

# Exfoliated CdPS<sub>3</sub> Single Layers and Restacked Films

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The layered compound CdPS<sub>3</sub> has been exfoliated to form a suspension by ion exchange and washing in distilled water. The X-ray diffraction patterns of the suspension show that the material is two-dimensional, indicating the formation of single molecular layers of Cd<sub>0.8</sub>PS<sub>3</sub>. The 3.5 eV optical band-gap absorption and the refractive index of bulk CdPS<sub>3</sub> have been measured. The measured absorption of single layers of Cd<sub>0.8</sub>PS<sub>3</sub> in water suspension indicates that there is no significant change in electronic structure for the single layers. Single layers of Cd<sub>0.8</sub>PS<sub>3</sub> have been restacked with different included molecules, opening up another approach for the synthesis of new layered nanocomposites. © 2002 Elsevier Science (USA)

**Key Words:** cadmium phosphorous trisulfide; layered compound; exfoliation; X-ray diffraction; optical properties.

## 1. INTRODUCTION

Single molecular layers ("single layers") of MoS<sub>2</sub>, WS<sub>2</sub> and MoSe<sub>2</sub>, dispersed in suspension in water, have been prepared by exfoliation (1, 2). These two-dimensional (2-d) materials are readily identified by their unique powder X-ray diffraction patterns. To our knowledge, no other layered compounds have been clearly demonstrated to be in the single-layer form.

In recent years, there has been increasing interest in transition metal phosphorous trisulfide layered compounds, such as CdPS<sub>3</sub> and MnPS<sub>3</sub> (3). These compounds are transparent in the visible region, and hence have potential applications in many areas of optoelectronics (4, 5). The transition metal phosphorous trisulfides have a layered structure where a molecular layer is made up of sheets of Cd and P atoms located between two sheets of S atoms, which is similar to that of transition metal dichalcogenides. Clement and co-workers (6) have developed an ion-exchange intercalation chemistry for transition metal phosphorous trisulfides which allows the synthesis of

many stable intercalation compounds. In this paper, we report that CdPS<sub>3</sub> can be exfoliated into single molecular layers suspended in water using the ion-exchange method. We have studied the structure of the exfoliated layers by X-ray diffraction and have also measured their optical absorption. New inclusion solids and excellent oriented films can be formed by restacking the exfoliated layers with different molecules included between layers.

## 2. EXPERIMENTAL

Crystals of CdPS<sub>3</sub> were grown by heating a mixture of stoichiometric amounts of elemental Cd, P and S powder in an evacuated quartz tube at 800–900°C for 10 days. The resulting material contains mostly small crystals, but includes a few large, thin single crystals about 1 cm<sup>2</sup> in area and 5–20 μm in thickness. The large crystals were used in our optical absorption studies. Some crystals were ground into powder (10–50 μm size) for the exfoliation work.

For potassium ion exchange, we followed the method of Lagadic *et al.* (4), where 1 g of CdPS<sub>3</sub> powder is treated in a mixture of 50 ml of 2 M KCl aqueous solution and 10 mL of 0.1 M EDTA in 1 M K<sub>2</sub>CO<sub>3</sub>/KHCO<sub>3</sub> buffer at room temperature for 24 h. This leads to the formation of Cd<sub>0.8</sub>K<sub>0.4</sub>PS<sub>3</sub>(H<sub>2</sub>O)<sub>y</sub>, where the interlayer spacing expands from 6.55 to 9.41 Å. This material is then centrifuged and decanted. The potassium ions are exchanged for lithium ions by adding about 40 ml of a 3 M LiCl solution to the Cd<sub>0.8</sub>K<sub>0.4</sub>PS<sub>3</sub>(H<sub>2</sub>O)<sub>y</sub>, and stirring for 1 h. According to Lagadic *et al.*, the resulting material is Cd<sub>0.8</sub>Li<sub>0.4</sub>PS<sub>3</sub>(H<sub>2</sub>O)<sub>x</sub> where Li<sup>+</sup> is located in the interlamellar space, on either side of a Cd vacancy, with an interlayer spacing of 12.0 Å. We have determined that this spacing is the same whether the material is in the form of a wet slurry or a nominally dry powder. We have not measured the lithium content of our samples, but assume Lagadic's nominal value of 0.4 which compensates for the loss of Cd. We wash and centrifuge the material three times with water. Lagadic *et al.* have noted that after several water washes, the product was

