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# Synthesis of Polyoxometalate-Pillared Layered Double Hydroxides via Calcined Precursors

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Layered double hydroxides (LDHs) represent an important group of solids.[1–6] They consist of positively charged metal oxide/hydroxide sheets with intercalated anions and water molecules[1,2,7,8] and are, therefore, mirror images of the much studied family of cationic clay minerals.[2] They may be represented by the general formula

$$M^{2+}{}_aM^{3+}{}_b(OH)_{2a+2b}(X^-)_b{\cdot}xH_2O$$

where $M^{2+}$ may be Mg, Ni, Co, Zn, or Cu and $M^{3+}$ may be Al, Cr, or Fe. $M^{2+}/M^{3+}$ ratios between 1 and 5 are possible.[4,9] Such LDHs have attracted attention as precursors for the generation of solid base catalysts[4,10] as well as being intermediates in the synthesis of more conventional catalysts, e.g., in the formation of copper/cobalt bimetallic catalysts supported on ZnO.[5]

$Cl^-$, $OH^-$, and $CO_3{}^{2-}$ are frequently cited as the charge-balancing anions, although recent attempts have aimed at incorporating other guests, for example, $[V_{10}O_{28}]^{6-}$ and $\alpha$–$\omega$-carboxylic acids (see ref 3 and 6). The high charge densities associated with LDHs, however, suggest that there may be some difficulty in intercalating such large species. Consequently two strategies have been described. The first strategy makes use of the fact that $Cl^-$ or $NO_3{}^-$ anions are significantly easier to displace than, for example, $CO_3{}^{2-}$;[11] for this reason Kwon et al.[3] and Woltermann[12] made use of the $Cl^-$ and $NO_3{}^-$ forms, respectively, in their studies. The second strategy has relied upon an approach whereby the LDH is initially synthesized with a large organic anion (typically the terephthalate dianion) as the intercalated species.[6]

Here we present a third and a particularly straightforward procedure for synthesizing polyoxometalate-pillared LDHs that requires only direct exposure of a calcined precursor to a solution of the pillaring species, i.e., $[V_{10}O_{28}]^{6-}$ or $[Mo_7O_{24}]^{6-}$. Our previous work in this area has concentrated on inserting organic molecules into LDHs.[13] Regeneration of the original LDH structure (typically hydrotalcite) by hydration of the calcined material in carbonated water has been reported elsewhere.[13–18]

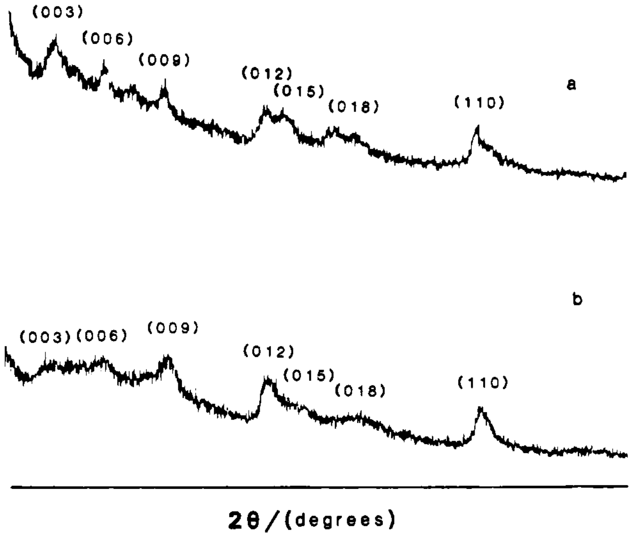

**Figure** 1. X-ray powder diffraction patterns of (a) Mg–Al–$V_{10}O_{28}$ ($d$ = 11.8 Å) and (b) Mg–Al–$Mo_7O_{24}$ ($d$ = 12.0 Å) prepared via calcined precursor. Miller indices are shown.

