

## Luminescence properties of $\text{Nd}^{3+}$ , $\text{Sm}^{3+}$ and $\text{Eu}^{3+}$ intercalated $\text{CdPS}_3$

Rene Clément<sup>a,\*</sup>, Anne Léaustic<sup>a</sup>, Kimberly Marney<sup>b</sup>, A.H. Francis<sup>b</sup>

<sup>a</sup>Laboratoire de Chimie Inorganique: U.R.A. 420, Bt 420, Université de Paris Sud, 91405 Orsay Cedex, France

<sup>b</sup>Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109, USA

### Abstract

$\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$  have been intercalated by cation exchange into  $\text{CdPS}_3$ . The photoluminescence and IR spectra show the creation of cadmium cation vacancies. Crystal field analysis indicates that the rare earths have entered the intralamellar vacancies and formed a complex defect center with  $C_2$  or lower symmetry.

### 1. Introduction

Transition metal trichalcogenides  $\text{MPS}_3$ , where M is a divalent transition metal, form a broad class of lamellar semiconductors. The  $\text{MPS}_3$  structure consists of slabs constructed from face-sharing  $\text{MS}_6$  and  $\text{P}_2\text{S}_6$  octahedra. Adjacent slabs are held together by relatively weak van der Waals forces to form easily accessible interstitial spaces called “van der Waals gaps” (vWG). When crystalline  $\text{MPS}_3$  materials are placed in contact with solutions containing monovalent, divalent or trivalent cations, the solute cations enter the vWG and lattice cations are in turn displaced into the solution [1]. Fig. 1 is a schematic of the cation exchange process in these materials.

In the present work we have employed photoluminescence (PL) spectroscopy to examine the structure of centers formed by the intercalation of tripositive rare earth (RE) cations. The tripositive

RE cations retain many of their atomic-like properties in the lattice and sharp, well resolved PL spectra characteristic of f-electron transitions are observed. The details of the crystal coordination environment can be derived from the relatively weak crystal field effects observed in the spectra [2].

### 2. Experimental

The experimental procedures for the PL spectra and for sample preparation have been previously described [3]. X-ray diffractograms were obtained at several temperatures between 20°C and 300°C using a McPherson powder diffractometer with a  $\text{CuK}_\alpha$  ( $\lambda = 1.5405 \text{ \AA}$ ) source. The basal spacings of all freshly prepared samples were  $\sim 13 \text{ \AA}$ , but upon standing for one month approximately half of the material converted to a dehydrated form with a  $\sim 6.6 \text{ \AA}$  basal spacing. All crystals undergo rapid conversion back to the original  $\sim 6.6 \text{ \AA}$  basal spacing when dehydrated by heating to 120°C under

\* Corresponding author.

