

Layered MPS₃ (M = Mn, Cd) Thin Films as Host Matrixes for Nonlinear Optical Material Processing

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The possibility of processing MPS₃ (M = Mn, Cd) layered materials as thin films capable of intercalating nonlinear optical chromophores is investigated. Two different synthetic routes are presented. The first method (solution approach) involves the coprecipitation of transition-metal ions Mn²⁺ with ligands (P₂S₆⁴⁻) followed by casting on a glass substrate. Such films have a composition similar to the high-temperature-synthesized MnPS₃ phase but exhibit a much lower crystallinity. However, XRD patterns reveal a preferential orientation of the layers parallel to the support. The second process (solid-state approach) uses the ability of the MPS₃ layered compounds to be exfoliated through the successive intercalations of K⁺ and Li⁺ cations. The resulting compounds of formula M_{1-x}PS₃Li_{2x}·nH₂O (x = 0.18 for the manganese derivative and 0.16 for the cadmium derivative) readily form highly orientated thin films. Highly transparent thin films were obtained from the CdPS₃ starting material. The lithium intercalate thin films were characterized by thermogravimetric techniques, IR spectroscopy, and X-ray diffraction. Their mechanical stability was found to be slightly better than that of the solution-approach-based thin films. The intercalation of a nonlinear optical chromophore (4-[4-(dimethylamino)-α-styryl]-1-methylpyridinium) was performed in these thin layered films, which were found to be much more reactive than the parent bulk MPS₃.

Introduction

Theoretically, organic second-order nonlinear optical (NLO) chromophores have the potential to supplant inorganic crystals as the materials of choice for many optoelectronic devices. At the *molecular* level, many of them exhibit NLO responses several orders of magnitude higher than those of a single molecule of inorganic crystals currently available.³ However, one of the main bottlenecks in the development of these chromophores in optical materials is their processing in macroscopic systems. It is well-known that second-order nonlinearities require materials exhibiting noncentrosymmetric structures.⁴ Therefore, molecular materials exhibiting such properties must necessarily be engineered into acentric environments if the molecular hyperpolarizability (β) is to contribute to an observable bulk nonlinearity (χ^2). The problems related to efficient and time-stable poling of chromophores into acentric envi-

ronments have not been overcome yet, although many processing methods such as sol-gel methods,⁵ molecular acentric arrangements in single crystals,⁶ and the promising high- T_g poled polymer approach⁷ have been explored. During the past decade, it has been reported that intercalation into organic⁸ or inorganic^{9,10} host compounds could be an alternative method in spontaneously aligning organic chromophores into an acentric arrangement without the need for an external electric field. Efficiencies several times greater than that of urea were achieved even when the parent compounds could not frequency-double. These processes, which could also provide materials with thermodynamic stability and then avoid any decay rate of the NLO signal, are especially worthwhile for ionic or nonpolar guests

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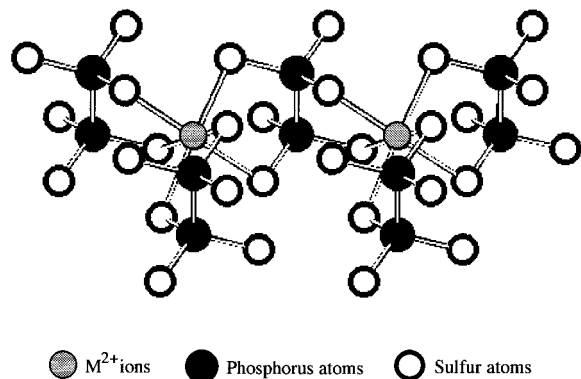
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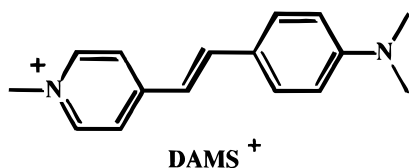
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Scheme 1



(for example, octupolar chromophores¹¹) since poling fields usually require neutral species and nonzero dipole moments, even if alternative routes have been recently proposed to overcome this problem.¹²

Two of us recently reported¹³ the preparation of a new class of multifunctional materials combining magnetism and NLO properties via intercalation of an organic dye, 4-[4-(dimethylamino)- α -styryl]-1-methylpyridinium¹⁴ (DAMS⁺) into the inorganic lamellar compounds MPS₃ (M = Mn, Cd).¹⁵



These compounds of formula M_{0.86}PS₃(DAMS)_{0.28} were obtained as powders showing NLO efficiencies in second harmonic generation (SHG) of several hundred times (750 times for the cadmium derivative) that of urea and a permanent magnetization below 40 K for the manganese derivative. However, the practical applications of intercalation materials are rather limited because many of them are usually available only in fine powders. To be appropriate in optical devices for further potential applications, these materials must be easy to process and possess good transparency. Single crystals and thin films generally meet these requirements.

In the present work, we investigated the possibility of processing MPS₃ materials as layered thin films capable of intercalating nonlinear optical chromophores. Two different approaches were selected to achieve this goal. The first method (A) describes the preparation of MPS₃ thin films involving the unusual aqueous chemistry of the MPS₃ phases (solution approach). As mentioned in previous work,¹⁶ MPS₃ slab behaves as a coordination compound made up of M²⁺ cations coordinated to P₂S₆⁴⁻ bridging ligands (Scheme 1). It was reported¹⁷ that MPS₃ materials can then be synthesized

by the usual techniques of coordination chemistry, i.e., by coprecipitating the transition-metal ions (Mn²⁺ or Cd²⁺) and the ligands (P₂S₆⁴⁻).

The second method (B) is based on the exfoliation technique (solid-state approach). For the past 10 years, much work has been focused on developing film-forming properties of several layered compounds, such as dichalcogenides¹⁸ (MoS₂, TaS₂), metal oxides¹⁹ (titanate, alumina), or clay minerals²⁰ (montmorillonite) through their ability to be exfoliated to single layers. The exfoliation technique, which can be done by chemical, electrochemical, or ultrasonical treatment, allows layer stacking to collapse and the dispersion into colloidal nanosheet suspensions. These suspensions can be spread on a support and upon drying the nanosheets reassemble into a stack so that the final materials are well-ordered layered thin films. This technique was successfully applied to the MPS₃ materials via a lithium intercalate (chemical exfoliation). Herein is the description of the preparation of MPS₃ layered thin films by the two methods mentioned above and their possible application as starting materials for the intercalation of NLO chromophores (C).

