

An inorganic–organic intercalated nanocomposite, BEDT-TTF into layered MnPS_3

Huiqiong Zhou · Li Zou · Xingguo Chen ·
Chuluo Yang · Makoto Inokuchi · Jingui Qin

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Abstract In this paper we report the synthesis and magnetic properties of an inorganic–organic hybrid, $\text{Mn}_{0.84}\text{PS}_3(\text{BEDT-TTF})_{0.35}$ (BEDT-TTF = bis(ethylenedithio) tetrathiafulvalene), which is obtained by the intercalation of pre-intercalation compound $\text{Mn}_{0.90}\text{PS}_3(\text{Phen})_{0.32}$ (Phen = 1,10-phenanthroline) with $(\text{BEDT-TTF})_2\text{I}_x$. The lattice spacing expansion (Δd) of 4.0 Å compared with the pristine MnPS_3 indicates that the molecular plane of BEDT-TTF is arranged parallel to the host layer. From the magnetic measurements it was found that two magnetic phase transitions occur. Above 50 K it shows paramagnetism in well agreement with Curie–Weiss law. Around 40 K it exhibits spin-glass transition and at 5 K a ferrimagnetic phase transition occurs, which is confirmed by M–H at different temperatures.

Keywords Intercalation · BEDT-TTF · Layered MnPS_3 · Magnetic property

Introduction

The organic–inorganic hybrid nanocomposite is a kind of the most attractive functional materials due to the promising application in many fields [1], and intercalation provides an effective approach to design and synthesize these hybrid

materials [2, 3]. Via intercalation organic species can be arranged in well-ordered orientation through the interlayered space limitation of the layered inorganic solids to produce the low-dimensional functional materials and even multifunctional materials [4, 5]. For example, the insertion of 4'-dimethylamino-*N*-methylstilbazolium (DAMS) into MnPS_3 had produced a multifunctional material simultaneously showing the large second-order nonlinear optical property and spontaneous magnetization below 40 K [6].

Due to the interesting electronic and magnetic properties, MPS_3 intercalation compounds have attracted a considerable attention in the past decades [7]. Several transition metal hexathiodiphosphates, MPS_3 (M = Mn, Fe etc.) are layered anti-ferromagnetic compounds [8], and they possess a unique non-redox intercalation reaction based on the cation-exchange between the intralamellar M^{2+} ions of the host and the guest cations in the solution where the inserted guests can compensate the intralamellar M^{2+} ion vacancies to maintain the charge balance [9]. The departure of intralayered M^{2+} ions can destroy the balance of antiferromagnetic interaction of MPS_3 slab, leading to spontaneous magnetization at low temperature for many MPS_3 intercalation compounds [10–13].

Tetrathiafulvalene (TTF) and its derivatives such as bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), as the excellent organic π -electron-donors, have constituted a series of organic conductors and superconductors [14]. The inorganic–organic hybrids based on the inorganic anions and TTF type salts have been extensively studied and some of them exhibited novel solid-state physical properties such as paramagnetic superconductivity [15] and metallic-like conductive ferromagnetism [16]. In addition, TTF type salts had been chosen as the guest to be intercalated into some layered inorganic solids such as FeOCl [17, 18], Montmorillonite (MT) [19] and MPS_3 [20] to give rise to some intercalation

H. Zhou · L. Zou · X. Chen (✉) · C. Yang · J. Qin
Department of Chemistry, Hubei Key Lab on Organic and Polymeric Opto-electronic Materials, Wuhan University,
Wuhan 430072, China
e-mail: xgchen@whu.edu.cn

M. Inokuchi
Department of Materials Science and Engineering, Science
University of Tokyo in Yamaguchi, Onoda, Yamaguchi
756-0884, Japan

compounds exhibiting much higher electrical conductivity than that of the corresponding pure host compounds owing to their column stacking arrangement of the mixed-valence TTF type molecules between the host layers. Bringley and coworkers firstly reported BEDT-TTF-FeOCl intercalation compound in 1990 [21], and a BEDT-TTF intercalation compound based on MnPS_3 had been presented [22], in which the long C_2 axial of BEDT-TTF molecule was arranged in a canted angle from the perpendicular with respect to host layer. Here we successfully obtained a new intercalation compound also based on BEDT-TTF molecule into layered MnPS_3 , in which the guest molecule of BEDT-TTF was arranged in its molecular plane parallel to host layer. And its synthesis, structural characterization and magnetic properties were also presented in this paper.

