

无机-有机纳米复合材料:有机氮氧自由基/MnPS₃ 夹层物的合成与磁性

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摘要: 合成了一个无机/有机纳米复合物(MPYNN)_{0.14}Mn_{0.93}PS₃,即有机氮氧自由基 MPYNN(*N*-甲基吡啶阳离子自由基)的 MnPS₃ 夹层化合物。通过 X-射线粉末衍射和红外光谱等对其结构进行了表征,根据其 0.56 nm 的层间距扩大值推测夹层化合物中的客体分子在层间采取了分子平面近乎垂直于主体层的排列方式。通过 SQUID 测试了所得到的夹层化合物的磁性,结果表明夹层化合物(MPYNN)_{0.14}Mn_{0.93}PS₃ 在 10 K 以上具有顺磁特性,而在 7 K 时出现了一个明显的磁相变,表现出自发磁化。

关键词: 夹层; 氮氧自由基; 层状 MnPS₃; 磁性

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Synthesis and Magnetism of an Inorganic-organic Nanocomposite: Nitronyl-nitroxide Radical Intercalated into Layered MnPS₃

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Abstract: The synthesis and magnetism of an intercalation compound were studied based on 2-(4'-*N*-methylpyridinium)-4,4,5,5-tetramethyl-imidazolyl-1-oxyl-3-oxide (Methylpyridinium nitronyl nitroxide, MPYNN) radical into layered MnPS₃. The lattice expansion of 0.56 nm suggests that the guest molecule plane of pyridine in MPYNN is arranged almost perpendicular to the host layer. Magnetic measurements by SQUID indicates that the intercalation compound of (MPYNN)_{0.14}Mn_{0.93}PS₃ exhibits paramagnetism above 10 K, and then spontaneous magnetization occurs at 7 K.

Key words: intercalation; nitronyl nitroxide radical; layered MnPS₃; magnetic property

In the past decades intercalation materials have attracted considerable attention for their promising application as cathode materials, catalysts, solid ionic conductors, anisotropic electronic conductors, low-dimensional molecular magnets and nonlinear optical

materials^[1,2].

Layered manganese phosphorous trisulfide, MnPS₃, is an antiferromagnet with Neel temperature of 78 K^[3,4]. However, after intercalation the magnetic properties of this system are sometimes dramatically changed^[5-7]. For

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example, some intercalation compounds from inorganic, organic, metal complex cationic and organometallic cationic species into MnPS_3 show a variety of interesting magnetic properties^[8-11] and even multifunctional properties^[12]. This provides an effective route to design the functionally magnetic inorganic-organic hybrid materials.

Since the discovery of the organic magnet based on nitronyl nitroxide radical in 1990's^[13] much attention has been focused on the synthesis and application of pure organic ferromagnets^[14,15] as well as molecular-based magnets using nitronyl nitroxide radical as building block^[16-18]. In addition, some stable free radicals have been inserted into the layered solids such as transition metal hydroxide^[19] and layered double hydroxides (LDHs)^[20] to study the magnetic properties of the products. In order to search for some new molecular-based magnetic materials, we have selected 2-(4'-*N*-methylpyridinium)-4,4,5,5-tetramethyl-imidazolyl-1-oxyl-3-oxide (Methylpyridinium nitronyl nitroxide, MPYNN) radical as a guest to be inserted into layered MnPS_3 host. Here we report the synthesis and structural characterization of an intercalation compound of $(\text{MPYNN})_{0.14}\text{Mn}_{0.93}\text{PS}_3$ as well as its solid state magnetic property.

1 Experimental

1.1 Materials and characterizations

XRD patterns were recorded on a Dmaxr A X-ray diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda=0.15418$ nm). Fourier transform infrared (FTIR) spectra were recorded on a Shimadzu Testscan FTIR 3000 series (Osaka, Japan) in the region of $4000\sim 400$ cm^{-1} on KBr pellets. Elemental analysis of carbon, hydrogen and nitrogen was performed on a VarioEL-III microanalyzer. The content of manganese and phosphorus were measured by the method of ICP-AES with an Atomscan-2000 instrument. The magnetic property was studied by SQUID-magnetometer (MPMS, Quantum Design).