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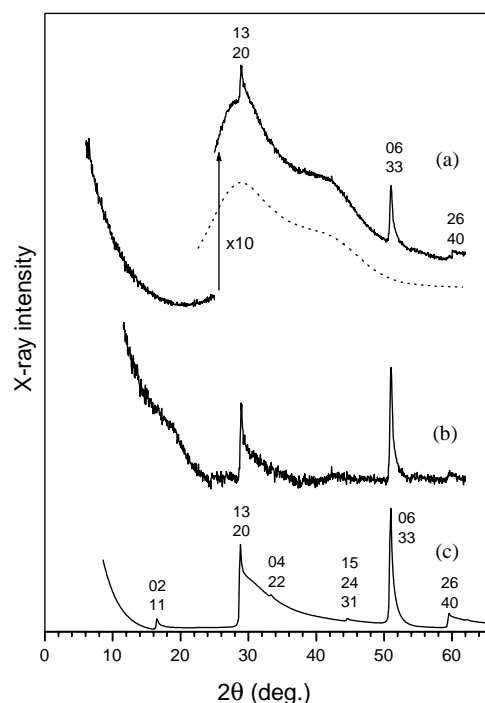
highly dispersed and formed what they described as a colloidal suspension. However, they did not carry out any structural work on this suspension.

X-ray diffraction patterns reported here were obtained with a Siemens D-5000 diffractometer using Cu  $K\alpha$  radiation. Our optical data were obtained with a Cary 3E UV-visible spectrophotometer.

### 3. RESULTS AND DISCUSSION

#### 3.1. Identification of Single Layers of $Cd_{0.8}PS_3$

Suspensions obtained after three water washes were examined with X-ray diffraction. A suspension was first centrifuged to obtain a more dense paste-like suspension to enhance the diffraction signal. Figure 1a shows the X-ray diffraction pattern of a concentrated suspension. Since the sample contains more than 95% water by weight, the pattern has a strong water background. In order to show the diffraction pattern more clearly, we subtracted the water background from the raw data. This water background was obtained by measuring the diffraction from a pure water sample. The result is shown in Fig. 1b. There are only three peaks in Fig. 1b and they all have an asymmetric line shape, indicating the formation of 2-d single molecular layers. There are two unique features in



**FIG. 1.** (a) Experimental X-ray diffraction powder pattern of single layers of  $Cd_{0.8}PS_3$  in water suspension (the dotted line shows the water background); (b) pattern with water background subtracted; and (c) calculated pattern for randomly oriented single layers of  $CdPS_3$ .

powder X-ray diffraction patterns of 2-d materials which differ from those of 3-d materials (7, 8). First of all, because there is no periodicity in the third dimension, only  $(hk0)$  peaks result, and all  $(00l)$  and mixed  $(hkl)$  peaks are absent. Thus only two indices  $(hk)$  are required to denote a Bragg peak for a 2-d system. Secondly, the shape of Bragg peaks is highly asymmetric, with a rapid increase on the low-angle side and a long tail on the high-angle side, due to the so-called Warren effect. The Warren tail is modulated by the structure factor, and hence the actual shape of a Bragg peak depends on the structure of the layer.

