

Preparation of α -MnO₂ with an Open Tunnel

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A single-phase α -MnO₂ without any large stabilizing cations was successfully prepared by starting from hollandite-type (NH₄)_xMn₈O₁₆ and quenching from 440°C during heating in flowing Ar. The unit-cell dimension was determined by XRD analysis to be $a = 10.308(2)$ Å and $c = 2.854(1)$ Å. In comparison with that of the starting material ($a = 9.896(1)$ Å and $c = 2.859(1)$ Å), the a dimension increased while the c dimension changed little. No presence of ammonium ions in the structure of this specimen was shown by IR spectroscopy, the Kjeldahl analysis, or temperature-programmed-desorption (TPD) measurement. The structural change from the hollandite phase to Mn₂O₃ was observed at 540°C. TPD analysis indicates the presence of nitrogen other than ammonium ions in the hollandite material we prepared, and also suggests that this nitrogen might have a strong chemical interaction to the hollandite structure. © 1999

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Key Words: α -MnO₂; hollandite structure; ammonium ion; quench; 440°C.

INTRODUCTION

α -MnO₂s naturally occur as manganese dioxide minerals like cryptomelane, hollandite, and coronadite. Originally α -MnO₂s were named for products obtained by the reduction of a KMnO₄ solution with various reducing agents (1,2). Recently, α -MnO₂s have come to refer to isostructural minerals and the artificial MnO₂ that have the so-called hollandite structure. In these materials, manganese ions are in MnO₆-octahedra, which are linked to form double octahedral zigzag chains along the c axis by edge-sharing, as shown in Fig. 1a. These chains share their corners with each other to form approximately square tunnels parallel to the

c axis (Fig. 1b). The large cations are located within the tunnels, being surrounded by eight oxygen ions. The crystal symmetry is mostly tetragonal (space group; $I4/m$), but monoclinic ($I2/m$) symmetry was observed in some hollandites (3). The general formula of α -MnO₂ is given as $A_{2-x}Mn_{8-y}X_{16}$ (A represents the ions such as K⁺, Ba²⁺, Pb²⁺ or NH₄⁺, and X is O²⁻ or OH⁻) and the charge of the large cations is compensated by reducing Mn oxidation state in the framework. For many years, it was assumed that Mn²⁺ was present based on oxidation-reduction potential arguments that Mn²⁺ and Mn⁴⁺ are more stable than Mn³⁺. But recent results of structure refinements for hollandite and cryptomelane reported by Post and Yamamoto tend to support the conclusion that Mn³⁺ is the reduced form of Mn, because the mean Mn–O bond lengths in MnO₆ octahedron calculated from the refinement suggest that Mn³⁺ is more easily accommodated in the structures than the larger Mn²⁺ (3,5). α -MnO₂s have been intensively examined as superionic conductors (6,7) and as possible encapsulators for radioactive waste (8–10).

It has been considered for a long time that some large cations in the square tunnel are necessary to prevent collapse of the hollandite structure. Sreenivas investigated the structural stability of cryptomelane by removing some parts of K⁺ ions from the tunnel by means of electro dialysis (11). They found that cryptomelane became more and more distorted in attempting to keep a hollandite framework as the amount of K⁺ ions decreased and was finally converted into γ -MnO₂. The potassium-free cryptomelane was discovered in nature by Neganna, and the presence of that manganese oxide free of potassium was revealed (12). The first preparation of α -MnO₂ without any large stabilizing cations in the tunnel was reported by Rossouw (13). This

