Hydrothermal Synthesis of Rb-Containing Manganese Dioxides Polymorphs Having Structures of 2×∞, 2×5 and 2×2 Tunnel Sizes

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Manganese dioxide polymorphs of $2 \times \infty$, 2×5, and 2×2 tunnel sizes were obtained by using hydrothermal reaction. The particle shape was found to be characteristic to each polymorph, namely, hexagonal plate-like shape for $2 \times \infty$ and needle-like for 2×5 and 2×2 tunnel sizes. IR spectra of these polymorphs are also reported.

I. INTRODUCTION

Manganese dioxide has a group of polymorphs the structure of which is called tunnel structures.[1] The polymorphs are made up from MnO_6 octahedra linked by sharing their edges or corners. The linkage results in one dimensional hollow pipes in manganese dioxide crystals and thus the pipes are called tunnel structures. The tunnel have cross-sections of various sizes which depend on the way of MnO_6 octahedra linkage. A few amounts of foreign ions, such as alkaline or alkaline earth ions, are usually included in a tunnel and the exact chemical formula of the compound is rather expressed as A_xMnO_2, where A is a foreign ion. The tunnel size is given from its cross-section as $n \times m$ where n and m are the numbers of MnO_6 octahedra constructing the width (wall) and the length of the cross section (roof), respectively. For example, the tunnel size of the crystal in Fig. 1 is expressed as 2×3. We adopted this representation to distinguish the tunnel structures. The
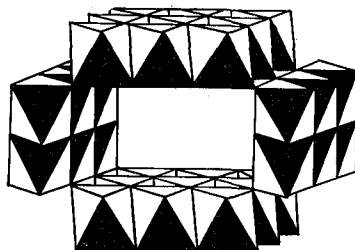

Fig. 1. The tunnel structure of having the size of 2×3.

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description of the overall types of the tunnel structures was presented by Buseck et al. They studied polymorphs of manganese dioxide minerals by HRTEM technique and found coexistence of lattice images of different sizes even in a specimen with macroscopically single phase. The observed sizes of the lattice images were 2×2, 2×4, 2×5, 3×2, 3×5, 3×9 and so on. Based on the results, they classified the manganese dioxide polymorphs into three groups with respect to the tunnel wall height. The first group has a wall height of one MnO_6 octahedron, the second two octahedra and third three octahedra.[2~5] In each group the tunnel roof length can vary from one MnO_6 ($n\times1$) to an infinite number of MnO_6 ($n\times\infty$). The tunnel of the infinite roof length ($n\times\infty$) is just the layer structure. So far only five kinds of tunnel sizes have been confirmed by using single crystal specimen. They are 1×1 of pyrolusite,[6] 1×2 of ramsdellite,[7] 2×2 of hollandite and cryptomelane,[8,9] 2×3 of psilomelane[10] and 2×5 of $Rb_{0.27}MnO_2$.[11] The last one with the biggest tunnel size has recently been prepared in our study by using a hydrothermal technique and the exact crystal structure has also been determined.[12] As a part of studying the manganese dioxide polymorphs, we will report here further experimental study on the formation of polymorphs in Rb-Mn-OH stsyem.