The powder diffraction pattern for single layers can be computer generated using the Debye formula (8, 9). Figure 1c gives calculated powder diffraction patterns for single molecular layers of  $CdPS_3$  with a layer size of  $60 \times 60$  unit cells ( $\approx 400 \times 600 \text{ \AA}^2$ ). There are two strong peaks, the  $(13)/(20)$  and  $(06)/(33)$  peaks, and several weaker peaks in the calculation range. Calculation shows that as the layer size increases, the  $(06)/(33)$  peak becomes relatively stronger and narrower (9). We have determined that a layer size of  $60 \times 60$  unit cells provides the best fit with the experimental data. Our calculations also show that there are no significant differences between diffraction patterns for  $CdPS_3$  single layers and  $Cd_{0.8}PS_3$  single layers with random Cd vacancies. The experimental pattern (Fig. 1b) is in good agreement with the calculated pattern (Fig. 1c), except that the weak  $(02)/(11)$ ,  $(22)/(04)$  and  $(15)/(24)/(31)$  peaks do not show up in the experimental data. From a comparison of Fig. 1b and 1c, we can conclude that the suspension is actually made up of randomly oriented single layers of  $Cd_{0.8}PS_3$  with a correlation size (coherence distance) of about  $60 \times 60$  unit cells. Note that the actual layer size may be much larger than the coherence size since the layers will not be perfectly flat.

We observed that single layers of  $Cd_{0.8}PS_3$  can remain suspended in water for months without significant flocculation (restacking). This indicates that there is a repulsion between the layers. We have also observed that when an electric field is applied to a single-layer suspension the layers migrate to and deposit on the positive electrode. We applied 5 V across  $2 \times 2 \text{ cm}^2$  parallel planar Ni electrodes, separated by 2 cm. The deposit demonstrates that there is a net negative charge associated with the single layers and that Coulomb forces between the layers prevent them from restacking to form a 3-d material. In addition, X-ray diffraction of the deposit on the positive electrode shows that it consists of restacked single layers with an interlayer spacing of  $6.58 \text{ \AA}$ . This value is to be compared to the original  $CdPS_3$  layer spacing of  $6.55 \text{ \AA}$  and the restacked  $Cd_{0.8}Li_xPS_3(H_2O)_y$ , with a larger spacing of  $12.16 \text{ \AA}$ . We have found that restacked  $Cd_{0.8}Li_xPS_3(H_2O)_y$  is stable in air and will not lose the water unless heated above  $200^\circ\text{C}$ . We thus conclude that the positive electrode deposit is restacked  $Cd_{0.8}PS_3$ , without Li and its associated  $H_2O$ . It

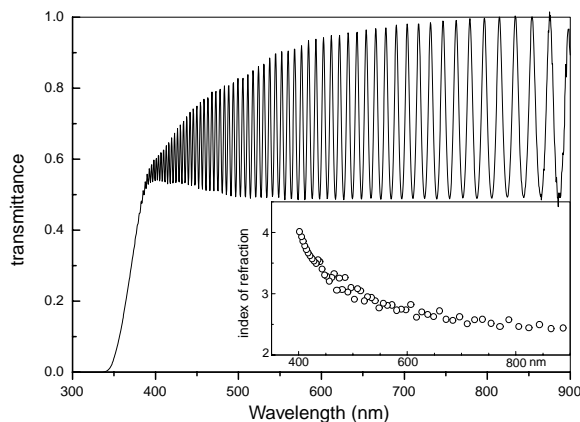
appears that in a single-layer suspension, Li<sup>+</sup> ions form electrical double layers with polarized water molecules around Cd<sub>0.8</sub>PS<sub>3</sub> single layers. The applied electric field separates the Li ions from the layers, giving rise to negatively charged Cd<sub>0.8</sub>PS<sub>3</sub> single layers which are attracted to the positive electrode.

### 3.2. Optical Absorption

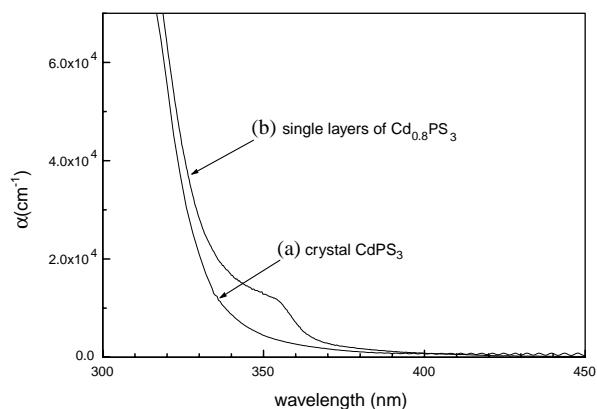
The measurement of the optical absorption coefficient can provide valuable information about the band structure of the material. The energy gap of CdPS<sub>3</sub> crystals has been determined to be around 3.5 eV (10); however, no detailed data have been published.