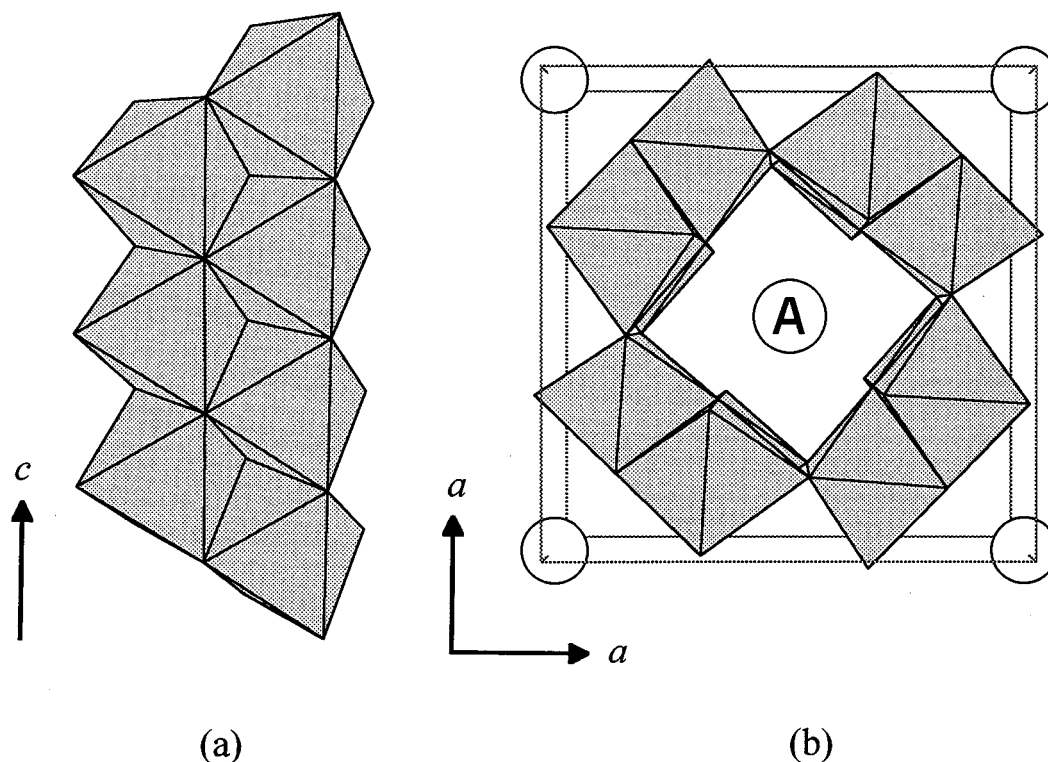


FIG. 1. Representation of the hollandite structure of $A_{2-x}Mn_8O_{16}$ (A represents ions such as K^+ , Ba^{2+} , Pb^{2+} , or NH_4^+) projected (a) along c axis and (b) along a axis.

material was synthesized by almost entire dehydration of its hydrated compound, $MnO_2 \cdot 0.2H_2O$ at $300^\circ C$, which was prepared by acid treatment of Li_2MnO_3 . They also found that the α - MnO_2 framework was retained up to at least $400^\circ C$.

The purpose of this work is to prepare α - MnO_2 without any large stabilizing cations in the tunnel. The material is prepared by starting from the hollandite-type $(NH_4)_xMn_8O_{16}$ and heating to remove all ammonium ions from its structure. The first step is to synthesize $(NH_4)_xMn_8O_{16}$ as a starting material and to study the thermal stability of its hollandite structure. The prepared compounds are characterized by X-ray powder diffraction, electron diffraction, infrared absorption, and Kjeldahl analysis.

EXPERIMENTAL

The starting material, $(NH_4)_xMn_8O_{16}$ was prepared from Mn_2O_3 by a wet method reported by Ohzuka (14). The powder of Mn_2O_3 was heated at $800^\circ C$ before use. A 250-ml H_2SO_4 solution with 0.5 M $(NH_4)_2SO_4$ was heated in a flask at $95^\circ C$, and then 10 g of Mn_2O_3 was added into this solution. This solution was kept at $95^\circ C$ for 7 days and cooled to room temperature. The crystalline product was

isolated by suction filtration, washed with distilled water, and then preheated at $60^\circ C$ in air. Finally, the product was dried under vacuum at $150^\circ C$ for 24 h. The prepared samples were examined by X-ray powder diffraction (XRD) using monochromated $CuK\alpha$ radiation. Both thermogravimetric and differential thermal analyses (TG-DTA) were done using a Sinku-Riko TGA-7000. Temperature-programmed-desorption (TPD) analysis was carried out using a BEL Japan Inc. Multitask T.P.D., with Ar as an internal standard. The unit-cell dimension was determined from the observed d spacings by least-squares method. Electron diffraction (ED) work was carried out using a 200-kV electron microscope (JEOL 2000EX) with a sample holder of tilt angle $\pm 60^\circ$. The presence of ammonia was examined by infrared (IR) spectroscopy and the Kjeldahl method.

