kinetic diameter of the two gases. A similar result was obtained with an alumina-pillared montmorillonite[17] characterized by an interlamellar distance of 7.4 Å.

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# Soft Chemical Synthesis of New Compounds with the Hexagonal Molybdenum Oxide Structure

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## Introduction

Many transition-metal oxides are of great interest for catalytic and electrochemical applications, and metastable structures often demonstrate new or enhanced properties compared to their thermodynamically stable forms. These materials can often be prepared at low temperatures by electrochemical intercalation, inorganic ion exchange, or organic precursor methods. In this paper we report the synthesis in aqueous acid of $A'_{0.13}V_{0.13}Mo_{0.87}O_3\cdot nH_2O$ (A′ = H, Na) from the compounds $AVMoO_6$ (A = Li, Na) which have the layered brannerite structure (Figure 1a). The framework of the new structure is isotypic with the hypothetical hexagonal "tunnel" structure of $MoO_3$[2,4] shown in Figure 1b. Although previous syntheses have been used to stabilize this structure by incorporating large cations or hydrated $Na^+$ into the tunnels,[3,4] there have been no reports of the successful preparation of the structure containing empty tunnels. In the current work, we have found that the alkali-metal brannerites undergo a novel "leaching" reaction, which for A = Li leads to the formation of $H_{0.13}V_{0.13}Mo_{0.87}O_3\cdot nH_2O$. Subsequent dehydration of this compound permits the preparation of a "microporous" form of hexagonal $MoO_3$, $V_{0.13}Mo_{0.87}O_{2.935}$, in which the one-dimensional tunnels are empty.

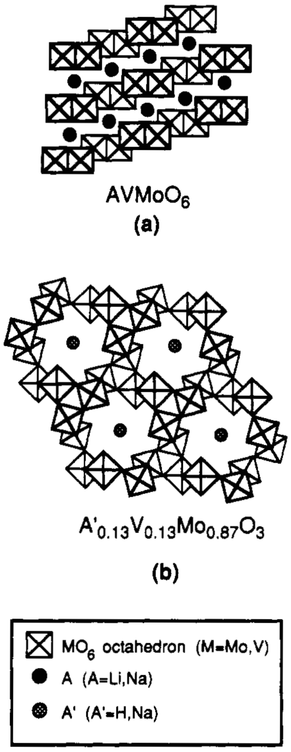

**Figure 1.** Structures of (a) brannerite and (b) hexagonal molybdenum oxide.

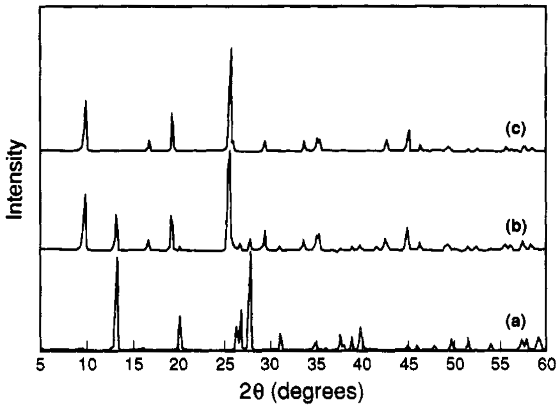

**Figure 2.** Powder X-ray diffraction patterns of $NaVMoO_6$ (a) before, (b) after one treatment, and (c) after two treatments in 0.25 M HCl.

## Experimental Section

The new materials have been prepared by a novel soft chemical route involving the acid treatment and dehydration of alkali-metal brannerites. Lithium and sodium brannerites were prepared by solid-state reaction of $AVO_3$ (A = Li, Na) and $MoO_3$ as reported by Galy et al.[5] The Na brannerite was stirred in 0.25 M HCl for 12 h at 60°C, and the solid was recovered by vacuum filtration. The process was repeated to ensure complete conversion of the brannerite to the tunnel structure. $LiVMoO_6$ was immersed in 0.25 M HCl for 36 h with stirring at 60 °C. The solution was then

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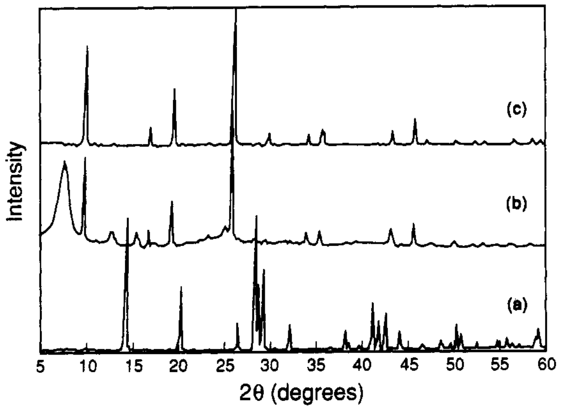

**Figure 3.** Powder X-ray diffraction patterns of $LiVMoO_6$ (a) before, (b) during, and (c) after treatment in 0.25 M HCl.

acidified with 1 M HCl and stirred for 2 h before isolating the product by vacuum filtration. The products were analyzed by thermogravimetric analysis (TGA), X-ray diffraction (XRD), atomic absorption spectroscopy (AAS), and powder neutron diffraction.