Figure 2 shows a plot of optical transmittance vs wavelength in the region of 300–900 nm for a CdPS<sub>3</sub> crystal flake of size 5 × 5 mm<sup>2</sup> for unpolarized light at perpendicular incidence. The sample was unsupported and all measurements were taken in air. The graph shows that significant absorption occurs in the UV region and that the sample is essentially transparent in the visible region. Strong interference is observed in the region 400–900 nm, showing that the thickness of the crystal is very uniform. This can be used to determine the thickness of the crystal and the index of refraction as shown below.

Assume the film to be nonabsorbing and uniform in thickness. Let  $r$  be the amplitude–reflection coefficient at the interface (reflectivity of electric field), and  $n$  the index of refraction. Multiple-beam interference occurs between the two sample surfaces. The maximum intensity of transmitted light for constructive interference must be 100% as observed in Fig. 2 for  $\lambda = 800$ –900 nm. The minimum intensity of the transmitted light,  $T_{\min}$ , depends on the index of refraction of the material. By measuring  $T_{\min}$ , the amplitude–reflection coefficient  $r$  and the index of refraction



**FIG. 2.** Optical transmission in visible and UV region for a CdPS<sub>3</sub> crystal 7.16 μm thick; inset shows refractive index  $n$  as a function of wavelength.



**FIG. 3.** Comparison of optical absorption coefficients in crystal CdPS<sub>3</sub> and water suspension of single layers of Cd<sub>0.8</sub>PS<sub>3</sub>.

tion  $n$  can be determined from (11)

$$r^2 = \frac{1 - \sqrt{T_{\min}}}{1 + \sqrt{T_{\min}}} \quad \text{and} \quad n = \frac{1 + r}{1 - r}.$$

Using the wavelengths of two consecutive transmission maxima (or minima),  $\lambda_m$  and  $\lambda_{m+1}$ , the thickness of the film,  $d$ , can be determined from

$$d = \frac{\lambda_m \lambda_{m+1}}{2n(\lambda_{m+1} - \lambda_m)}.$$

For our sample, the minimum intensity  $T_{\min} = 0.49$ . The thickness and the index of refraction of the film are determined to be 7.16 μm and 2.45, respectively, for  $\lambda = 800$ –900 nm.

Once the thickness is known, the dependence of index of refraction on wavelength can be obtained from the interference pattern. The inset of Fig. 2 gives the graph of  $n$  vs  $\lambda$ .

Knowing the thickness of the crystal, the optical absorption coefficient,  $\alpha$ , can be derived from the optical absorbance in the UV region. Figure 3a is the graph of  $\alpha$  as a function of  $\lambda$ , which shows an absorption edge at 350 nm ( $\approx 3.55$  eV). The absorption coefficient increases rapidly below 330 nm and reaches  $1 \times 10^5 \text{ cm}^{-1}$  at about 310 nm.

Next we try to obtain the optical absorption coefficient for single layers of Cd<sub>0.8</sub>PS<sub>3</sub> by directly measuring the absorbance of a suspension. The sample holder was a quartz cell with a sample thickness of 1 mm. The concentration of the suspension was 3.6 mg/mL, equivalent to a crystal thickness of 1.0 μm. In deriving the absorption coefficient for single layers, we have assumed that the layers are oriented perpendicular to the direction of the incident light. This assumption is not expected to have a large effect on the magnitude of the absorption coefficient. However, scattering effects have to be considered. The suspension scatters the incident light strongly, and the

