810. *Some Structural Properties of* α-MnO_2 *containing* NH_4^+, K^+, Na^+, Ca^{++}, *and* Ba^{++} *Ions.*

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Methods of obtaining α-MnO_2 containing Na^+, K^+, NH_4^+, Ca^{++}, and Ba^{++} ions, either directly or by sintering manganous manganite, are described. The formation of the α-phase is shown to be accompanied by a loss in oxygen until the ratio oxygen : manganese reaches the value 1·88 characteristic of the α-form. The structures of the materials were examined by *X*-ray and electron diffraction and electron microscopy. The macroscopic crystals of the potassium- and ammonium-containing oxides are straw-shaped; the others do not show this habit. All the oxides have layers of MnO and either γ-Mn_2O_3 or Mn_3O_4 on the surface.

THE designation α has been applied to varieties of naturally occurring manganese dioxide containing foreign ions and crystallising with a tetragonal, or pseudo-tetragonal (monoclinic, $\beta \gtrsim 90°$; $a_0 \gtrsim c_0$), structure with a large axial ratio. An approximate general formula for these oxides is $M_xMn_8O_{16}$, where M is the foreign metal ion and x varies, but is usually less than 2.

Much of the work on these oxides has been carried out with naturally occurring minerals and relevant details are given on p. 4213. Our interest in the systems arises out of our investigations on the synthetic production of different types of manganese dioxide. The problem has been studied to some extent by other workers; *e.g.*, Sakar and Dhar (*Z. anorg. Chem.*, 1922, **121**, 135) investigated the precipitation of manganese dioxide from manganese sulphate by potassium permanganate in the presence of foreign ions. Many of the oxides obtained had a general formula of $MO,7MnO_2$ with a high but variable water content, *e.g.*, $CaO,7MnO_2,14H_2O$. Oxides of similar composition can also be prepared by shaking freshly precipitated manganese dioxide with a solution containing the foreign ion. We have already obtained indications that M may be ammonium (Butler and Thirsk, *Acta Cryst.*, 1952, **5**, 288). Other references to the preparation of oxides having an α-MnO_2 structure are by Dubois (*Ann. Chim.*, 1936, **5**, 401), who also claimed to have prepared an α-MnO_2 containing no foreign ion by decomposing permanganic acid. It is possible that his preparation may contain some barium. These results have led us to investigate the possibility of preparing α-oxides with M = Ba, Ca, K, or Na.

We have either used a method whereby α-MnO_2 is produced directly, or have prepared samples of manganous manganite, which is known to yield the α-oxide on sintering. By manganous manganite, we mean essentially finely divided oxides giving prominent diffractions near d_{hkl} = 7·3, 3·6, 2·45, and 1·41 Å, and we thus use the designation due to Feitknecht and Marti (*Helv. Chim. Acta*, 1945, **28**, 129) in classifying certain preparations from *X*-ray data. We do not, however, limit ourselves, as they do, to a method of preparation by oxidation of alkaline manganese solutions.

The chemical compositions have been determined of the precipitates (i) as originally formed, after suitable methods of drying, and (ii) during the sintering processes at different temperatures. The changes in the structure of the oxides during the heating process have been examined by *X*-ray and electron diffraction. Electron microscopy has been used in an attempt to follow changes in the shape of the micro-crystals of the oxides during the sintering process, and electron diffraction in an attempt to increase the resolution of the diffraction method particularly in size ranges where *X*-rays give diffuse patterns. By using the EM3 Metropolitan-Vickers microscope, a simultaneous search of the oxide specimen by microscopy and diffraction was possible. As shown previously (Butler and Thirsk, *loc. cit.*) in certain cases, the high resolution of the instrument makes it possible to ascribe a particular orientation to the unit cell in the observed crystals.

EXPERIMENTAL

X-*Ray, Electron-microscope, and Election-diffraction Techniques.*—Photographs of the manganese oxides were taken on a Metropolitan-Vickers demountable *X*-ray set, a 9-cm. powder camera being used. Unfiltered iron radiation was used, the manganese dioxide specimen acting as its own β-filter. This resulted in a somewhat darkened back-ground but only the weakest reflections are lost. The normal exposure at 44 kv and 18 mA was 90 minutes.