## Results and Discussion

In contrast to the ion-exchange reactions observed and characterized for many layered transition-metal oxides, in weak mineral acids the sodium and lithium brannerites participate in an unusual "leaching" reaction. The vanadium is preferentially dissolved from the brannerite framework, leaving a structure in which the Mo:V ratio has increased from 1:1 to 6.7:1. In the case of $NaVMoO_6$, the process proceeds through a two-phase mixture of the starting structure and the final product, $Na_{0.13}V_{0.13}Mo_{0.87}O_3 \cdot 0.26H_2O$, which XRD (Figure 2) confirmed to have the hexagonal $MoO_3$ structure (S. G. $P6_3$) with $a$ = 10.626 (1) Å and $c$ = 3.696 (1) Å. TGA of the single-phase final product indicates that $Na_{0.13}V_{0.13}Mo_{0.87}O_3 \cdot 0.26H_2O$ can by fully dehydrated at 300 °C. The structure rehydrates immediately upon cooling, indicating that the tunnels, with a minimum diameter of 3.2 Å, are too large for $Na^+$ to occupy without coordination by water molecules. XRD confirms that the tunnel structure is maintained throughout the dehydration/rehydration process.

Although the reaction of $LiVMoO_6$ in HCl also yields new phases with the hexagonal $MoO_3$ structure, the nature of the reaction is quite different. Upon immersion in dilute HCl, the material dissolves, leaving only a small amount of amorphous residue. XRD (Figure 3) of the recovered solid products indicates that, with continued stirring at 60 °C, the hexagonal tunnel structure begins to crystallize from solution. After 36 h of reaction, small amounts of the remaining amorphous phase were removed by acidification of the solution leaving a yellow, single-phase "hexagonal $MoO_3$" product consisting of needlelike particles approximately 1–10 μm in length. Atomic absorption shows that the Mo:V ratio is 6.7:1 and the material contains only trace amounts of lithium (Mo:Li > 20:1). The stoichiometry of the final product, as gauged by TGA, is $H_{0.13}V_{0.13}Mo_{0.87}O_3 \cdot nH_2O$, with $n \approx 0.26$, and the lattice parameters are $a$ = 10.583 (1) Å, $c$ = 3.698 (1) Å. Dehydration of this acidic product permits the preparation of a hexagonal $MoO_3$ structure in which the one-dimensional tunnels are empty. TGA (Figure 4) indicates that after the loss of surface water, water molecules which are presumably located in the tunnels are removed, leading to the formation of $H_{0.13}V_{0.13}Mo_{0.87}O_3$ at approximately 225 °C. During the final weight loss, which corresponds to 0.065($H_2O$), the residual protons are apparently abstracted from the structure with a small amount of oxygen from the framework, leaving a yellow-green sample with the stoichiometry $V_{0.13}Mo_{0.87}O_{2.935}$. The color change, which may indicate the presence of a small amount of $V^{4+}$, was independent of the atmosphere used during dehydration. Rietveld refinement of powder neutron diffraction data has confirmed that the fully dehydrated and dehydroxylated product retains the hexagonal $MoO_3$ structure, with $a$ = 10.560 (2) Å and $c$ = 3.695 (2) Å, and contains no species in the tunnels. Subsequent studies of the thermal stability of $V_{0.13}Mo_{0.87}O_{2.935}$ indicate that the open structure is kinetically stable to at least 450 °C. The absence of any ions in the channels after complete dehydroxylation is reflected by the difference in the rehydration characteristics of $V_{0.13}Mo_{0.87}O_{2.935}$ as compared to the Na tunnel structure. Whereas the latter rehydrates immediately during cooling from 400 °C, the former does not rehydrate when cooled under dry helium. This is most likely a direct result of the large reduction in the chemical driving force for the incorporation of molecular $H_2O$ into the empty channel structure.

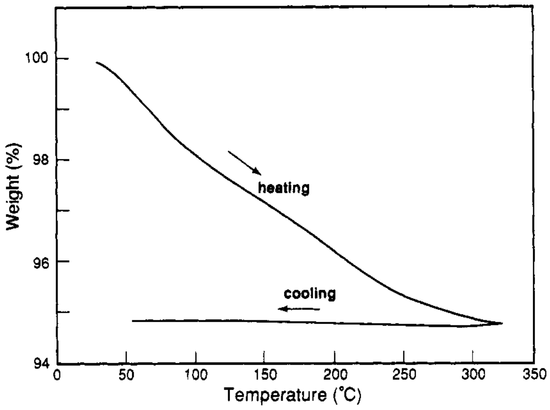

**Figure 4.** TGA of $H_{0.13}V_{0.13}Mo_{0.87}O_3 \cdot nH_2O$ ($n \approx 0.26$).

Preliminary experiments indicate that this new compound can be readily inserted with a variety of monovalent cations, such as $H^+$, $Li^+$, and $Na^+$, leading to a new series of reduced compounds with the hexagonal $MoO_3$ structure. These and other experiments are currently being performed to clarify the mechanisms of these unusual reactions and to explore the chemical, catalytic and electronic properties of these unique vanadium–molybdenum oxides.

## Conclusion

The reactions of alkali-metal brannerites $AVMoO_6$ in weak mineral acids have been used to develop a novel method for the synthesis of new hexagonal vanadium/molybdenum oxides. Neutron diffraction and chemical and thermal analyses have confirmed that dehydration of the product of the reaction of Li brannerite leads to the formation of hexagonal $V_{0.13}Mo_{0.87}O_{2.935}$ in which the large one-dimensional channels are empty. This structure can be used as a host for a variety of insertion reactions.

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