transmitted light is not 100% even in the long wavelength region. We assume the scattered light obeys Rayleigh's law, in which the intensity of scattered light is inversely proportional to the fourth power of wavelength. To obtain the absorption coefficient of single layers, this scattering factor has to be subtracted from the raw data. The proportionality constant in Rayleigh's law is adjusted so that the absorption curve is completely flat in the wavelength region of 400–900 nm. The result is given in Fig. 3b. The single layer absorption has a shoulder at 360 nm ( $\approx 3.45$  eV). The strong absorption edge (below 330 nm) is basically the same as that of the crystal sample. This shows that there is no significant change in the band structure of the single layer relative to the bulk. The absorption shoulder on the band edge may be related to the fact that for the single layers, 20% of Cd sites are vacant or may be due to a small change in the band structure due to the layer separation.

### 3.3. Restacked Films from Single Layers of $Cd_{0.8}PS_3$

Single layers of  $Cd_{0.8}PS_3$  can be restacked in different ways, and this opens up a new approach for the synthesis of new materials. A unique feature of the restacked materials is that they can form very highly oriented films on various substrates. Figure 4 shows the results for two examples of restacked films prepared from single layers of  $Cd_{0.8}PS_3$ . Figure 4a is the X-ray diffraction pattern for a restacked  $Cd_{0.8}Li_xPS_3(H_2O)_y$  film. The sample was pre-

pared by dropping the single-layer suspension onto a glass slide and drying at room temperature for 24 h. Only interlayer (00 $l$ ) peaks were observed in the XRD pattern (we have observed ten (00 $l$ ) peaks for this sample), indicating that the film is oriented with the basal planes parallel to the glass substrate. The X-ray rocking curve shows that the layers are parallel to the substrate to within  $0.5^\circ$ . The interlayer spacing is 12.16 Å, an increase of 5.6 Å from the original 6.55 Å, corresponding to two layers of water. The full-width at half-maximum (FWHM) of the (001) peak is  $0.13^\circ$ , which gives a coherence thickness of about 600 Å, or 50 layers. We have determined by vacuum heating and weighing that the  $y$  value in  $Cd_{0.8}Li_xPS_3(H_2O)_y$  is  $\approx 4$ . A calculation gives  $y \approx 6$ , assuming close packing of the water between the layers.

Figure 4b shows the X-ray diffraction pattern of a restacked  $Cd_{0.8}Li_xPS_3(PEG)_{2.0}$  film (where we use the 2.0 value for PEG obtained by intercalation into  $Cd_{0.8}K_{0.4}PS_3(H_2O)_y$ ). The sample was prepared by mixing the single-layer suspension of  $Cd_{0.8}PS_3$  and a solution of poly(ethylene glycol) (PEG, molecular weight 1000). The mixture did not flocculate, but remained in suspension. Films of  $Cd_{0.8}Li_xPS_3(PEG)_{2.0}$  were formed by dropping the mixture on glass substrates and drying in air. The interlayer spacing is 14.78 Å. The (001) peak has an FWHM of  $0.09^\circ$ . The coherent thickness is about 900 Å, or 60 layers. Sharp (00 $l$ ) peaks and extremely clean backgrounds imply that the restacked film is remarkably well ordered with a uniform interlayer spacing.

$Cd_{0.8}Li_{0.4}PS_3(PEG)_{2.0}$  powders have already been synthesized by intercalation of the polymer into  $Cd_{0.8}K_{0.4}PS_3(H_2O)_y$  (12–15). Single layers of  $Cd_{0.8}Li_xPS_3$  provide a simple alternate approach for synthesis of inclusion compounds. Most water-soluble polymers, such as poly(vinylpyrrolidone) (PVP), poly(ethylenimine) (PEI) and poly(acrylic acid) (PAA), can also be included by restacking in the same manner as PEG, but with different interlayer spacings. In some cases, inclusion compounds can have more than one phase. For example, we find that  $Cd_{0.8}Li_xPS_3(PVP)_y$  can have two phases with distinct spacings of 23.9 and 31.7 Å. Table 1 summarizes the interlayer spacings of restacked  $Cd_{0.8}Li_xPS_3$ /polymer systems. We have also formed restacked systems with