Rod-shaped specimens of diameter about 0·3 mm. were made by intimately mixing the oxide with gum tragacanth, moistening it with water to a very stiff paste, and rolling it between two glass slides until dry. These rods were mounted centrally in the camera in the usual way.

The line positions on the films were measured by means of an instrument designed by Gibson (*J. Sci. Instr.*, 1946, **23**, 159). The wave-length of the α-radiation of iron was taken to be 1·9373 Å. Some use was made, in addition to the EM3 instrument, of an electron-diffraction camera of the type described by Finch and Wilman (*Ergebn. exakt. Naturwiss.*, 1937, **16**, 353).

The specimens for examination in these two instruments were supported on Collodion or Formvar films picked up on the standard copper gauzes used in the electron microscope. Deposits were made either by precipitation from air (Drummond *et al.*, *J. Roy. Micros. Soc.*, 1950, **70**, 32), or by evaporation of a drop of an aqueous suspension which was placed on the film by means of a platinum ring. We could not detect any difference between the results by the two methods.

For an accurate determination of the interplanar spacings, we used thallous chloride as standard, and $a_0 = 3{\cdot}834$ Å was taken as the length of the edge of the simple cubic unit cell. This standard was suggested by Boswell (*Proc. Phys. Soc.*, 1951, *A*, **64**, 465), and we found that the material gave very sharp lines whether it was evaporated on to the oxide specimen or co-deposited from a solution containing the suspended oxide.

All the plates were measured by a travelling microscope adapted to project the image of a cross-wire on to the photographic plate.

Preparative and Analytical Techniques.—" AnalaR " reagents were used for all preparations and analyses.

Preparation 1. The procedure was similar to that used by Selwood, Eischens, Ellis, and Wethington (*J. Amer. Chem. Soc.*, 1949, **71**, 3039) for the preparation of the oxide they describe as γ(I)-MnO_2. 50 G. of hydrated manganese sulphate and 100 ml. of 2N-sulphuric acid were dissolved in 1 l. of water. The solution was then heated to boiling, and 113 g. of ammonium persulphate were added in small portions during ½ hour. The precipitate formed was washed by decantation with boiling water and finally collected and washed again with hot water. Preparation 1(*a*) was dried for 6 days at 60°, and 1(*b*) for 6 days in a vacuum-desiccator (P_2O_5).

Preparation 2. The method was similar to that used by Selwood *et al.* (*loc. cit.*) for the preparation they name γ(II)-MnO_2. A solution of hydrated manganese sulphate (36 g.) and potassium nitrate (24 g.) in water (about 2 l.) was heated to boiling, and 2% potassium permanganate solution slowly added until present in excess. The precipitate was washed by decantation with boiling water (6 × 1 l.), then filtered off and washed again. Preparations 2(*a*) and 2(*b*) were dried as for 1(*a*) and 1(*b*), respectively.

Preparation 3. 5N-Solutions were made of the permanganates of (*a*) potassium, (*b*) sodium, (*c*) calcium, and (*d*) barium. 60 ml. of each of the solutions were boiled, and 15 ml. of *ca.* 6N-hydrochloric acid (redistilled) slowly added. The precipitates were washed with boiling water and dried as for preparations (*b*), above.

Analysis. The oxides were analysed for manganese, available oxygen (*i.e.*, the excess over that required for MnO), water, and the foreign ion.

Manganese was determined volumetrically by means of the pyrophosphate complex of tervalent manganese (Goffart, Michel, and Pitance, *Anal. Chim. Acta*, 1947, **1**, No. 6, 393). To this end, the oxide was dissolved in a small amount of hydrochloric acid, and the solution made up to 300 c.c. by addition of a freshly saturated solution of sodium pyrophosphate. The pH of the solution was then adjusted to between 6 and 8 by addition of sodium hydroxide solution, litmus paper being the indicator. The resulting solution was titrated with standard potassium permanganate, the end-point being detected by a platinum and silver/silver chloride electrode connected externally to a micro-ammeter. The permanganate solution was standardised against sodium oxalate (Fowler and Bright, *J. Res. Nat. Bur. Stand.*, 1935, **15**, 497).

