Communications

Hydrated Lithium Intercalation Compounds of Misfit Layer Sulfides

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Monolayer and bilayer solvation of intercalated cations may take place simultaneously with an intercalation reaction. Thus, hydrated alkali-metal ions are guest species when aqueous solutions of dithionites are used as insertion reagents.[1] Similarly, alkali-metal solutions in liquid ammonia give rise to intercalation of ammoniated ions into SnS_2.[2] Co-intercalation of ammonium ions and ammonia was recently reported for TiS_2.[3] The preparation of insertion compounds in an inert atmosphere avoids simultaneous solvation. Exposure of the products to an appropriate solvation agent atmosphere or liquid can be used to obtain solvated species in the interlayer space.[4] Further reactions of these species can be used to obtain monolayer materials.[5]

Misfit layer sulfides have $MM'S_3$ and MM'_2S_5-like stoichiometry and their structures consist of an intergrowth of MS and $M'S_2$ layers with distorted NaCl and CdI_2 structures, respectively.[6,7] These will be henceforth referred to as C and H, respectively. Two possible arrangements are found: ...HCHC... for $MM'S_3$ and ...HHCHHC... for MM'_2S_5.[6] Lithium intercalation into misfit layer sulfides by chemical procedures was recently reported.[8] Irrespective of the metal atoms present in the sulfides, phases with $MM'S_3$ composition allow for lower Li contents than does a MM'_2S_5 phase. In this work we studied the hydration properties of Li intercalation products of Pb/Ti misfit layer sulfides.

"$PbTiS_3$" and "$PbTi_2S_5$" samples were prepared from the elements in evacuated quartz ampules heated at 900 °C for 14 days. The semiquantitative atomic percentages of Pb, Ti, and S determined by energy-dispersive X-ray microanalysis in the platelike particles obtained by this procedure are listed in Table I. These results are consistent with $(PbS)_{1+x}TiS_2$ and $(PbS)_{1+x}(TiS_2)_2$ stoichiometries, as found for "$PbTiS_3$"[6] and other 1:1:3 and 1:2:5 misfit layered materials.[7] However, the exact value of x must be derived from the ratio between a unit cell parameters in the H and C sublattice, obtained by single-crystal X-ray diffraction procedures. Recently,[12] this value was calculated for the 1:1:3 phase, and a structure-derived stoichiometry was obtained of $(PbS)_{1.18}TiS_2$. Powder X-ray and electron diffraction data (Figure 1) show that the samples contain high-purity misfit phases. The X-ray diffraction patterns allow to determine basal spacings of 23.7_4 and 34.9_0 Å, which are characteristic of HCHC and HHCHHC structural units, respectively.

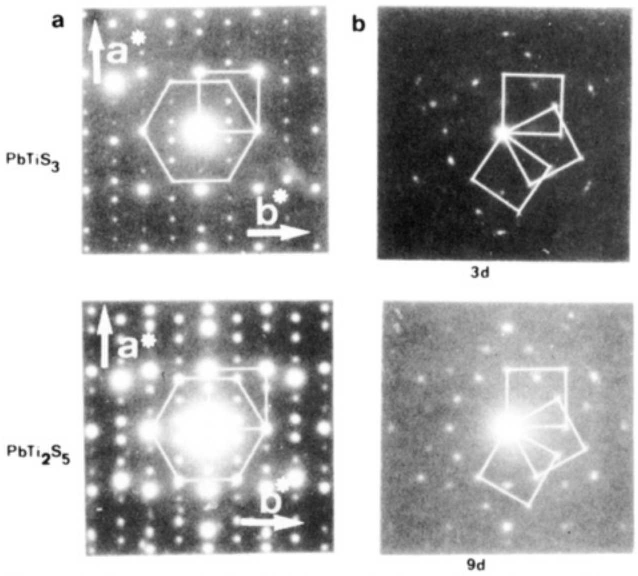

Figure 1. Representative [001] zone electron diffraction patterns of (a) "$PbTiS_3$" and "$PbTi_2S_5$" and (b) the same samples after lithium intercalation reactions with n-butyllithium during 3 and 9 days, respectively.

