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.

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.

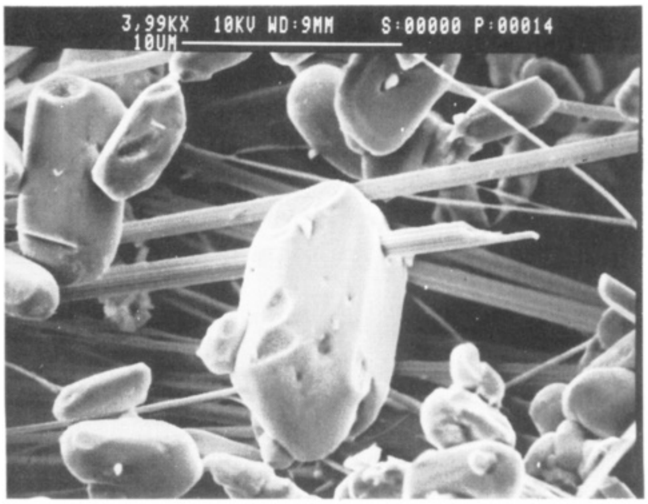

Figure 1. Representative SEM photograph of a $NbSe_3$ fiber penetrating a crystal of Nb_2Se_9. Note the identical banding features on both sides of the crystal. Several crystals in the photograph exhibit a "potato stub" appearance due to fibers that either are beginning to grow from the crystals or are 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_2Se9 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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[1] Langer, J. S. *Science* **1989**, *243*, 1150.

[2] Herring, G.; Galt, J. K. *Phys. Rev.* **1952**, *85*, 1060.

[3] For a review, see: Brenner, S. S. *Science* **1958**, *128*, 569.

[4] Many thorough reviews are available. See, for instance: (a) Rouxel, J., Ed. *Crystal Chemistry and Properties of Materials with Quasi-One-Dimensional Structures*; D. Reidel Publishing: Dordrecht, The Netherlands, 1986. (b) Delhaes, P., Drillon, M., Eds. *Organic and Inorganic Low-Dimensional Crystalline Materials*; Plenum Press: New York, 1987. (c) Legrand, A. P., Flandrois, S., Eds. *Chemical Physics of Intercalation*; Plenum Press: New York, 1987. (d) Sunshine, S. A.; Keszler, D. A.; Ibers, J. A. *Acc. Chem. Res.* **1987**, *20*, 395.

[5] (a) Meerschaut, A.; Rouxel, J. *J. Less Common Met.* **1975**, *39*, 197. (b) Hodeau, J. L.; Marezio, M.; Roucau, C.; Ayroles, R.; Meerschaut, A.; Rouxel, J.; Monceau, P. *J. Phys. C: Solid State Phys.* **1978**, *11*, 4117.

[6] Meerschaut, A.; Guemas, L.; Berger, R.; Rouxel, J. *Acta Crystallogr.* **1979**, *B35*, 1747.

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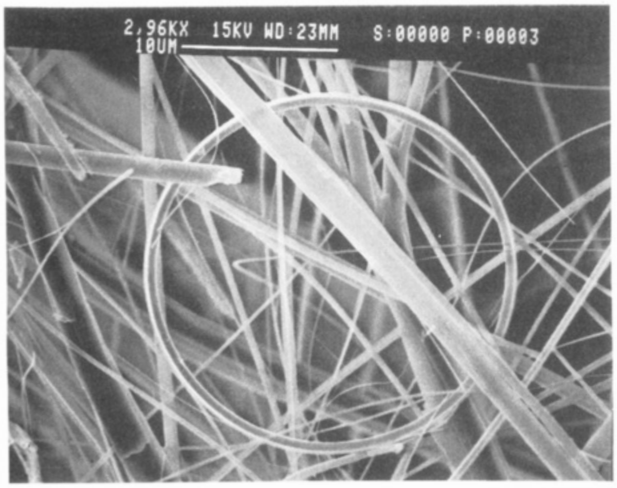

Figure 2. SEM photograph of a very "clean" $NbSe_3$ hoop in a background of many similar sized $NbSe_3$ fibers.

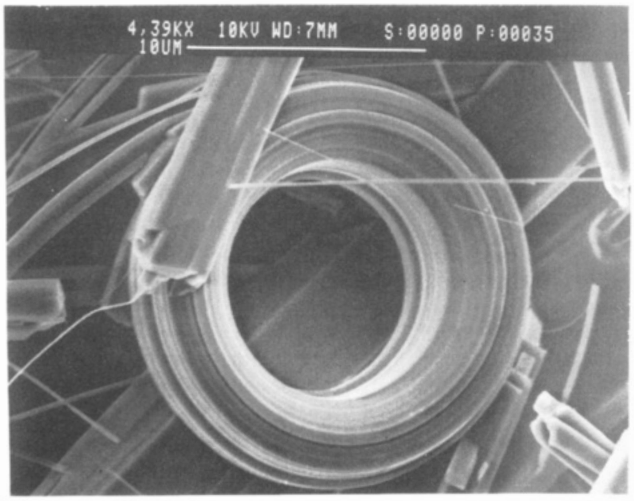

Figure 3. SEM photograph of a bulky $NbSe_3$ circular object. Note the continuity of the circular "banding", i.e., it is not the spirallike effect that one might expect from the winding of ribbons.