Pure MnPS_3 was synthesized by reaction of stoichiometric amounts of high-purity elements (>99.9%) in an evacuated quartz tube at 650 $^\circ\text{C}$ as described in the literature^[21,22]. It was identified by means of XRD and indexed as a monoclinic unit cell (space group $C2/m$),

in which $a=0.6094$ nm, $b=1.0589$ nm, $c=0.6817$ nm, $\beta=107.23^\circ$. Methylpyridinium nitronyl nitroxide (MPYNN) iodide was synthesized as described in ref^[23].

1.2 Synthesis of intercalation compounds

Pre-intercalate $\text{Mn}_{1-x}\text{PS}_3(\text{K})_{2x}\cdot(\text{H}_2\text{O})_y$ was obtained from pure MnPS_3 reacting with KCl in aqueous solution for two days. Then 0.20 g of $\text{Mn}_{1-x}\text{PS}_3(\text{K})_{2x}\cdot(\text{H}_2\text{O})_y$ and 0.50 g of MPYNN iodide in 25 mL methanol were put into an ampoule and oxygen was removed under nitrogen atmosphere. The mixture was kept in dark and heated at 60 $^\circ\text{C}$ for about 2 weeks. The solids were filtered and washed with methanol for 3 times and light yellow solids were obtained. The elemental analysis leads to the stoichiometry of $(\text{MPYNN})_{0.14}\text{Mn}_{0.93}\text{PS}_3$ for the intercalation compound. Anal. Calcd (%): C, 10.14; H, 1.38; Mn, 23.75; N, 2.36; P, 14.67. Found (%): C, 10.25; H, 1.26; Mn, 23.97; N, 2.76; P, 14.53.

2 Results and discussion

Fig.1 lists the XRD patterns of the intercalation compound. Also listed are those of the pre-intercalate $\text{Mn}_{1-x}\text{PS}_3\cdot\text{K}_{2x}\cdot(\text{H}_2\text{O})_y$ and pure MnPS_3 for comparison. As can be seen from XRD patterns, the final product of $(\text{MPYNN})_{0.14}\text{Mn}_{0.93}\text{PS}_3$ shows a series of new $00l$ reflections such as those at $2\theta=7.28^\circ(001)$ and $14.50^\circ(002)$, which are different from those of the pre-intercalate $\text{Mn}_{1-x}\text{PS}_3\cdot\text{K}_{2x}\cdot(\text{H}_2\text{O})_y$ ($2\theta=9.38^\circ(001)$, $18.86^\circ(002)$) and pure MnPS_3 ($2\theta=13.68^\circ(001)$, $27.54^\circ(002)$). This

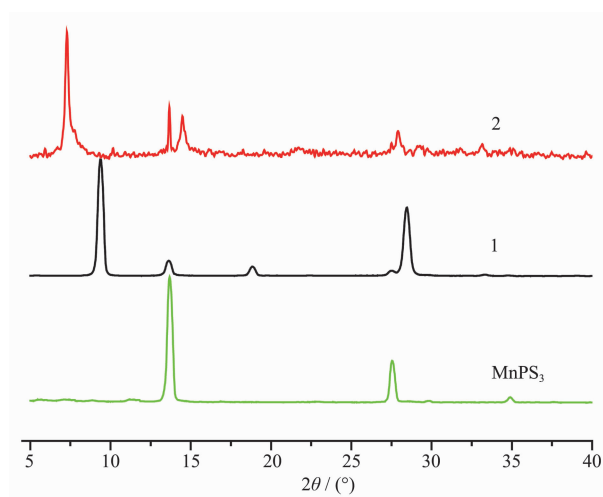


Fig.1 XRD patterns of pure MnPS_3 , pre-intercalate $\text{Mn}_{1-x}\text{PS}_3\cdot\text{K}_{2x}\cdot(\text{H}_2\text{O})_y$ (1) and intercalate $(\text{MPYNN})_{0.14}\text{Mn}_{0.93}\text{PS}_3$ (2)

