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The Preparation and Structure of Cadmium Rhenium Oxide, $Cd_2Re_2O_7$

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A cadmium rhenium oxide has been prepared with the formula $Cd_2Re_2O_7$. Its structure is of the pyrochlore type. For the face-centered cubic unit cell, $a = 10.219$ Å. The room temperature resistivity is about 2×10^{-3} ohm cm.

Introduction

A new cadmium rhenium oxide was found to be the primary constituent of the products of an experiment originally devised to prepare the cadmium analog of the magnetic compound Ca_2ReFeO_6. The product was first thought to be a single magnetic phase,[1] but further investigation by microscope and by powder X-ray diffraction showed the presence of several phases, one of which was purple and highly crystalline. The powder diffraction pattern of this phase suggested a structure of the pyrochlore type.

Experimental

A direct synthesis of the phase was carried out by heating in an evacuated silica ampoule at 1000° the mixture of finely ground powders indicated by the equation

$$^5/_3ReO_3 + {}^1/_3Re + 2CdO \longrightarrow Cd_2Re_2O_7$$

The single phase appeared as small octahedral crystals adhering to the walls of the ampoule.

A powder X-ray diffraction pattern was taken and indexed on the basis of a face-centered cubic unit cell with $a = 10.219$ Å. The density determined pycnometrically was 8.82 ± 0.03 g./cc., which compares well with the theoretical density of 8.83 g./cc. for $Cd_2Re_2O_7$.

The fact that crystals adhered to the walls of the ampoule suggested that the formation of the phase proceeded by a vapor transport mechanism. A likely process would be reaction between the volatile compound Re_2O_7 and Cd vapor; the Re_2O_7 could be formed from the reduction of CdO to Cd and the oxidation of ReO_3 to Re_2O_7.

A vapor phase synthesis of $Cd_2Re_2O_7$ was carried out by the following procedure: Re_2O_7 was prepared in a silica tube.[2] A stoichiometric quantity of cadmium metal was placed in the tube about 3 cm. from the Re_2O_7 deposit, care being taken to exclude moisture. The tube was evacuated, sealed, and heated at 800° for 12 hr. Crystals of $Cd_2Re_2O_7$ measuring about 1 to 4 mm. on an edge were deposited on the cooler portions of the tube.

Four-probe resistivity measurements were made on a test piece of several intergrown crystals. Electrical connections to it were made by soldering with indium. A graph of resistivity *vs.* temperature is shown in Figure 1.

Structure Analysis

X-Ray data were collected from a single crystal with dimensions ranging between 0.1 and 0.18 mm. using the precession camera and Mo Kα radiation. Since the powder data had strongly suggested the pyrochlore structure, the crystal was examined as a possible example of this structure type.

The pyrochlore structure has been studied extensively. It was first determined by Bystroem[3] as belonging to the cubic $E8_1$ structure type. Pyrochlore itself is $CaNaNb_2O_6F$ (the natural mineral contains additional elements); there are eight formula units in the unit cell. The formula suggests what is in fact the case—with proper charge balance, variability in anion content is possible. Ferroelectric behavior has been found in a compound of the pyrochlore type, $Cd_2Nb_2O_7$[4]; dielectric, optical, and X-ray studies have been carried out on single crystals of $Cd_2Nb_2O_7$.[5]

The space group for pyrochlore is Fd3m, and, since it was compatible with the X-ray data collected, that was the space group assumed. Intensities were measured visually. After averaging the intensities of symmetry related reflections 66 independent values were obtained. Lorentz and polarization corrections were made and absorption was corrected for by assuming the crystal to be a sphere of equal volume. Structure factors were calculated using the positions listed in Table I.

TABLE I

ATOMIC POSITIONS FOR $Cd_2Re_2O_7$

Space Group 227, Fd3m

$(0, 0, 0;\ 0, {}^1/_2, {}^1/_2;\ {}^1/_2, 0, {}^1/_2;\ {}^1/_2, {}^1/_2, 0)+$

16 Re	c	$0, 0, 0;\ 0, {}^1/_4, {}^1/_4;\ {}^1/_4, 0, {}^1/_4;\ {}^1/_4, {}^1/_4, 0$
16 Cd	d	${}^1/_2, {}^1/_2, {}^1/_2;\ {}^1/_2, {}^1/_4, {}^1/_4;\ {}^1/_4, {}^1/_2, {}^1/_4;\ {}^1/_4, {}^1/_4, {}^1/_2$
48 O(1)	f	$x, {}^1/_8, {}^1/_8;\ \bar{x}, {}^7/_8, {}^7/_8;\ {}^1/_4 - x, {}^1/_8, {}^1/_8;\ {}^3/_4 + x, {}^7/_8, {}^7/_8;\ {}^1/_8, x, {}^1/_8;\ {}^7/_8, \bar{x}, {}^7/_8;\ {}^1/_8, {}^1/_4 - x, {}^1/_8;\ {}^7/_8, {}^3/_4 + x, {}^7/_8;\ {}^1/_8, {}^1/_8, x;\ {}^7/_8, {}^7/_8, \bar{x};\ {}^1/_8, {}^1/_8, {}^1/_4 - x;\ {}^7/_8, {}^7/_8, {}^3/_4 + x$
8 O(2)	b	${}^3/_8, {}^3/_8, {}^3/_8;\ {}^5/_8, {}^5/_8, {}^5/_8$

$x = 0.3089 \pm 0.0073$

Atomic scattering factors were corrected for the real part of anomalous dispersion,[6] and the single position parameter and isotropic temperature factors were refined using the Busing, Martin, and Levy least-squares program. The final R factor was 7.0% with the oxygen position parameter 0.3089 ± 0.0073. Temperature factors for the cations were small and in the final calculation were simply taken as zero. For the 48-fold oxygen, the temperature factor was 3 ± 1; for the 8-fold oxygen the temperature factor was 3 ± 4. Observed and calculated structure factors are listed in Table II.

