

promise that some of these complex perovskite-type compounds will find electronic application in the near future.

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Crystal Data of Mn_5O_8 and $Cd_2Mn_3O_8$

RECENTLY, a new phase of manganese oxide with the ideal composition $MnO_{1.6}$ or Mn_5O_8 has been obtained by several reactions: (a) Oxidation of Mn_3O_4 of suitable particle size (specific surfaces between 10 and ~ 80 m²/g) in nitrogen-oxygen mixtures with oxygen contents of 5-100 per cent at temperatures varying from 250° to 550° C (refs. 1, 2 and 3). (b) Decomposition of β - $MnOOH$ in air at similar temperatures¹. (c) Topotactic decomposition of γ - $MnOOH$ (synthetic and natural manganite) at low oxygen pressures at 400° C (ref. 1).

The compound has a characteristic X-ray powder diagram, showing partially a resemblance to a pattern published earlier by Le Blanc and Wehner⁴ ($MnO_{1.57-1.58}$ obtained by thermal decomposition of $MnCO_3$). Another resemblance exists possibly between the reflexions of Mn_5O_8 and a diagram by Klingsberg and Roy⁵ ($MnO_{1.81}$ in a mixture with β - MnO_2). Analyses of numerous samples of Mn_5O_8 resulted in the limits of composition of: $MnO_{1.58}-MnO_{1.84}$. These specimens were always fine-grained, black powders, showing often broadened X-ray reflexions. For purest samples giving practically sharp powder lines, an ideal Mn:O ratio of 1:1.60 is found. Differential thermal analyses and thermogravimetric analyses in air and oxygen atmosphere have shown that Mn_5O_8 decomposes at 550° C to α - Mn_2O_3 .

The analytical method of de Wolff⁶ enabled us to index completely the Mn_5O_8 X-ray powder diagram, taken on a Nonius-de Wolff Guinier camera with iron $K\alpha$ radiation. Purest potassium chloride was used as an internal standard. The dimensions of the monoclinic unit cell are:

$$\begin{array}{lll} a = 10.34, \text{ \AA} & b = 5.72, \text{ \AA} & c = 4.85, \text{ \AA} \\ \beta = 109^\circ 25' & V = 271.0 \text{ \AA}^3 & D_{\text{obs}} = 4.85 \text{ g cm}^{-3} \\ Z = 2 [Mn_5O_8] & D_{\text{calc}} = 4.93 \text{ g cm}^{-3} & (\text{Pycnometric in decaline at } 20^\circ \text{ C}) \end{array}$$

Space group $C2/m$ or $C2$.

The calculated and measured interplanar spacings are in good agreement (Table 1). Furthermore, the cell dimensions obtained were corroborated by selected area electron diffraction and single-crystal (Weissenberg) X-ray photographs of highly oriented, pseudomorphous Mn_5O_8 obtained from natural manganite needles by reaction c.

Table 1. X-RAY POWDER DIAGRAM OF Mn_5O_8

I/I_0	D_{obs}	D_{calc}	hkl	I/I_0	D_{obs}	D_{calc}	hkl
10	4.876	4.879	200	<1	2.042	2.042	40 $\bar{2}$
5	4.087	4.083	201	2	1.954	1.954	112
<1	3.674	3.676	11 $\bar{1}$	7	1.896	1.896	421
6	3.103	3.104	111	4	1.848	1.848; 1.847	202; 510
4	2.893	2.893	201	1	1.787	1.787	022
3	2.861	2.861	020	<1	1.772	1.773	131
4	2.820	2.828	310	3	1.663	1.662	422
6	2.797	2.794	31 $\bar{1}$	3	1.640	1.639	331
1	2.532	2.531	401	4	1.603	1.600	60 $\bar{2}$
5	2.470	2.469	220	6	1.586	1.586	421
2	2.440	2.440	400	2	1.552	1.553; 1.552	222; 511
8	2.425	2.426	021	2	1.525	1.525	003
2	2.400	2.400	20 $\bar{2}$	3	1.478	1.477	021
7	2.343	2.343	221	2	1.457	1.457	33 $\bar{2}$
4	2.286	2.288	002	1	1.445	1.446	402
<1	2.222	2.223	11 $\bar{2}$	5	1.429	1.431; 1.430	040; 711
1	2.102	2.100	81 $\bar{2}$	7	1.407	1.408; 1.406	223; 132