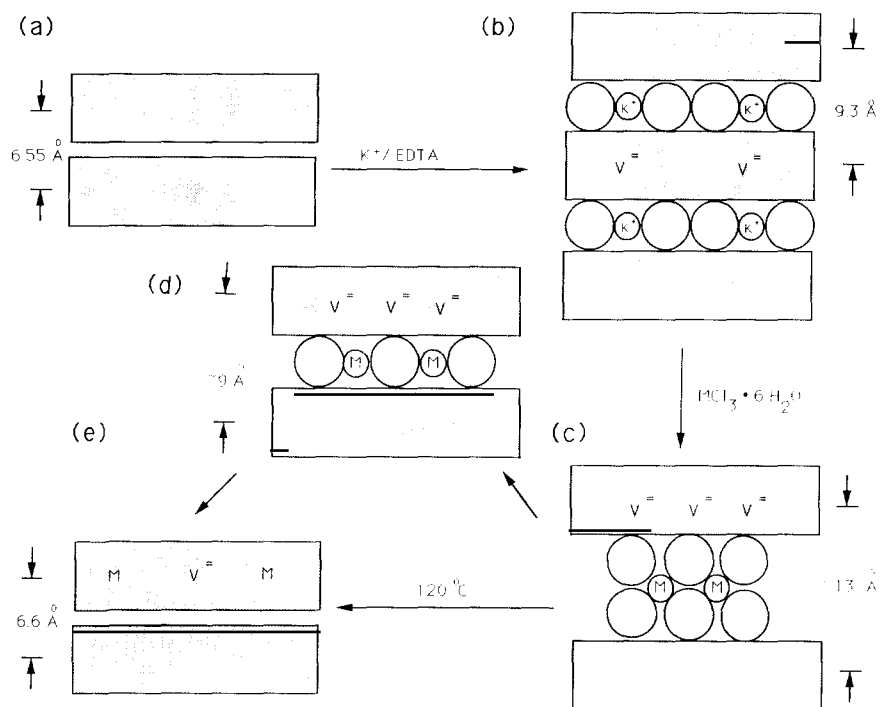


Fig. 1. Schematic of the cation exchange process in the  $\text{MPS}_3$  layered chalcogenide lattices: (a) pristine  $\text{CdPS}_3$ , (b)  $\text{CdPS}_3:\text{K}^+$ : monolayer of  $\text{H}_2\text{O}$ , (c)  $\text{CdPS}_3:\text{RE}^{3+}$ : bilayer of  $\text{H}_2\text{O}$  ( $\text{M} = \text{RE}^{3+}$ ), (d) partially dehydrated  $\text{CdPS}_3:\text{Eu}^{3+}$ : monolayer of  $\text{H}_2\text{O}$  and (e) dehydrated  $\text{CdPS}_3:\text{RE}^{3+}$  samples.

vacuum. The loss of all water at 120 C was confirmed by TGA.

### 3. Results

PL spectra for the  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$  exchanged crystals are shown in Fig. 2. Luminescence was stimulated most efficiently by broad-band excitation between 3300 and 4000 Å for  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$  and by the 5145 Å line of an Argon ion laser for  $\text{Nd}^{3+}$ . The PL spectra consisted of both rare earth emission and the broad-band luminescence between 16 500 and 20 600  $\text{cm}^{-1}$ , characteristic of lattice cation vacancies,  $\text{V}^{2+}$ . In the  $\text{CdPS}_3:\text{Nd}^{3+}$  sample, the vacancy luminescence is partially reabsorbed by  $\text{Nd}^{3+}$  giving rise to several regions of sharp-line absorption. The general positions of the  $J$ -multiplets are typical of  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$  in other crystal lattices [4].

### 4. Discussion

#### 4.1. Cation exchange chemistry

After cation exchange with  $\text{RE}^{3+}$ , the basal spacing of the host  $\text{CdPS}_3$  lattice increases by about 6.8 Å. This increase approximately corresponds to the RE cation diameter plus twice the van der Waals diameter of water (2.8 Å). The bilayer solvation model shown schematically in Fig. 1 is consistent with the increase in basal spacing. Upon dehydration, the basal spacing of the hydrated phases returns to nearly that of the host lattice. This suggests that the RE cations have entered Cd vacancies. The ionic radii of  $\text{Nd}^{3+}$  (0.995 Å),  $\text{Sm}^{3+}$  (0.964 Å) and  $\text{Eu}^{3+}$  (0.950 Å) allow them to insert into the  $\text{Cd}^{2+}$  vacancy ( $\sim 1.1$  Å) [4].

The substitution of  $\text{RE}^{3+}$  for  $\text{Cd}^{2+}$  requires a clustering of ions and vacancies to achieve charge neutrality. A simple cluster of two  $\text{RE}^{3+}$  and a  $\text{V}^{2+}$

