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Thermal and Physical Properties of Hollandite-Type $K_{1.3}Mn_8O_{16}$ and $(K,H_3O)_xMn_8O_{16}$

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Two kinds of samples of cryptomelane: synthetic single crystals of $K_{1.33}Mn_8O_{16}$ (A) and $(K,H_3O)_xMn_8O_{16}$ powder prepared by aqueous chemistry (B) were studied by thermogravimetry, magnetic, and electrical (dc and ac) measurements. B loses water at 100–185°C. A and B are decomposed in the range 460–610°C into Mn_2O_3 in air and MnO, under vacuum. They are antiferromagnetic with T_N 18 K (A), 11 K (B). A is a semiconductor with $\sigma(300\text{ K}) \sim 3\ \Omega^{-1}\text{ m}^{-1}$ and $E_\sigma = 0.38$ eV. The ac measurements did not reveal any significant contribution of ionic conduction up to 740 K.

Introduction

In spite of the wide applications of manganese dioxide, the knowledge of the basic structural and physical properties of this material is very incomplete. Its crystal chemistry is complex (*1–3*). Well-characterized samples or single crystals are difficult to obtain (*1, 4*). Most "MnO_2" allotropic forms are actually nonstoichiometric. This happens in α-MnO_2, also known by the names "cryptomelane" and "hollandite," corresponding to minerals containing potassium or barium as other major constituents, respectively. The hollandite structure (see Fig. 1) contains large square channels between double rutile-like chains of (MnO_6) octahedra (*5*). It is stabilized by partial occupation of the channels by uni- or divalent cations of suitable size (Na, K, Ba, Pb), so that the actual formula of "α-MnO_2" is $A_x^+Mn_{8-x}^{4+}Mn_x^{3+}O_{16}$ ($x < 2$) where A is a univalent cation.

Because of their channel structure, hollandite-type compounds have been intensively studied recently as candidates for either one-dimensional fast ionic conduction (*6*) or as host materials for nuclear waste immobilization (*7*). Most works in this field dealt with titanium hollandites, $A_x(Ti_{8-y}B_y)O_{16}$, where the A-cation charge is compensated by replacing yTi^{4+} by di- or trivalent cations B of suitable size. These compounds are very stable and easy to prepare by standard solid state chemistry techniques (*8*).

Manganese hollandites $A_xMn_8O_{16}$, which are actual mixed-valence compounds, have been studied to a lesser degree. Available data are limited to (i) structure refinements on natural crystals containing a variety of impurities on A and Mn sites (*9*), (ii) hydrothermal crystal synthesis by Yamamoto *et al.* (*10*), who reported the compound to be antiferromagnetic below ~24.5 K. Another point of interest is the electrical conductiv-

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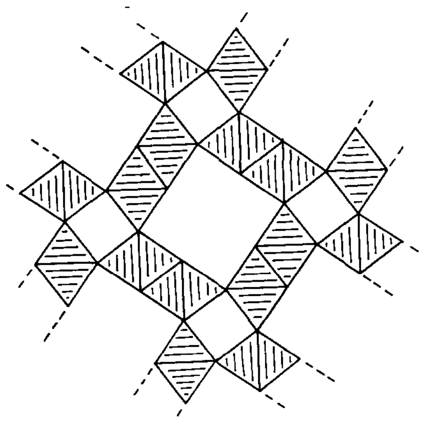

FIG. 1. Projection of the cryptomelane/hollandite structure along c (tetragonal). Only (MnO_6) octahedra are shown; the A cations lie in the large channels.

ity (ionic and electronic). The latter has been a subject of controversy for "MnO_2." The only available single-crystal measurements on stoichiometric, (rutile-type) β-MnO_2 showed a peculiar (metallic) temperature dependence of the resistivity (*13*), while polycrystalline samples were reported as semiconductors (*12–14*). There is no data available for $A_xMn_8O_{16}$ hollandites.

We succeeded in growing single crystals of cryptomelane $A_xMn_8O_{16}$ (A = K, Rb) using an electrolytic technique (*4*). Here we report the results of physical studies on single-crystal $K_xMn_8O_{16}$ as well as on the powdered hydrated samples with the same structure. A detailed crystallographic study of $K_xMn_8O_{16}$ will be published elsewhere (*15*).