Synthesis of the parent LDH followed closely the method of Reichle.[4] A typical composition for the starting material was $Mg_6Al_{3.3}(OH)_{18.6}(CO_3)_{1.7}{\cdot}4H_2O$. The LDH was then calcined in air at 450 ± 10 °C for 18 h prior to the following treatments:

**$V_{10}O_{28}$-Pillared Mg–Al LDH**: 0.2 g of calcined Mg–Al LDH powder and 0.3 g of $NaVO_3$ were added to 10 mL of decarbonated deionized water at room temperature. The mixture was stirred for 10–15 min before the addition of 2 M HCl dropwise with vigorous stirring (acid was added until the pH dropped to 4.5). The pH was observed to drop from 8.8 to 4.5 and maintained at 4.5 for 20–25 min. The products were then filtered and washed thoroughly with hot deionized water. The resulting yellow product was allowed to partially dry under $N_2$ before further drying in an oven at 110 °C overnight. The product gave a powder X-ray diffraction pattern indicative of a regenerated layered double hydroxide in expanded form,[19] an observation similar to that of the intercalation of organic species.[13] A basal spacing ($d_{003}$) of 11.8 Å was observed (Figure 1a). Acidification of the calcined LDH in the presence of $NaVO_3$ results in the oligomerization of the metavanadate to form the polyvanadate, and it is this species that is believed to be intercalated. The observed basal spacing is in good agreement with previously reported values of 11.9 and 11.8 Å and corresponds to gallery heights of 7.0 Å and to a $V_{10}O_{28}{}^{6-}$ orientation in which the $C_2$ axis is parallel to the host layers.[3,6] The observed reflections

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[19] The IR spectrum of the treated material shows the absence of an absorption due to carbonate incorporation; elemental analysis gave Mg 11.2%, Al, 10.0%, and V 24.8% in agreement with a formula of $Mg_6Al_{3.8}(OH)_{19.6}(V_{10}O_{28})_{0.6}{\cdot}6H_2O$.

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are quite weak, probably due to the fact that the exchange was carried out at room temperature and hence the crystallites did not grow appreciably.[20] The exchange of organic anions at higher temperatures, typically 70 °C, allowed larger crystallites to form.

**$Mo_7O_{24}$-Pillared Mg–Al LDH**: 0.5 g of the calcined Mg–Al LDH was added to a solution of 7.0 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 160 mL of decarbonated deionized water at room temperature. The pH of the $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ solution was observed to be 5.2. On addition of the calcined material the pH changed to 5.6. This was controlled to pH 4.5 by the addition of 2 M HCl in order to minimize the hydrolysis of the $Mo_7O_{24}^{6-}$ species. The pH was maintained at 4.5 for 60–90 min before the material was filtered, washed several times with hot deionized water, and partially dried under $N_2$ prior to drying in the oven overnight at 110 °C. The powder X-ray diffraction pattern of the nearly white product was characteristic of a regenerated layered double hydroxide in an expanded form with a basal spacing of $d_{003}$ = 12.0 Å (Figure 1b) and corresponds to the $Mo_7O_{24}^{6-}$ orientation in which the $C_2$ axis is perpendicular to the brucite layers as observed by Drezdzon.[6] Surface area and elemental composition follow the trends established for the $V_{10}O_{28}^{6-}$ pillared material.[21]

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[20] Surface area measurements indicate a slight increase as a result of incorporation of $V_{10}O_{28}^{6-}$: pure LDH = 42 $m^2/g$; calcined LDH = 180 $m^2/g$; $V_{10}O_{28}^{6-}$-pillared LDH = 59 $m^2/g$. These results are comparable to those reported by Drezdzon[6] and Kwon et al.[3]

[21] Elemental analysis gave Mg 12.7%, Al 6.4%, and Mo 28.9% (corresponding to $Mg_6Al_{2.7}(OH)_{17.4}(Mo_7O_{24})_{0.5}\cdot 6H_2O$) in agreement with total replacement of carbonate. Surface area for $Mo_7O_{24}^{6-}$-exchanged LDH was 57 $m^2/g$.