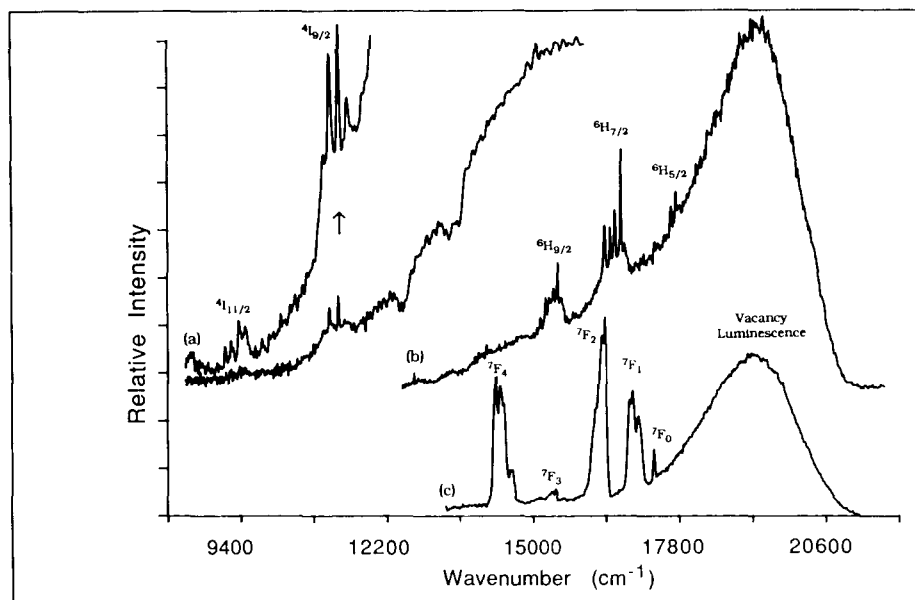


Fig. 2. Photoluminescence spectra of CdPS<sub>3</sub> exchanged with (a) Nd<sup>3+</sup> (hydrated), recorded at 77 K, (b) Sm<sup>3+</sup> (dehydrated) at 4 K and (c) Eu<sup>3+</sup> (hydrated) at 4 K.

form a M–V–M neutral center. If a monovalent ion (M') is present, an M–M' center can be formed and a lattice vacancy is not required. Monovalent ions, K<sup>+</sup> and H<sup>+</sup>, are present in the aqueous cation exchange solution and could participate in the exchange scheme. However, the M–V–M structure is preferred since the PL and IR data reveal the presence of vacancies. In each case, the symmetry of the RE<sup>3+</sup> is C<sub>2</sub> or lower.

#### 4.2. CdPS<sub>3</sub> photoluminescence

Well annealed crystals of the CdPS<sub>3</sub> host lattice are only weakly luminescent. However, after treatment with aqueous solutions containing solute cations (G<sup>n+</sup>), the CdPS<sub>3</sub> lattices exhibit an intense, broad luminescence between 16 500 and 21 400 cm<sup>-1</sup>. The luminescence is long-lived (~65 μs) and originates from cation vacancy sites created by cation exchange according to the reaction, CdPS<sub>3</sub> + yG<sup>n+</sup> ↔ Cd<sub>1-ny/2</sub>G<sub>y</sub>PS<sub>3</sub> + (ny/2)Cd<sup>2+</sup>.

The presence of cation vacancies is also indicated by changes in the IR spectrum. The PS<sub>3</sub> asymmetric

stretch, observed at 570 cm<sup>-1</sup> in the IR spectrum of CdPS<sub>3</sub>, is split into 2 components at 605 and 555 cm<sup>-1</sup>. It is well established that this effect in the IR spectrum is caused by the creation of intralaminar vacancies in MPS<sub>3</sub> intercalates [5].

#### 4.3. RE<sup>3+</sup> luminescence and coordination geometry

Additional luminescence bands due to RE cations appear superimposed on the V<sup>2-</sup> luminescence. The RE<sup>3+</sup> luminescence arises from intra-configurational, 4f-electron transitions and is typically sharp and well resolved. The luminescence studied in this work is derived from the following RE<sup>3+</sup> free-ion transitions:

$$\text{Nd}^{3+} (4f^3): {}^4F_{3/2} \rightarrow {}^4I_J \quad (J = \mathbf{1}, \mathbf{2}, \mathbf{3}, \mathbf{4}, \mathbf{5}, \mathbf{6}),$$

$$\text{Sm}^{3+} (4f^5): {}^4G_{5/2} \rightarrow {}^6H_J \quad (J = \mathbf{1}, \mathbf{2}, \mathbf{3}, \mathbf{4}, \mathbf{5}, \mathbf{6}),$$

$$\text{Eu}^{3+} (4f^6): {}^5D_0 \rightarrow {}^7F_J \quad (J = \mathbf{0}, \mathbf{1}, \mathbf{2}, \mathbf{3}, \mathbf{4}, \mathbf{5}, \mathbf{6}).$$

In each case the emitting state is the lowest level of the first excited term. Only the J-states of the ground term shown in bold were observed. The

remaining transitions are unobservable due either to host lattice emission/absorption or because they lie beyond the long-wavelength limit of the phototube.