The tetragonal and orthorhombic unit cells proposed by Le Blanc and Wehner⁴ and Klingsberg and Roy⁵ respectively could not be confirmed.

Three main compositions of Mn_5O_8 are possible: $Mn_4^{III}Mn^{IV}O_8$, $Mn_3^{II}Mn_2^{IV}O_8$ and $Mn^{II}Mn_3^{III}Mn_2^{IV}O_8$. Recently, Toussaint⁷ has found a mixed oxide $Cd_2Mn_3O_8$. We have reproduced this phase which gives a very sharp X-ray powder diagram, and it was possible to index this complex pattern completely. The resulting unit cell bears a close resemblance to that of Mn_5O_8 :

$$\begin{array}{lll} a = 10.80, \text{ \AA} & b = 5.80, \text{ \AA} & c = 4.93, \text{ \AA} \\ \beta = 109^\circ 32' & V = 291.7 \text{ \AA}^3 & \text{Space group } C2/m \text{ or } C2 \end{array}$$

Tentative structure factor calculations based on a provisional structure model confirm that both compounds are indeed isotypic. Hence, the true formula of Mn_5O_8 must be $Mn_3^{II}Mn_2^{IV}O_8$. The complete structure determinations based on the present X-ray data are in progress and will be reported elsewhere.

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CHEMISTRY

Metal Complexes of Diphenylmethylarsine Oxide Involving Co-ordinated Perchlorate Ions

In recent years, a number of tertiary arsine oxide¹ and tertiary phosphine oxide² complexes of metal salts have been prepared. The metal atom, in all cases, has been shown, using magnetic and spectral data, to display the usual tetrahedral or octahedral stereochemistry. We report here a new class of compound, using diphenylmethylarsine oxide as ligand, in which the metal atom is five co-ordinate with a tetragonal pyramid structure, the fifth position being occupied by a perchlorate group*. Complexes of the composition $M(II)(Ph_2MeAsO)_4(ClO_4)_2$, $M = Mn, Fe, Co, Ni, Cu, Zn$, are obtained from alcoholic solutions of the arsine oxide and the corresponding perchlorate. X-ray powder photographs indicate that these substances are isostructural. The infra-red spectra of the manganese, cobalt, nickel and zinc complexes in the 1,100 cm⁻¹ region indicate the presence of both co-ordinated and uncoordinated perchlorate groups, while the spectra of the corresponding iron and copper salts indicate the presence of ionic perchlorate only³.

For cobalt(II) and nickel(II), two related series of complexes have been prepared; $[M(Ph_2MeAsO)_4](NO_3)_2$ and $[M(Ph_2MeAsO)ClO_4]NO_3$. The infra-red spectra of the nitrate complexes indicate the presence of both a co-ordinated and a free anion, absorption bands occurring at 1,420(m.w), 1,370(m), 1,300(s), 1,025(w); the band at 1,370 cm⁻¹ is, no doubt, associated with the free nitrate ion and the other bands with the co-ordinated species⁴. The mixed perchlorate-nitrate complexes are of special interest, as the infra-red spectra indicate that the nitrate groups are co-ordinated while the perchlorate group is ionic. In agreement with this, the ultra-violet and visible spectra of the nitrate and the nitrate-perchlorate complexes are identical for both nickel and cobalt salts; and while the perchlorate complexes have a similar pattern of bands these occur at slightly different wave-lengths. The spectra of all these complexes are not readily assigned on the basis of either octahedral or tetrahedral symmetry;