II. EXPERIMENTAL AND TESULRS

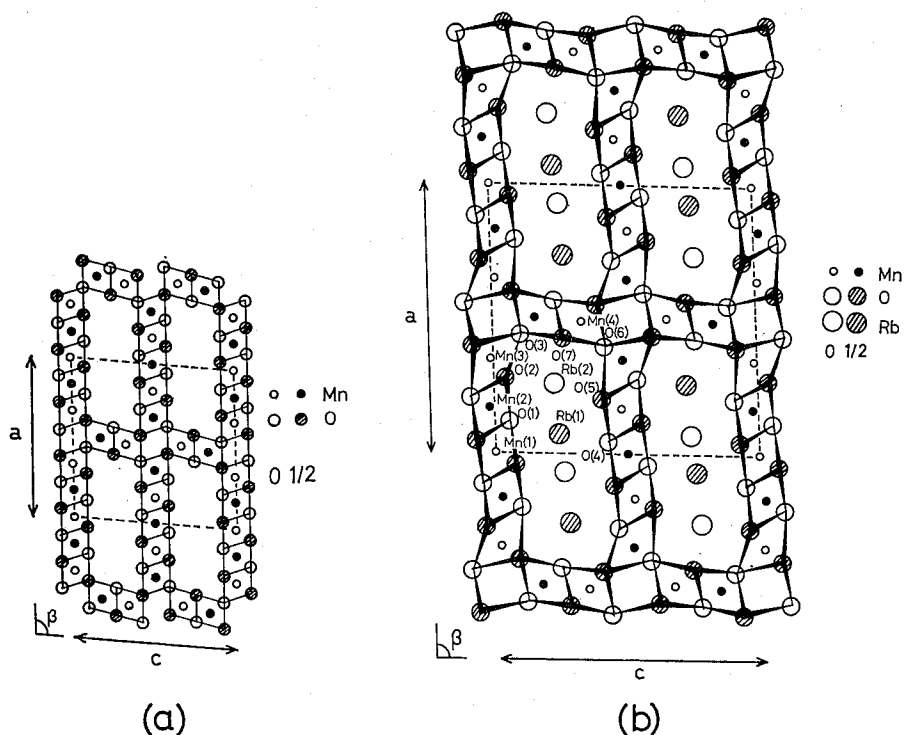1. Powder XDR Pattern of a Model: At first we have calculated powder XDR

Fig. 2. The adopted model (a) and the obtained real structure (b) of 2×5 tunnel.
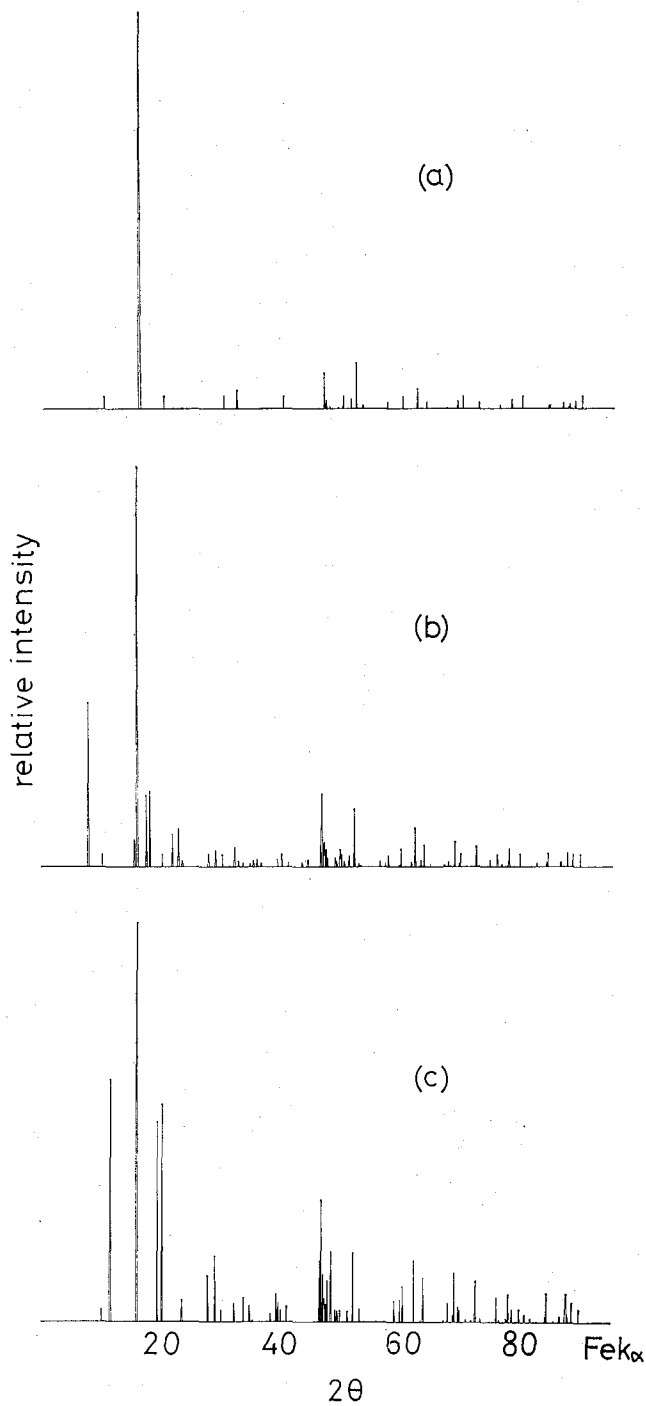
Fig. 3. The calculated powder XDR patterns of various tunnel sizes.
(a) $2 \times \infty$, (b) 2×5 and (c) 2×3.