Experimental

The crystal growth procedure has been described in detail previously (*4*). All single crystals used here were obtained from a single electrolysis run (run C in Ref. (*4*)) which was carried out at 778 K from a molten potassium vanadate flux containing $MnCO_3$. Crystals deposited by oxidation on the anode were needles up to 2 mm long, with a length/width ratio ≈ 10. The needle direction corresponded to the hollandite tetragonal c-axis. Powder samples were prepared following the procedure given by Parida *et al.* as "sample 3" (*16*), which involves (a) reduction of aqueous $KMnO_4$ by 6 M HCl at 80°C, (b) leaching the precipitate in boiling 3 M HNO_3. Crystals were examined by scanning electron microscopy and electrode microprobe analysis. Powders were analyzed by atomic absorption spectrophotometry for K and total Mn, and by thermogravimetry for H_2O. Additional redox titrations by the oxalate method (*24*) were carried out to determine the actual oxidation state of manganese in powder samples.

Magnetic susceptibilities were determined using the Faraday technique in a 660 kA/m field in the temperature range 3–300 K. No correction for core diamagnetism was applied. The dc electrical resistance R along c was measured on several crystals using a collinear 4-probe arrangement between 77 and 300 K. Voltage drop at low temperatures was measured by a Keithley Model 610 electrometer (input impedance 10^{14} Ω). Contacts were made with ultrasonically applied indium; they were found to be ohmic. The ac measurements were carried out above room temperature, using the complex impedance method (*17*), with platinum-paste contacts. Plots will be given as R vs $1/T$ as we estimate the error on values of the resistivity ρ (or conductivity σ) to be as large as 20%, due to the uncertainty in determining the geometrical factors (measured optically). Values of R and relative variation with T, however, were accurate and reproducible. The ac conductance was also measured on powdered samples, which were pelletized in a belt-type press at 2 GPa.

Results and Discussion

1. Characterization and Thermal Behavior

The K/Mn ratio in cryptomelane single

crystals (sample A) was found to be 0.16 ± 0.01 (electron microprobe analysis), in agreement with the structure refinement giving the formula $K_{1.33}Mn_8O_{16}$ (*15*). Lattice parameters were $a = 980.0(3)$, $c = 287.6(1)$ pm (tetragonal symmetry). No traces of vanadium from the melt were detected.

Powdered samples prepared by wet chemistry from $KMnO_4$ had K/Mn ratios of 0.057–0.072 (from atomic absorption analysis), and a variable water content depending on the drying conditions. A sample B dried over P_2O_5 under vacuum contained 0.12 mole H_2O per mole Mn (from thermogravimetry), while samples that were not vacuum-dried contained as much as 0.4 H_2O/Mn, (compare to Parida's analysis for compounds prepared by the same procedure and dried over silica gel (*16*): K/Mn = 0.058, H_2O/Mn = 0.26). Samples annealed at 200°C regained 41% of the lost weight within a 90-min exposure to air. X-Ray patterns of powder samples exhibit broad lines (due to small grain size or to monoclinic distorsion) corresponding to $a \simeq 985$, $c = 285.6$ pm.

The aqueous chemical synthesis yields $A_xMn_8O_{16}$ phases with low potassium content but, with high x values. Redox titration on sample B gave $x = 2.0$, i.e., full occupation of the channel sites (two per Mn_8O_{16} framework unit). As potassium accounts for only $x = 0.55$ in B, there must be extensive incorporation of H_3O^+ in the structure channels during the acidic treatment. Bode and Schmier (*18*) noted indeed that the second step in the chemical preparation (leaching in hot HNO_3) favors the crystallization of the hollandite phase, but removes part of its potassium content, and presented evidence of ion exchange of potassium by hydronium ions in acidic medium.

The thermogravimetric curve of sample B (see Fig. 2) shows two mass losses: (a) from 100 to 185°C, (b) from about 460 to 610°C. The (a) corresponds to dehydration; it occurs above 100°C, supporting the idea of strong bonding of (H_2O or H_3O^+) in the structure, which is consistent with the presence of H_3O^+ in the channels. The second mass loss on heating (b) corresponds to the thermal decomposition of the compound. Both the mass loss and the X-ray powder pattern of the resulting phase indicate that transformation into Mn_2O_3 occurred in air between 460 and 610°C.