Experimental Section

Starting Materials and Equipment. MnCl₂·4H₂O was purchased from Janssen Chimica and used without further purification. Na₄P₂S₆·6H₂O and DAMS⁺I⁻ were synthesized according to the procedures previously described.^{21,22}

Elemental analyses were performed by the Centre National de la Recherche Scientifique (CNRS) in Gif sur Yvette (France). Infrared spectra were obtained on a Perkin-Elmer 883 spectrometer from 200 to 4000 cm⁻¹. The samples were prepared as KBr pellets. The films were taken off their glass support and diluted 1 wt % in KBr. XRD patterns were obtained on a Siemens diffractometer using a generator voltage of 40 kV and a generator current of 20 mA. A step size of 1°/min was used. The XRD patterns of the samples were directly recorded on glass slides at room temperature (20 °C) and for some of them after heating at 40, 60, 80, 120, and 160 °C. The thermal analysis (TGA and DTA) experiments were performed in air, using a nickel/cobalt thermocouple from room temperature to 250 °C. Approximately 30 mg of sample was used for each run. The DAMS insertion was followed by XRD and also by UV-visible spectroscopy performed directly on the films deposited on the glass slides. UV-visible spectroscopy experiments were carried out on a Varian 2300 spectrometer from 800 to 200 nm.

(A) Preparation of Thin Films (Solution Approach).

To a solution of 90 mg of Na₄P₂S₆·6H₂O in 2 mL of distilled water was added 400 mg of MnCl₂·4H₂O (large excess) in 2 mL of distilled water. The milky suspension that instantaneously formed was centrifugated and washed several times with water. The mixture was then dispersed in 5 mL of

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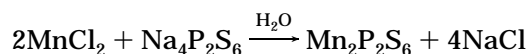
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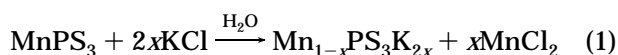
distilled water and a few drops were cast on a glass support and were allowed to dry very slowly for about 2 days in air. The opaque white suspensions turned into highly transparent green film with a thickness from 1 to 5 μm . The films were stored at 120 °C to ensure complete dryness. The chemical reaction describing this process is given by the following equation:



(B) Preparation of Thin Films (Solid-State Approach).

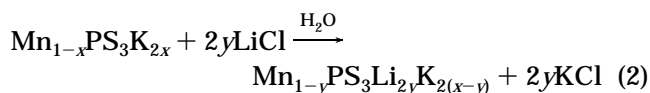
Pure MnPS_3 and CdPS_3 were synthesized as previously described²³ via a high-temperature process by heating a stoichiometric mixture of the elements at 750–780 °C for a few days in a sealed evacuated quartz tube. The preparation of the thin films is a two-step process.

Potassium ion intercalation: 200 mg of the polycrystalline powdered MPS_3 ($\text{M} = \text{Mn}, \text{Cd}$) samples were first soaked at room temperature in an aqueous solution of KCl (0.5 mol L^{-1}) for 1 h to yield to the intercalate compound $\text{M}_{0.8}\text{PS}_3\text{K}_{0.2}\cdot\text{H}_2\text{O}$ where the electrical charge of the entering solvated cation (K^+) is counterbalanced by the removal of some intralayer M^{2+} cations from the solid (eq 1). In the case of CdPS_3 , this reaction



requires a complexing agent such as EDTA be added to the aqueous solution to help the Cd^{2+} ions leave the host lattice. EDTA (5 mL, 0.1 mol L^{-1}) is then added to the 0.5 mol L^{-1} buffered solution ($\text{K}_2\text{CO}_3/\text{KHCO}_3$) of KCl in which 200 mg of CdPS_3 is stirred for 3 h at room temperature. The intercalated compounds are washed several times with distilled water.

Potassium ion exchange with lithium ions: During the second step, the interlamellar solvated K^+ ions are exchanged with solvated Li^+ ions (eq 2): the potassium intercalated



powdered samples previously obtained from the MnPS_3 phase as well as the CdPS_3 phase are treated by a highly concentrated (3 mol L^{-1}) aqueous solution of LiCl for 1 h at room temperature. After 1 h, some K^+ ions were exchanged by Li^+ ions in the interlayer space, the LiCl solution was renewed, and the powder was allowed to react for one more hour at room temperature. The powder was first washed with three dilute LiCl solutions (0.5, 0.25, and 0.1 mol L^{-1}), then many times with distilled water. The pH of the washing solutions was also measured after each washing. The pH of the first washing solution was found to be around 8, whereas after the second washing the pH drops to 7 and stabilizes around 6 after the third washing. We also observed that in the case of the manganese-based compound, these washing solutions were black. This could be attributed to different hydroxides of manganese III and IV resulting from the oxidation of the Mn^{2+} ions in basic solution. When the pH dropped below 7, some H_2MnO_3 could also form. These solutions turn colorless after exposure to the light for few hours suggesting that acid/base equilibria occurred. After the last water washing, the powder was highly dispersed and formed a colloidal suspension; pale green and milky white with MnPS_3 and CdPS_3 , respectively, as starting materials. Black particles for MnPS_3 and orange particles for CdPS_3 were also observed in the more dense part of the suspension and were identified as MnS and CdS particles. Drops of these suspensions were then deposited on glass slides and allowed to slowly dry in air for a few days. Lithium intercalate thin films, with a thickness around 1–3 μm were obtained. They are slightly opaque for the MnPS_3 phase but fully transparent for the CdPS_3 phase. This

transparency can further be improved by sifting the starting CdPS_3 powder in order to obtain a grain size lower than 75 μm .

