

Synthesis of potassium manganese oxides under hydrothermal conditions

T. ENDO AND S. KUME

College of General Education, Osaka University

AND

M. SHIMADA AND M. KOIZUMI

Institute of Scientific and Industrial Research, Osaka University

SUMMARY. A 1 M solution of potassium permanganate was sealed in a gold capsule and was treated under conditions of temperature and pressure up to 800 °C and 2.5 kb. Different kinds of products were produced under different conditions of synthesis, and potassium manganate, birnessite, cryptomelane, hausmannite, manganosite, and a new phase appeared. The chemical composition of the new phase was determined as $K_2Mn_4O_9$ and its X-ray powder diffraction pattern was indexed on a hexagonal cell with a 11.295 and c 21.870 Å.

SEVERAL minerals containing potassium and manganese as the main constituent elements are known in nature. In relation with the natural occurrences and geneses, laboratory preparations of these materials have been undertaken (McMurdie and Golovato, 1948; Cole *et al.*, 1947; Dubois, 1936; Pauling *et al.*, 1960) but few attempts at the synthesis of related substances have been made under hydrothermal conditions, although some minerals such as cryptomelane or coronadite have often been found in hydrothermal ore deposits (Roy, 1968; Hewett, 1971). The authors tried a series of experiments on hydrothermal syntheses using a solution of potassium permanganate as starting material.

Experimental. The starting material was a 1 M solution of potassium permanganate. About 1 ml of the solution was carefully sealed in a gold capsule and was subjected to the conditions up to 800 °C in temperature and 2.5 kb in pressure using a test-tube type bomb (Roy and Tuttle, 1956). After the completion of the run, the bomb was quenched to room temperature in several minutes. The shape of the gold capsule was slightly deformed and the size shrunk. No damage, however, was seen on either welding or other parts of the capsule and accordingly it was considered that contamination of the sample with materials outside the capsule had hardly occurred.

The product was identified by X-ray powder diffraction with filtered $Cu-K\alpha$ radiation. Optical and electron microscopic observations were undertaken. Chemical analyses by means of photometric and flame spectrophotometric methods were performed to determine the chemical formula of the product and the valence state of manganese ions in it. The presence of OH^- ion or H_2O molecule in the sample was

checked by infra-red absorption; the absorption spectra were measured in the range from 4000 to 650 cm^{-1} by both Nujol mull and KBr disc methods. The amount of water contained in the product and the dehydration temperature were determined by TG and DTA.