RESULTS AND DISCUSSION

Figure 2 shows the X-ray powder diffraction pattern of the starting material. By XRD analysis, this material was found to be a single phase. The XRD pattern is similar to that of $(NH_3)_2Mn_8O_{16}$ in the JCPDS files (No. 29-105) and is indexed with a tetragonal cell. The a and c dimensions of the starting material were determined to be $a = 9.896 \text{ \AA}$ and $c = 2.859 \text{ \AA}$. This value is in good agreement with that of the

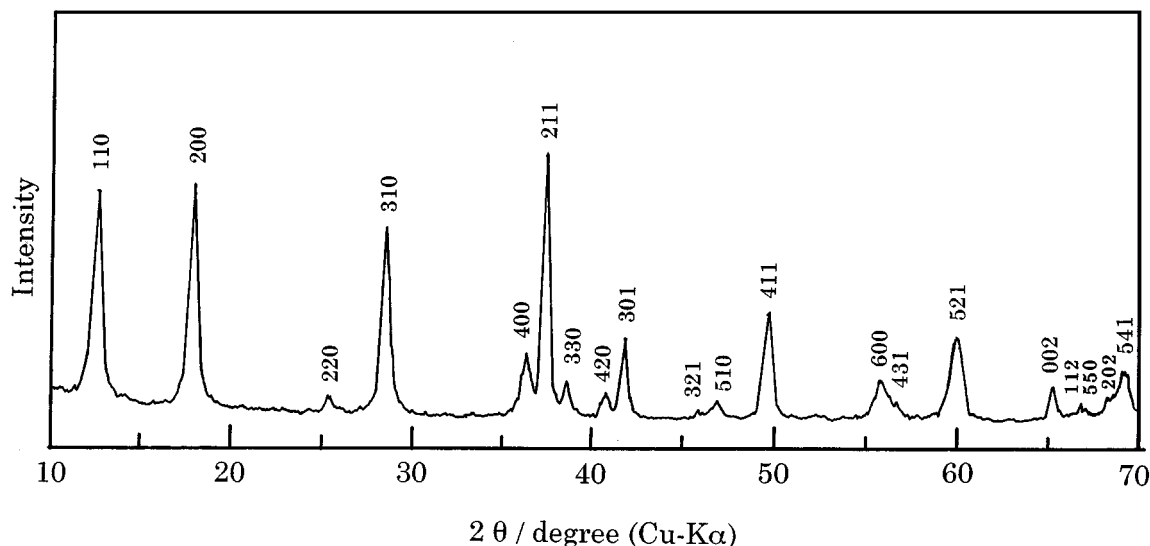


FIG. 2. X-ray powder diffraction pattern of the starting material, $(\text{NH}_4)_x\text{Mn}_8\text{O}_{16}$.

previous work (14). The tetragonal symmetry of the starting material was also confirmed by ED studies. The presence of ammonium ions in the starting material was confirmed by both infrared spectroscopy and the Kjeldahl method.

Both thermogravimetry and differential thermal analyses of the starting material were carried out up to 700°C at a heating rate of $5^\circ\text{C}/\text{min}$ in flowing Ar. The obtained TG-DTA curve is shown in Fig. 3. The weight decreased only slightly up to 220°C , and then a remarkable weight decrease started. This weight change became less remarkable at around 400°C , and again started to decrease from 450°C . No more significant weight loss was observed above 570°C . On the other hand, an exothermic peak was observed at 540°C , accompanied with the weight loss. The origin of this peak will be discussed later.

The starting material was quenched to room temperature from various temperatures during heating in flowing Ar and the obtained specimens were examined by XRD. XRD measurements were carried out in air. These quenched specimens were hygroscopic, but were checked by TGA not to absorb water during XRD measurements in air. As will be shown, no band attributed to absorbed water (around 1600 cm^{-1}) was observed either during IR spectroscopy. After the measurement, the specimens were kept in a dry box.