Heating a single crystal of $K_{1.33}Mn_8O_{16}$ above about 550°C resulted in a similar decomposition, which is in agreement with a study on natural crystals by Faulring *et al.*,

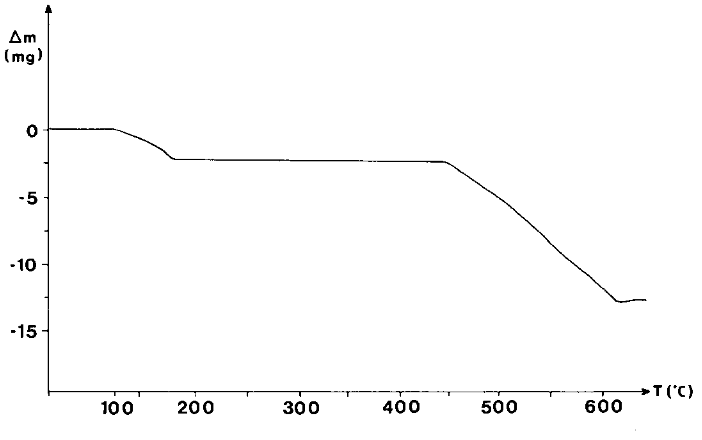

FIG. 2. Thermogravimetric curve of powdered cryptomelane (sample B, see text) prepared by the wet chemical method. Sample mass: 161.0 mg; heating rate: 2°C/mn.

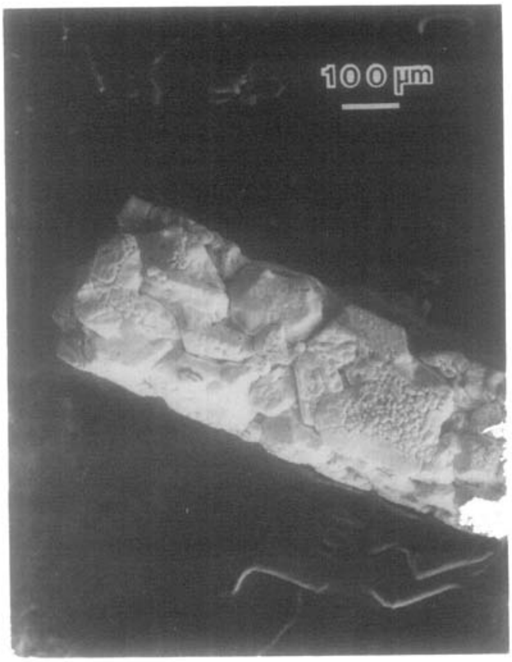

FIG. 3. Electron micrograph of a $K_{1.33}Mn_8O_{16}$ columnar crystal after annealing at 550°C under vacuum, showing oriented crystals of MnO.

who reported a decomposition temperature of 600°C (*19*). These authors found the transformation to be "topotactic," as the resulting Mn_2O_3 crystallites are highly oriented. We were able to carry the reduction further by heating a single crystal under vacuum at 550°C. The original cryptomelane crystal has a columnar shape similar to those shown in Figs. 2 and 3 of Ref. (*4*). The end product is shown in Fig. 3. It consists of oriented crystallites identified as MnO. Many of them have ⟨110⟩ edges parallel to the original column direction, i.e., the hollandite *c*-axis.

2. *Magnetic Properties*

The magnetic susceptibility vs temperature (Fig. 4) shows evidence of antiferromagnetic ordering at 18 K for sample A (crystals) and at 11 K for a powder sample C with K/Mn = 0.057 and unknown water content prepared by the wet chemical method. These T_N values are significantly lower than those reported in a previous paper (*10*), where neither the $\chi(T)$ curve nor the sample composition were given. The discontinuity in $\chi(T)$ is much sharper for the single-crystal sample (Fig. 4, inset). Curie constants and paramagnetic Curie temperature are given in Table I. For the crystal sample, the magnetic moment per Mn atom is 4.00 μ_B in excellent agreement with the spin-only value 4.04 μ_B calculated from the formula unit $K_{0.16}MnO_2$. The powder sample has a higher Curie constant, indicating a higher Mn(3+) content, i.e., a larger x in $A_x^+Mn_{8-x}^{4+}Mn_x^{3+}O_{16}$. As its potassium content was actually lower than that of the crystal sample, the additional Mn(3+) must be balanced by H_3O^+ cations in the channels. The Mn^{3+} fraction (= total A^+ frac-

TABLE I

SUMMARY OF PHYSICAL PARAMETERS OF SYNTHETIC CRYPTOMELANE SAMPLES

	Curie constant	θ_p (K)	Activation energy of conductivity (eV)	Conductivity (Ω^{-1} m^{-1})
Crystal $K_{0.16}MnO_2$	2.00	315	($T < 150$ K : 0.015)[a] ($T > 220$ K : 0.38)	(294 K : 3.0)[a] (354 K : 40)
Powder $(K,H_3O)_xMnO_2$[c]	2.16	319	($300 < T < 367$ K : 0.31)[b] ($495 < T < 715$ K : 0.16)	(308 K : 0.023)[b] (367 K : 0.17)

[a] From dc measurement.