(C) DAMS Intercalation. DAMS⁺ ions were first intercalated in MnPS_3 thin films obtained via the solution approach. The MnPS_3 films were kept for few hours in 60 mL of a solution of 183 mg (2×10^{-4} mol) of DAMS⁺I⁻ in ethanol containing various amounts of water (absolute ethanol, 95/5, 90/10, 50/50 ethanol/water ratio). The resulting films were washed with ethanol and allowed to dry without any special care (room temperature, in air). The kinetics of the intercalation turns out to be very dependent on the water concentration (see Results and Discussion) but the elemental analysis of any intercalates yields to the formula $\text{Mn}_{0.85}\text{PS}_3(\text{DAMS})_{0.3}(\text{H}_2\text{O})_{0.5}$. Elemental analyses (wt %) found (calculated): C 22.18 (22.64), H 2.56 (2.65), N 3.08 (3.30), Mn 17.78 (18.34). The absence of iodine was also carefully confirmed.

The DAMS⁺ intercalation into the thin films obtained from the solid approach was done with the MnPS_3 and CdPS_3 phases as starting materials. In a typical experiment, a thin film of CdPS_3 lithium intercalate was kept in a solution of 200 mg of DAMS⁺I⁻ in 75 mL of ethanol at 60 °C for 2 h. The resulting red film was washed with ethanol and dried in air.

Results and Discussion

(A) Thin Films from Solution Approach. MnPS_3 films obtained by coprecipitation of $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ and $\text{Na}_4\text{P}_2\text{S}_6\cdot 6\text{H}_2\text{O}$ in aqueous solution exhibit similar structural features as a MnPS_3 phase synthesized via a high-temperature solid-state process.²¹ Elemental analyses (wt %) found (calculated for MnPS_3): Mn 29.49 (30.17), P 16.96 (17.01), S 52.33 (52.82), H 1.22 (0.00). However, the crystallinity of these thin films is much lower than that of the high-temperature synthesized phase as can be observed on the XRD patterns (Figure 1). The XRD patterns show the 00 l reflections which yield to the interlamellar distance. This distance is the same for the high-temperature synthesized MnPS_3 phase (Figure 1a) as it is for the MnPS_3 thin films (Figure 1b): 6.5 Å ($2\theta = 13.5^\circ$), but the peaks of the thin films are much larger: 1.2° versus 0.2°, indicating that this material is less ordered. However, it is obvious from the XRD patterns that the films show a preferential orientation in the deposition process with the layers parallel to the substrate. The crystallite size was estimated, from the XRD line broadening, at 150 Å. A similar experiment was attempted to obtain CdPS_3 by coprecipitation of CdCl_2 and $\text{Na}_4\text{P}_2\text{S}_6$ in aqueous solution but remained unsuccessful. This can be reasonably understood with the mechanism previously described¹⁷ to relate the ion-exchange intercalation chemistry of the MPS_3 phases to the heterogeneous equilibrium occurring between the MPS_3 solid phase and the ionic constitutive species: $(\text{P}_2\text{S}_6)^{4-}$ and M^{2+} . Such an equilibrium is not expected to take place for the less labile Cd(II) ions.

A crucial question related to the suitability of such MnPS_3 films is their poor mechanical stability. We have noticed that although dry films were mechanically resistant, they undergo dramatic changes, such as loss of transparency and mechanical stability, while exposed to air saturated with water. In the search for improving the mechanical properties, we found that using water containing poly(ethylene glycol) (PEG; 300 mg of PEG of average molecular weight 7000 in 10 mL of distilled water) as solvent for the synthesis of starting MnPS_3 thin films significantly increased the stability and quality of the samples. However, further experiments were no longer pursued, as it turned out that the

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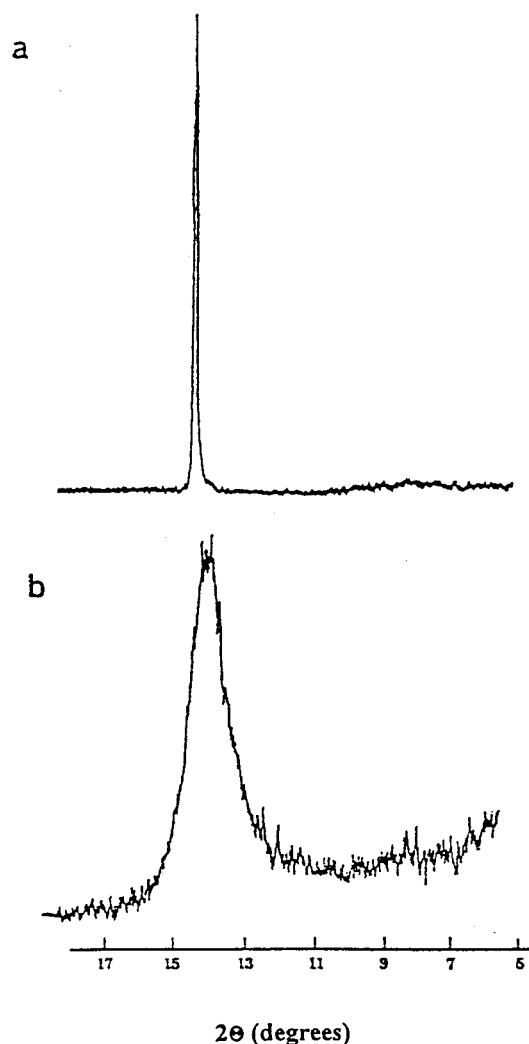


Figure 1. XRD patterns of (a) high-temperature-synthesized MnPS₃ and (b) MnPS₃ thin films (solution approach).

Table 1. Elemental Analyses in Weight Percent (wt %) of MnPS₃-Based Li Intercalate and CdPS₃-Based Li Intercalate Thin Films

	M	P	S	Li	K	Cl	H
MnPS ₃ -based Li intercalate	18.67	13.37	40.07	1.00	<0.09	0.30	2.63
CdPS ₃ -based Li intercalate	35.48	11.55	35.85	0.92	<0.20	0.37	1.63

presence of polymer significantly decreased the intercalation process kinetics.