Available oxygen was determined by Eberius and Le Blanc's modification (*Z. physikal. Chem.*, 1932, **160**, *A*, 129) of Bunsen's method. The oxide was heated with hydrochloric acid, and the chlorine evolved carried by a stream of carbon dioxide into the absorption vessels containing potassium iodide solution. The iodine liberated was titrated with sodium thiosulphate solution which had been standardised against potassium iodate.

The combination of these two methods has the advantage that the oxygen : manganese ratio can be determined rapidly on a sample of manganese dioxide without any standardisation of solution or weighing: the available oxygen is first determined on any weight of manganese dioxide and the remaining solution is used for determination of the manganese. Water was determined by Penfield's method (*Amer. J. Sci.*, 1894, **48**, 30) modified to accommodate the very bulky specimens by blowing a bulb on the end of the tube containing the dioxide. Potassium was determined by means of a flame photometer, barium and calcium by precipitation as sulphate, and the sodium by difference. Ammonia was determined by a modified Kjeldahl method.

Sintering Experiments.—The specimens of the oxide were sintered by heating them in a hard-glass tube which had a small furnace placed round the centre. A current of dry oxygen was passed over the specimen, and the temperature measured by means of a thermocouple. The apparatus permitted sintering to be carried out at temperatures up to about 580°. Two of the preparations, those containing calcium and barium, were also sintered at a red heat but in this case they were exposed to the air. A preliminary survey of the behaviour of the oxide on heating was carried out by differential thermal analysis. The conditions of sintering were then chosen so that, except for Preps. 3(*c*) and (*d*) at above 500°, very little decomposition of the oxide was believed to occur. Heating was for 24 hours at each temperature except where otherwise noted.

Results.—*Preparation* 1. Prep. 1(*a*) had a composition by analysis of $(NH_4)_{0\cdot016}MnO_{1\cdot884},0\cdot33H_2O$; and 1(*b*) of $(NH_4)_{0\cdot022}MnO_{1\cdot951},0\cdot26H_2O$. *X*-Ray data gave evidence in 1(*a*) of equal amounts of α- and γ-oxide. Previous workers had found only the γ-phase; we have also prepared the pure γ-form by using this method. The lines were broad, indicating very fine crystals. The dimensions of the unit cell of the α-form were $a_0 = 9\cdot87 \pm 0\cdot02$ Å, $c_0 = 2\cdot849 \pm 0\cdot005$ Å, $a/c = 3\cdot46$. Similarly, Prep. 1(*b*) was also a mixture of α- and γ-MnO_2. Heating to 200° gave very similar diffraction patterns, but from the increased sharpness of the 002 diffraction it seems clear that the crystallinity of the specimens was improved. No further heating was carried out on this preparation because the crystallites seemed quite well developed; examination in the electron microscope showed that they were about 1 μ long. From the electron-diffraction patterns it was calculated that the material had an α-MnO_2 structure, with unit cell of $a_0 = 9\cdot88 \pm 0\cdot03$ Å, $c_0 = 2\cdot845 \pm 0\cdot005$ Å, $a/c = 3\cdot47$. The c_0 axis of the unit cell has been shown to lie parallel to the long axis of the needle-like aggregates (Butler and Thirsk, *loc. cit.*). The surface of the oxide showed the presence of MnO and also of either γ-Mn_2O_3 or Mn_3O_4. It is impossible to distinguish between these two oxides except by chemical analysis, since the recorded *X*-ray patterns seem to be identical.

Preparation 2. Initially Prep. 2(*a*) had the constitution $K_{0\cdot092}MnO_{1\cdot911},0\cdot34H_2O$, and Prep. 2(*b*) $K_{0\cdot085}MnO_{1\cdot931},0\cdot40H_2O$; after 24 hours' heating at 200° the compositions were $K_{0\cdot092}MnO_{1\cdot941}$ and $K_{0\cdot085}MnO_{1\cdot944}$, respectively.