[b] From ac measurement.

[c] Samples of variable (H_2O or H_3O^+) content (see text); K/Mn was 0.07.

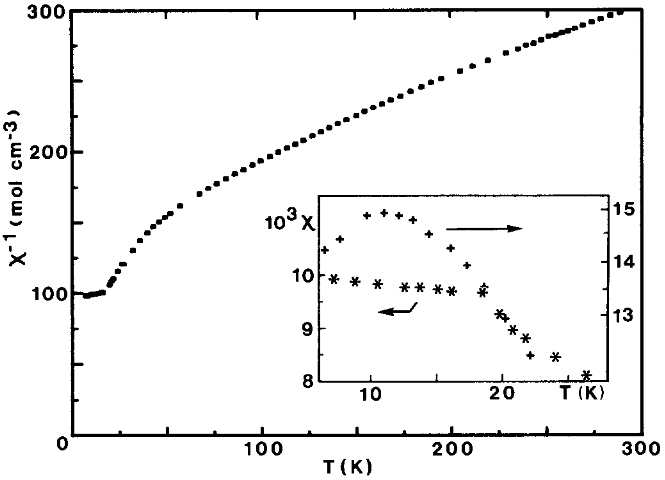

FIG. 4. Reciprocal magnetic susceptibility of $K_{1.33}Mn_8O_{16}$ as a function of temperature. Inset: detail of low-temperature region: (■) $K_{1.33}Mn_8O_{16}$ crystals (sample A); (+) $(K,H_3O)_2Mn_8O_{16}$ (sample C).

tion) deduced from the Curie constant is 0.26 per Mn atom, corresponding to $x = 2.1$, i.e., to full occupation of the channel sites. This is confirmed by redox titration on C giving $x \simeq 1.90$.

3. *Electrical Properties*

The temperature variation of the resistance of two single crystals of cryptomelane (Fig. 5) shows that the compound is a semiconductor. It exhibits two separate ranges of exponential variation of R versus reciprocal temperature, with respective activation energies 0.015 and 0.38 eV (see Table I). The low-temperature part, which is characterized by a very low activation energy, can be attributed to impurity levels. The material has a room-temperature conductivity σ of about 3 Ω^{-1} m^{-1}. This is comparable to that of other forms of nonstoichiometric "MnO_2" (see Table 2 in Ref. (*20*)), whereas the electrical behavior of the only stoichiometric form, the rutile-type β-MnO_2, is definitely different when determined on single crystals: its conductivity is higher ($\sim 10^3$ Ω^{-1} m^{-1} at 300 K) and does not follow an $\exp(E/kT)$ dependence (*11*). Yet, both $K_{0.16}MnO_2$ (cryptomelane) and β-MnO_2 have very similar structural features in the direction of shortest Mn–Mn distances, which are equal and oriented along the rutile chains in both compounds. Moreover, $K_{0.16}MnO_2$ has a smaller conductivity than β-MnO_2, in spite of the presence of additional electrons in the MnO_2 framework, compensating for the channel cation charge.

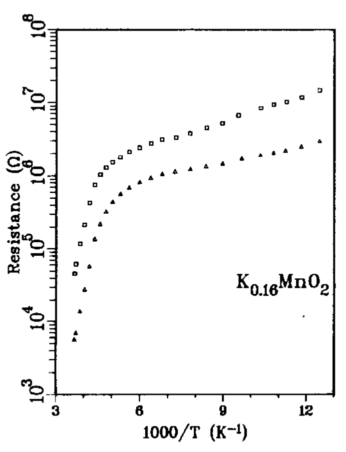

FIG. 5. The dc electrical resistance of $K_{1.33}Mn_8O_{16}$ crystals as a function of reciprocal temperature.