indicates that successful intercalation occurs and the layered structure is maintained with the space expansion in the *c* direction compared with the pristine MnPS₃. The biggest lattice spacing corresponding to $2\theta=7.28^\circ$ is about 1.21 nm, which is expanded by 0.56 nm with respect to the pristine MnPS₃ ($d_{001}=0.65$ nm). The value of 0.56 nm is roughly the width of pyridine ring. Therefore, the XRD result suggests that the pyridine ring plane of the guest MPYNN is arranged almost perpendicular to the host layer, similar to the intercalation of pyridine into layered MnPS₃, where the lattice expansion is 0.58 nm^[24]. The possible orientation of MPYNN in the host is illustrated in Fig.2.

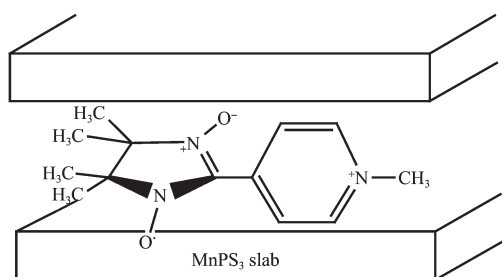


Fig.2 Possible orientation of the guest molecule in the host

Fig.3 lists the IR spectra of the intercalation compound, (MPYNN)_{0.14}Mn_{0.93}PS₃, and the guest molecule, MPYNN, for comparison. It can be seen from IR spectrum of (MPYNN)_{0.14}Mn_{0.93}PS₃ that the stretching vibration absorption band of $\nu(\text{PS}_3)$ at 570 cm⁻¹ for pure MnPS₃ has been split into three sharp absorptions at 610, 590, 558 cm⁻¹, indicating the presence of intralamellar Mn²⁺ ion vacancies in the host layer^[25]. In addition,

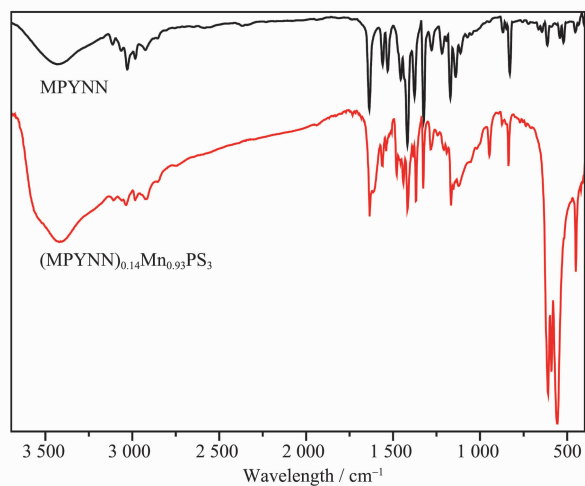


Fig.3 Infrared spectra of (MPYNN)_{0.14}Mn_{0.93}PS₃ and MPYNN

ion, some IR absorption bands of (MPYNN)_{0.14}Mn_{0.93}PS₃ in the range of 3 100~600 cm⁻¹ such as those at 3 063, 3 035, 2 985, 2 922, 1 636, 1 560, 1 540, 1 441, 1 418, 1 370, 1 327, 1 285, 1 166, 838, are similar to those of MPYNN molecule (at 3 067, 3 031, 2 982, 2 925, 1 639, 1 563, 1 532, 1 438, 1 418, 1 379, 1 325, 1 282, 1 169, 832 cm⁻¹). Especially, the IR absorption of 1 379 cm⁻¹ for pure nitronyl nitroxide radical^[26] has been shifted to 1 370 cm⁻¹ due to the interlayered space limitation in the host.