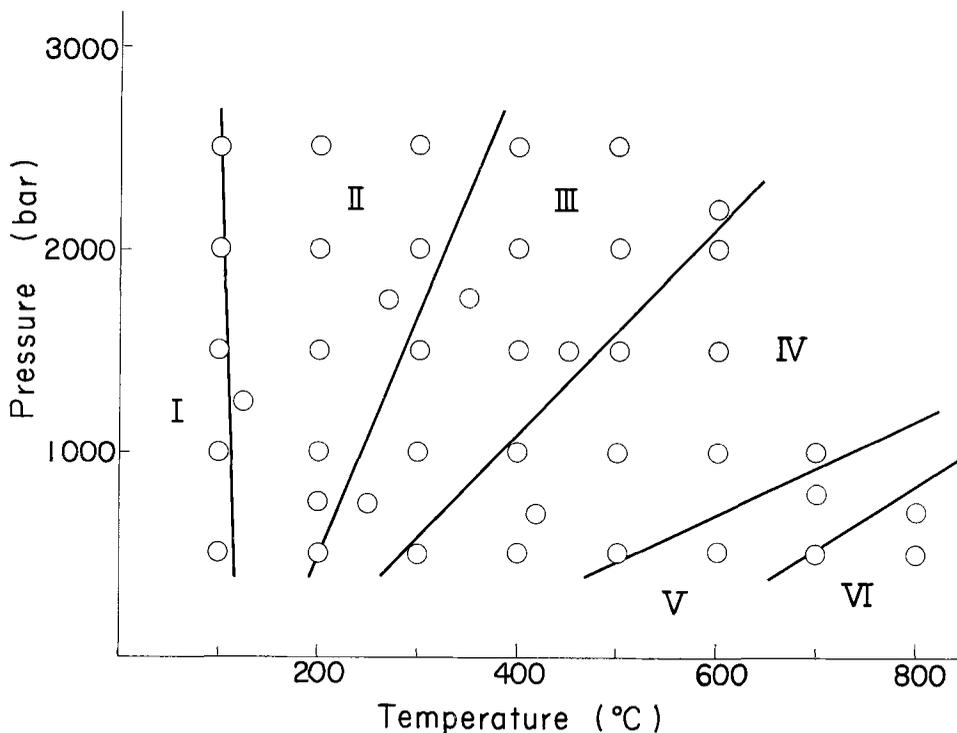


FIG. 1. Results of synthesis experiments. Circles show the conditions of temperature and pressure at which experiments were undertaken.

I: Region where potassium permanganate was formed. II: Region where the products consisted of two phases, potassium manganate and a new phase. III: Region where the products consisted of two phases, a new phase and birnessite. IV: Region where cryptomelane was formed. V: Region where hausmannite was formed. VI: Region where manganosite was formed.

Results and discussion. The results of the synthetic experiments are summarized in fig. 1. The relation illustrated in this diagram is not always in equilibrium but the diagram only shows the experimental results. As shown in the region I of the diagram, potassium permanganate KMnO_4 crystallized when the experimental conditions of temperature and pressure were relatively low.

The product obtained in region II consisted of two phases. One of them was easily identified as potassium manganate K_2MnO_4 . When the product was washed with 2N KOH solution, K_2MnO_4 dissolved and the residue was a brownish-black powder. An electron micrograph (fig. 2) indicated that the grains are scaly thin plates. The electron diffraction patterns illustrated in fig. 3 were perfectly indexed by assuming that the

crystal had a hexagonal symmetry, the unit cell being a 11.3, c 21.9 Å. More precise lattice constants were determined to be a 11.295 and c 21.870 Å by means of X-ray powder diffraction. The agreement of the calculated d -spacings with the observed values is excellent as seen in Table I.



FIGS. 2 and 3: FIG. 2 (left). Electron micrograph of a new phase $K_2Mn_4O_9$.
FIG. 3 (right). Electron diffraction pattern of $K_2Mn_4O_9$.

TABLE I. X-ray powder data for $K_2Mn_4O_9$; calculated d -values for a hexagonal cell with a 11.295, c 21.870 Å

d_{obs}	I	hkl	d_{calc}	d_{obs}	I	hkl	d_{calc}
9.781	vs	100	9.782	2.095	vvw	412	2.095
5.646	w	110	5.648	1.702	vw	245	1.703
4.062	m	203	4.061	1.411	w	440	1.412
3.062	w	116	3.063	1.221	vvw	800	1.223
2.445	s	400	2.445	1.184	w	456	1.184
2.196	m	322	2.198	1.093	vvw	555	1.094

Although the infra-red spectra did not show any absorption band attributable to the presence of OH^- ions or H_2O molecules, two endothermic reactions were observed at 108 °C and 918 °C in DTA and the corresponding weight losses were seen in TG. Since the sample began to change to hausmannite at 918 °C, the reaction occurring at 918 °C is due to a decomposition; the reaction at 108 °C is presumed to be the evaporation of adsorbed water. The X-ray diffraction pattern of the sample once heated at 850 °C in air for 24 hours was exactly the same as that before heating and DTA and TG of the heated sample did not show any anomaly in the temperature range up to 900 °C. Chemical analysis of the heat-treated sample gave K_2O 21.21 %, MnO_2 79.15 % (total Mn as MnO_2), sum 100.36 %. Accordingly, the chemical formula of the sample is $K_2Mn_4O_9$, a new phase.

