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A Method for Controlled Stoichiometry Intercalation of Alkali Metals in Layered Metal Dichalcogenide Crystals*

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Crystals of Li_yTiS_2 ($0 < y < 1$) and 2H–A_yTaX_2 (A = Li, Na, K; $0 < y < 1$; X = S, Se) have been prepared by equilibration of the unintercalated crystals with a source powder of the desired alkali ion stoichiometry via the alkali vapor pressure of the compounds at 400–650°C. Crystals of 1 cm^2 area were intercalated. The final stoichiometry of the crystals is in good agreement with that expected from the source. © 1987 Academic Press, Inc.

Alkali metal intercalation chemistry continues to generate considerable interest due to the many fascinating physical properties exhibited by intercalation compounds and also by their possible secondary battery applications. A wide variety of transition metal oxide and chalcogenide intercalation species have been prepared using well established ambient temperature chemical and electrochemical techniques (*1–3*). Desired intercalation stoichiometries can generally be obtained in polycrystalline powders through application of appropriate reagents and conditions. However, these same reagents have been less successful for making single crystal intercalation compounds. The problems encountered with single crystals relate to cointercalation of solvents, relatively slow diffusion of the alkali in the host, changes in volume which tend to break the crystals, and most importantly, lack of control over stoichiometry. There have been successful intercalation reactions on small perfect crystals of TiS_2 with n-BuLi (*4*), and crystals of $A_{.5}MS_2$ (A = Li, Na, K, Rb, and Cs; M = Ti, Nb) have been grown directly from alkali halide melts (*5*). In general, relatively few physical properties have been measured on single crystals.

This paper reports a method for intercalation of alkali metals (Li, Na, K) into crystals of MX_2 (M = Ta, Ti; X = S, Se) which utilizes the small, alkali metal vapor pressure of A_yMX_2 (A = Li, Na, K) at temperatures in the range of 300–650°C. The method affords control of stoichiometry by equilibrating MX_2 crystals with a large excess of the desired A_yMX_2 stoichiometry.

Experimental

TaS_2 and TiS_2 powders were prepared by standard high temperature techniques (*6–8*). Crystals of TaS_2, $TaSe_2$, and TiS_2

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were grown by iodine vapor transport. Polycrystalline $LiTaS_2$ and $LiTiS_2$ powders were prepared by reaction with *n*-BuLi at room temperature. $NaTiS_2$ and $KTaS_2$ powders were prepared by reaction of TiS_2 and TaS_2 with Na and K naphthalide in THF. These powders were mixed with varying amounts of TiS_2 or TaS_2 to give a source charge of the intended final stoichiometry. Typical reaction mixtures contained approximately 200 mg of powders, and crystals on the order of approximately 1 to 5 mg. The powders and crystal were loaded in fused silica ampoules, keeping the powders and crystal physically separated. The tubes were sealed under vacuum (~60 mTorr) and placed in an oven at appropriate temperatures (300–650°C). TaS_2 samples were heated to 650°C for 7–10 days. TiS_2 and $TaSe_2$ crystals were heated to 400°C for 7–10 days. Intercalation of crystals could also be accomplished using another already intercalated single crystal as the source for the alkali ion. The sample tubes were allowed to cool slowly in the furnace before their transfer and storage in a dry box.

X-ray diffraction as well as atomic emission analysis were performed on the crystals and powders. X-ray diffraction patterns were obtained from a Rigaku miniflex powder X-ray diffractometer. Atomic emission was performed on a Perkin Elmer 3030 Atomic absorption spectrophotometer.