Nb_2Se_9 crystals, and often to the Nb_2Se_9 crystal from which it appeared to originate.

It is well-known that once $NbSe_3$ fibers are nucleated, fibers a few micrometers in cross section and several centimeters in length can be obtained. Whether this unimpeded fiber growth involves a vapor–liquid–solid (VLS) mechanism[7] or some other growth mechanism is presently unknown. The spearing effect probably involves the nucleation of $NbSe_3$ when a growing $NbSe_3$ fiber comes in contact with a thermodynamically unstable Nb_2Se_9 crystal. Clearly, this would be accompanied by the formation of selenium liquid and/or vapor. Then, once nucleated, the $NbSe_3$ fiber could propagate through the Nb_2Se_9 crystal by way of epitaxial addition of the more stable phase ($NbSe_3$) until it emerges from the other side where normal fiber growth could resume.

"Circular $NbSe_3$" Growth Morphologies. "Circular $NbSe_3$" morphologies were first noticed during optical microscope studies on the decomposition temperature of Nb_2Se_9 in evacuated quartz tubes. SEM studies revealed an even richer variety of "circular $NbSe_3$" specimens. Figure 2 shows an elegantly simple, "pure" hoop, but more massive objects such as the one in Figure 3 are best described as "doughnuts" or "tires". Truly surprising is that variations on these types of morphologies were common and, like snowflakes, no two identical specimens were ever found.

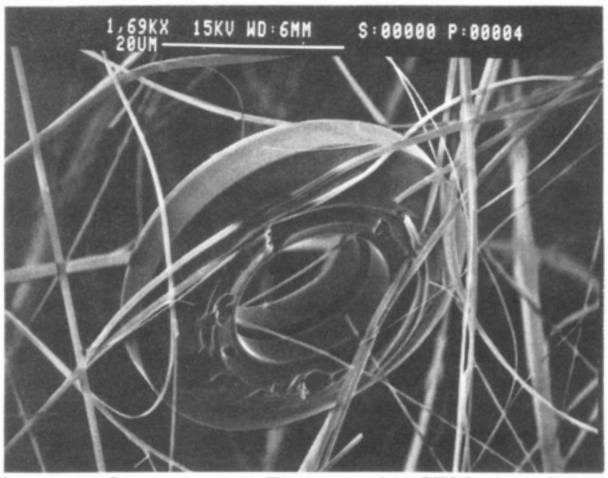

Figure 4. In contrast to Figure 3, this SEM view shows a "smooth" $NbSe_3$ object which is remarkably featureless, i.e., no bands, but it does have a curious inner void.

As a very obvious formation process, we note the following. Many hoops could often be seen to "attract" neighboring fibers. These fibers would "wrap" around and become incorporated to form more massive objects, the shapes of which presumably depend on the number and nature of the surrounding fibers. After retrieval of some of these hoops by hooking them with 0.001-in.-diameter wire, they could actually be unwound by pulling the fibers with tweezers and using the wire as the mandrel. On the other hand, the continuity of the "circular twin lines" such as the ones in Figure 3 suggest yet another growth mechanism that may be similar to a winding type mechanism but nonetheless quite different.

Finally, in stark contrast to such a "spool of thread", the specimen in Figure 4 is an example of the "circular $NbSe_3$" morphologies that are "smooth and solid". This object is remarkably free of entwining structure and is, except for a few defective areas, virtually featureless, perhaps due to some sort of agglomeration or liquid flux effect. Whether such a "smooth" specimen *becomes* a "spool of thread" or *evolves from* a "spool of thread" is, of course, a valid question.

Interestingly, "circular $NbSe_3$" is not the only system to display circular phenomena. Guemas et al.[8] recently reported similar cylindrical morphologies in the ternary $PbNb_2S_5$ system. Apparently, $PbNb_2S_5$ shares some basic structural features with the "$LaCrS_3$" order–disorder structure presented by Kato et al.[9] However, Hyde and co-workers[10-13] have extensively investigated "$LaCrS_3$" and found it unnecessary to invoke the severe disorder originally suggested[9] by instead using $La_{1.2}CrS_{3.2}$ as the formula and by recognizing similarities to the layered misfit structures of which the cylindrite minerals are also a member.[14,15] To this extent we mention "$LaCrS_3$" (i.e.,

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(7) (a) Wagner, R. S.; Ellis, W. C. *J. Met.* **1963**, *15*, 76. (b) Wagner, R. S.; Ellis, W. C. *Appl. Phys. Lett.* **1964**, *4*, 89.

(8) Guemas, L.; Rabu, P.; Meerschaut, A.; Rouxel, J. *Mater. Res. Bull.* **1988**, *23*, 1061.

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(13) Otero-Diaz, L.; Fitzgerald, J. D.; Williams, T. B.; Hyde, B. G. *Acta Crystallogr.* **1985**, *B41*, 405.

(14) Makovicky, E.; Hyde, B. G. *Struct. Bonding* **1981**, *46*, 101.