(B) Thin Films from the Solid-State Approach.

The preparation of oriented thin films via the exfoliation process which occurs after lithium intercalation in the MPS₃ phases was investigated as an alternative to the solution approach in the case of the CdPS₃ phase. As mentioned above, it has been impossible to synthesize this phase by coprecipitation of the constitutive ions: Cd²⁺ and P₂S₆⁴⁻ as it was done with the manganese phase. However, the CdPS₃ starting material was anticipated to show very promising optical properties as the monocrystals obtained via a high-temperature synthesis process are almost transparent. The processing of this phase as layered thin films was hence of great interest to us. It should also be noted that the starting CdPS₃ compound behaved toward the lithium intercalation the same way as the MnPS₃ phase did, as we will discuss below.

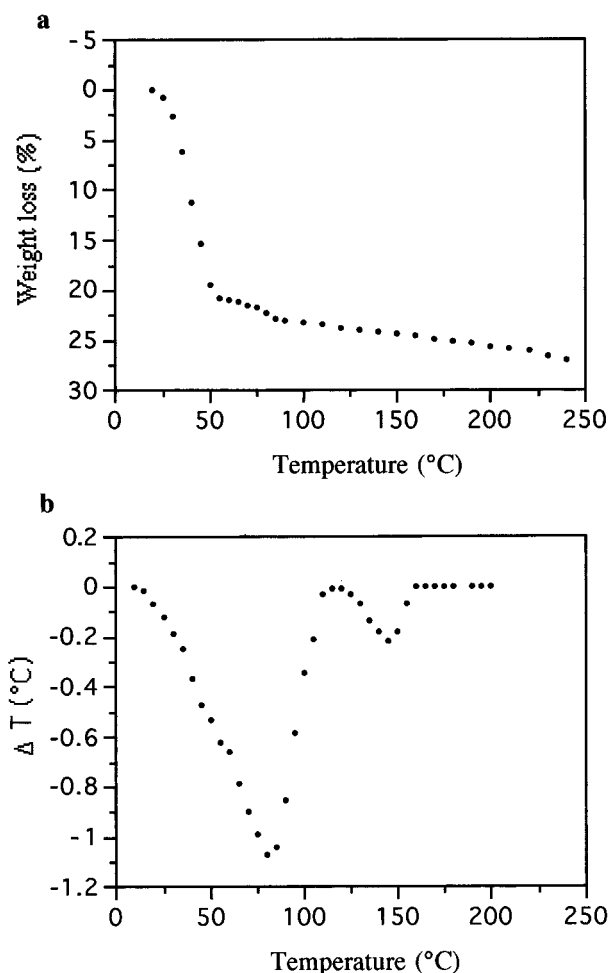


Figure 2. (a) TGA and (b) DTA curves of MnPS₃ lithium intercalate thin film.

The MPS₃ (M = Mn, Cd) lithium intercalate thin films were characterized by elemental analyses, thermogravimetric techniques (TGA, DTA), X-ray diffraction, and IR spectroscopy in order to find an explanation for the solid-phase dispersion occurring upon Li⁺ ion intercalation. The stability of these films toward heat treatment and exposure to different solvents was also investigated. The elemental analyses of these two compounds, as shown in the Table 1, yield to the formulas: Mn_{0.82}PS₃·Li_{0.34}·3H₂O and Cd_{0.84}PS₃Li_{0.35}·2H₂O. The number of H₂O molecules in each of these compounds was also confirmed by the TGA results. Despite many water washings, Cl⁻ ions were not totally eliminated. Also, not all K⁺ ions were exchanged for Li⁺ ions in the interlamellar space. However, their concentration remained low compared to the Li⁺ ion concentration. Figures 2 and 3 show the TGA and DTA curves recorded in the 20–250 °C range (in air) of the MnPS₃ lithium intercalate and the CdPS₃ lithium intercalate, respectively. Both compounds underwent a very fast weight loss (20%) at room temperature (25 °C). This weight loss, which probably started before the beginning of the data recording, was assigned to the elimination of the remaining water due to a partial drying of the sample. Another weight loss occurred around 50 °C and corresponds to only 5% of the MnPS₃-based sample total weight and 3% of the CdPS₃-based sample total weight. This loss is also attributed to water molecules present in the interlamellar space. Because they are more strongly bound to the lattice, their removal from the

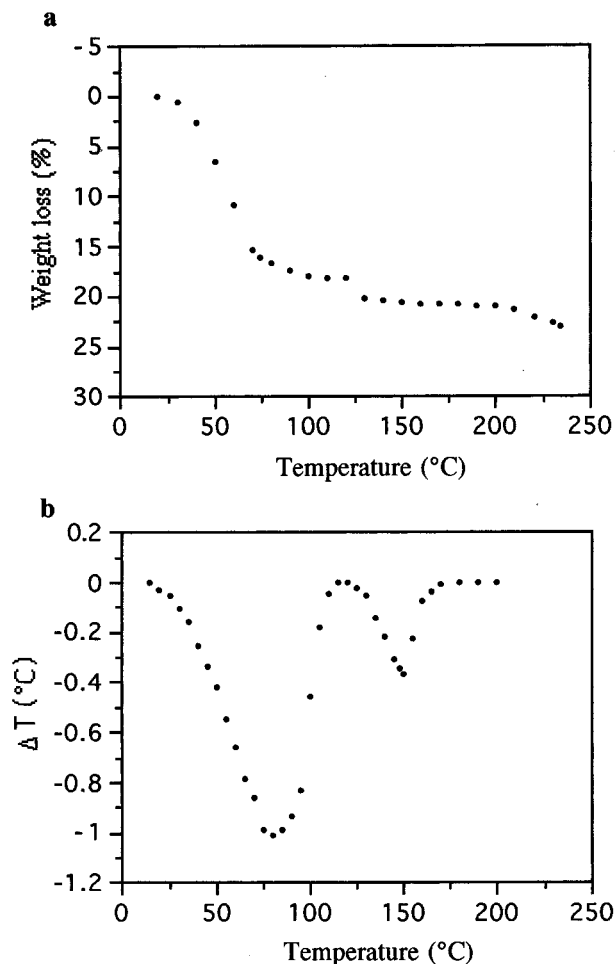


Figure 3. (a) TGA and (b) DTA curves of CdPS₃ lithium intercalate thin film.

interlayer space is more difficult and requires a higher temperature. The DTA data (Figures 2b and 3b) also show in both cases endothermic effects attributed to water elimination from the interlayer space.