Results and Discussion

The ability to prepare crystals of intercalation compounds in order to measure physical properties which cannot be obtained from polycrystalline powders led us to attempt to prepare crystals of 2H–Li_yTaS_2 ($0 < y < 1$) using the *n*-butyl lithium technique on 2H–TaS_2 crystals of about 1 cm^2 area. We were able to prepare crystals of $LiTaS_2$ using this reaction with an excess of *n*-BuLi for 10 days at 50°C. However, stoichiometry for intermediate compositions could not be controlled. Partial reactions showed regions of complete lithiation and regions of no lithiation by X-ray diffraction. These samples could be homogenized by annealing at 400°C. in evacuated silica ampoules. We could not, however, correlate reaction time with the final Li stoichiometry. In the course of annealing samples to homogenize them, a few crystals were placed in the same tube without physical contact. Following the anneal we were surprised to find that each crystal had the same stoichiometry and we postulated that Li was being transferred via the vapor phase. This was checked by using one lithiated crystal and one pure 2H–TaS_2 crystal and again the two crystals attained the same composition. The final stoichiometry was now readily determined by the total Li/Ta ratio in the tube.

We have generalized this method to use lithiated polycrystalline powders as the source of Li. An excess of powder of the desired composition is used to fix the stoichiometry. The crystals intercalated to date have been wide thin platelets (~1 cm^2 × 5–50 μm) which required ~7–10 days to reach equilibrium. The composition of the alkali ion source and resultant crystals for several runs are given in Table I along with the interlayer separation. The majority of the samples prepared to date are Li intercalated species. A few examples of Na and K intercalated crystals are presented. The interlayer distances are compared with literature values in Figs. 1 and 2 for Li_xTaS_2 and Li_xTiS_2, respectively. The two curves exhibit close agreement between the experimental and previously published data. Several crystals heated for shorter periods of time exhibited sharp (001) reflections indicative of lower than expected Li intercalation. This is in contrast to incomplete reaction of crystals with *n*-BuLi which show regions of high Li concentration and regions of low concentration and leads to

TABLE I

Li source composition	Crystal stoichiometry	Interlayer spacing (Å)
$Li_{1.0}TaS_2$	$Li_{0.95}TaS_2$	6.465
$Li_{.50}TaS_2$	$Li_{.50}TaS_2$	6.450
$Li_{.33}TaS_2$	$Li_{.34}TaS_2$	6.425
$Li_{.25}TaS_2$	$Li_{.29}TaS_2$	6.360
	TaS_2	6.040
$Li_{1.0}TiS_2$	$Li_{1.0}TiS_2$	6.203
$Li_{.5}TiS_2$	$Li_{.5}TiS_2$	6.184
$Li_{.25}TiS_2$	$Li_{.08}TiS_2$	5.843
	TiS_2	5.699
$Li_{1.0}TaSe_2$	$Li_{.92}TaSe$	6.791
$Li_{.20}TaSe_2$	$Li_{.20}TaS_2$[a]	6.440
	$TaSe_2$	6.360
$Na_{1.0}TiS_2$	$Na_{.94}TaS_2$	14.67
$Na_{1.0}TaS_2$	$Na_{.92}TaS_2$	14.65
K_xTiS_2[a]	$K_{.80}TaS_2$	16.30

[a] Not analized by atomic emission spectrophotometry.

the conclusion that the rate limiting step for the vapor phase method is mass transport of Li through the vapor.

The fact that the Li is nearly homogeneous throughout a crystallite during the intercalation aids in minimizing any strain between regions of different Li concentration. This low strain, coupled with increased flexibility of the structure at high temperature, probably helps prevent cracking or exfoliation of the crystals.

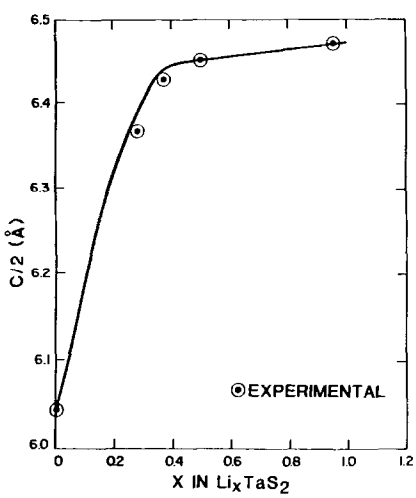

FIG. 1. Experimental and literature values for the interlayer spacing of Li_xTaS_2.