Due to the small size of samples, no thermoelectric power measurements could be carried out to identify the sign or temperature variation of the carrier density n. Taking the maximum n equal to the density of electrons compensating the channel cations charge, then

$$n = Zx/V_c = 4.64 \times 10^{27}\ \mathrm{m}^{-3},$$

where Z is the number of formula units per unit cell and V_c the cell volume. In this hypothesis, the carrier mobility $\mu = \sigma/ne$ is of the order of 4×10^{-9} m^2/V sec at room temperature; this mobility range would be typical of localized carrier, small-polaron-type conduction (hopping between Mn^{3+} and Mn^{4+} sites).

Given the particular features of the structure, ac measurements were carried out to check for possible ionic conduction by the potassium ions in the channels. However, the range of electronic conductivity of this material makes it difficult to detect ionic conduction. Most studies in hollandite-type titanates gave room-temperature conductivities $\sigma_{RT} < 10^{-2}\ \Omega^{-1}\ \mathrm{m}^{-1}$ (*21, 22*), although σ_{RT} values as high as $2\ \Omega^{-1}\ \mathrm{m}^{-1}$ have been reported (*6*). Complex impedance plots of single-crystal and pellet cryptomelane are given in Fig. 6. The material behaves like a pure resistor, showing no evidence of space charge and electrode polarization. Similar impedance diagrams were obtained at temperatures up to 740 K. Note that the total conductivity of the pelletized material is significantly lower than that of a crystal along c. This can be due to grain boundary resistances and to anisotropy of conductivity (the c direction being the likely direction of easy conduction).

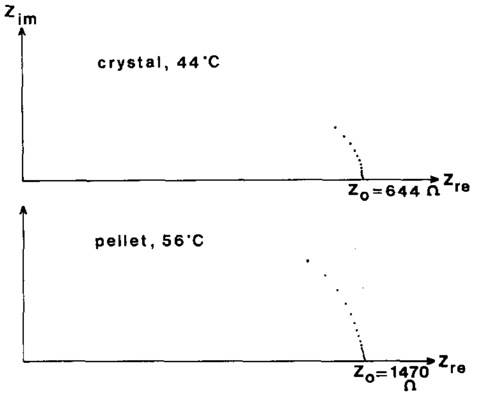

FIG. 6. Typical complex impedance plots of cryptomelane. The frequency range was 10^2 to 10^6 Hz.

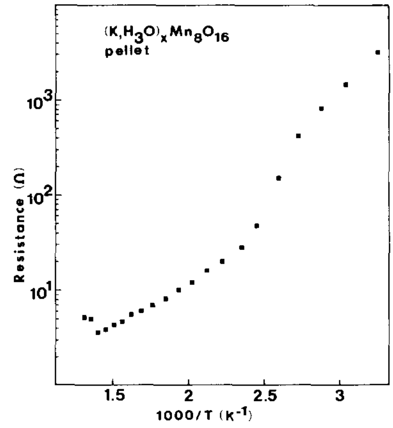

FIG. 7. The ac electrical resistance of $(\mathrm{K,H_3O})_x\mathrm{Mn_8O_{16}}$ pellet as a function of reciprocal temperature.

The pellet $R(T)$ curve (Fig. 7), determined in the 300–780 K temperature range, confirms the results of thermal analysis. A kink appears at 367–495 K (dehydration), followed by a zone of lower activation energy (see Table I). The latter is interrupted by an abrupt resistance increase at ~720 K, corresponding to the beginning of the decomposition of cryptomelane in air. Similar breaks in $R(T)$ occur for powdered β-$\mathrm{MnO_2}$ at 450–490°C (*13, 20*). In both cases (crystal or pellet), ionic conductivity in cryptomelane, if existing at all, is several orders of magnitude lower than the electronic conductivity. This agrees with previous reports stating that no high ionic conductivity should be expected in a purely one-dimensional structure, because long-range motion in channels is easily blocked by crystal defects or impurities (*23*). Further facts supporting cation blocking are the narrowness of channel bottlenecks in the hollandite structure (*25*) and cation ordering in $K_{1.33}Mn_8O_{16}$ channels (*15*).

Conclusion

The study of manganese dioxide and its derivatives is frequently beset by uncertainties about their composition, water content, homogeneity, and thermal stability (*3, 13, 20*). We have examined the magnetic and electrical properties of well-characterized synthetic single-crystal cryptomelane $K_{1.33}Mn_8O_{16}$. We have shown that samples prepared by wet chemical methods have a variable (H_2O or H_3O^+) content and partial occupation of the channels by H_3O^+. Their composition is constant in the temperature range 185–460°C only. Both phases are poor ionic conductors, probably due to the isolated one-dimensional character of the channels in their structure.

Acknowledgments

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