Lithium insertion reactions of these samples were carried out in an argon-filled glovebox (M. Braun; water content lower than 2 ppm). Samples were covered with a plastic film inside the glovebox for the recording of X-ray diffraction patterns. The intercalated products were obtained after similar 4-day periods of treatment of 200 mg of the original samples with a 1.6 M n-butyllithium solution in hexane at room temperature. These products had the Li contents and basal spacings given in Table I. Previous results on the lithiation of misfit layer chalcogenides[8] indicate that the rate of lithium insertion is higher in 1:2:5 phases as compared with 1:1:3 phases. After similar periods of reaction, we always find a higher lithium content in 1:2:5 phases. At present we have no satisfactory explanation for these differences in the kinetics, although it may be suggested that they are related with the higher interactions between Li^+ ions and Pb ions in C layers at both sides of an H layer for 1:1:3 compositions. Second, these compositions were chosen because further lithiation leads to a deterioration of the structure finally reaching an amorphous state in both cases and samples were needed in which crystallinity is sufficient to study the hydration process. As earlier noted,[8] the 1:1:3 phase had a less significant increase in its basal spacing. This behavior may be a result of the presence of two consecutive H layers

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Table I. Chemical Composition and Basal Spacings of Lithium Intercalated/Hydrated Phases[a]

idealized Pb:Ti:S	original sample experimental atomic % (EDX) Pb	Ti	S	lithiated sample (AAS) Li/Pb	basal spacing, nm c^{MF}	c^0	c^1	c^2
1:1:3	21.8	20.0	58.2	0.2	2.37_4	2.38_9		
1:2:5	12.5	23.0	64.6	2.0	3.47_0	3.58_4	4.04_6	4.61_3

[a] EDX: energy-dispersive X-ray microanalysis. AAS: atomic absorption spectrometry. MF: original nonlithiated misfit phase. ^{0,1,2} Number of layers of water molecules per structural unit HHC in lithiated phases.

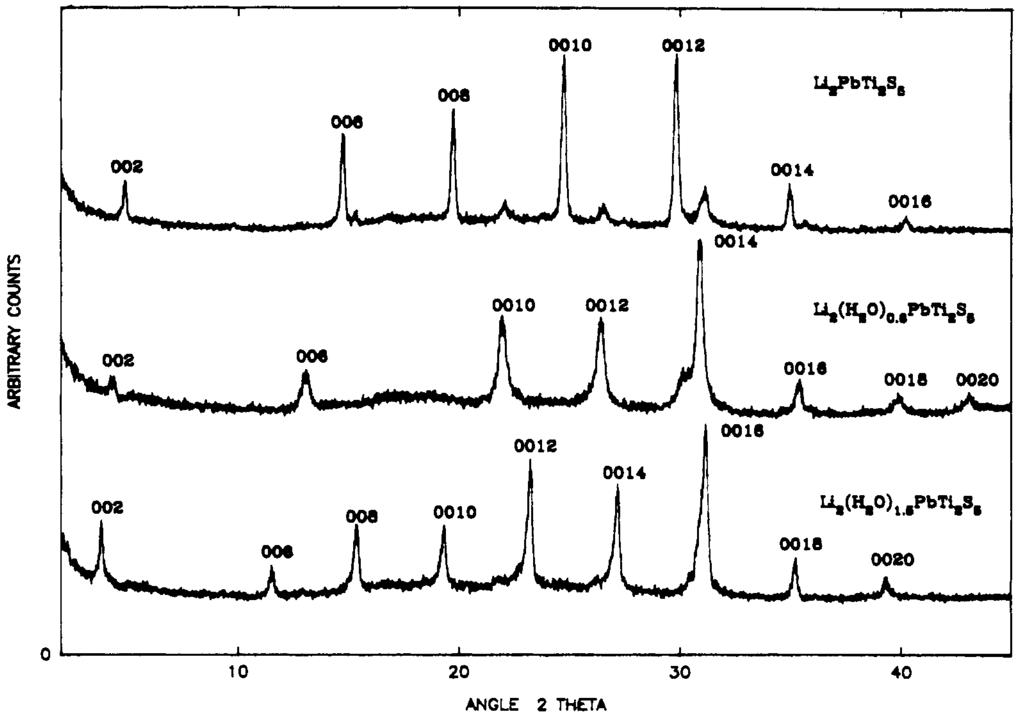

Figure 2. Powder X-ray diffraction patterns of partially hydrated $Li_2PbTi_2S_5$ and samples containing one and two layers of water molecules per structural unit HHC.

separated by a van der Waals gap in the structure of the 1:2:5 phase. However, no van der Waals gap connects two $M'S_2$ sublattices in the 1:1:3 phase because of the layer sequence ...HCHC....