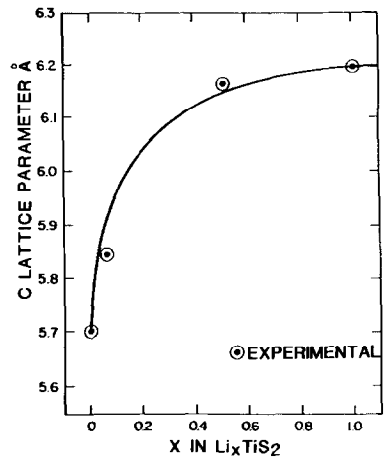

FIG. 2. Experimental and literature values for the interlayer distances of Li_xTiS_2.

In the case of 2H–$TaSe_2$, we were able to prepare crystals of $LiTaSe_2$ by heating 2H–$TaSe_2$ crystals with $LiTaS_2$ powder, even though the standard reaction using *n*-BuLi at room temperature led to exfoliation of the crystal. This example highlights the fact that the vapor method operates close to equilibrium reduction potentials whereas chemical reagents, such as the alkali napthalides, provide alkali ions at higher activities.

Although lithium has a substantial vapor pressure at moderate temperature (10^{-2} Torr at 650°C) (*9*), it is somewhat surprising that the intercalation compounds Li_yMX_2 have a significant vapor pressure since they are generally formulated as $Li_y^+M^{y-}X_2$. Estimates of the degree of charge transfer in $LiMX_2$ from ^{7}Li NMR data indicate ~90% charge transfer from Li to *M* (*10*). To a first approximation, the Li vapor pressure should be reduced from pure Li by the

percentage of charge transferred, e.g., 90% for $LiTiS_2$. This would still leave a substantial vapor pressure of 10^{-3} Torr at 650°C. In general, we expect that the Li vapor pressure will depend on the activity of Li in the intercalation compound. The Li activity, and thus the vapor pressure, is related to the EMF of $Li/Li^+/Li_yMX_2$ cells, with lower cell voltages giving higher activities and vapor pressures. Intercalation systems exist with a wide range of Li activities and, thus, Li vapor pressures.

These intercalation reactions were accomplished in sealed fused SiO_2 tubes. Thermodynamic calculations indicate that the Li vapor pressure would have to be $<10^{-15}$ Torr in order to prevent reaction with the tube. Pressures greatly in excess of this must be present in order to have any appreciable mass transport. Therefore, in order to have sufficient Li vapor to react with the MX_2 and still not react with SiO_2, we must propose either slow kinetics for the Li–SiO_2 reactions and/or formation of a thin passivating film on the SiO_2. Above 750°C attack of the silica tubes becomes substantial. Na and K have even higher vapor pressures than Li (at 400°C, 0.4 Torr for Na and 3 Torr for K). Thermodynamic calculations for Na and K also show that a suitable vapor pressure can only be attained kinetically.

Theoretically any other sources of alkali ion of appropriate activity can be used for intercalation. Attempts to use Li–Al alloy (20% Li) as a source for a higher activity of Li resulted in severe attack of the silica tube at typical reaction temperatures (500°C). Reaction with silica ampoules may be a problem even with low activity sources in those cases where long reaction times are needed. Nonreactive metal tubes could be used as a substitute for silica in those cases.

Conclusion

This paper presents a new method for preparing large single crystals of Li, Na, and K intercalation compounds of layered transition metal dichalcogenides. The availability of these crystals should make possible a number of experiments in which only single crystals can be used. The method should also be applicable to the other alkali ions, Cs and Rb, as well as other metals of similar vapor pressures (e.g., Zn, Hg, Mg). This is the first such technique to provide easy control over the alkali ion stoichiometry in large single crystals.

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