Ba_2(CrTa)O_6$

HKL[a]	d_{obs}	d_{cal}[b]	I_{obs}	I_{cal}[c]	HKL[a]	d_{obs}	d_{cal}[b]	I_{obs}	I_{cal}[c]
002	9.40	9.39	5.1	19.0	300	1.656	1.656	19.1	17.8
100	4.97	4.97	3.7	7.4	1011	1.614	1.615	11.4	21.4
101	4.81	4.80	2.4	5.7	216	1.610	1.610		
103	3.89	3.89	3.5	2.2	209	1.598	1.598	2.0	1.3
104	3.41	3.41	10.5	10.1	1110	1.571	1.572	4.8	1.4
105	2.996	2.997	79.1	73.8	2010	1.498	1.498	7.7	6.7
110	2.868	2.868	100.0	100.0	1012		1.493		
112	2.744	2.743	2.0	7.3	220	1.434	1.434	14.5	15.9
106	2.648	2.649	18.1	26.4	2011	1.407	1.407	3.6	9.6
200	2.484	2.484	1.4	2.2	219	1.395	1.396	2.2	1.2
202	2.401	2.401	1.6	0.4	311	1.373	1.374	1.0	0.3
008	2.347	2.348	1.4	1.1	1112		1.374		
203	2.308	2.309	0.8	0.5	2110	1.328	1.328	8.6	6.0
204	2.196	2.196	6.8	7.5	2012		1.325		
205	2.073	2.072	37.9	40.3	1014	1.294	1.296	10.4	9.6
206	1.946	1.946	11.2	16.1	315		1.294		
109	1.924	1.925	3.2	1.9	2111	1.263	1.264	4.3	12.8
0010	1.878	1.879	1.9	2.7	316	1.261	1.261		
210		1.878			3010	1.242	1.242	1.3	0.9
211		1.868			400		1.240		
1010	1.757	1.757	9.1	7.2	401		1.239		
214	1.744	1.744	2.0	2.6	1114	1.215	1.216	2.9	0.7
215	1.680	1.680	24.3	25.1	1015		1.215		

a) HKL with four numbers have L index greater than 9.

b) Calculated using a hexagonal cell with a=5.7369 Å, c=18.782 Å.

c) Calculated on the basis of an ideal 8-layer sequence shown in Fig. 1.

hedra linked by corners to corner-shared octahedra, and has been observed only in $Ba_4(LiM^{5+}{}_3)O_{12}$ with M=Nb and Ta.[6)] In these two compounds the Li^{1+} and M^{5+} ions are ordered in the face-shared octahedra and the symmetry is therefore reduced to $P6_3mc$. If 8-layer $Ba_2(CrTa)O_6$ has a 25% cubic stacking, its X-ray density must be smaller than that of a 6-layer phase with a 33.3% or 66.7% cubic stacking. However, the X-ray density of 8-layer $Ba_2(CrTa)O_6$ (7.47 g/cm³) was larger than that of the 6-layer form (7.39 g/cm³).[1)] It is reasonable therefore to conclude that 8-layer $Ba_2(CrTa)O_6$ has a 75% cubic stacking with $P6_3/mmc$ symmetry. The most likely arrangement of B ions in the octahedral sites is shown in Fig. 1, in which only the Cr^{3+} ions occupy the face-shared octahedra. The atomic possitions based on an ideal 8-layer stacking sequence with $P6_3/mmc$ symmetry are as follows: 2 Ba at (a), 2 Ba at (d), 4 Ba at (f), z=1/8; 4 Cr at (e), z=3/16; 4 Ta at (f), z=9/16; 6 O at (g), 6 O at (h), x=5/6, 12 O at (k), x=5/6 and z=1/8.

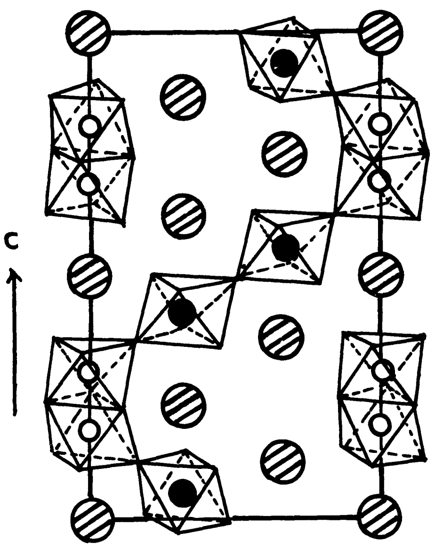

Fig. 1. 8-layer structure of $Ba_2(CrTa)O_6$. Striped circles are Ba; white circles are Cr; black circles are Ta. Cations shown lie in the (110) plane.

In order to confirm the proposed superstructure, the reflection intensities for 8-layer $Ba_2(CrTa)O_6$ were calculated using the ideal atomic positions and an overall temperature factor B=1.0 Å² (a typical value for inorganic compounds), and are compared with the observed intensities in Table 1. The calculated and observed intensities are qualitatively in good agreement. The reliability factor R for the intensities of 37 peaks was 23.2%.

Next, three other possibilities for the B cation distribution were examined. The second possibility is the case in which the Ta^{5+} ions instead of Cr^{3+} ions occupy the face-shared octahedra. The corresponding R value was 57.2%. The large discrepancy indicates that the pairing of highly charged cations like Ta^{5+} ions in the face-shared octahedra is difficult to achieve, as seen in the examples of 5-layer $Ba_5Ta_4O_{15}$[7)] and 12-layer $Sr_2La_2(MgW_2)O_{12}$[8)] in which one of the three face-shared octahedra is vacant. The next type of ordering would place the Cr^{3+} and Ta^{5+} ions alternately in the face-shared and corner-shared octahedra. The symmetry is reduced to $P6_3mc$ as in $Ba_4(LiNb_3)O_{12}$[6)]. However, the R value was 36.1%. Finally, we could have a disordered distribution of the Cr^{3+} and Ta^{5+} ions in all the octahedral sites. In this case the R value was 32.9%. Thus these three possibilities are unlikely compared with the proposed superstructure shown Fig. 1.

In conclusion, 8-layer $Ba_2(CrTa)O_6$ has a 75% cubic stacking with $P6_3/mmc$ symmetry and only the Cr^{3+} ions occupy the sites of face-shared octahedra. Cation ordering in this compound is considered to arise from the nature of Cr^{3+} ion. From electrostatic considerations, a Cr^{3+}-Cr^{3+} pair is favorable for the occupation of the face-shared octahedra as compared with a Cr^{3+}-Ta^{5+} or Ta^{5+}-Ta^{5+} pair. For Cr^{3+} ions without e_g electrons, the electron clouds of oxygens in the octahedra would be strongly attracted to the cations since the repulsion between the cationic e_g and the oxygen P_σ electrons does not exist. In consequence, the covalent character of Cr-O bond and the oxygen polarization increase, and the effective charges of cations decrease. In the case when cations occupy in pairs the face-shared octahedral sites, the repulsion between Cr^{3+} ions would be smaller than that between transition metal cations with e_g electrons. For this reason, a Cr^{3+}-Cr^{3+} pairing in the face-shared octahedra occurs in 8-layer $Ba_2(CrTa)O_6$ in contrast with the cubic perovskites $Ba_2(FeTa)O_6$ and $Ba_2(MnTa)O_6$ 3). The unique 8-layer stacking sequence in $Ba_2(CrTa)O_6$ is stabilized by cation ordering of the Cr^{3+} and Ta^{5+} ions.

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