On the other hand, it is known that multiple orientations of H or C layers have been reported in distorted regions of samples of nonintercalated misfit layer compounds.[9,10] The original $PbTiS_3$ and $PbTi_2S_5$ samples were carefully observed in the electron microscope, and practically all the observed particles showed a single orientation of the C sublattice. On the contrary, the vast majority of the particles of the lithiated samples showed the characteristic patterns of Figure 1b. The origin of this distortion can be ascribed to the interactions of the incoming Li^+ with the Pb ions. This cation is coordinated to five sulfur atoms in the C sublattice forming roughly a square pyramide. Thus Li intercalation between C and H layers may cause a displacement of both sublattices, as a result of the repulsions of both positive charges.

Lithiated phases were extracted from the drybox in an argon-filled closed vessel and then exposed to O_2-free water vapor. Consecutive recordings of XRD patterns (Figure 2) showed the gradual appearance of two new sets of 00*l* lines corresponding to hydrated phases in "$PbTi_2S_5$", whereas no changes were observed for "$PbTiS_3$". The basal spacings of the hydrated phases are listed in Table I. It should be noted that during the recording of the XRD pattern of the lithiated phase $Li_{2.0}PbTi_2S_5$ (Figure 2) a partial hydration took place, as shown by the low-intensity set of lines corresponding to a higher basal spacing. This is probably a result of the nonhermeticity of the plastic cover used for XRD experiments and the ease of hydration of this phase. Moreover, the intensity of the line set with a basal spacing of 40.46 nm decreased as the phase characterized by a basal spacing of 46.13 nm became more prominent as a longer hydration period was allowed. These values were initially ca. 3 Å and finally ca. 6 Å larger for each HHC unit than were those of the lithiated phase. These values are quite consistent with 1 and 2 times the van der Waals diameter of a water molecule (ca. 2.8 Å). The absence of hydration in the 1:1:3 phase may indicate that water molecules are inserted between H layers of the misfit structure.

The TG traces recorded under a dynamic nitrogen atmosphere for those samples previously exposed to water vapor are shown in Figure 3 and agree with previous interpretations. Thus, a significant weight loss is observed for the 1:2:5 stoichiometry as compared with the 1:1:3 stoichiometry. Indeed, the weight loss for the latter system between room temperature and 150 °C is negligible and falls within the resolution range of the thermobalance. In addition, the fact that two steps with similar weight-loss percentage are present in the dehydration curve implies

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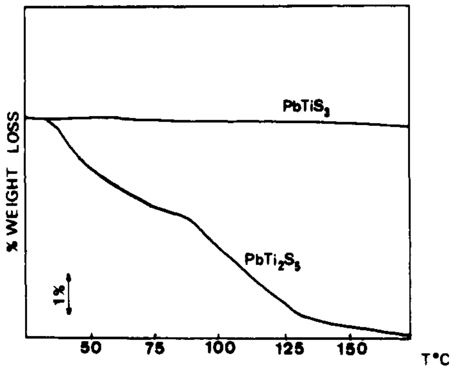

Figure 3. TG traces of $Li_{0.2}PbTiS_3$ and $Li_{2.0}(H_2O)_{1.5}PBTi_2S_5$. These samples were prepared from lithiated samples after being exposed to water vapor.

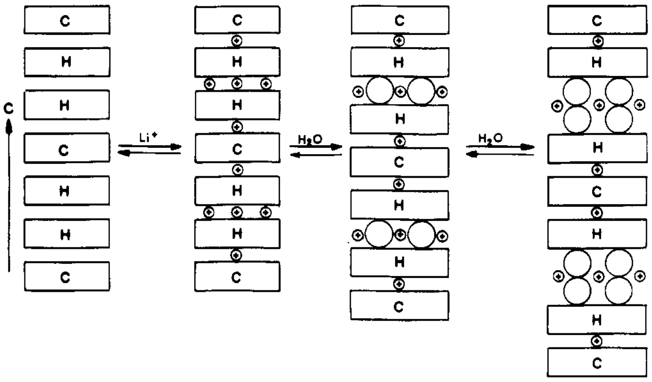

Figure 4. Scheme of lithiation/hydration reactions of $PbTi_2S_5$. C and H denote PbS (NaCl related) and TiS_2 (CdI_2 related) negatively charged layers.

