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Crystallographic data for potassium manganate K_2MnO_4. By F. H. HERBSTEIN, *National Physical Research Laboratory, Council for Scientific and Industrial Research, Pretoria, South Africa*

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Crystallographic data for potassium manganate K_2MnO_4 were required in order to check reports that this compound is one of the products of the thermal decomposition of potassium permanganate $KMnO_4$ below 250 °C (early work in this field is summarized by Mellor (1932, p. 307) while some more recent results have been given by Glemser & Butenuth (1953)). K_2MnO_4 was prepared by the method of Scholder & Waterstradt (1954); the crystals obtained were thin purple laths elongated along [001] and showed straight extinction. Single crystals were stable in air for at least some weeks and did not require protection during photography.

Oscillation and Weissenberg photographs (Cu $K\alpha$, Ni filter) showed the crystals to be orthorhombic with the following cell dimensions and systematic absences:

$$a=7\cdot66\pm0\cdot01,\ b=10\cdot33\pm0\cdot01,\ c=5\cdot89\pm0\cdot01\ \text{Å}\ .$$

$h0l$ absent for h odd; $0kl$ absent for $k+l$ odd. The calculated density for four K_2MnO_4 molecules per cell is 2·81 g.cm.$^{-3}$, close to that of $KMnO_4$ (2·70 g.cm.$^{-3}$). The possible space groups are C_{2v}^9–Pna and D_{2h}^{16}–$Pnam$; the latter is preferred because of the isomorphism of K_2MnO_4 and low K_2SO_4.

The axial ratios calculated from the diffraction measurements ($a:b:c=0\cdot7415:1:0\cdot5702$) are in reasonably good agreement with those measured about 1831 by E. Mitscherlich (0·7570:1:0·5638) (see Mellor, 1932, p. 285). Mitscherlich also pointed out that K_2MnO_4 is isomorphous with K_2SO_4, K_2SeO_4 and K_2CrO_4. This is borne out by the present results and the crystallographic data for the last three compounds summarized by Donnay & Nowacki (1954).

Table 1. *Powder pattern of* K_2MnO_4

Index hkl	d_o (Å)	d_c (Å)	Relative observed peak intensity
020	5·17	5·165	19
120	4·29	4·283	36
111	4·26	4·256	15
200	3·83	3·830	39
210	3·59	3·591	9
130	3·15	3·142	5
211	3·08	3·062	100
031	2·978	2·975	37
002	2·940	2·945	16
040	2·596	2·583	21
230 } 022 }	2·570	2·562 2·558	33
310	2·483	2·482	32
320	2·291	2·290	13
311	2·283	2·283	5
212	2·276	2·276	5
141	2·260	2·260	5
132	2·147	2·148	16
321 } 222 }	2·132	2·133 2·125	5
330	2·057	2·050	37
400	1·918	1·915	11
401	1·824	1·821	4
340 } 250 }	1·821	1·819 1·819	5
060 } 213 }	1·729	1·722 1·721	8
160	1·678	1·682	4
430	1·675	1·672	4

Table 2. *Extra lines in* K_2MnO_4 *pattern*

d (Å)	Observed relative intensity
4·88	*w*
4·18	*vw*
3·65	*vvw*
3·57	*vw*
3·25	*w*
2·89	*w*
2·88	*vvw*
2·38	*w*

The powder pattern of K_2MnO_4 was obtained on a Philips high-angle diffractometer, using filtered Cu $K\alpha$ radiation. As powdered K_2MnO_4 decomposes in a few days, measurements were always made on freshly-prepared samples. Light grinding of the crystals produced a very sharp pattern with the $hk0$ intensities intensified because of preferred orientation; this sample was used for spacing measurements (Table 1). Further grinding removed nearly all the orientation but at the cost of broadening the lines; this sample was used for measuring the relative peak intensities given in Table 1. All but a few weak lines (Table 2) could be satisfactorily indexed on the basis of the single-crystal data. The source of the extra lines has not been identified (it is not $KMnO_4$) but they are presumably due to a small amount of decomposition product formed on grinding. No extra spots or lines were seen on the single-crystal photographs. If powdered K_2MnO_4 is left in air for a few days, it does transform into $KMnO_4$, the powder pattern being very broadened but still recognizable. No other crystalline transformation product was observed but this could have been due to the broadening of the $KMnO_4$ pattern.

The powder pattern of the decomposition products from $KMnO_4$ heated to constant weight in air at 220 °C. consists of a broadened K_2MnO_4 pattern and three broad lines at $d=7\cdot08$, 3·55 and 2·45 Å. The latter pattern is similar to that reported for δ-MnO_2 (Cole, Wadsley & Walkley, 1947).

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