The preparations gave broad diffraction lines by *X*-ray analysis and indicate almost equal amounts of α- and γ-oxide. It is considered that the increase in ratio (available O_2)/Mn on sintering is due to the γ-phase which can absorb oxygen up to practically the theoretical amount; whereas (see table) the α-phase loses oxygen when heated, approaching the limiting ratio $MnO_{1\cdot88}$ as crystal growth occurs. On balance, this mixed phase absorbs a small amount of oxygen on being heated. Heating to 200° produced a slight improvement in the crystallinity. By electron diffraction the preparation gave evidence for MnO, and γ-Mn_2O_3 or Mn_3O_4. It was clear from examination of the electron-microscope pictures that the needles of α-MnO_2 observed were much more finely divided than in Preps. 1(*a*) and 1(*b*). The α-MnO_2 pattern corresponded to a body-centred tetragonal lattice with $a_0 = 9\cdot83 \pm 0\cdot01$ Å, $c_0 = 2\cdot862 \pm 0\cdot003$ Å, $a/c = 3\cdot434$. The elongation of the crystals in the direction of the c_0 axis in the unit cell was not so marked as in the first preparation.

Preparation 3. The preparation was analysed in its initial form, and after it had been heated at 200° and at 400°, the compositions were $K_{0\cdot278}MnO_{2\cdot00},0\cdot82H_2O$, $K_{0\cdot278}MnO_{1\cdot928}$, and $K_{0\cdot278}MnO_{1\cdot892}$, respectively.

Prep. 3(*a*) gave four broad refractions characteristic of manganous manganite. At 200° the crystallinity was improved, the unit-cell dimensions being $a_0 = 10\cdot3$ Å, $c_0 = 2\cdot83$ Å. At 400° manganous manganite was transformed with considerable improvement in crystallinity into α-MnO_2, with unit-cell parameters $a_0 = 9\cdot82 \pm 0\cdot01$ Å, $c_0 = 2\cdot858 \pm 0\cdot005$ Å. The improvement in crystallinity at 200° was quite noticeable by electron microscopy, but no preferred direction of growth could be observed in the crystalline aggregates. At this temperature no α-MnO_2 was detectable, although the diffraction rings for the γ-Mn_2O_3 or Mn_3O_4 were broken, indicating that the lower dioxide particles were of greater size than in the original preparation. Heating at 400° caused a marked change, and the preparation showed well-developed needle-like crystals, giving an α-MnO_2 pattern similar to that of Preps. 1 and 2. The c_0 axis in the unit cell was again seen to lie in the direction of the long axis of the needles.

Prep. 3(*b*) was very similar to 3(*a*) and at 200° the unit-cell dimensions of the manganous manganite were as recorded for 3(*a*). The following analytical data were obtained. For the original preparation the formula was $Na_{0·218}MnO_{1·987},1·14H_2O$; after heating to 200°, $Na_{0·218}MnO_{1·932}$, and after heating to 400°, $Na_{0·218}MnO_{1·895}$. It was noted from *X*-ray diffraction that at 400° transformation took place into α-MnO_2, with a body-centred tetragonal unit cell: $a_0 = 9·81 \pm 0·02$ Å, $c_0 = 2·858 \pm 0·005$ Å. This preparation gave much more diffuse reflections than the α-MnO_2 from Prep. 3(*a*). On examining the specimen by electron microscopy it was noticed that the crystals, although giving α-MnO_2 diffraction patterns, had grown in quite a uniform crystal habit. No evidence was found on further examination by electron diffraction of any preferred external shape or internal structure for the α-MnO_2. The diffraction spots lying on the diffraction rings corresponding to α-MnO_2 were quite round and not elongated in specific directions.

