is not necessarily reestablished even after the oxided electrode is reduced back to the metal. Figure 2A shows the result of the LEED experiment performed after extensive anodic oxidation of the Pd(100) electrode; the absence of discernible LEED spots betrays the high degree of disorder of the oxided surface. Figure 2B shows the LEED pattern generated when the oxide-coated Pd(100) electrode was immersed, at room temperature and at potentials where the metal oxide is reduced, in a solution of 0.5 mM NaI at pH 10. It is easy to see that this LEED pattern is identical to that for the initially ordered Pd(100) electrode (Figure 1B). The Auger spectrum for the reordered interface is likewise identical with that for the unoxidized surface. It is thus clear that the oxided, disordered Pd(100) surface has been reordered by electrochemical reduction and subsequent iodine chemisorption. Since the reordering occurs under conditions where Pd dissolution is negligible,[10] the driving force for this disorder-to-order surface reconstruction is most probably the formation of the highly stable Pd(100)c(2X2)-I adlattice.

The present results demonstrate that the in situ regeneration of clean and ordered single-crystal electrode surfaces from the simple sequence of oxidation, reduction, and iodine chemisorption, first reported by us for Pd(111),[6,7] is also applicable to Pd(100). The iodine-free single-crystal surface could then be prepared according to published procedures.[4,7] On-going studies are aimed at (i) exploring the applicability of the iodine-chemisorption reordering method to other electrode surfaces and (ii) identifying other reagents which can effect this in situ chemisorption-induced reordering phenomenon.

Acknowledgment. Acknowledgement is made to the National Science Foundation (Presidential Young Investigator program, DMR-8958440) and the Robert A. Welch Foundation for support of this work.

Registry No. Pd, 7440-05-3; I_2, 7553-56-2; NaI, 7681-82-5.

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$InMnO_3$: A New Transition Metal Oxide with an Unusual ABO_3 Structure

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Received August 24, 1992

We report the synthesis and structure of a new, unusual indium manganese oxide, $InMnO_3$, with a hexagonal layered structure containing manganese in trigonal bipyramidal coordination. Several common ABO_3 structural types are known, such as perovskite, corundum, ilmenite, and bixbyite,[1-9] and radius ratio rules, such as Goldschmidt's tolerance factor,[10] will generally predict which structural type will form for any given pair of cations. Two common ABO_3 structural families are characterized by (1) A and B cations of approximately equal size and of a size suitable for octahedral coordination by oxygen and (2) an A cation comparable in size to O^{2-}, which together with oxygen can form AO_3 closest-packed layers.[11] Oxides of the first group tend to adopt sesquioxide structures, such as corundum (α-Al_2O_3)[8,11] (a random distribution of cations in octahedral interstices, preferred by cations having the same oxidation state and/or similar radii) or ilmenite[12,13] (an ordered cation distribution preferred by cations having different oxidation states and/or different radii). Oxides of the second group form linked BO_6 octahedra and AO_3 closest-packed layers, such as perovskite,[1,2] $BaNiO_3$,[14] or hexagonal $BaTiO_3$ type structures,[15] as well as uncommon structural types,[16,17] e.g., the tunnel structure of $KSbO_3$.[18,19] $InMnO_3$, intriguingly, is not a member of these known structural families.

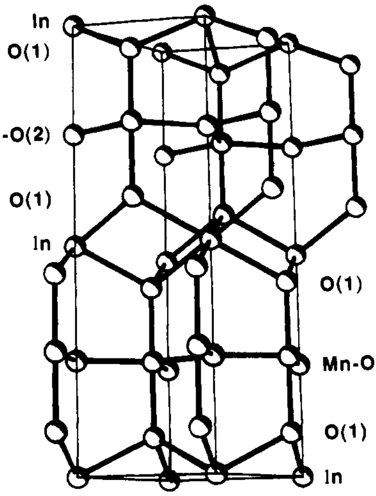

Figure 1. PLUTO drawing of the structure of $InMnO_3$. Selected bond lengths are In–O(1) = 2.202 (3), In–O(2) = 2.869 (nonbonding), In–Mn = 3.4756 (1), Mn–O(1) = 1.870 (8), Mn–O(2) = 1.9621 (1), Mn–Mn = 3.3985 (2), In–In = 3.3985 (2) Å.