Experimental

X-ray powder diffraction (XRD) patterns were obtained with Dmaxr A X-ray diffractometer using Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$). FTIR were recorded on a PerkinElmer-2 spectrometer. Elemental analysis of C, H and N was performed with a Carlorba-1106 micro-analyzer. The content of Mn and P were measured by the method of ICP-AES with an Atomscan-2000 instrument. Magnetic properties were studied by SQUID-magnetometer (MPMS, Quantum Design).

Pure MnPS_3 was synthesized as described by Taylor [23], which was identified by means of XRD [24]. (BEDT-TTF) $\cdot\text{I}_x$ was prepared as in reference [25]. And some other reagents are purchased commercially without further purification.

Pre-intercalation compound $\text{Mn}_{0.90}\text{PS}_3(\text{Phen})_{0.32}$ was synthesized as in reference [26], in which MnPS_3 (0.30 g) reacted with 1,10-phenanthroline (0.55 g) in the presence of HOAc (0.5 mL) in 15 mL of ethanol for 5 days. Anal. Calcd. (%): C, 19.66; H, 1.24; Mn, 21.08; N, 3.82; P, 13.20. Found (%): C, 19.04; H, 1.05; Mn, 20.52; N, 3.85; P, 12.68. IR (cm^{-1}): 1617, 1596, 1545, 1520, 1497, 1423, 1142, 1100, 842, 783, 723, 610, 591, 558.

$\text{Mn}_{0.84}\text{PS}_3(\text{BEDT-TTF})_{0.35}$ was obtained by treating $\text{Mn}_{0.90}\text{PS}_3(\text{Phen})_{0.32}$ (0.30 g) with (BEDT-TTF) $\cdot\text{I}_x$ (0.25 g) in acetonitrile (15 mL) for one and half months at 65°C , followed by filtration and washing with acetonitrile and dichloromethane. Anal. Calcd. (%): C, 13.65; H, 0.92; Mn, 14.99; P, 10.06. Found (%): C, 13.05; H, 0.95; Mn, 14.46; P, 9.57. IR (cm^{-1}): 1515, 1413, 1289, 1230, 1221, 998, 882, 917, 773, 611, 590, 556.

Results and discussion

Figure 1 lists the X-ray powder diffraction (XRD) patterns of final intercalation compound as well as the pre-

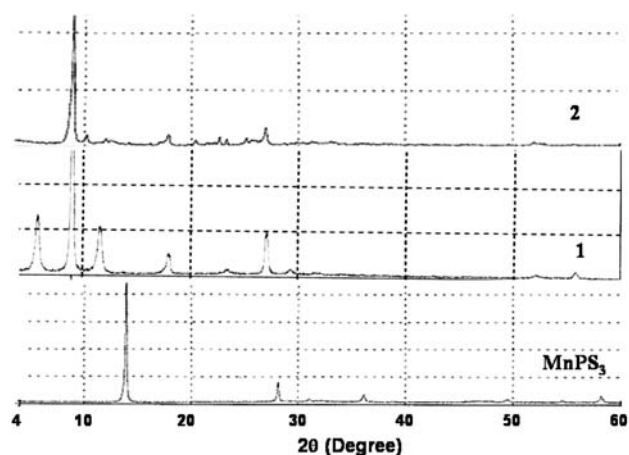


Fig. 1 The XRD patterns of pure MnPS_3 , pre-intercalation compound $\text{Mn}_{0.90}\text{PS}_3(\text{Phen})_{0.32}$ (1) and intercalation compound $\text{Mn}_{0.84}\text{PS}_3(\text{BEDT-TTF})_{0.35}$ (2)