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(2) A. D. Melaven, *et al.*, *Inorg. Syn.*, **3**, 88 (1950).

(3) A. Bystroem, *Arkiv. Kem. Mineral Geol.*, **18A**, No. 21 (1944).

(4) W. R. Cook, Jr., and H. Jaffe, *Phys. Rev.*, **88**, 1426 (1952).

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(6) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, pp. 213–216.

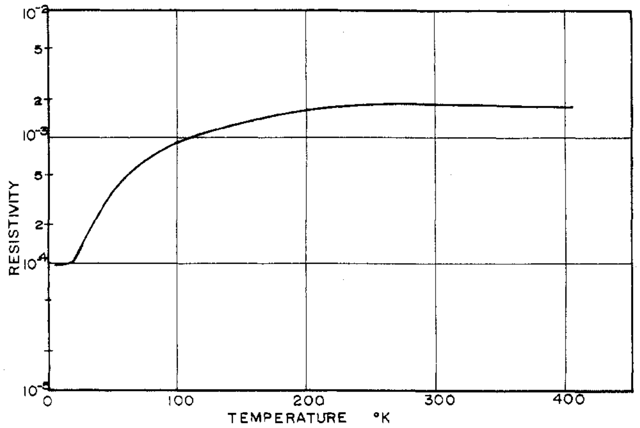

Figure 1.—Plot of resistivity (ohm cm.) *vs.* absolute temperature for $Cd_2Re_2O_7$. This information was kindly provided by Dr. J. L. Gillson.

TABLE II

H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL
0	0	12	147	134	2	2	10	162	161	4	4	12	147	134
0	4	4	211	230	2	2	14	118	128	4	8	8	170	148
0	4	12	146	142	2	6	6	174	177	4	8	12	122	123
0	8	12	139	128	2	6	10	156	147	5	5	5	24	21
1	1	7	25	30	2	6	14	116	121	5	5	7	30	27
1	1	11	22	22	3	3	5	35	38	5	5	9	26	25
1	1	13	22	23	3	3	7	19	19	5	5	11	20	20
1	3	3	13	15	3	3	9	19	19	5	7	7	28	24
1	3	5	26	30	3	3	11	23	25	5	7	9	23	23
1	3	7	32	34	3	3	13	30	24	5	7	11	25	22
1	3	9	27	30	3	5	5	25	28	5	7	13	20	19
1	3	11	23	24	3	5	7	24	25	5	9	9	24	22
1	5	5	27	37	3	5	9	23	22	5	9	11	25	21
1	5	7	25	26	3	5	11	23	22	6	6	6	173	161
1	5	9	25	24	3	5	13	24	22	6	6	10	143	136
1	5	11	24	25	3	7	7	30	28	7	7	9	19	21
1	7	7	20	24	3	7	9	29	27	7	7	11	25	21
1	7	9	22	22	3	7	11	24	22	7	9	9	16	20
1	7	11	26	22	3	9	9	29	25	7	9	11	24	20
1	9	9	22	21	3	9	11	21	20	8	8	8	122	129
1	9	11	24	21	4	4	4	191	199	8	8	12	111	115
2	2	6	182	161	4	4	8	180	165	9	9	11	20	19

Bond distances in $Cd_2Re_2O_7$ are as follows: Re–O(1) = 1.90 ± 0.02 Å., Cd–O(1) = 2.66 ± 0.05 Å., Cd–O(2) = 2.21 Å.

The condition for regular octahedral environment around Re is that the x parameter equal 0.312. The value for x found in this study is 0.309 ± 0.007. There is thus no definite evidence for distortion of the ReO_6 octahedra.

Discussion

A cadmium rhenium oxide has been prepared which has been shown to have the pyrochlore structure. In this structure, one-seventh of the anions are not needed for a stable framework, so that the formula $Cd_2Re_2O_6$ is conceivable. On the other hand, vacancies exist which could accommodate additional oxygens. Were these sites occupied, the formula would be $Cd_2Re_2O_8$. The structure would then be similar to fluorite with both Cd and Re having oxygen coordination numbers of eight. Chemical analysis of the compound was carried out.[7] *Anal.* Calcd. for $Cd_2Re_2O_7$: Re, 52.51; Cd, 31.70. Calcd. for $Cd_2Re_2O_8$: Re, 51.35; Cd, 31.00. Found: Re, 51.49; Cd, 31.97. The results clearly establish the Re:Cd ratio as essentially 1:1, but if we take this ratio to be 1, they do not distinguish between $Cd_2Re_2O_7$ and $Cd_2Re_2O_8$. On this point, however, the structure refinement did provide strong evidence. The least-squares refinement proceeded normally for $Cd_2Re_2O_7$. When a refinement was attempted for $Cd_2Re_2O_8$, the temperature factor for the eighth oxygen grew very large (reaching almost 200 and forcing the program to stop). This extra oxygen atom was thus being "smeared out" in the calculation by tremendous thermal vibration to indicate that this atom did not belong. Thus, although the chemical analysis was inconclusive in establishing the oxygen content, the starting composition, the density, and the structure refinement establish the formula $Cd_2Re_2O_7$.

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(7) By Ledoux and Company, Teaneck, N. J.