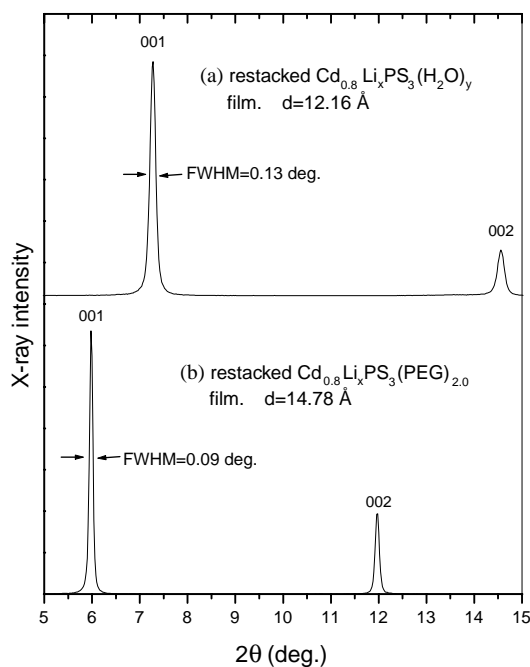


FIG. 4. X-ray diffraction patterns for restacked oriented films of (a)  $Cd_{0.8}Li_xPS_3(H_2O)_y$  and (b)  $Cd_{0.8}Li_xPS_3(PEG)_{2.0}$ .

TABLE 1  
Interlayer Spacings, Obtained from X-Ray Diffraction,  
for Restacked  $Cd_{0.8}Li_xPS_3$ /Polymer Systems

Polymer	Interlayer spacing (Å)
PEG	14.78
PVP	23.9, 31.7
PEI	10.6
PAA	13.0, 24.0

molecules that are insoluble in water. Single-layer restacking provides an alternate to the intercalation approach and will be useful in cases where intercalation does not occur or occurs at an unacceptably slow rate. This approach has the additional advantage of being able to form oriented films rather than randomly oriented powders.

#### ACKNOWLEDGMENT

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#### REFERENCES

1. P. Joensen, R. F. Frindt, and S. R. Morrison, *Mater. Res. Bull.* **21**, 457 (1986).
2. D. Yang and R. F. Frindt, *J. Phys. Chem. Solid.* **57**, 1113 (1996).
3. R. Brec, *Solid State Ionics* **22**, 3 (1986).
4. I. Lagadic, P. G. Lacroix, and R. Clement, *Chem. Mater.* **9**, 2004 (1997).
5. P. G. Lacroix, A. V. V. Lemariner, R. Clement, K. Nakatani, and J. A. Delaire, *J. Mater. Chem.* **3**, 499 (1993).
6. R. Clement, in "Hybrid Organic-Inorganic Composites," (J. Marks, C. Lee, and P. Bianconi, Eds.), pp. 29-41. ACS Press, 1995.
7. B. E. Warren, *Phys. Rev.* **59**, 693 (1941).
8. D. Yang and R. F. Frindt, *J. Appl. Phys.* **79**, 2376 (1996).
9. A. Guinier, "X-ray Diffraction in Crystals, Imperfect Crystals, and Amorphous Bodies." Dover, New York, 1994.
10. R. Brec, D. M. Schleich, G. Ouvrard, A. Louisy, and J. Rouxel, *Inorg. Chem.* **18**, 1814 (1979).
11. E. Hecht, "Optics," 4th ed. Addison-Wesley, Reading, MA, 2001.
12. D. Yang and R. F. Frindt, *J. Mater. Res.* **15**, 2408 (2000).
13. P. Jeevanandam and S. Vasudevan, *Chem. Mater.* **10**, 1276 (1998).
14. I. Lagadic, A. Leautic, and R. Clement, *J. Chem. Soc., Chem. Commun.* 1396 (1992).
15. C.O. Oriakhi, R.L. Nafshun, and M.M. Lerner, *Mater. Res. Bull.* **31**, 1513 (1996).