intercalation compound and pristine MnPS_3 for comparison. The pre-intercalation compound $\text{Mn}_{0.90}\text{PS}_3(\text{Phen})_{0.32}$ showed the coexistence of two phases similar to that of 1,10-phenanthroline into layered FePS_3 [26], where one phase is corresponding to the lattice spacing of $\sim 15.5 \text{ \AA}$ and the other is corresponding to a lattice spacing of 9.9 \AA . After intercalation a new series of reflection patterns appeared, which is different from those of pre-intercalate $\text{Mn}_{0.90}\text{PS}_3(\text{Phen})_{0.32}$ as well as pristine MnPS_3 . This indicated that a full intercalation product is obtained. Elemental analyses lead to its stoichiometry to be $\text{Mn}_{0.84}\text{PS}_3(\text{BEDT-TTF})_{0.35}$. From XRD it is found that the lattice spacing of it is about 10.5 \AA , expanding by 4.0 \AA with respect to the pristine MnPS_3 ($d = 6.52 \text{ \AA}$), suggesting that the orientation of BEDT-TTF molecular plane is parallel to the host layer. This is similar to that of TTM-TTF molecule into layered MnPS_3 [27] and BEDT-TTF into layered FePS_3 [28].

A stretching band $\nu(\text{PS}_3)$ at 570 cm^{-1} for pure MnPS_3 has been split into three sharp absorptions at 612 , 590 and 556 cm^{-1} in $\text{Mn}_{0.84}\text{PS}_3(\text{BEDT-TTF})_{0.35}$, indicating the presence of intralamellar Mn^{2+} ion vacancies in the host layer [29]. In addition, some IR absorptions such as at 1413 , 1288 and 916 and 773 cm^{-1} for $\text{Mn}_{0.84}\text{PS}_3(\text{BEDT-TTF})_{0.35}$ is similar to those of BEDT-TTF molecule [30] as well as BEDT-TTF into layered FePS_3 [28], further suggesting that BEDT-TTF has been inserted into the interlayer space of the host layers.

The magnetic property of $\text{Mn}_{0.84}\text{PS}_3(\text{BEDT-TTF})_{0.35}$ was studied with SQUID. Figure 2 shows its plots of χ (susceptibility)– T (temperature) and χT – T as well as $1/\chi$ – T . As can be seen from χT – T curve, there are two magnetic phase transitions occurring at 40 and 5 K , respectively. The decrease of χT from 300 to 40 K indicates that the interaction of the Mn^{2+} spins is antiferromagnetic in the paramagnetic

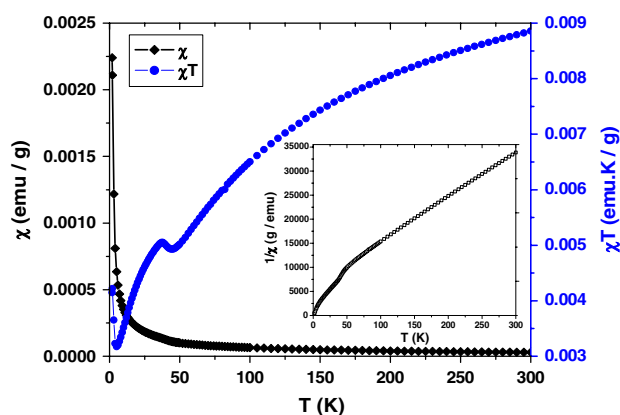


Fig. 2 The plots of χ - T and χT - T as well as $1/\chi$ - T (inset)

range. Above 50 K $1/\chi$ - T curve is in well agreement with Curie–Weiss Law. The Curie–Weiss temperature (θ) is -62.3 K also reflecting the localized antiferromagnetic coupling interaction between the Mn^{2+} ions, which is much weaker than pure MnPS_3 ($\theta = -268$ K) owing to the strong dilution of the more intralamellar Mn^{2+} ion vacancies in $\text{Mn}_{0.84}\text{PS}_3(\text{BEDT-TTF})_{0.35}$. At 40 K χT value exhibits weak upward indicating the occurrence of a magnetic phase transition. This magnetic behavior possibly derives from the spin-glass transition produced by the competition between antiferromagnetic interaction and ferromagnetic interaction induced by intercalation. From 25 to 5 K the χT decreases monotonically again. However, at 5 K χT increases rapidly indicating that a ferrimagnetic phase transition occurs.