Intercalated water molecule mobility as well as structural modifications was evidenced by IR spectroscopy during a dehydration/rehydration cycle of the MnPS₃ and CdPS₃ lithium intercalates. A representative sample is illustrated on Figure 4 showing the IR spectra obtained after a dehydration/rehydration cycle of a MnPS₃-based sample, first dried in air (Figure 4a), then heated to 80 °C (Figure 4b), and finally exposed again to air for few hours (Figure 4c). In Figure 4a the broadband at 3391 cm⁻¹ as well as the peak at 1618 cm⁻¹ are respectively attributed to the ν_{OH} and the δ_{OH} of the water molecules still present in the interlayer space. The two peaks respectively located at 558 and 605 cm⁻¹ correspond to a splitting of the asymmetric stretching bond ν(PS₃). It has been shown²⁴ that the ν(PS₃) asymmetric stretching band located at 570 cm⁻¹ in the pure MPS₃ compounds is systematically split into two components (558 and 605 cm⁻¹) in intercalated materials. This splitting was explained as a consequence of the release of metallic ions from the layers occurring upon intercalation that makes the PS₃, and hence the P–S bonds, inequivalent, as some of them are

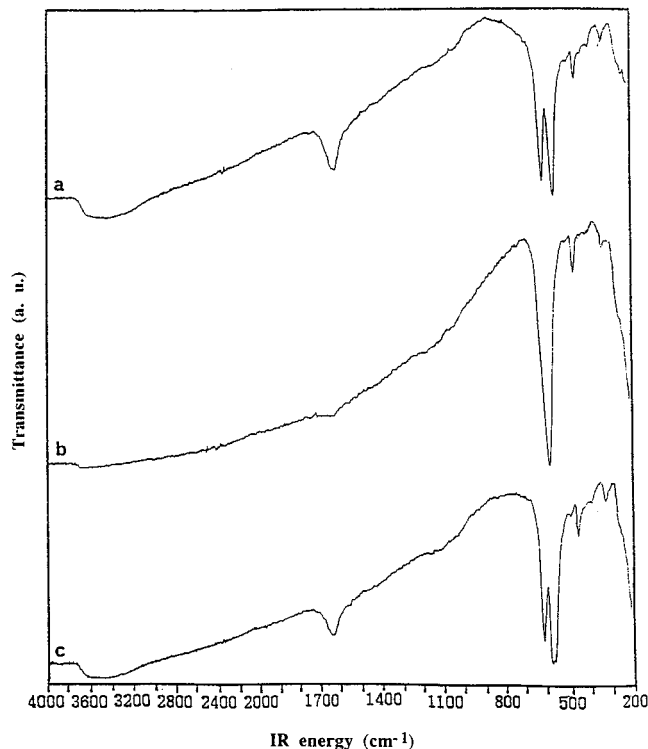


Figure 4. IR spectra of MnPS₃ lithium intercalate thin film after (a) drying in air, (b) heating to 80 °C, and (c) reexposed to air for few hours.

surrounding metallic vacancies while others are still bound to transition-metal ions. Finally, in Figure 4a, the 450 cm⁻¹ band was attributed to P–P vibrations.^{24b} When heating the compound to 80 °C (Figure 4b), some changes were observed in the IR spectrum. The bands assigned to the water molecules disappeared and, more importantly, the ν(PS₃) splitting into two components also disappeared. Instead, one peak was observed, located at the same wavelength (571 cm⁻¹) as in the pure MnPS₃ phase^{24b} but slightly wider, suggesting that the PS₃ vibrators are now all equivalent and no intralamellar metallic vacancies were present in the compound. The dehydration of the lithium intercalates is a reversible process as shown by the IR spectrum (Figure 4c) recorded after rehydration of the sample. This spectrum is very similar to the spectrum recorded after drying in air (Figure 4a) with the bands attributed to the water molecules (broad band between 3600 and 3400 cm⁻¹ and peak at 1626 cm⁻¹) and the two peaks (605 and 558 cm⁻¹) corresponding to the ν(PS₃) splitting due to the intralamellar vacancies. Upon the rehydration process, some ionic species are then able to leave their intralamellar sites as discussed later.

The XRD characterization of the lithium intercalates was carried out during a dehydration/rehydration cycle for the MnPS₃ derivative as was done for the IR spectroscopy study and upon heating at different temperatures for the CdPS₃ derivative. The XRD patterns are shown on Figures 5 and 6. These patterns exhibit only 00 l reflections indicating a preferential orientation of the layered thin films with the sheet stacking parallel to the substrate. The interlayer distances are deduced from the d_{00l} spacings, which are obtained using the first rational orders corresponding to the 00 l reflections. Figure 5 shows the XRD patterns of the MnPS₃ lithium intercalate film during a dehydration/rehydration cycle,