patterns of tunnel structures having a fixed wall height of two MnO_6 octahedra $(2 \times m)$. A structure model was based on the psilomelane of 2×3 tunnel size in which each MnO_6 octahedron has a non-distorted ideal form. The tunnel size becomes larger with increasing m or the number of MnO_6 octahedra forming tunnel roof. The crystal symmetry is assumed to be monoclinic ($\beta = 92.5°$) after the psilo-melane crystal. As an example the adopted model of the 2×5 tunnel size is shown in Fig. 2, together with the MnO_6 octahedra arrangement of the real crystal struc-ture, where accommodation of foreign ions in a tunnel is neglected. For the $2 \times \infty$ tunnel size, the atomic scattering factor of MnO_6 octahedra forming a wall is as-sumed to be zero in order to represent the infinite number of tunnel length. The calculated XDR patterns for $FeK\alpha$ radiation are shown in Fig. 3. Two XDR patterns for the 2×5 tunnel size, one is obtained from the real lattice parameters and the other from the model calculation are in good agreement. For the 2×3 tunnel size, the calculated XDR pattern is also in good agreement with the observed one for psilomelane. In the case of the 2×2 tunnel size, however, the observed XDR pattern is much simpler than the calculated one. The discrepancy is rather natural for MnO_6 octahedra in hollandite crystal (real crystal of the 2×2 tunnel
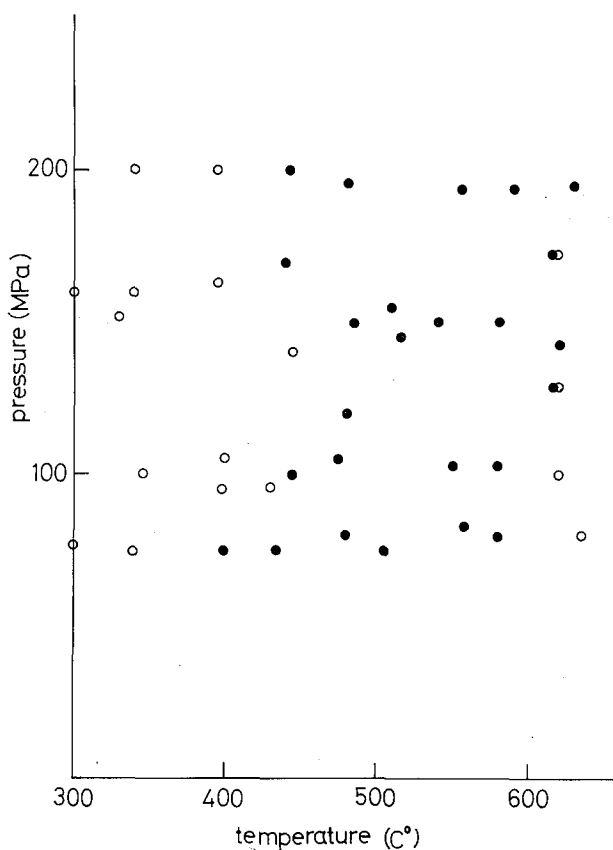

Fig. 4. The formation diagram of Rb-Mn-OH system where saturated RbOH solution being used as a reagent. ● 2×5, ○ $2 \times \infty$ tunnel sizes,

size). The distortion of the octahedron brings the crystal lattice in higher symmetry than that of the adopted model. As a whole, in spite of rough approximation, the model is in good approximation to the real crystal structure and the calculated powder XDR pattern can be used as the standard to identify the phase of products.