Table I

atom	x	y	z	B_{eq}
In	0	0	0	1.97 (5)
Mn	$^2/_3$	$^1/_3$	$^1/_4$	1.05 (6)
O(1)	$^2/_3$	$^1/_3$	0.0871 (07)	2.0 (2)
O(2)	0	0	$^1/_4$	1.5 (4)

The Goldschmidt tolerance factor, $t = (r_A + r_O)/(2)^{1/2}(r_B + r_O)$, where r_A, r_B, and r_O are the ionic radii of A, B, and O^{2-}, respectively, predicts the perovskite structure for $1 > t > 0.8$ and the ilmenite structure for $0.8 \geq t$. In_2O_3 and Mn_2O_3 are known in both the bixbyite (an anion deficient fluorite structure) and corundum structures, and consequently, one would expect an ABO_3 indium manganese oxide to form a derivative of one of those two structural types. Furthermore, the tolerance factor for $InMnO_3$ is 0.80, confirming that ilmenite, the ordered corundum structure, should form. It is therefore surprising to find $InMnO_3$ in this very simple, yet unusual, layered hexagonal structure with two different cation coordination environments: octahedral and trigonal bipyramidal.

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0002-7863/92/1514-10952$03.00/0

Single crystals of InMnO$_3$ were prepared from In$_2$O$_3$ (Cerac, 99.99%) and Mn$_2$O$_3$ (Cerac 99.99%) in a Bi$_2$O$_3$ (Cerac 99.9%) flux. Approximately 3 mmol of the binary oxides was ground together and pelletized. The pellet was heated at 950 °C for 3 days in air on platinum foil and quenched to room temperature. Partial melting of the pellet occurred during the heating cycle, and black hexagonal plates were visible on the surface of the pellet. The flux matrix was weakened with concentrated nitric acid, and crystals were mechanically separated.

InMnO$_3$ is a low-temperature structure and decomposes above 1000 °C. The spinel solid solution, In$_{2-x}$Mn$_{1+x}$O$_4$,[20] is the stable In–Mn–O structure above 1000 °C and forms preferentially if a mixture of In$_2$O$_3$ and Mn$_2$O$_3$ is ground together and heated in air. Polycrystalline InMnO$_3$ can be prepared via a nitrate decomposition route, although care must be taken not to exceed 1000 °C, at which point InMnO$_3$ powder decomposes into In$_2$O$_3$ and Mn$_2$O$_3$.

The structure of InMnO$_3$,[21] shown in Figure 1, consists of alternating layers of octahedrally coordinated indium and trigonal bipyramidally coordinated manganese. The manganese and indium coordinations are fixed by symmetry (atomic positions are shown in Table I) and, consequently, have ideal D_{3h} and near-ideal octahedral symmetry, respectively. The structure of InMnO$_3$ may be described as a stuffed delafossite structure,[22] in which an extra oxygen, O(2), has been inserted into the manganese plane; instead of the linear coordination of B found in ABO$_2$ delafossite, manganese is trigonal bipyramidally coordinated. Alternatively, the InMnO$_3$ structure may be described as related to the CdI$_2$ structure,[23] except instead of empty octahedral sites located between a layer of filled sites, an MnO hexagonal net (6,3)[24] has been inserted between slabs of InO$_6$ octahedra in which all octahedral interstices are filled. The trigonal bipyramidally coordinated manganese layers repeat with every second layer. The staggered arrangement of the manganese atoms results in only limited communication between the transition metal oxide planes. It has been shown that transition metal structures with low dimensional units have the potential for interesting magnetic and electronic effects.[25-30] The low dimensional InMnO$_3$ structure, thus, should give rise to strong intralayer manganese–manganese interactions, while oxygen-mediated interlayer interactions are not expected to be significant except at very low temperatures. Preliminary measurements indicate that InMnO$_3$ orders antiferromagnetically with a complex applied magnetic field dependence. We will report on the magnetic properties of InMnO$_3$ at a later date.