X-Ray evidence showed that Prep. 3(*c*) was very poorly crystalline indeed. On heating to 400°, three diffuse lines were obtained. These could be indexed on a unit cell with $a_0 = 10·5$ Å and $c_0 = 2·82$ Å, assigned as 200, 121, and 002 reflections; manganese manganite gives 110, 220, 121, and 002 reflections. Attempts to improve the crystallinity of this oxide by sintering were unsuccessful. At 580° the oxide obtained was shown to be a mixture of α-MnO_2, with $a_0 = 9·78 \pm 0·02$ Å, $c_0 = 2·847 \pm 0·005$ Å, and cubic α-Mn_2O_3, with $a_0 = 9·40$ Å. The compositions were: as prepared, $Ba_{0·131}MnO_{2·00}$; at 400°, $Ba_{0·131}MnO_{1·937}$, and at 500°, $Ba_{0·131}MnO_{1·910}$. Prep. 3(*d*) was also very poorly crystalline. Its chemical composition varied in a similar manner to that of 3(*c*). Initially the composition was $Ca_{0·125}MnO_{1·986}$, and after heating at 200° $Ca_{0·125}MnO_{1·937}$, and at 500°, $Ca_{0·125}MnO_{1·859}$. As will be noticed in the analysis slight decomposition had occurred at 500°.

On heating to 400°, no improvement in the crystallinity or additional diffraction lines were observed. At 500° α-MnO_2 was formed, and the crystallinity was slightly improved by further heating at 580°. The dimensions of the body-centred tetragonal unit cell were $a_0 = 9·83 \pm 0·02$ Å, $c_0 = 2·847 \pm 0·005$ Å. This oxide was stable for a short period at red heat. Similar comments can be made on the results from the electron microscope and diffraction examination. Both Preps. 3(*c*) and 3(*d*) gave sharp diffraction patterns after being heated at 580°. An attempt was made with Prep. 3(*d*) to produce further growth in the crystals by heating at a red heat, and evidence was obtained that the α-MnO_2 had decomposed considerably. The electron micrographs showed a beautiful effect: very sharply defined and regularly shaped rod-like crystals grew out of the crystalline matrix. It is considered that these crystals may be single crystals of either γ-Mn_2O_3 or Mn_3O_4, and the nature of the phase change is still being investigated. Some importance is attached to the observation that with these two preparations containing calcium and barium, increase in crystal size by sintering was much less than with α-MnO_2 containing sodium and potassium.

The final specimen examined was a commercial B.D.H. sample of composition $K_{0·212}MnO_{1·916},1·09H_2O$, which gave originally a manganous manganite pattern. After 100 hours' heating at 530°, it had crystallised as α-MnO_2 with $a_0 = 9·828$ Å, $c_0 = 2·862$ Å, $a/c = 3·434$.

DISCUSSION

In the following discussion we have represented our oxides as anhydrous material based on a general formula $M_xMn_8O_y$. The experimental results are summarised in the table. It is convenient to relate a discussion of the results from our synthetic materials with relevant data for naturally occurring minerals. The mineral hollandite corresponds to $Ba_xMn_8O_{16}$. Byström and Byström (*Acta Cryst.*, 1950, **3**, 146) determined the unit cell to be monoclinic, with dimensions $a_0 = 9·91$ Å, $b_0 = 2·872$ Å, $c_0 = 9·97$ Å, and $\beta = 90·6°$. From the short M–M distance in the crystals, they consider that for large ions the maximum value of x is about unity. If the foreign ion is potassium, the corresponding mineral is $K_xMn_8O_{16}$, cryptomelane, and Byström and Byström (*loc. cit.*) consider that x must be about 1. Delano (*Ind. Eng. Chem.*, 1950, **42**, 523) considers the correct formula to be $x = 2$. The unit cell was thought by Ramsdell (*Amer. Min.*, 1942, **27**, 611) to be tetragonal with $a_0 = 9·82$ Å, $c_0 = 2·86$ Å, but Byström and Byström give the unit-cell dimensions $a_0 = 9·84$ Å, $c_0 = 2·85$ Å, and consider that the maximum difference in length of a_0 and b_0

Summary of experimental results.

