Photoluminescence and magnetic properties of CdPS$_3$ intercalated with rare earth ions

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Available online 19 April 2007

Abstract

We have investigated the photoluminescence (PL) and the magnetic properties of CdPS$_3$ intercalated with Ce and Eu ions. Two kinds of the intercalated phases are obtained. In the first phases (P_{Ce} and P_{Eu}), the hydrated rare earth ions exist in the van der Waals gap. The second phases (D_{Ce} and D_{Eu}) are obtained by the dehydration of P_{Ce} and P_{Eu}. Rare earth ions are inserted into the lamellar layers in them. All phases are paramagnetic. While the magnetic properties of P_{Ce}, P_{Eu} and D_{Ce} are explained by Ce^{3+} and Eu^{3+} ions, respectively, those of D_{Eu} suggest the coexistence of Eu^{2+} and Eu^{3+} ions. In the PL spectra at 4.2 K, while 4f $\rightarrow$ 5d transition of Ce^{3+} ions is observed in D_{Ce}, 4f $\rightarrow$ 4f transition of Eu^{3+} ions and 4f $\rightarrow$ 5d transition of Eu^{2+} ions are observed in D_{Eu}. These are consistent with the magnetic properties.
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PACS: 68.65.−k; 71.20.Eh; 71.70.Gm

Keywords: Rare earth; Luminescence; Magnetization; Layered compound

1. Introduction

Transition metal phosphorus trichalcogenides MPX$_3$ (M: transition metal ion, X: chalcogen ion) are cation ordered CdCl$_2$-type layered compounds. These crystal structures belong to the monoclinic system with the space group *C*2/*m*. The physical properties and intercalation chemistry of these compounds have been studied during several decades [1–4]. Recently, we have investigated the magnetic properties of MPX$_3$ (M = Mn, Fe) and clarified the relation between the magnetic properties and the interlayer distance of MnPS$_3$ by intercalating pyridine or by applying high pressure [5,6]. On the other hand, CdPS$_3$ is known to be nonmagnetic and transparent at visible wavelengths region. While Clement et al. studied the luminescence properties of CdPS$_3$ intercalated with Eu, Sm and Nd ions [3], the systematic study on the luminescence and the magnetic properties of CdPS$_3$ intercalated with rare earth ions has not been reported.

Ce ion is an optically active ion in the lanthanide series. Eu ion is known to have two different valence states, divalent and trivalent states, and they show quite different magnetic proper-

ties. Then, in this study, we have prepared CdPS$_3$ intercalated with Ce and Eu ions and investigated the magnetic and the photoluminescence properties of them.

2. Experimental

Single crystal of CdPS$_3$ was grown by a chemical vapor transport method. The proper weights of starting materials (cadmium, phosphorus and sulfur powders) were thoroughly mixed with iodine in an Ar atmosphere. They were sealed in an evacuated quartz tube ($\sim$2 × 10^{-5} Torr). The chemical vapor transport reaction was carried out in a two-zone electric furnace for 120 h. The distance between the charge zone and the growth zone is about 10 cm. The temperatures of the charge zone and the growth zone are 953 and 903 K, respectively. Ce and Eu ions were intercalated into CdPS$_3$ by the following way [3]. Single crystalline CdPS$_3$ plates were firstly immersed in a potassium chloride solution. Hydrated potassium ions were intercalated into the van der Waals gap of CdPS$_3$. After this process, above materials were immersed in a rare earth chloride solution. Potassium ions were substituted by rare earth ions, accompanying the removal of Cd ions from the lamellar layers. The phases obtained by above process were denoted by P_{Ce} and P_{Eu} for Ce and Eu intercalation, respectively. By dehydrating P_{Ce} and P_{Eu} at 393 K under a vacuum during 20 h, new phases were obtained. Rare earth ions were inserted into the lamellar layers of CdPS$_3$. They were denoted by D_{Ce} and D_{Eu} for Ce and Eu intercalation, respectively.

The powder X-ray diffraction (XRD) measurements were performed using XRD diffractometer (RINT 1100, Rigaku) with a Cu Kα (λ = 1.5405 Å). The quantitative analysis of elements were carried out using inductively coupled plasma atomic emission spectrometer (ICP-AES) (SPS-1200A, Seiko Instru-

ment). Compositions of the inorganic elements (Cd, P, Eu and Ce) of samples were directly estimated using ICP-AES. Composition of sulfur was estimated by subtracting the amounts of Cd, P, Eu and Ce from the total amount of the sample. The magnetization was measured by a superconducting quantum interference device (SQUID) (MPMS, Quantum Design) magnetometer in a temperature range between 5 and 300 K. Photoluminescence (PL) measurements were carried out using (ATRAS-25, Bunkoh-Keiki Co. Ltd.) with a He–Cd Laser ($\lambda = 325$ nm) at 4.2 K.