2. Formation diagram of Rb-Mn-OH system: Experimental facility is a conventional reaction vessel of test-tube type. A mixture of 10 mg β-MnO_2 and 0.3 cc RbOH solution of the desired concentration was sealed in an Ag-tube ($0.5\phi \times 60$ mm). The tube was inserted into the reaction vessel and heat treated for 48 h. After the reaction the vessel was quenched to room temperature, the obtained precipitate was filtered, washed with distilled water and dried at room temperature. Phase identification of the product was carried out by a conventional XDR method. Particle shape was observed by a SEM measurement. The reaction conditions were between 300°C and 600°C and up to 200 PMa. An example of the formation diagram of Rb-Mn-OH system is given in Fig. 4 where saturated RbOH solution was used as a starting reagent. The formation of two kinds of the compounds are found in the diagram. One of them is obtained in the intermediate range of the reaction temperature and confirmed to be the manganese dioxide of 2×5 tunnel size. This compound has a platy needle-like shape as shown in the SEM photograph of Fig. 5 (b). In both regions of the lower and the higher temperatures, precipitates of hexagonal plate-like shape were obtained. Though the reaction
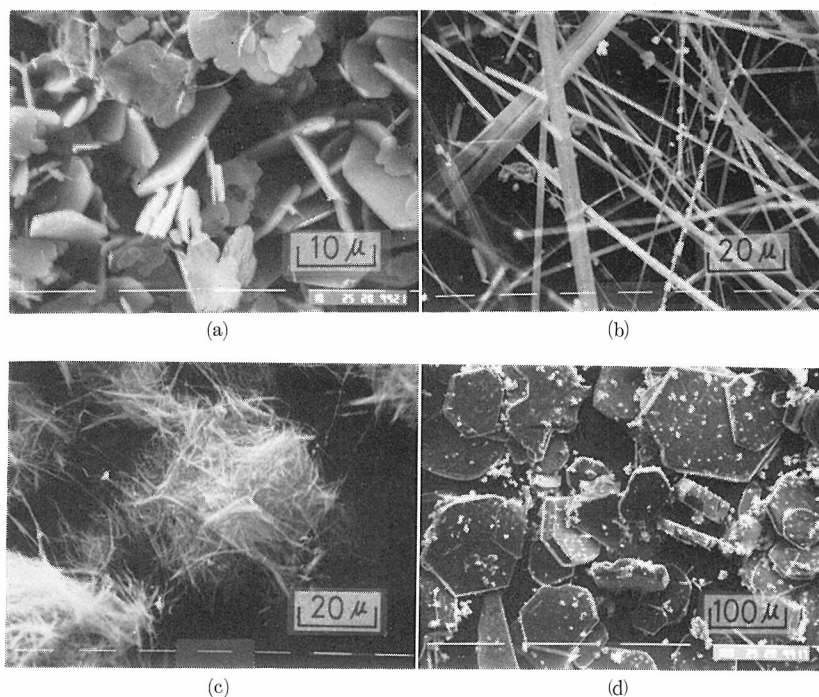

(a)

(b)

(c)

(d)

Fig. 5. The SEM photographs of manganese dioxide polymorph of various tunnel size
(a) $2 \times \infty$, (b) 2×5, (c) 2×2 and (d) $2 \times \infty$.