The magnetic property of (MPYNN)_{0.14}Mn_{0.93}PS₃, was studied with SQUID. Fig.4 and 5 show the plots of χ (susceptibility)-*T*(temperature) and $\frac{1}{\chi}$ -*T*, as well as χT -*T*, respectively. As can be seen from Fig.4, the $\frac{1}{\chi}$ -*T* curve is in good agreement with Curie-Weiss Law above 50 K. The Curie-Weiss temperature (θ) is -59 K also reflecting the localized antiferromagnetic coupling interaction between the Mn²⁺ ions, which is much weaker than pure MnPS₃ ($\theta=-268$ K) owing to the magnetic dilution of the intralamellar Mn²⁺ ion vacanci-

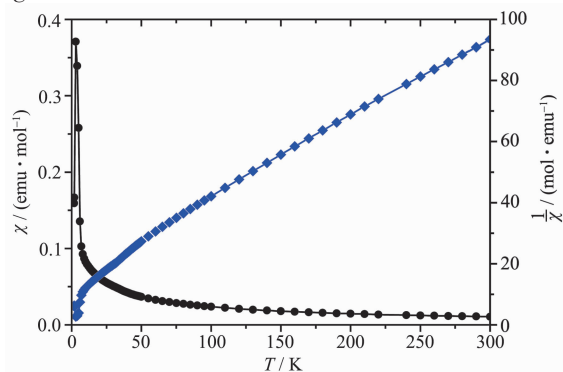


Fig.4 Temperature-dependent magnetic susceptibility for (MPYNN)_{0.14}Mn_{0.93}PS₃

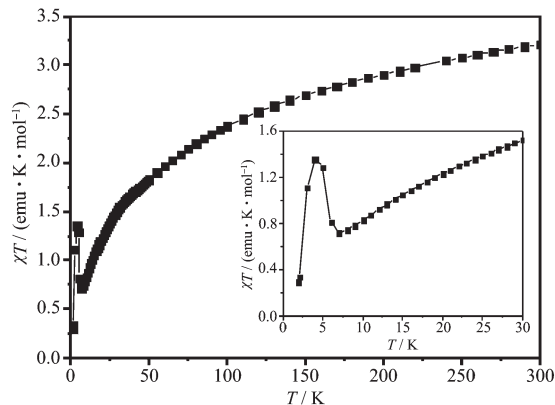


Fig.5 χT vs *T* curve for (MPYNN)_{0.14}Mn_{0.93}PS₃

es in $(\text{MPYNN})_{0.14}\text{Mn}_{0.93}\text{PS}_3$. In Fig.5 the χT value monotonically decrease from 300 K to 7 K indicating that the interaction of the spins is antiferromagnetic in the paramagnetic range. However, there exists a rapid upward for χT value at around 7 K (Fig.5), indicating the occurrence of a spontaneous magnetization.

Generally, some MnPS_3 intercalation compounds exhibit the spontaneous magnetization at 30~40 K^[27-30]. The origin of the spontaneous magnetization for these intercalates has been suggested^[31] as that there are ordered manganese ion vacancies within the MnPS_3 layers, so that a ferrimagnetic ground state could arise from incomplete compensation of the antiferromagnetically coupled Mn^{2+} spins. However, in the intercalate of $(\text{MPYNN})_{0.14}\text{Mn}_{0.93}\text{PS}_3$, its magnetic phase transition occurs at 7 K, which is much lower than that of some other related MnPS_3 intercalation compounds. It can be inferred that there may exist the magnetic interaction between the free radical spin and layered MnPS_3 magnetic slab. Similar behavior had been observed in the intercalation compounds of free radical into layered metal hydroxide such as $\text{M}_2(\text{OH})_3\text{OAc}$ ($\text{M}=\text{Cu}$ and Co)^[32].

3 Conclusions

An intercalation compound, $(\text{MPYNN})_{0.14}\text{Mn}_{0.93}\text{PS}_3$, was synthesized via the ion-exchange intercalation. XRD results suggest that the pyridinyl plane in MPYNN is oriented almost perpendicular to the host layer. The magnetic measurements indicate that it shows paramagnetism above 10 K, and at 7 K a magnetic phase transition occurs and spontaneous magnetization is observed.

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