Figure 4 shows the X-ray diffraction patterns of specimens quenched from several temperatures. The X-ray diffraction pattern of the specimen quenched from 280°C (Fig. 4a) shows little change from that of the starting material. At 350°C (Fig. 4b), although the starting material phase was retained, the peak intensity got weaker and the peak width at low angles became broader than that of the starting material. In addition, a few new peaks appeared at angles

lower than (310) and (211) peak positions. In the X-ray diffraction pattern at 440°C (Fig. 4c), a new ($h00$) peaks appeared at lower angles than the corresponding ($h00$) peaks of the starting material, although the peaks at lower angles showed weaker intensity. This indicates that the a dimension increased from that of the starting material. The specimen quenched from 440°C was found to be a single phase and indexed with the same tetragonal symmetry as the starting material, implying that the tetragonal

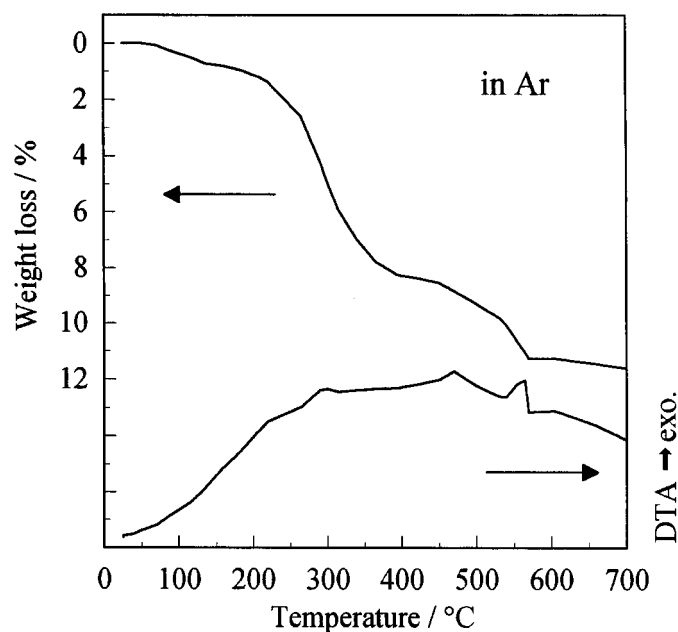


FIG. 3. Weight loss of the starting material with a heating rate of $5^\circ\text{C}/\text{min}$ in flowing Ar.

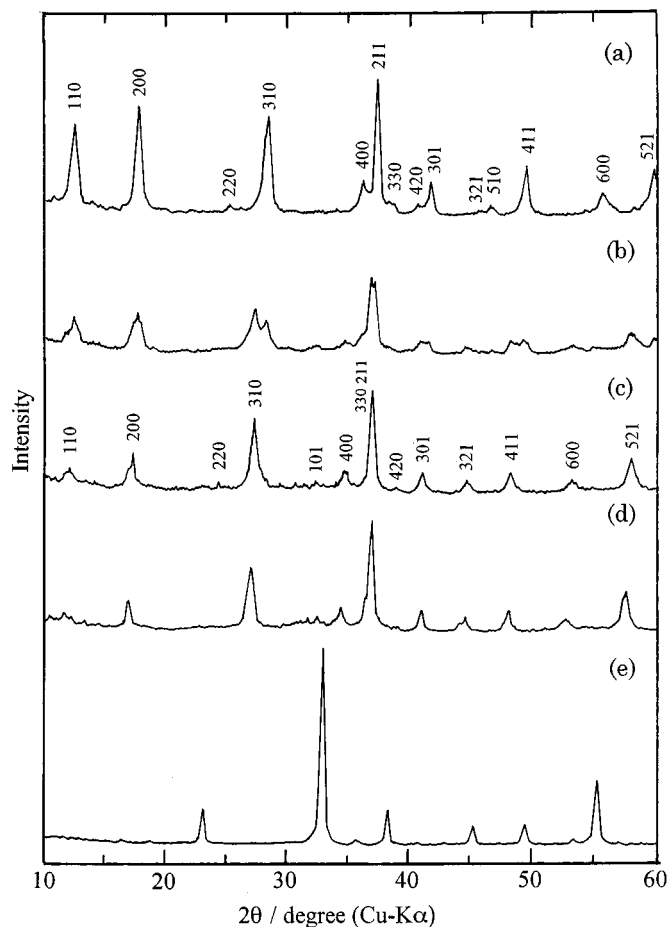


FIG. 4. X-ray powder diffraction patterns of the specimens quenched to room temperature from (a) 285°C, (b) 350°C, (c) 440°C, (d) 525°C and (e) 670°C.

hollandite structure was still retained up to at least 440°C. A similar X-ray diffraction pattern was observed 525°C (Fig. 4d), while the (110) peak almost disappeared. The starting material phase changed completely to Mn₂O₃ pattern at 670° (Fig. 4e).