temperatures were quite different, the both precipitates gave the same XDR pattern. By comparison with the calculated XDR patterns, the observed pattern of the hexagonal shaped precipitate is in qualitative agreement with the calculated pattern of $2 \times \infty$ tunnel size. The discrepancy of the peak heights between the observed and the calculated pattern is considered to arise from the following reasons, the existence of foreign ions and the distortion of MnO_6 octahedra of the real lattice were neglected in the calculation. Therefore we may concluded that the hexagonal
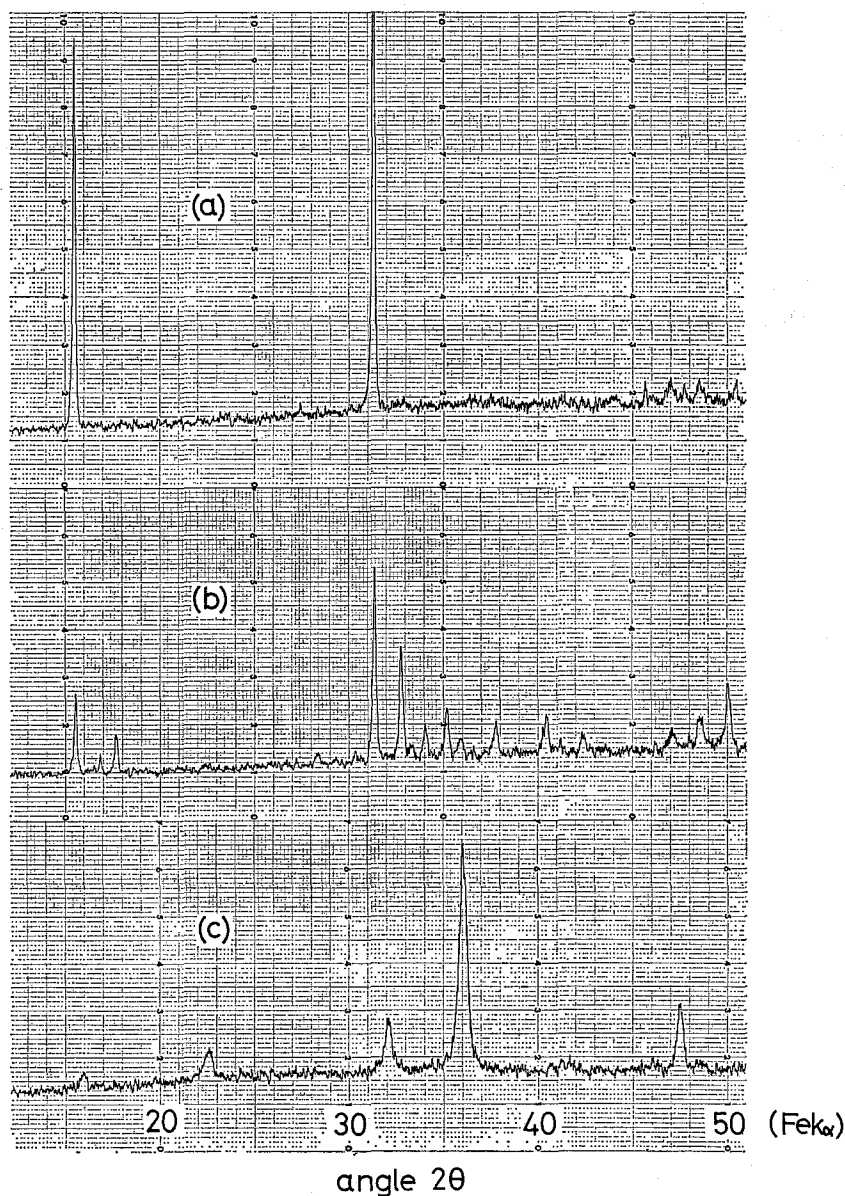

Fig. 6.   The observed powder XDR patterns (a) $2 \times \infty$, (b) 2×5 and (c) 2×2.

plate-like shaped crystal is of the $2 \times \infty$ tunnel size or layer structure. The lattice parameters of the crystal are $a=4.8$ Å, $b=2.9$ Å, $c=14.32$ Å and $\beta=92.5°$. The chemical analysis showed that the compound has a chemical formula of $Rb_{0.3}$ MnO_2. When concentration of RbOH solution was diluted to less than 6N, the hollandite type of 2×2 tunnel size appeared instead of the polymorph of 2×5 tunnel size. In Fig. 5 (c), a SEM photograph of the compound of 2×2 tunnel size is shown, the compound also has a needle-like crystal shape. The powder patterns of the obtained three polymorphs are shown in Fig. 6.