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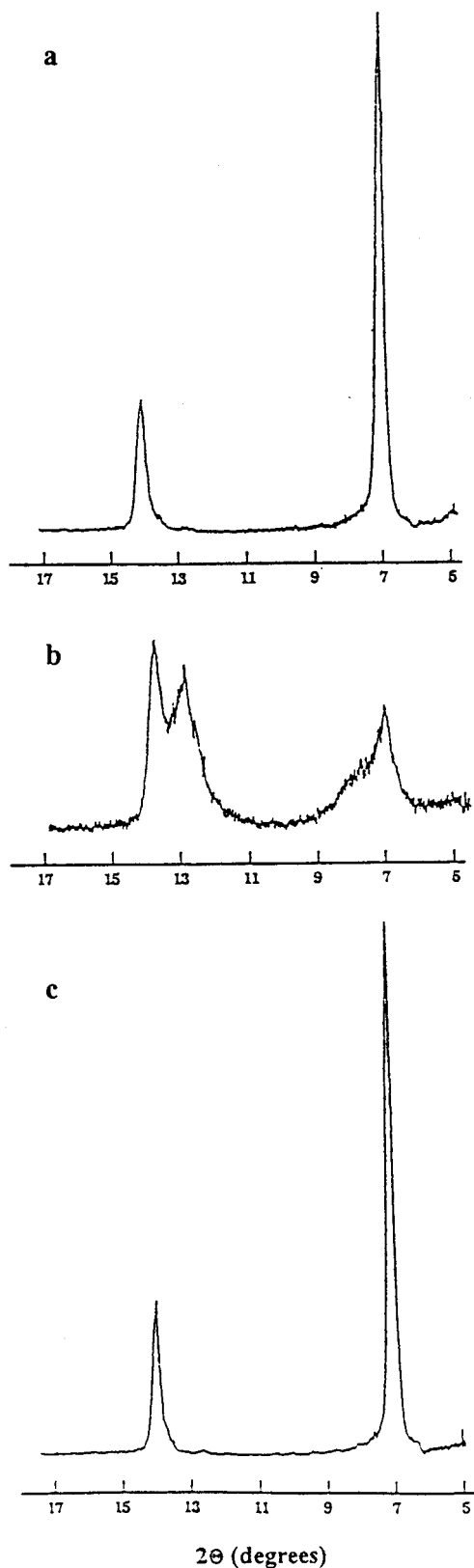


Figure 5. XRD patterns of MnPS_3 lithium intercalate thin film during a dehydration/rehydration cycle: (a) after drying in air, (b) after heating to 120°C , and (c) after rehydration at room temperature in air.

the dehydration temperature being 120°C . After drying in air (Figure 5a), the sample exhibits $00l$ reflections leading to a basal spacing of 12.62 \AA . Taking into account the basal spacing of the starting MnPS_3 material (6.5 \AA), the increase of the interlamellar distance

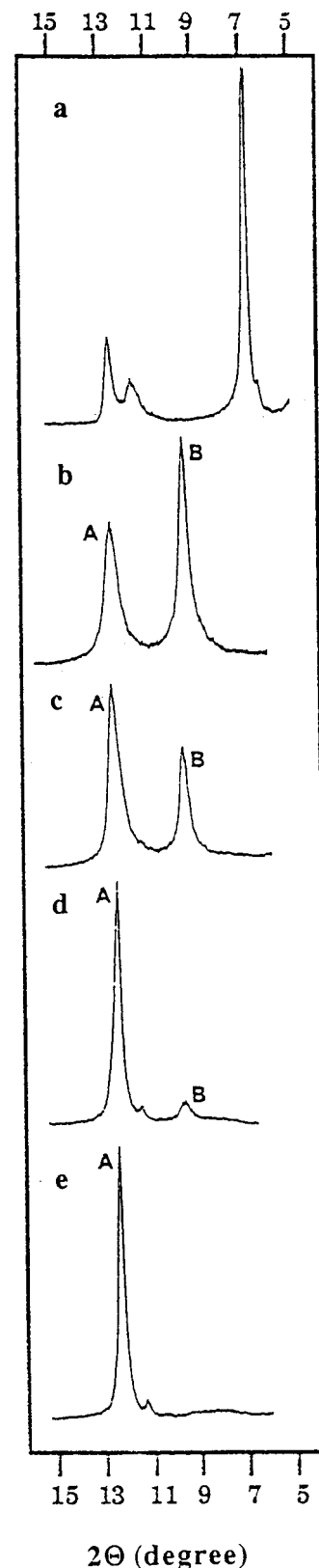
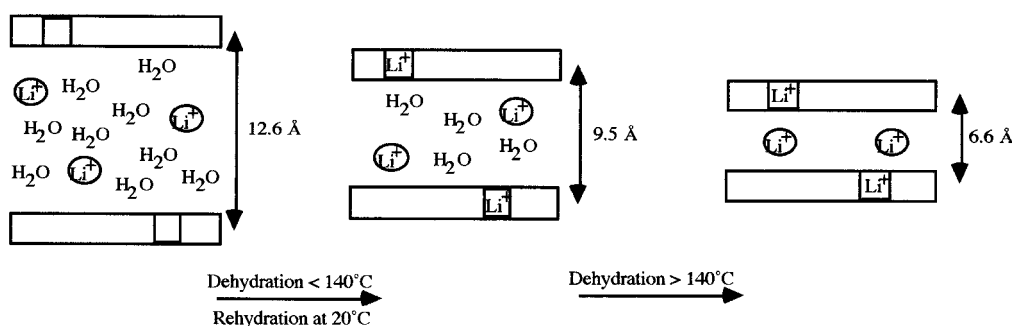


Figure 6. XRD patterns of CdPS_3 lithium intercalate film as a function of the drying temperature: (a) at 20°C , (b) at 40°C , (c) at 80°C , (d) at 120°C , and (e) at 160°C .

resulting from the Li^+ ion intercalation is 6.12 \AA , suggesting that the intercalated lithium ions are highly solvated by water molecules. The sharpness of these peaks also indicates that the compound is well-ordered. This is not the case after the sample has been heated to 120°C (Figure 5b). The $00l$ reflections are much