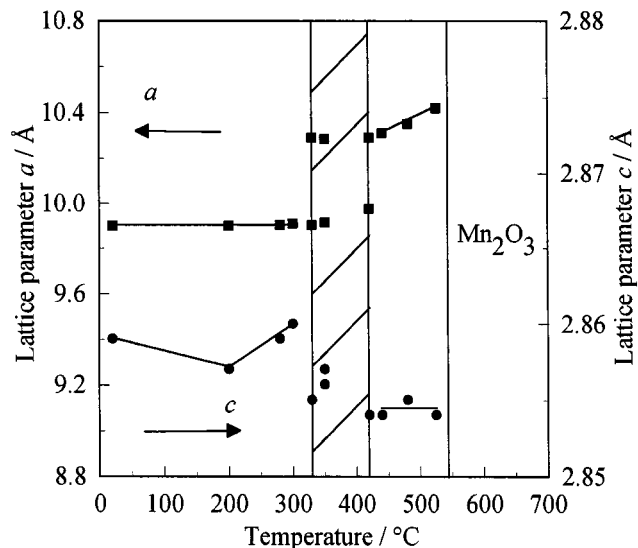


FIG. 5. Dependence of a (closed squares) and c (closed circles) dimensions on the various quenched temperatures.

Dependence of a and c dimensions on the various quenched temperatures is shown in Fig. 5. The a dimension of the starting material did not change significantly up to about 300°C. The specimens quenched in the temperature range from 320 to 420°C, where the weight decreased remarkably, were composed of mixed phases of the starting material with $a = 9.90$ Å and the specimen with $a = 10.30$ Å. The a dimension increased with increasing quenched temperature from $a = 10.31$ Å at 440° to $a = 10.41$ Å at 525°C. The specimen was found to become Mn₂O₃ above 570°C, indicating that the exothermic peak observed at 540°C corresponds to the structural change from the hollandite α -MnO₂ to Mn₂O₃. This means that the hollandite structure of (NH₄)_xMn₈O₁₆ is stable up to 540°C, higher than that reported by Rossouw (13). The c dimension decreased slightly up to 220°C and then increased in the temperature range of $220^\circ\text{C} \leq T \leq 300^\circ\text{C}$, where a large weight loss was observed by TG measurements. The c dimension of the specimen quenched

TABLE 1
The Structural Symmetry, a and c Dimensions, and Unit-Cell Volume of the Starting Material, the Specimen Quenched from 440°C, Li_x(NH₄)_{1.41}Mn₈O₁₆ and Dehydrated α -MnO₂

Materials	Structural symmetry	a dimension/Å	c dimension/Å	Unit-cell volume /Å ³	References
Starting material	Tetragonal	9.896(1)	2.859(1)	280.0(1)	This work
Specimen quenched from 440°C	Tetragonal	10.308(2)	2.854(1)	303.3(1)	This work
Li _x (NH ₄) _{1.41} Mn ₈ O ₁₆ with increasing x	Tetragonal	9.90–10.40	2.85	279–308	(14)
Dehydrated α -MnO ₂	Tetragonal	9.7876	2.8650	274.45	(13)

TABLE 2

Observed d Values and Intensities of the Diffraction Lines for the Starting Material ($a = 9.896(1) \text{ \AA}$ and $c = 2.859(1) \text{ \AA}$) and the Specimen Quenched from 440°C ($a = 10.308(2) \text{ \AA}$ and $c = 2.854(1) \text{ \AA}$) with a Tetragonal Cell

Starting material			Specimen quenched from 440°C		
hkl	$d_{\text{obs.}}/\text{\AA}$	Intensity	hkl	$d_{\text{obs.}}/\text{\AA}$	Intensity
110	7.0	77	110	7.3	13
200	4.94	85	200	5.15	36
220	3.49	7	220	3.64	9
310	3.12	71	310	3.26	70
400	2.468	24	101	2.754	8
211	2.398	100	400	2.577	18
330	2.330	13	330/211	2.427	100
420	2.208	10	420	2.305	6
301	2.159	30	301	2.197	19
321	1.975	3	321	2.020	14
510	1.937	6	411	1.880	21
411	1.835	40	600	1.717	11
600	1.644	15	521	1.589	32
431	1.626	13			
521	1.543	31			

above 440°C was almost constant, but slightly smaller than that of the starting material.