Owing to the small spatial extent of the  $f$ -orbitals, the RE transitions are only weakly perturbed by the crystalline lattice. The detailed splitting and intensity patterns within each multiplet, however, are sensitive to both the strength and symmetry of the crystal field. The crystal field interaction has two primary effects: it partially or completely removes the degeneracy of the free ion  $J$ -states into a number of  $|M_J|$  levels determined by the site symmetry of the ion, and it changes the relative intensity of the free-ion transitions.

The PL spectrum of  $\text{CdPS}_3:\text{Eu}^{3+}$  yields considerable information about the coordination environment of intralamellar  $\text{Eu}^{3+}$  in the dehydrated phase. The appearance of a single, strong  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$  transition (Fig. 2(c)) reveals immediately that  $\text{Eu}^{3+}$  resides in a single emission site with  $\text{C}_{3v}$  or lower symmetry [4]. Moreover, an intense transition is usually indicative of a strong crystal field. This analysis agrees with the  $\text{C}_2$  RE $^{3+}$  site symmetry predicted by charge compensation requirements.

The crystal field splitting of the  $J = 1$  and 2 transitions also support these conclusions. It is seen that the degeneracy of each  $J$ -state is completely lifted by the low site symmetry. For the best resolved multiplets, the number of components observed is equal to the maximum degeneracy. Other multiplets exhibit fewer than the maximum number of components, probably due to lack of adequate resolution. The observation of three well resolved components for the  $J = 1$  state is consistent with the proposed site symmetry.

The dipole selection rules for RE cations with half-integral  $J$ -states are less restrictive than those for integral  $J$ -states. As a result, the spectra of the  $\text{Nd}^{3+}$  and  $\text{Sm}^{3+}$  intercalates are less diagnostic than those of the  $\text{Eu}^{3+}$  compound. Nevertheless, the PL spectra of the dehydrated phases of  $\text{CdPS}_3:\text{Nd}^{3+}$  and  $\text{CdPS}_3:\text{Sm}^{3+}$  (Fig. 2(a) and (b)) are consistent with and support the analysis of the  $\text{Eu}^{3+}$  intercalate spectrum. For example, the  $\text{CdPS}_3:\text{Nd}^{3+}$   ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$  transition is fully

resolved into its five crystal field components as predicted for trigonal or lower site symmetry. The spectra of  $\text{Sm}^{3+}$  reveals the  $J$ -multiplet splitting of the  ${}^6\text{H}_{5/2}$ ,  ${}^6\text{H}_{7/2}$  and  ${}^6\text{H}_{9/2}$  manifolds. In each case, the number of lines observed is equal to the number expected for trigonal or lower symmetry: three for the  ${}^6\text{H}_{5/2}$  manifold, four for the  ${}^6\text{H}_{7/2}$  manifold and five for the  ${}^6\text{H}_{9/2}$  manifold.

## 5. Conclusion

Analysis of the luminescence spectra of three RE $^{3+}$  cations inserted into the lamellar host  $\text{CdPS}_3$  via cation exchange in aqueous media suggests that a single emissive site is present in each case. Based on the number of  $J$ -multiplet components observed in the emission spectrum of each ion and charge compensation requirements, the site must have  $\text{C}_2$  or lower symmetry. The symmetry reduction probably results from the pairing of RE cation sites with other RE cations, with vacancies or with monovalent cations in order to preserve local charge neutrality.

## Acknowledgement

The authors would like to acknowledge support from the National Science Foundation (DMR 8818371). International collaboration was greatly assisted by funds from the NATO research program.

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