The magnetization at different temperatures (from 35 to 1.85 K) (Fig. 3) as well as the magnetic hysteresis at 1.85 and 35 K (Fig. 4) also support the occurrence of this ferrimagnetic phase transition. The saturation trend of magnetization is observed from M - H curve at 1.85, 3.0 and 5.0 K, respectively. However, M - H curves from 5 to 35 K show almost linear relationship with temperature increment even

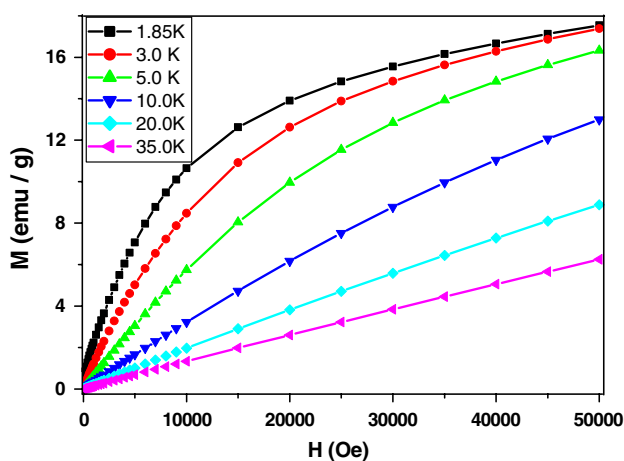


Fig. 3 The plots of M - H at different temperatures

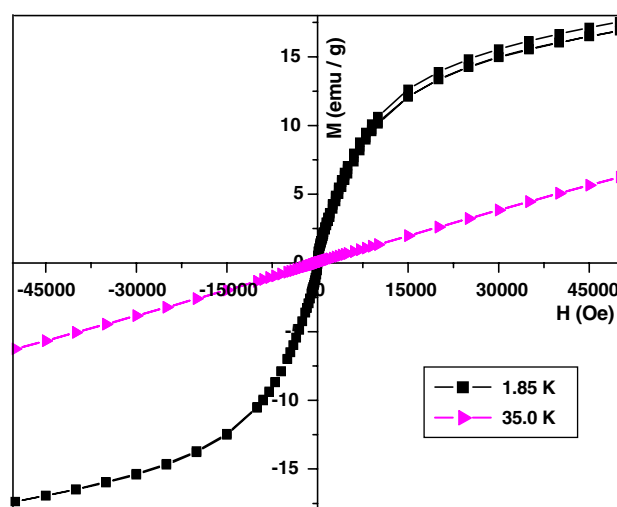


Fig. 4 The magnetic hysteresis at 1.85 and 35 K

up to 50 KOe. Similar magnetic behavior was observed in the intercalation compound of $\text{Mn}_{0.83}\text{PS}_3(\text{Tm-TTF})_{0.50}$ [27], in which the molecular plane of the guest (Tm-TTF) was also arranged in the parallel way to the MnPS_3 layer. But the intercalation compound with the long C_2 axial of BEDT-TTF molecule arranged in a canted angle from the perpendicular to MnPS_3 layer only exhibited paramagnetism in the range of 2–300 K [22]. It seems that the magnetic property is related to the arrangement of guest molecule in the interlayer space of the host. However, the relationship of magnetic property and guest molecular arrangement is still not clear and needs to be further studied.

Conclusions

Via the ion-exchange intercalation we synthesize an intercalation compound, $\text{Mn}_{0.84}\text{PS}_3(\text{BEDT-TTF})_{0.35}$, in which the BEDT-TTF molecular plane is arranged in parallel orientation to the host layer. Two magnetic phase transitions are observed at 40 and 5 K, respectively. Above 50 K it shows paramagnetism and obeys Curie–Weiss Law. Around 40 K a magnetic transition occurs due to spin disorder and below 5 K it exhibits a ferrimagnetic phase transition, which is further confirmed by M - H behavior at different temperatures.

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