The structural symmetry, a and c dimensions, and the unit-cell volume of the starting material and the specimen quenched from 440°C are shown in Table 1 together with those of $\text{Li}_x(\text{NH}_4)_{1.41}\text{Mn}_8\text{O}_{16}$ (14) and dehydrated $\alpha\text{-MnO}_2$ (13) for comparison. Indices, d values, and intensities of the starting material and the specimen quenched from 440°C are shown in Table 2. The a and c dimensions of the quenched specimen were estimated to be $10.308(2)$ and $2.854(1) \text{ \AA}$, showing that the a dimension increased by about 0.4 \AA from that of the starting material, while the c dimension changed little. The unit-cell volume of the quenched specimen was estimated to be $303.3(2) \text{ \AA}^3$, which was larger by 8.3% than that of the starting material ($280.0(1) \text{ \AA}^3$). The unit-cell dimension of the quenched specimen is different from that of dehydrated $\alpha\text{-MnO}_2$ but similar to that of $\text{Li}_x(\text{NH}_4)_{1.41}\text{Mn}_8\text{O}_{16}$ prepared by inserting lithium ions into the tetragonal hollandite-type material, $(\text{NH}_4)_{1.41}\text{Mn}_8\text{O}_{16}$. Considering that the reduction of manganese in $(\text{NH}_4)_{1.41}\text{Mn}_8\text{O}_{16}$ occurred due to the insertion of lithium ion, we suggest that the manganese ions in the starting material were reduced during heating up to 440°C in flowing Ar.

Electron diffraction (ED) patterns of the specimen quenched from 440°C , taken with the incident electron beam parallel to the $[010]$ and $[1\bar{1}1]$ direction, are shown in Figs. 6a and 6b, respectively. They were quite similar to those of the starting material, indicating that the two structures are closely related. These patterns can be indexed

with tetragonal symmetry. The a and c dimensions estimated from ED were consistent with those determined from XRD analysis. However, some diffraction patterns show streaking or even some diffuse rows, which could be attributed to some defects in the MnO_2 octahedral stacking. These features may relate to the broad and weak intensity of