Scheme 2

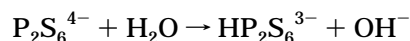


broader, which means that the compound tends to become amorphous. The peak corresponding to 12.62 Å significantly decreased, while a broad reflection associated with a 6.55 Å interlayer distance, close to the pure MnPS_3 phase basal spacing, appears. The disordered material resulting from the water molecule removal appears like a two-phase compound since some areas display an interlamellar distance close to that of the pure phase. After rehydration at room temperature in air, the material is again well-ordered as shown on Figure 5c by the very sharpness of the 00/ peaks and displays only one interlamellar distance (12.62 Å) corresponding to intercalated lithium ions fully solvated by water. The evolution of the interlamellar distance as a function of the temperature was studied on a CdPS_3 lithium intercalate film and the XRD patterns recorded at 20, 40, 80, 120, and 160 °C are shown in Figure 6. At room temperature (Figure 6a), the sharp reflections indicate that the well-ordered material mainly exhibits a 12.03 Å interlamellar distance corresponding to fully water solvated lithium ions present in the interlamellar space. However, the intercalation process was not totally complete, since a peak yielding to a basal spacing of 6.65 Å (basal spacing close to that of the pure CdPS_3 phase: 6.55 Å) still remained. Upon heating (Figure 6b–e), the peak (denoted A in the figures) associated to the intercalated phase in the material was first shifted to a interlayer distance of 9.5 Å, indicating the partial removal of water molecules, and its intensity decreased as the temperature increased. On the other hand, the peak (denoted B in the figures) corresponding to the interlamellar distance of the nonintercalated phase: 6.65 Å continued to increase in intensity. Heating the sample caused a conversion from the fully ($d = 12.03$ Å), then partially ($d = 9.5$ Å), hydrated phases to only a phase with a 6.65 Å interlamellar distance where all water molecules were removed from the interlayer space. After heating the sample to 160 °C, the rehydration process was not reversible as the water molecules did not enter the interlamellar space even after air exposure for many days. But as long as the compound still displayed both phases, this process was still reversible.

The XRD experiments carried out at different temperatures show the high mobility of the water molecules solvating the intercalated lithium ions as these molecules can easily leave and enter the interlamellar space during a dehydration/rehydration cycle at moderate temperatures. However, above 140 °C, the process is no longer possible, the reason probably being that the lithium ions cannot so easily interact with the water molecules. The water molecules are not the only species

mobile in these compounds. The IR spectroscopy study shows that the Li^+ ions are also mobile. The IR spectrum recorded after heating (Figure 4b) displays one $\nu(\text{PS}_3)$ vibration band located at the same wavelength as in pure MnPS_3 , suggesting that some Li^+ ions have migrated to the intralamellar vacancies. This migration process seems possible, as we compare the value of the respective ionic radii: 0.60 Å for Li^+ and 0.95 Å for Mn^{2+} . However, it is impossible to insert two monovalent lithium ions into one divalent vacancy. The charge balance of the compound is probably ensured by some lithium ions still present in the interlamellar space even at high temperature since the van der Waals gap of the MPS_3 phases (3.24 Å) can easily accommodate Li^+ ions without changing the interlayer distance.²⁵ Therefore, the compound heated at 160 °C still contains interlamellar Li^+ ions although the interlamellar distance (6.65 Å) is close to that measured in the pure CdPS_3 phase (6.55 Å). Upon rehydration the intralamellar Li^+ ions can leave the host lattice to the interlamellar space, giving rise to intralamellar vacancies, as evidenced by the $\nu(\text{PS}_3)$ vibration band splitting (Figure 4c). The lithium ion mobility depending of the temperature is shown in Scheme 2.

We also attempted to analyze the mechanism of the exfoliation process occurring upon lithium ion intercalation into the MPS_3 phases. Among all alkali ions that can be intercalated into these lamellar phases,^{16a} Li^+ ions are the only ones giving rise to a dispersion of the starting phases into colloidal suspensions. This observation can be attributed to the very high hydration energy (515.81 kJ)²⁶ of lithium ions. Upon intercalation, they bring many water molecules along into the interlamellar space, resulting in a very high hydration of the intercalated compound. In such conditions, a partial and local hydrolysis of the intralamellar $\text{P}_2\text{S}_6^{4-}$ species may occur according the reaction



This hydrolysis, responsible for the basicity of the washing solutions, would bring about a local and partial dissolution of the layers and therefore a dispersion of the starting phases into colloidal suspensions. In these intercalates, the lithium ions have a double role as they are responsible for the phase dispersion and ensure the electroneutrality of the compound. They can further be

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exchanged with other cationic species, as was described for the exfoliated dichalcogenides.^{18b,27} Like the dichalcogenide-based thin films,¹⁸ the XRD patterns of the MPS₃-based thin films dried in air showed 00 l reflections, suggesting that the layers pile up upon drying. An estimation of the crystallite size from the XRD broadening gives 1500 Å. In such a size range, the light scattering by the particles is negligible, which explains the high transparency of the films. These thin films are stable in air over long periods of time, and they quite strongly interact with the glass substrate. They do not come off the support after immersion in ethanol although they are sensitive to water.

(C) DAMS⁺ Insertion. *Intercalation into MnPS₃ thin films (solution approach):* We have reported above the high sensitivity of MnPS₃ thin films to water, probably due to a poor crystallinity of this phase. The role of water in the intercalation process, which involves heterogeneous equilibrium between the layered solid, the (P₂S₆)⁴⁻ ligand, and the Mn²⁺ cations, is readily evident when DAMS⁺ is intercalated into MnPS₃ made by the solution approach. It turned out that no intercalation of DAMS⁺ was observed in absolute ethanol, even with a solution refluxed for 2 days, whereas the films become dark red (color of DAMS⁺) after a few minutes at 40 °C in 95% ethanol. We have noticed that the sensitivity to water is such that the films are highly damaged if intercalations are carried out in solution containing more than 10% of water. Structurally speaking, the compound of formula Mn_{0.85}PS₃(DAMS)_{0.3}(H₂O)_{0.5} obtained after DAMS⁺ intercalation in the solution-approach-synthesized thin films exhibits most of the X-ray diffraction pattern and IR features of Mn_{0.83}PS₃(DAMS)_{0.34}(H₂O)_{0.9} and Mn_{0.86}PS₃(DAMS)_{0.28} previously reported.^{13,15} The basal spacing of 12.3 Å strongly suggests that the stilbazolium species are “edge-on” intercalated into the interlamellar space and the splitting of the ν (PS₃) band into two components confirms the presence of the intralamellar vacancies. Such DAMS⁺-intercalated thin films did not exhibit any signal in second harmonic generation, the reason being that the particles are too small (150 Å) to lead to a detectable signal.