Method of preptn.	Treatment	Formula	Comments (cell dimensions in Å)
Prep. 1. $MnSO_4$ + $(NH_4)_2S_2O_8$	1(*a*). Dried for 6 days at 60°	$(NH_4)_{0\cdot18}Mn_8O_{15\cdot1}$	Broad lines by *X*-ray diffraction. Approx. equal amounts of α- and γ-forms. Unit cell of α-form has $a_0 = 9\cdot87 \pm 0\cdot02$, $c_0 = 2\cdot849 \pm 0\cdot005$, $a/c = 3\cdot46$
	1(*b*). Dried for 6 days over P_2O_5 in vac. desiccator	$(NH_4)_{0\cdot18}Mn_8O_{15\cdot61}$	
	1(*b*). Heated to 200° for 24 hours in oxygen	$(NH_4)_{0\cdot18}Mn_8O_{15\cdot82}$	Electron microscopy shows α-form to exist as straw-shaped particles about 1 μ in length; electron diffraction demonstrated that the c_0 axis lay parallel to the long axis of the crystals and gave the following dimensions for the unit cell: $a_0 = 9\cdot88 \pm 0\cdot03$, $c_0 = 2\cdot845 \pm 0\cdot005$, $a/c = 3\cdot47$. Also present were MnO, and γ-Mn_2O_3 or Mn_3O_4 on the surface
Prep. 2. Boiling solution of $MnSO_4$ and KNO_3 to which $KMnO_4$ was added	2(*a*). Dried for 6 days at 60°	$K_{0\cdot73}Mn_8O_{15\cdot29}$	Heating to 200° gives a slight improvement in crystallinity. Approx. equal amounts of α- and γ-oxides present. Less well-developed crystals of α-form than for Prep. 1. Unit cell: $a_0 = 9\cdot83 \pm 0\cdot01$, $c_0 = 2\cdot862 \pm 0\cdot03$, $a/c = 3\cdot434$
	2(*a*). Heated at 200° in oxygen for 24 hours	$K_{0\cdot73}Mn_8O_{15\cdot53}$	
	2(*b*). Dried for 6 days at 60°	$K_{0\cdot68}Mn_8O_{15\cdot46}$	
	2(*b*). Heated at 200° in oxygen for 24 hours	$K_{0\cdot68}Mn_8O_{15\cdot56}$	
Prep. 3(*a*). 6N-HCl added dropwise to a boiling 5N-solution of $KMnO_4$	3(*a*). Dried *in vacuo* over P_2O_5 for 6 days	$K_{2\cdot22}Mn_8O_{16\cdot00}$	Four broad manganous manganite reflections
	3(*a*). Heated at 200° in oxygen for 24 hours	$K_{2\cdot22}Mn_8O_{15\cdot42}$	Improved crystallinity: $a_0 = 10\cdot3$, $c_0 = 2\cdot83$
	3(*a*). Heated at 400° in oxygen for 24 hours	$K_{2\cdot22}Mn_8O_{15\cdot14}$	Similar shape of crystals to Preps. 1 and 2. Unit cell has: $a_0 = 9\cdot82 \pm 0\cdot07$, $c_0 = 2\cdot858 \pm 0\cdot005$
Prep. 3(*b*). 6N-HCl added dropwise to a boiling 5N-$NaMnO_4$ solution	3(*b*). Dried *in vacuo* over P_2O_5 for 6 days	$Na_{1\cdot75}Mn_8O_{15\cdot90}$	Manganous manganite
	3(*b*). Heated at 200° for 24 hrs. in oxygen	$Na_{1\cdot75}Mn_8O_{15\cdot46}$	Much as above; slightly more crystalline
	3(*b*). Heated at 400°	$Na_{1\cdot75}Mn_8O_{15\cdot20}$	α-MnO_2 with unit cell: $a_0 = 9\cdot81 \pm 0\cdot02$, $c_0 = 2\cdot858 \pm 0\cdot005$ No preferred direction of growth of crystalline material
3(*c*). 6N-HCl added to boiling 5N-$Ba(MnO_4)_2$	3(*d*). Dried *in vacuo* over P_2O_5 for 6 days	$Ba_{1\cdot05}Mn_8O_{16\cdot00}$	Very poorly crystalline manganous manganite
	3(*d*). Heated at 400° in O_2	$Ba_{1\cdot05}Mn_8O_{15\cdot50}$	Three broad lines from *X*-rays: $a_0 = 10\cdot5$, $c_0 = 2\cdot82$
	3(*d*). Heated at 500° in O_2	$Ba_{1\cdot05}Mn_8O_{15\cdot28}$	Little change in appearance. Finely divided α-form; some decomposition.
	3(*d*). Heated at 580° in O_2		A mixture of α-MnO_2 ($a_0 = 9\cdot87 \pm 0\cdot02$, $c_0 = 2\cdot845 \pm 0\cdot005$) and cubic Mn_2O_3 ($a_0 = 9\cdot404$). Sharp diffraction patterns
3(*d*). 6N-HCl added to boiling 5N-$Ca(MnO_4)_2$	3(*c*). Dried *in vacuo* over P_2O_5 for 6 days	$Ca_{1\cdot00}Mn_8O_{15\cdot90}$	
	3(*c*). Heated to 200° in O_2	$Ca_{1\cdot00}Mn_8O_{15\cdot74}$	Very poorly crystalline
	3(*c*). Heated to 400° in O_2		
	3(*c*). Heated to 500° in O_2	$Ca_{1\cdot00}Mn_8O_{14\cdot87}$	Some α-MnO_2 formed. Some decomposition to Mn_2O_3
	3(*c*). Heated to 580° in O_2		Improved crystallinity but also considerable decomposition. Unit cell of α-MnO_2 is $a_0 = 9\cdot83 \pm 0\cdot02$, $c_0 = 2\cdot847 \pm 0\cdot005$