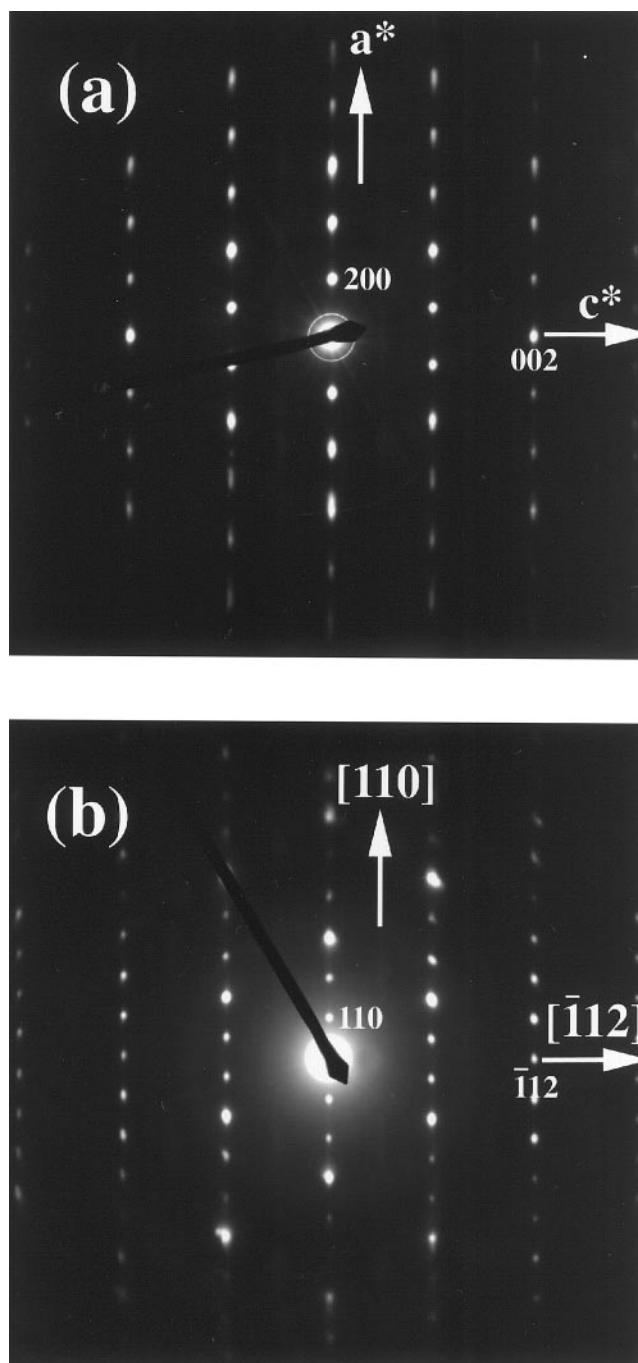


FIG. 6. Electron diffraction patterns of the specimen quenched from 440°C taken with the incident electron beam parallel to the (a) $[010]$ and (b) $[1\bar{1}1]$.

the peaks observed in the X-ray diffraction pattern of the specimen quenched from 440°C, as shown in Fig. 4c.

Figures 7a and 7b show the IR spectra of the starting material and the specimen quenched from 440°C, respectively. The starting material exhibited a small band at 3178 cm⁻¹ and a narrow band at 1407 cm⁻¹. These two bands agree with the frequencies of the stretching the deformation vibrations of ammonium ion (15). The spectra below 1000 cm⁻¹ exhibited approximately the same bands at ca. 715, 523, and 475 cm⁻¹ as those of cryptomelane reported previously (16). Interestingly, the intensity of the band at 1407 cm⁻¹ disappeared in the IR spectrum of the specimen quenched from 440°C (Fig. 7b). This suggests that there are no ammonium ions in the quenched specimen. Nonexistence of ammonium ions was also confirmed by the Kjeldahl method. This is in good agreement with the result of IR spectroscopy.

The TG and temperature-programmed-desorption (TPD) measurements of the specimen quenched from 440°C were carried out at a heating rate of 5°C/min in flowing Ar. The TG curve and TPD analysis are shown in Figs. 8a, 8b, and 8c, respectively. In Fig. 8a, the weight change exhibited two steps: the first weight change took place gradually up to about 200°C and then started again at 400°C as a second step. According to the results of TPD analysis in Fig. 8b, the first step was due to the desorption of water molecules from the structure. This was caused by the removal of adsorbed waters in the structure, showing that this quenched specimen absorbed waters in spite of having been kept under a dry condition. More in detail, the desorption of water was observed a few times in this step, suggesting that there are a few kinds of adsorbed water with different chemical environment in the structure. The second step corresponded to the loss of oxygen from the structure and total weight change in this step was estimated to be about 3.4%, which is

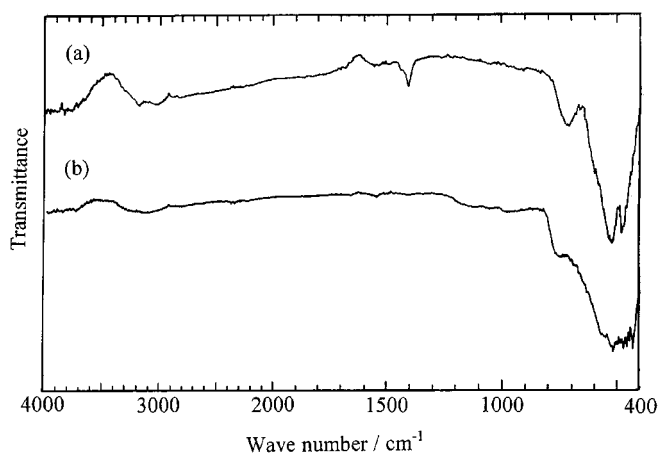


FIG. 7. IR spectrum of (a) the starting material and (b) the specimen quenched from 440°C.