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# Unusual Crystal Growth Morphologies in the Niobium–Selenium System

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Researchers in materials chemistry, especially crystal growth, often encounter crystals of unusual beauty or morphology. Dendritic crystal growth and pattern formation, for example, is a topic of considerable research and, as Langer[1] points out, dates back to the centuries-old appeal of the snowflake. Similarly, crystal whiskers were known for centuries, but not until the 1950s[2,3] did they become of technical interest. For low-dimensional metal chalcogenides, the observation of unusual crystal growth or polymorphism has been of interest to both chemists and physicists in terms of synthesis, crystal structure, and physical properties.[4] For this reason, it is the purpose of this communication to report the novel occurrence of two unusual types of morphological features observed in crystal growth studies of $NbSe_3$[5] and $Nb_2Se_9$.[6] The first involves the "spearing" of $Nb_2Se_9$ crystals by growing $NbSe_3$ fibers. The second, more fascinating feature is the curious formation of "circular $NbSe_3$". The very occurrence of these ringlike crystals clearly raises many questions as to why they occur and certainly as to how they grow.

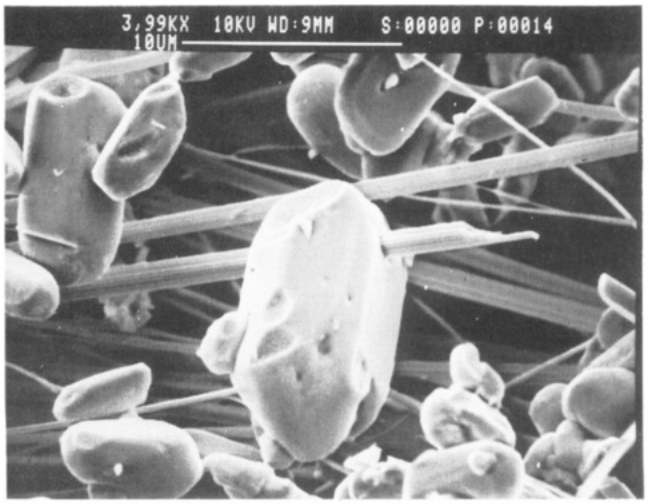

**Figure 1.** Representative SEM photograph of a $NbSe_3$ fiber penetrating a crystal of $Nb_2Se_9$. Note the identical banding features on both sides of the crystal. Several crystals in the photograph exhibit a "potato stub" appearance due to fibers that either are beginning to grow from the crystals or are fibers just barely piercing the crystal surface.

Synthetic conditions required to obtain these results were reactions based on pure elements and/or binary precursors in evacuated quartz tubes. The most success was typically achieved when the conditions were such that microcrystalline $Nb_2Se_9$ was allowed to decompose (600–630 °C, 3–6 h) to $NbSe_3$. These preliminary results are from studies utilizing scanning electron microscopy (SEM) with a Cambridge S-90B SEM. The chemical formulas $Nb_2Se_9$ and $NbSe_3$ are used as a general result of semiquantitative microprobe measurements. As usual, these are restricted in accuracy and do not guarantee the absence of slight nonstoichiometry.

**Penetration of $Nb_2$Se9 Crystals.** The first indication that crystals of $Nb_2Se_9$ could be "speared" by $NbSe_3$ fibers is shown in Figure 1. Manipulation inside the SEM of samples such as this one conclusively showed that $Nb_2Se_9$ crystals could be penetrated by $NbSe_3$ fibers. Note how the striations of the fiber are identical on both sides of the $Nb_2Se_9$ crystal. Repeated instances of $NbSe_3$ fibers penetrating $Nb_2Se_9$ crystals were found. Also visible in Figure 1 are what appear to be small stubs emanating from the surfaces of $Nb_2Se_9$ crystals. Obviously, these could be $NbSe_3$ fibers in the early stages of either formation or emergence from a $Nb_2Se_9$ crystal. In many cases, a penetrating $NbSe_3$ fiber could be traced through several

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