allowable would be 0·02 Å and the difference of β from 90° is less than 0·3°. Recently, however, Mathieson and Wadsley (*ibid.*, 1950, **35**, 99) have reported the existence of a monoclinic cryptomelane with $a_0 = 9{\cdot}79$ Å, $b_0 = 2{\cdot}86$ Å, $c_0 = 9{\cdot}94$ Å, $\beta = 90° 37$. It is readily seen that these values are very close to the hollandite parameter reported above. Although the ratio of barium content to the potassium content is 1 : 6, the barium content is higher than for many other crypotmelanes, and we consider that Mathieson and Wadsley are dealing with a material similar to the mineral hollandite rather than cryptomelane.

Prep. 1 containing ammonium has a remarkably low value of x. The ammonium ion seems to be very firmly held, since heating at 200°, whilst serving to remove water from the specimen, made no other appreciable difference in the composition. This low proportion of ammonium ion might reasonably be assumed to be due to adsorption rather than the formation of a compound if it were not for certain other features of the preparation. It was a most satisfactory method of obtaining a product at room temperature possessing the characteristic microcrystalline cryptomelane structure. Recent unpublished work by the authors has also shown that the specific resistance corresponds to that of α-MnO_2 and is of the order of 10^3 less than that of the manganous manganite preparations. Since there is no well-substantiated preparation of α-MnO_2 without a foreign ion in the lattice, we regard this preparation as analogous in form to the other preparations.

Consideration of the table shows that the potassium content varies from less than 1, the limit suggested by Byström and Byström, to a figure corresponding to Delano's formulation with $x = 2$. These results imply that the foreign ion content may vary widely, although a determination of the actual quantity in the lattice is not possible owing to the poor crystallinity of the specimens preventing the use of a more refined X-ray technique. Although there must have been considerable adsorption of potassium on the enormous surface area of manganous manganite, this can hardly account for such a high percentage of potassium. The same effect was noted with the sodium, barium, and calcium products. Of these three, the barium-containing material corresponds very closely to $x = 1$, agreeing with Byström and Byström.

From an examination of our X-ray results and from experimental results of Copeland, Griffiths, and Schertzinger (*Trans. Electrochem. Soc.*, 1947, **92**, 127), the improvement in crystallinity, which may perhaps also be associated with the entry of the foreign ion into the manganese dioxide lattice, can be shown in the case of potassium to alter the c/a ratio of the tetragonal cell, mainly because of a marked decrease in the a_0 value.

It has been suggested by Sakar and Dhar (*loc. cit.*) and by Gruner (*Amer. Min.*, 1943, **28**, 496) that the oxides under discussion resembled the zeolites, since the exchange of foreign ion can be readily carried out by washing with a solution containing a replacing ion in a manner analogous to zeolitic behaviour. This point has not been examined in this work but it would seem from our results that there would be a limit to the extent to which this process can be carried out in view of the markedly differing external crystal habits of the oxides on sintering.

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