3. IR spectrum: Potter and Rossman measured IR spectra of the manganese dioxide polymorphs systematically for various kinds of samples and found the following experimental rule.[13] When plotted the wave numbers of major bands for lattice vibration mode to the numbers of shared edges per MnO_6 octahedron, the major bands shift to lower wave number with increasing the number of shared edges. We measured IR spectra of the newly obtained two species of 2×5 and $2 \times \infty$ tunnel sizes and examined whether the experimental rule of Potter and Rossman can be applied to the new species. The polymorph of 2×5 tunnel size is constructed with the mixture of three MnO_6 octahedra of having six shared edges and four MnO_6 octahedra of having four shared edges. Therefore the number of average shared edges per MnO_6 octahedron is 4.86. The layer structure of the $2 \times \infty$
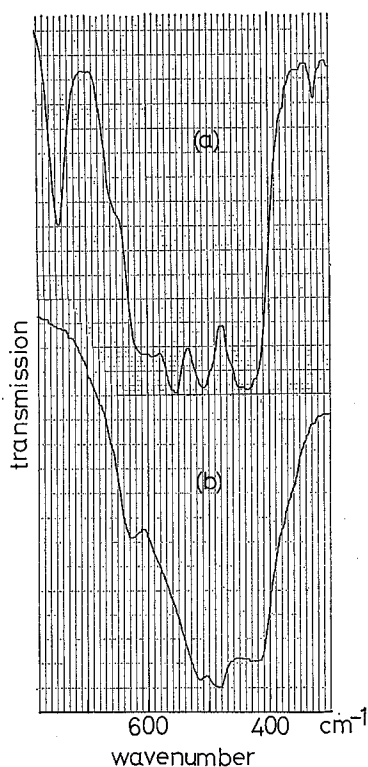

Fig. 7. The observed IR spectra of two tunnel sizes (a) 2×5 and (b) $2 \times \infty$.
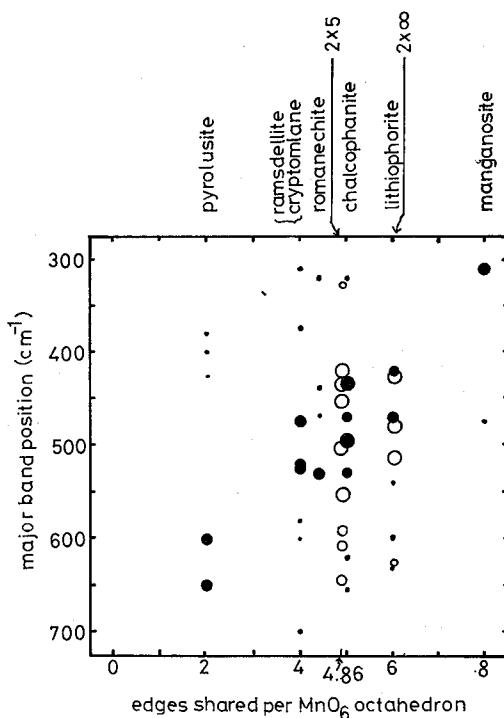
Fig. 8. Correlation of wave numbers vs. number of shared edges
per MnO_6 octahedron in various kinds of manganese
dioxides (The graph dotted with solid circle being copied
from R.M. Potter and G.R. Rossman, Amer. Minel., **64**
1219 (1979)), observed wave numbers by this work of
$2 \times \infty$ and 2×5 tunnel size being given by open circles.

tunnel size has six shared edges per MnO_6 octahedron. The observed IR spectra
for the two new polymorphs are shown in Fig. 7. The IR spectra for polymorphs
of 2×5 and $2 \times \infty$ tunnel sizes have peaks at 745, 610, 590, 550, 510, 445, 430 and
325, and 630, 515, 480 and 420 cm^{-1}, respectively. In Fig. 8 the graph of wave
number vs. number of shared edges per MnO_6 octahedron is reinserted which was
given by Potter and Rossman. The experimental data of the present study are
also given in the figure with open circle. It is found that the Potter and Rossman's
rule is well adopted for the polymorph of 2×5 tunnel size. Of newly obtained
specimen of layer structure the rule is also roughly adopted.

III. CONCLUSION

In Rb-Mn-OH system it was affirmed that at least three polymorphs of man-
ganese dioxide were obtained by hydrothermal reactions. Existence of manganese
polymorphs which have the other tunnel sizes as predicted by Buseck et al from
their HRTEM study is still the problem left behind.

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