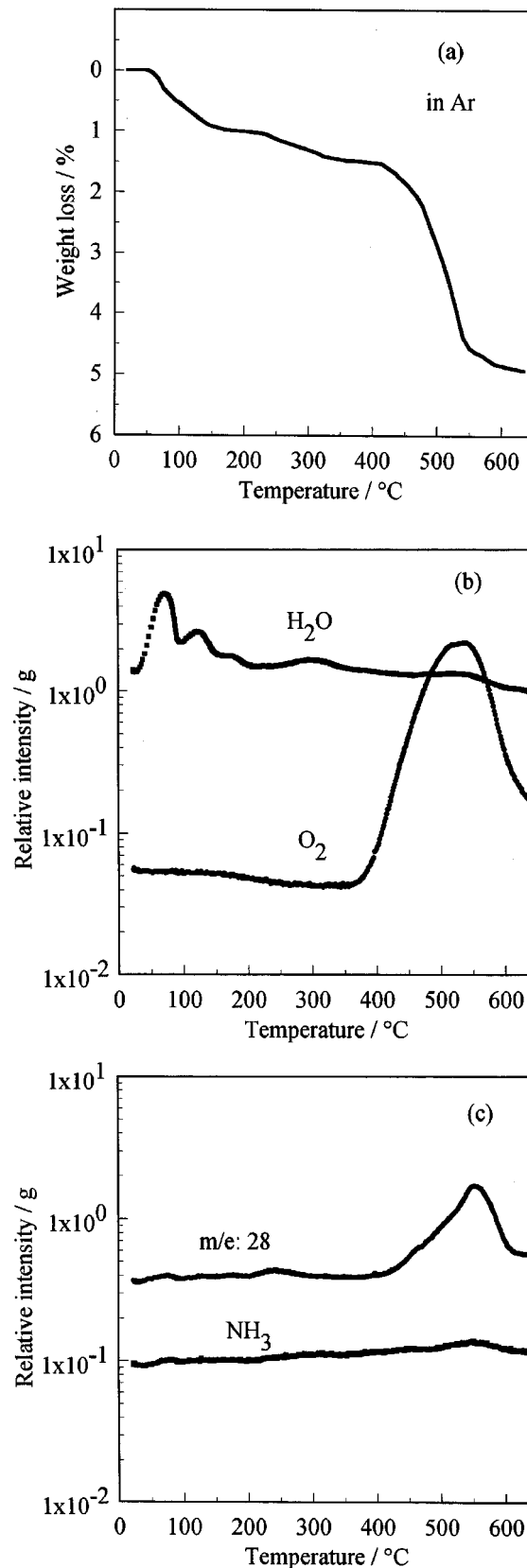


FIG. 8. (a) Weight loss, and both (b) and (c) TPD analysis of the specimen quenched from 440°C with a heating rate of 5°C/min in flowing Ar.

consistent with that shown in Fig. 3 (3.2%). Manganese ions in the structure were reduced by this oxygen removal and according to the previous report (14), this reduction of manganese causes the expansion of the a dimension of the hollandite structure, as shown in Fig. 5.

In Fig. 8c, ammonia was not significantly detected by TPD analysis of the quenched specimen, which is in good agreement with the results of both IR spectroscopy and Kjeldahl analysis. These results indicate that the ammonium-free α -MnO₂ was successfully prepared by starting from the hollandite-type (NH₄)_xMn₈O₁₆ and quenching from 440°C in flowing Ar. Interestingly, a gas species with mass number 28 was detected during the second step in the temperature range from 400 to 650°C. The mass number 14 was also observed in this temperature region with the same temperature dependence as the mass number 28. This suggests that both two gas species with different mass number come from the same source. In this case, nitrogen can be proposed as a source, implying that some nitrogens still remain in the structure as an ionic form. Considering the result that the mass number 28 was detected mostly around 540°C, where a structural change from hollandite phase to Mn₂O₃ was observed, we suppose that there are some kinds of strong chemical interactions between nitrogen and the hollandite structure. Further work would be necessary to discuss the presence of nitrogen and its role in the hollandite structure.

CONCLUSION

The α -MnO₂ without any large stabilizing cations in its tunnel was successfully prepared by starting from the hollandite-type (NH₄)_xMn₈O₁₆ and quenching from 440°C in flowing Ar. This hollandite structure was verified by XRD and ED analyses. No NH₄⁺ in the structure of this specimen

was detected by the IR spectroscopy, the Kjeldahl analysis, or TPD measurement. The hollandite phase was found to be stable up to 540°C in flowing Ar. TPD analysis suggested the presence of nitrogen other than ammonium ions in the hollandite material, and also that this nitrogen had a strong chemical interaction to the hollandite structure.

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