Intercalation into MnPS₃ and CdPS₃ (solid-state approach): The solid-state-approach-based films seem to be more promising host materials in the DAMS⁺ intercalation. Unlike the solution approach, this approach allows the use of the CdPS₃ phase as starting material to obtain thin films exhibiting a high degree of transparency which is obviously an advantage in the insertion of optical active species. A significant role of water was not observed in the exchange kinetics occurring upon DAMS⁺ intercalation. Figure 7 shows the XRD pattern of a representative sample made via this approach. The interlamellar distance (12.6 Å) calculated from the 00 l diffraction peaks is not significantly different from that of the starting lithium intercalate compounds, suggesting that the intercalation of the DAMS⁺ cations simply proceeds through an ion exchange process and does not involve any major structural modifications in the layer stacking. As lithium

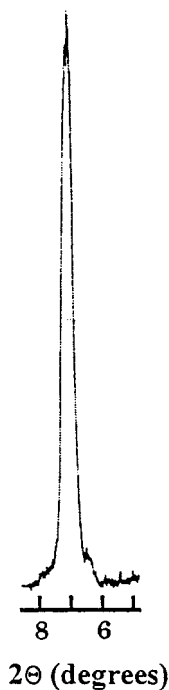


Figure 7. XRD pattern of the DAMS⁺ intercalated CdPS₃ compound obtained after DAMS⁺ intercalation into a solid-state-approach-synthesized thin film.

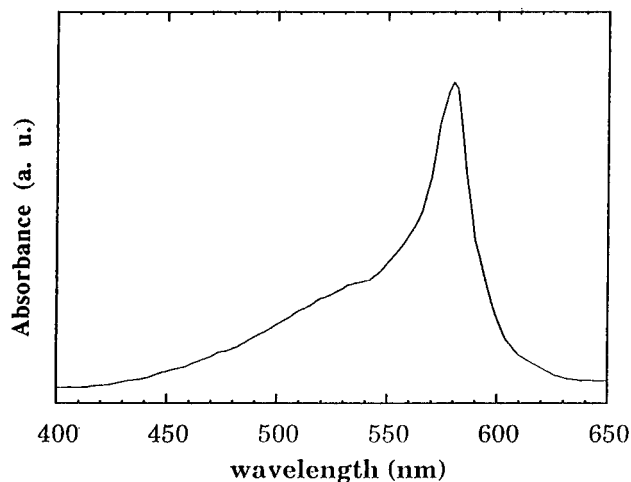


Figure 8. UV-visible spectrum of a DAMS⁺ intercalated thin film obtained via solid-state approach from the CdPS₃ starting phase.

ions were replaced by cations of the same valency, no more intralamellar metal ions M²⁺ were removed from the core of the slabs, ensuring the two-dimensional structure. These observations may also explain the rather high mechanical stability exhibited by these DAMS⁺-intercalated films compared to the solution approach-based films. The sharpness of the XRD peaks should be noted (0.4°), revealing a good crystallinity which is an important factor when cooperative interactions, such as second-order nonlinearities are required. The UV-visible spectra of DAMS⁺ intercalated into MPS₃ thin films are closely related to those recorded after intercalation into the bulk MPS₃ materials and described in a previous work.^{15,28} Figure 8 shows a representative UV-visible spectrum of DAMS⁺-intercalated thin film obtained via solid-state approach from the CdPS₃ starting phase. This spectrum displays a broad and intense absorption band in the range 580–

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600 nm with a shoulder around 530 nm. This spectrum, red-shifted with respect to the spectrum of the pure solid DAMS⁺I⁻, may be explained by the arrangement of the DAMS species in the interlamellar space. The typical shape of this absorption band has been reported as characteristic of the formation of J-aggregates.²⁹ It has also been found that this J-aggregate formation is responsible for SHG properties resulting from the noncentrosymmetric packing of the interacting chromophores.^{30,31} As previously reported,²⁸ the red-shift of the absorption band relatively to the charge-transfer band of the pure solid DAMS⁺I⁻ would suggest that the DAMS molecules are packed "edge-on" relatively to the host lattice layer plans, allowing strong interactions between them to be developed. It is therefore expected that many cooperative interactions may occur enhancing the molecular optical property to an observable bulk characteristic. However, for high transparent films (particle size 0.15 μm), the efficiency in second harmonic generation (SHG), measured on a picosecond Nd:YAG pulsed (10 Hz) laser operating at 1.064 μm , has been found to be negligible (<0.1 times that of urea). It is well-known that in this range of size, the SHG efficiency is proportionnal to the average size of the particles.³² Homogeneous thin films made up with larger particles (size between 1 and 2 μm) will probably give a higher SHG efficiency. However, scattering by the particles may occur, decreasing the transparency of the material.

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Conclusion

We have shown that it is possible to overcome some of the problems related to practical applications of powdered intercalation compounds in optical devices, by processing them into thin films. The ability of the MPS₃ layered compounds to be exfoliated to single layers seems to be a particularly promising method in the development of orientated thin films. Although their mechanical properties are still modest, they are quite good, considering the fact that they are thin films prepared in very mild conditions. Depending on the optical quality of the starting material, the resulting thin films may exhibit a very high transparency, which is obviously a great advantage for the use in optical devices. The MPS₃ thin films were also found to be much more reactive than the parent bulk MPS₃ compounds in the intercalation process of the stilbazolium dye: 4-[4-(dimethylamino)- α -styryl]-1-methylpyridinium. The preliminary characterizations performed on these films after the stilbazolium species insertion suggest that a nonlinear signal may be expected from these materials. However, further experiments focusing on the preparation of homogeneous thin films made up with substantially larger crystallites are required in order to find a compromise between observable SHG efficiency and significant transparency.

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