3. Results and discussion

CdPS$_3$ is found to be almost single crystal phase. A basal spacing (a distance between Cd layers) of CdPS$_3$ is 6.6 Å and that of the potassium ion intercalated phase is 9.3 Å. While the basal spacings of P_{Ce} and P_{Eu} are about 13 Å, those of D_{Ce} and D_{Eu} are 6.6 Å and almost the same as that of CdPS$_3$. Details are shown in Table 1.

The results of ICP measurements of the phases, P_{Ce}, P_{Eu}, D_{Ce} and D_{Eu}, are also given in Table 1. The compositions of the intercalated rare earth ions almost correspond to the amount of the removed Cd ions. A part of sulfur is lost by the dehydration.

The temperature dependences of the inverse magnetic susceptibility of P_{Ce} and D_{Ce} are shown in Fig. 1. They obey the Curie–Weiss law above 100 K. The values of the effective magnetic moment μ_{eff} estimated from the slope above 100 K are 2.96 and 2.98 μ_B for P_{Ce} and D_{Ce}, respectively. They are slightly larger than the free ion value of Ce^{3+} (2.54 μ_B). The slight increase of μ_{eff} estimated from χ^{-1} above 100 K, and the rapid decrease of χ^{-1} below 100 K for D_{Ce} compared to P_{Ce} at low temperature may be explained by the crystal field effect. The

Table 1
The basal spacing and the composition of P_{Ce}, P_{Eu}, D_{Ce} and D_{Eu}

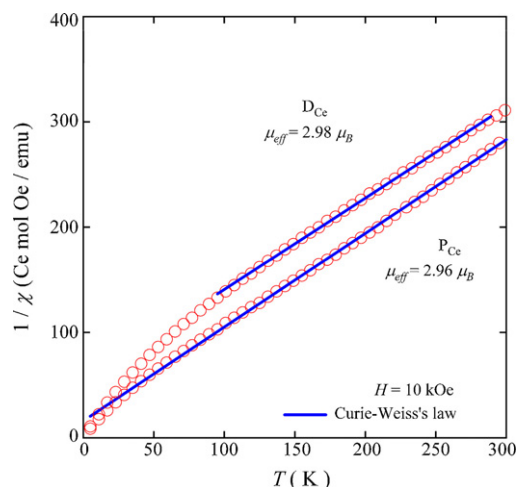| Sample	Basal spacing (Å)	Composition (at.%)
P_{Ce}	13.1	Cd$_{16.4}$P$_{20.6}$S$_{58.9}$Ce$_{4.1}$(H$_2$O)$_x$
P_{Eu}	12.9	Cd$_{18.0}$P$_{21.5}$S$_{56.1}$Eu$_{4.4}$(H$_2$O)$_x$
D_{Ce}	6.55	Cd$_{20.1}$P$_{25.3}$S$_{49.5}$Ce$_{5.1}$
D_{Eu}	6.6	Cd$_{17.8}$P$_{21.5}$S$_{55.9}$Eu$_{4.8}$

Fig. 1. Temperature dependences of the inverse magnetic susceptibility of P_{Ce} and D_{Ce}.
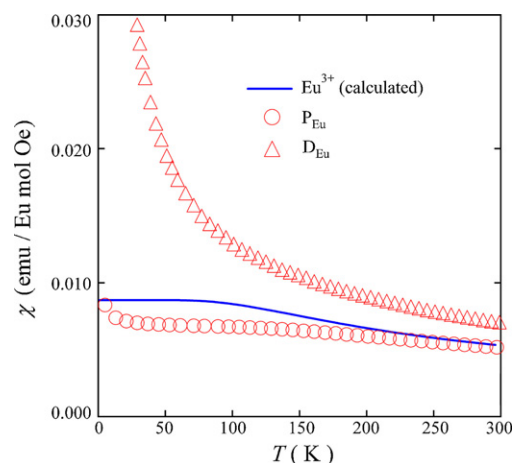

Fig. 2. Temperature dependences of the magnetic susceptibility of P_{Eu} and D_{Eu}. Solid line indicates the theoretical value of the van Vleck paramagnetism of Eu^{3+} ions.

crystal field effect in D_{Ce} is stronger than that in P_{Ce} because the effect of the surrounding ions is stronger in the lamellar layers than in the van der Waals gap. The temperature dependences of the magnetic susceptibility of P_{Eu} and D_{Eu} are shown in Fig. 2. While the behavior of the magnetic susceptibility of P_{Eu} is well explained by the van Vleck paramagnetism of Eu^{3+} ions, the magnetic susceptibility of D_{Eu} shows quite different tendency from that of P_{Eu} and obeys the Curie–Weiss law. As the μ_{eff} of D_{Eu} is 4.68 μ_B, it is considered that about a half of Eu^{3+} ions are changed to Eu^{2+} ions and that the coexistence of Eu^{2+} and Eu^{3+} ions takes place.