Two phases, birnessite and the above-mentioned $K_2Mn_4O_9$, existed in a sample synthesized under conditions of temperature and pressure represented by region III of fig. 1. The chemical analysis of birnessite showed that the potash content varied from 20.96 to 25.54 % K_2O and the ratio of oxygen to manganese ion was close to 2.0. The X-ray powder data were in good agreement with those given by Jones and Milne (1956).

The synthetic experiments under the conditions corresponding to region IV produced cryptomelane. From the X-ray diffraction pattern, the lattice constants were calculated to be a 9.86 and c 2.85 Å, which are the same as those reported by Butler *et al.* (1952). Chemical analysis gave 12.77 % K_2O . The results of infra-red absorption and TG indicated that neither H_2O molecules nor OH^- ions were present. The TG also showed that bixbyite was not produced from cryptomelane but the formation of hausmannite was observed.

In region V of fig. 1, single crystals of hausmannite, octahedral and from 1 to 2 mm long, were obtained. The calculated lattice constants, a 5.76 and c 9.49 Å, and the ferrimagnetic Curie temperature at 43 K were all consistent with the values already reported by Boucher *et al.* (1971).

Single crystals of manganosite were obtained by synthesis under the condition of region VI. The calculated lattice constant was a 4.44 Å, similar to that reported by Moore *et al.* (1950).

Conclusions. The experimental results may be summarized as follows:

When solutions of potassium permanganate are subjected to hydrothermal conditions up to 800 °C and 2.5 kb, six potassium manganese or manganese oxides, K_2MnO_4 , $K_2Mn_4O_9$, $K_2Mn_7O_{14}$, KMn_8O_{16} , Mn_3O_4 , and MnO are produced.

The valence of the manganese ion decreases when the conditions of temperature and pressure are elevated. Although the present investigation does not give enough proof, the reduction of manganese ions at high temperatures is believed to be due to hydrogen produced by the dissociation of water in the sample and also produced by the reaction of water with the test-tube bomb. Hydrogen possibly infiltrates through the wall of gold capsule as suggested by Laudise (1961).

Bixbyite is not obtained, and this result suggests that the bixbyite phase is unstable under a strongly alkaline environment.

A new oxide, $K_2Mn_4O_9$, with hexagonal symmetry, is produced in the region of relatively low temperature and pressure. Although this phase has not been found in nature so far, it is considered that it might be formed in a vein or a hydrothermal deposit if the environment at the time of its formation were strongly alkaline.

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REFERENCES

- BOUCHER (B.), BUHL (R.), and PERRIN (M.), 1971. *Journ. Appl. Phys.* **42**, 1615-17.
BUTLER (G.) and THIRSK (H. R.), 1952. *Acta Cryst.* **5**, 288-9.
COLE (W. F.), WADSLEY (A. D.), and WALKLEY (A.), 1947. *Trans. Electrochem. Soc.* **92**, 133-58.
DUBOIS (P.), 1936. *Ann. Chim.* **5**, 411-82.

- FAULING (G. M.), ZWICKER (W. K.), and FORGENG (W. D.), 1960. *Amer. Min.* **45**, 946-59.
HEWETT (D. F.), 1971. *Econ. Geol.* **66**, 164-77.
JONES (L. H. P.) and MILNE (A. A.), 1956. *Min. Mag.* **31**, 283-8.
LAUDISE, 1961. *Progress in Inorganic Chemistry*, **3**, 1. New York (Interscience).
MCMURDIE (H. F.) and GOLOVATO (E.), 1948. *Journ. Res. Nat. Bur. Stand.* **41**, 589-600.
MOORE (T. E.), ELLIS (M.), and SELWOOD (P. W.), 1950. *Journ. Amer. Chem. Soc.* **72**, 856-66.
ROY (R.) and TUTTLE (O. F.), 1956. *Physics and Chemistry of the Earth*, **1**, ch. 6, 143 (Ed. Ahrens
et al.). Oxford (Pergamon Press).
ROY (S.), 1968. *Econ. Geol.* **63**, 760-86.

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