that the pattern followed is that shown in Figure 4, which is similar to that described by Lerf and Schöllhorn.[4] This behavior was checked by halting the recording of the TG curve at the end of the first step and immediately recording the XRD pattern. The basal spacing of the low-temperature intercalation product was expanded by ca. 3 Å/HHC unit. The product obtained after the second step of the TG curve showed a similar basal spacing than the nonhydrated lithiated samples. Thus, the hydration seems to be a reversible process. Heating the samples above 175 °C led to a partial decomposition of the misfit structure, finally leading to an amorphous state. From the quantitative evaluation fo the TG data for the 1:2:5 phase, compositions of the hydrated phases close to $Li_2(H_2O)_{0.6}PbTi_2S_5$ and $Li_2(H_2O)_{1.5}PbTi_2S_5$ can be obtained. These values are similar to those found for $A_x(H_2O)_yMS_2$ (A: Na, K; M: Ti, Nb, Ta).[4] A final point of interest is the fact that no staging was observed in the hydrated phases. Staging has been found in amonium intercalates of TiS_2 and NbS_2.[11] Only stage I was detected in the hydrated samples, were the interlayer HH space of all HHC units contained 1 or 2 water molecules.

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Registry No. Pb, 7439-92-1; Ti, 7440-32-6; S, 7704-34-9; $PbTiS_3$, 12066-65-8; H_2O, 7732-18-5.

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Synthesis and Properties of Polyoxometalates Based Inorganic-Organic Polymers

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The synthesis of mixed organic-inorganic materials is a growing field of research.[1] The challenge for these new materials is to optimize both the inorganic and the organic components on a molecular scale. Such advanced materials must exhibit specific properties (electronic, optic, catalytic, ...) and easily be shaped as coatings or monoliths. Polyoxometalates (POM's) have been widely studied as small compact oxide clusters.[2] Their redox properties and high electronic density are ideal for their use as catalysts, stains for electron microscopy, cross-linking reagents, and photochromic or electrochromic materials.[3] Many studies are dealing with their stabilization by entrapment in polymeric networks.[4]

This communication presents for the first time, to the best of our knowledge, the synthesis and characterization of negatively charged macromolecules based on organically functionalized POM's anchored to an organic polymeric backbone. Organically modified POM's are anchored together through chemical bonds in order to obtain macromolecules. This study concerns the chemistry of a new class of organic-inorganic polymers. They could be promising materials for photo- or electrochromics.

The synthesis of mixed organic-inorganic polymers has been performed as follows: The organically modified POM precursors have been synthesized by reacting trichloro(or trialkoxy)silane with lacunar $K_4SiW_{11}O_{39}$ following a procedure previously described.[5-7] The organic functionalization is obtained via trichlorosilanes $RSiCl_3$ (R = vinyl ($CH{=}CH_2$), allyl ($CH_2CH{=}CH_2$), 3-(methacryloxy)propyl [methacryl] ($(CH_2)_3OC(O)C(CH_3){=}CH_2$)) purchased from Dynamit Nobel Company or triethoxystyrilsilane ($(OEt)_3Si(C_6H_4CH{=}CH_2)$) [styryl] synthesized by reaction of Grignard derivative with $Si(OEt)_4$ in THF.[8,9]

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(7) Triethoxystyrylsilane was added to a K_4SiW_{11} aqueous solution, under vigorous stirring, and the pH was adjusted to pH 1 by addition of HCl. After 20 h of stirring, NBu_4Br was added, and the precipitate was washed with water and *i*-PrOH, leading to styryl-derivitized heteropolytungstate (yield = 60%).

(8) $MgBrC_6H_4CH{=}CH_2$ was prepared by slow addition of 5.5 g (0.03 mol) of 4-bromostyrene to 0.73 g (0.03 mol) of magnesium turnings in THF, under argon atmosphere. The solution was kept boiling for 20 h. To this solution was added dropwise 5 g (0.024 mol) of tetraethoxysilane in THF. The solution was refluxed for 15 h. The resulting gum has been purified by vacuum distillation and 3 g (0.011 mol) of triethoxystyrylsilane ($(OEt)_3SiC_6H_4CH{=}CH_2$) was obtained (T_b = 120 °C/0.1 mmHg, yield = 50%, purity checked by NMR and mass spectrometry).

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