Fig. 3 shows the PL spectrum of D_{Ce} at 4.2 K. It is due to the $4f \rightarrow 5d$ transition of Ce^{3+} ions in the lamellar layers. It can be deconvoluted to four Gaussian spectra of which peak wave numbers are 13,250, 19,000, 22,600 and 24,200 cm^{-1}, respectively [7]. Each deconvoluted spectrum is considered to be originated
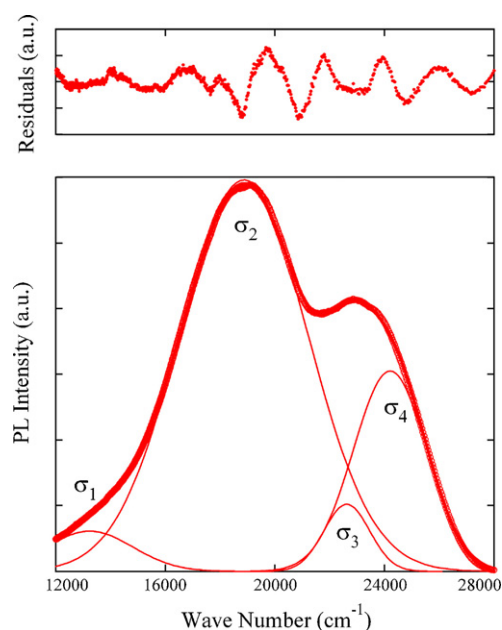

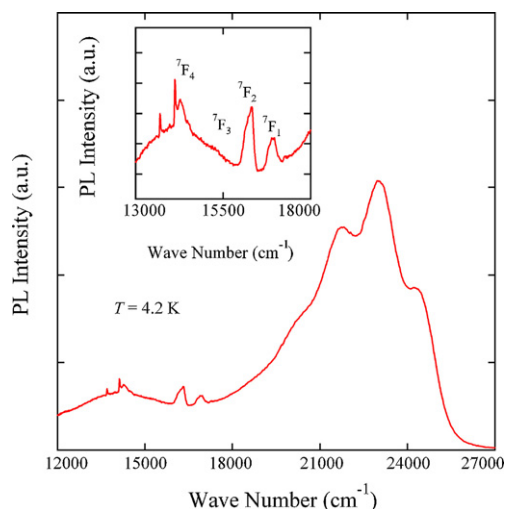Fig. 3. PL spectrum of D_{Ce} at 4.2 K.

Fig. 4. PL spectrum of D_{Eu} at 4.2 K.

from the different luminescent centers. In the present case, the photons with $\lambda = 325$ nm are mainly absorbed by $CdPS_3$ and then the energy is transfered from $CdPS_3$ to Ce^{3+} ions. Three peaks, σ_2, σ_3 and σ_4 are due to the transitions from several 5d levels to 4f levels of Ce^{3+} ions in the lamellar layers. The difference of energy between these peaks equal to the energy separations between $^2F_{5/2}$ and $^2F_{7/2}$ levels of the Ce^{3+} ions. On the other band, the peak σ_1 originates from the defect of $CdPS_3$. Fig. 4 shows the PL spectrum of D_{Eu} at 4.2 K. The mechanism of the energy transfer to Eu^{3+} ions is the same as that to Ce^{3+} ions. It consists of several sharp peaks and broad peaks. Sharp peaks between 13,000 and 18,000 cm^{-1} are due to the 4f' $\rightarrow$ 4f transition of Eu^{3+} ions in the lamellar layers. The peaks at 16,949, 16,287, 15,385 and 14,286 cm^{-1} correspond to ($^5D_0 \rightarrow {}^7F_J$)

($J = 1, 2, 3, 4$) $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, $^5D_0 \rightarrow {}^7F_4$ transitions of Eu^{3+} ions, respectively. Photons with $\lambda = 325$ nm can excite Eu^{2+} ions. Three peaks around 24,100 cm^{-1} are the 4f $\rightarrow$ 5d transitions of Eu^{2+} ions [8].

4. Conclusion

In the Ce or Eu intercalation to $CdPS_3$, two kinds of the intercalated phases are obtained. In hydrated phases (P_{Ce} and P_{Eu}), the hydrated rare earth ions exist in the van der Waals gap. In dehydrated phases (D_{Ce} and D_{Eu}), rare earth ions are inserted into the lamellar layers. From the magnetic properties and PL spectra, the valence of Ce ions in P_{Ce} and D_{Ce} is considered to be trivalent. On the other hand, although the Eu ions in P_{Eu} are also considered trivalent, the coexistence of Eu^{2+} and Eu^{3+} ions in D_{Eu} is strongly suggested.

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