(15) Hyde, B. G.; Andersson, S. *Inorganic Crystal Structures*; Wiley: New York, 1989; Chapter 12.

$La_{1.2}CrS_{3.2}$) and its relationship to cylindrite (ca. $FePb_3Sn_4Sb_2S_{14}$), since samples of cylindrite display a spiral morphology.[15,16] As one of the more complicated of these incommensurate structures, cylindrite may be suggestive of what is occurring in "circular $NbSe_3$", i.e., stacks of layers have a tendency to curl up into cylinders due to some sort of commensurability (or lack thereof) on a scale significantly larger than the simple unit cell. However, to the best of our knowledge and others[4,17] no polymorphs have ever been reported for $NbSe_3$. Perhaps, as in the case of o-TaS_3 and m-TaS_3[4a] or as has been suggested for $PbNb_2S_5$,[8] the chains in "circular $NbSe_3$" pack into the layers in a fashion only slightly different from traditional $NbSe_3$. It is after all not uncommon to obtain different low-dimensional systems (i.e., the condensate of clusters, chains, or layers) from similar substructures through different synthetic conditions, kinetic effects, and/or slight changes in constituents or composition.[18] The similar, but not identical, cylindrical phenomena reported for chrysotile[19] may also aid in further explaining "circular $NbSe_3$".

In conclusion, the occurrence of "circular $NbSe_3$" suggests either some type of polymorphism or another $NbSe_x$ phase. Perhaps, some of the answers may lie in the difficulty originally reported in the characterization of the $NbSe_x$ system, $3.0 < x < 4.5$,[20] as well as in the penetrability of Nb_2Se_9 by $NbSe_3$.

Registry No. Nb_2Se_9, 65762-16-5; $NbSe_3$, 12034-78-5.

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(16) Makovicky, E. *Neues Jahrb. Mineral., Abh.* **1974**, *126*, 304.

(17) Fleming, R. M., private communication.

(18) For example, we recently characterized CDW behavior in $K_3Cu_8S_6$, which, like $NbSe_3$, is a layer material composed of a chain substructure (infinite $[Cu_4S_4]^{n-}$ anions). Like the trigonal prismatic chains in certain Nb and Ta chalcogenides, the $[Cu_4S_4]^{n-}$ type chain can be found in several different systems; only the method of interchain connection varies. (a) ter Haar, L. W.; DiSalvo, F. J.; Bair, H. E.; Fleming, R. M.; Waszczak, J. V.; Hatfield, W. E. *Phys. Rev. B.* **1987**, *35*, 1932. (b) Fleming, R. M.; ter Haar, L. W.; DiSalvo, F. J. *Phys. Rev. B* **1987**, *35*, 5388.

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Reviews

The Potassium Titanyl Phosphate Structure Field: A Model for New Nonlinear Optical Materials

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Potassium titanyl phosphate (KTP) is unique in its overall qualifications for second-order nonlinear and electrooptic processes with a large hyperpolarizability, an excellent temperature window, a wide wavelength range for phase matching, and outstanding crystal stability. Until recently, only KTP and its arsenic analogue, potassium titanyl arsenate (KTA), had been structurally characterized. The structural properties of KTP make it possible to design and synthesize a large structural field (currently over 40 members) to fine-tune and modify optical properties. An unusual opportunity exists to develop a quantitative model for second-order nonlinear optic (NLO) effects that can handle large structural distortions in extended structures. Current nonlinear susceptibility models concur that the microscopic hyperpolarizability of an octahedral metal center increases with distortion of its geometry and that the Ti=O (titanyl) metal center is primarily responsible for KTP's optical nonlinearity. All models assume that bulk NLO properties can be defined in terms of local structural perturbations involving either the O–Ti–O trans bonds or the TiO_6 group, ignoring cation (K^+ in KTP) and secondary atom (P or As) contributions. Since the observed optical properties are particularly sensitive to crystal quality, this review focuses on the synthesis and ion-exchange chemistry and then considers chemical modification of the KTP structure and the consequent structural and optical implications in light of the present NLO structure/property models.

1. Prologue: Why Photons?

The possibility of studying and using "photonic" processes in which data transmission and storage are primarily initiated and executed by photons rather than electrons is an increasingly attractive alternative.[1] The motivations for this are numerous. The large bandwidths available in optical data transmission make it possible to manipulate and store visual images at a density of as high as 10^8 bits/cm^2. Third-order NLO properties can be used to greatly increase optical disk storage densities so that, for example, optical data storage may some day reduce large libraries to a few small rooms. The transmission of optical pulses on a picosecond or femtosecond rather than a nanosecond time scale adds another dimension to data processing.[2] In electronics binary states define device operation, while in photonics a "grey scale" of optical states might be accessible. The fact that fiber optics in telecommunications gives us a relatively "static" free carrier

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* Author to whom correspondence should be addressed.

(1) For a recent review of these applications see: *Photonic Materials*; MRS Bulletin, XIII, No. 8, Aug 1988.

(2) Fork, R. L.; Brito-Cruz, C. H.; Becker, P. C.; Shank, C. V. *Opt. Lett.* **1987**, *12*, 483.

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