The structures of InMnO$_3$ and (RE)AlO$_3$[31,32] (RE = Y, Eu, Gd, Tb, Dy, Ho, Er) are very similar, differing only in the coordination of the indium/RE site. In the case of YAlO$_3$, the yttrium is bound by six oxygen atoms at a distance of 2.274 Å and two additional oxygens, above and below at a distance of 2.63 Å. The higher coordination of the yttrium site causes the unit cell to be compressed in the c-direction, c = 10.52 Å. In the case of InMnO$_3$, on the other hand, indium interacts with O(2) only slightly, if at all. The indium–O(2) distance is 2.869 Å, more than 0.2 Å longer than the yttrium–O(2) distance in YAlO$_3$, even though the ionic radius of indium is 0.1 Å shorter than that of yttrium in octahedral coordination. Consequently, the c-axis in InMnO$_3$, c = 11.47 Å, is almost 1 Å longer than that of YAlO$_3$. This difference is even more pronounced in isostructural InFeO$_3$,[33,34] where the indium–O(2) distance is 3.044 Å and c = 12.175 Å. The structure of InMnO$_3$ is thus unique when compared to the YAlO$_3$ structure since the need of the rare earth atoms for higher coordination creates a shortening of the c-axis and a strong bond with O(2), which is not the case for InMnO$_3$. The difference is also evident in the chemical reactivity of rare earth aluminates, which transform to the perovskite structure above 1000 °C, unlike InMnO$_3$ which decomposes into the binary oxides.

It is unlikely that InMnO$_3$ is the only transition metal indate crystallizing in this structure, and in fact single crystals of the isostructural InFeO$_3$ compound have been prepared.[33] The syntheses of other members of this unusual structural family are in progress.

Acknowledgment. We thank W. M. Davis of the Single Crystal X-ray Diffraction Facility, Department of Chemistry, Massachusetts Institute of Technology, for collecting the crystallographic data set. We also thank Ken Poeppelmeier for valuable discussions. This work was supported by the Massachusetts Institute of Technology, Center for Materials Science and Engineering, Grant DMR 9022933.

Supplementary Material Available: Tables of positional and thermal parameters and crystal data for InMnO$_3$ (3 pages); table of observed and calculated structure factors (1 page). Ordering information is given on any current masthead page.

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(21) Crystal data for InMnO$_3$: Crystals were analyzed by microprobe (JEOL 781), indicating a stoichiometry of In:Mn of 1:1. The space group is $P6_3/mmc$ (No. 194), a = 3.3985 (2) Å, c = 11.4752 (6) Å, V = 114.78 (1) Å^3, Z = 2. Of 778 reflections collected 109 were unique. Data was corrected for absorption empirically, μ = 149.00 mm^{-1}. The secondary extinction coefficient = 0.1829 × 10^{-4}. All atoms were anisotropically refined. R = 3.3% and R_w = 3.5%.

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Absolute Configuration of Isoflurane

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Received August 17, 1992

The enantiomers of chiral anesthetic agent isoflurane (CF$_2$HOCHClCF$_3$)[1-3] have a 2-fold difference in their effectiveness on the anesthetic-activated potassium current and in their inhibition of current mediated by acetylcholine receptors. These differences were attributed to the stereospecific binding between the chiral isoflurane enantiomers and the anesthetic-sensitive proteins in the brain.[4,5] To understand these stereospecific interactions at the molecular level, it is necessary to know the absolute configurations of the isoflurane enantiomers and the conformations in which these isomers exist. Neither the configurational nor the conformational details are available in the lit-

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