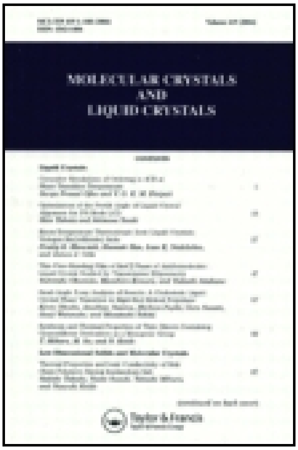

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Electrical Conduction Mechanisms of M_xPS_3, $M_{1-x}M'_xPS_3$ and their Intercalation Compounds

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In the M_xPS_3 and $M_{1-x}M'_xPS_3$ systems, the P_2S_6 cluster contributes to the poor electrical conductivity for the compounds in which the energy level of the metal 3d orbital is deeper than those of the P, S 3p orbitals. For the compounds in which metal 3d orbital is closed to P and S 3p orbitals and has mixed valency, the induced mixed valency of P_2S_6 cluster and/or hopping mechanism contribute to the electrical conductivity. In the organic electron donor intercalation into M_xPS_3 and $M_{1-x}M'_xPS_3$ compounds, the new intercalation reaction is discovered, in which formation of tris-complexes of metal ions with guest molecules occurs in the host interlayer.

Keywords: electrical conductivity; layered material; mixed valency; new intercalation route; X-ray photoelectron spectroscopy

INTRODUCTION

$FePS_3$, VPS_3 and $V_{0.78}PS_3$ crystals have electrical conductivity higher than 10^{-5} Scm^{-1}, while $MnPS_3$, $NiPS_3$, $ZnPS_3$, $In_{2/3}PS_3$ and $CoPS_3$ crystals lower than 10^{-9} Scm^{-1} at room temperature. The X-ray photoelectron spectra of V2p for VPS_3 and $V_{0.78}PS_3$ show that vanadium in $V_{0.78}PS_3$ is in a mixed valence state and the compound is expressed by the formula of $(V^{2+}_{0.3}V^{3+}_{0.7})_{0.78}PS_3$ [1]. The high conductivity of former crystals is attributed to their mixed valency on the metal and/or the S and P sites, which has been revealed by the X-ray photoelectron spectroscopy (XPS) [2]. Intercalation of pyridine or n-alkylamines to $ZnPS_3$ and that of n-alkylamines to $MnPS_3$ crystals have no influence on their electrical conductivity, while intercalation of pyridine to $MnPS_3$ crystal enhances its electrical conductivity more than 1000 times. The electrical conductivity is closely related to their electronic and crystal structures [3]. Vibrational spectra of pyridine-intercalated $MnPS_3$ (Py-$MnPS_3$) crystals reveal that a part of pyridine molecules in the interlayer space of $MnPS_3$ are converted to pyridinium cations (PyH^+) and then form hydrogen-bonded complexes with neutral pyridine molecules. Powder X-ray diffraction and polarized IR reflection spectra of Py-$MnPS_3$ crystals indicate that the majority of molecular planes of PyH^+ as well as neutral pyridine are oriented perpendicularly to the layers of $MnPS_3$ with the C_2 symmetry axes parallel to the layers [4]. Py-$MnPS_3$ single crystals show a discontinuity at about 2Gpa in the IR absorption frequency and intensity changes with increasing pressure. The discontinuity is attributable to a pressure-induced phase transition accompanied by an orientational change of the pyridine in the interlayer space [5]. TTF species intercalated in van der Waals gaps of $MnPS_3$ single crystals are in the state of mixed-valence, and their degree of ionicity is estimated at 0.8 from the Raman band observed at 1432 cm^{-1}. The frequency difference between the Raman band and the IR band of the same origin, of which IR intensity is enhanced through the vibronic intensity borrowing from the charge-transfer transitions, amounts to 120 cm^{-1}. This amount of frequency difference suggests that the intermolecular interaction between TTF species confined in $MnPS_3$ is stronger than that in TTF radical-salt crystals [6]. The UPS (Ultraviolet photoemission spectroscopy) spectral structures of $NiPS_3$ and $FePS_3$ change their intensities strongly with varying incident photon energy. The constant initial state spectroscopy, in conjunction with the photon energy dependence of the UPS spectra, provides the assignment of every UPS spectra feature. These results reveal that the electronic structures of $NiPS_3$ and $FePS_3$ differ from each other, suggesting an explanation for the difference in the electronic properties of these compounds [7]. In this study, electrical conduction mechanisms of M_xPS_3, $M_{1-x}M'_xPS_3$ and their intercalation compounds are investigated.

EXPERIMENTAL

The multiple transition-metal phosphorus trisulfide $Mn_{1-x}Zn_xPS_3$ and $Ag_xFe_{1-x}PS_3$ ($0.00 \leq x \leq 0.50$) were synthesized, and the intercalation compounds such as 2,2'-bipy- $Mn_{1-x}Zn_xPS_3$ and 1,10-phen- $Mn_{1-x}Zn_xPS_3$ were synthesized. These materials were characterized by means of powder X-ray diffractometry, XPS, infrared absorption, Raman, and ultraviolet-visible-near infrared absorption spectroscopies. Their temperature dependences of electrical conductivities were measured.

RESULTS AND DISCUSSION

In the Raman and infrared absorption spectra, the vibration modes of P_2S_6 cluster remained at essentially the same wavenumber. The Ag-substituted samples showed a new broad band appearing at about 2900-3100 cm^{-1} in their infrared absorption spectra with the full width of half maximum of 2000-3000 cm^{-1}. This band is assignable to the Fe^{2+}-Fe^{3+} intervalence transfer band. The absorption spectra in the visible and near infrared region of samples were measured by a Hitachi U-4000 spectrophotometer. All the samples showed the absorption edges at about 12000 cm^{-1} (1.5 eV) and there were no changes for the Ag-substituted samples. The conductivity of Ag-substituted samples was 10^{-2} Scm^{-1}, higher by three orders of magnitude than that of $FePS_3$. Logarithm of conductivity σ versus reciprocal temperature showed nearly linear relationships for all the materials, and the activation energy Ea defined by $\sigma=\sigma_0\exp(-Ea/kT)$ was determined. These values are listed in TABLE I. By the incorporation of Ag the activation energy decreased by a factor of more than two. It was concluded that the metal 3d electrons of $FePS_3$ and $NiPS_3$ do not contribute to the electric conduction from the UPS study. Therefore, it is concluded that P, S, or P-S bonding orbital and/or mixed valency contributes to the electric conduction. The measurement of X-ray photoelectron spectroscopy revealed the mixed valency between Fe^{2+} and Fe^{3+}, in $Ag_xFe_{1-x}PS_3$ (x=0.05, 0.10). This observation is in accordance with the appearance of intervalence transfer band discovered by the present study. Therefore, it is concluded that the enhancement of the electrical conductivity on $Ag_xFe_{1-x}PS_3$ is due to the mixed valency of Fe caused by the substitution of Ag: that is, the enhanced mixed valencies of P and S, or the hopping conduction between Fe^{2+} and Fe^{3+} which contributes to the decrease of activation energy.

TABLE I Electrical conductivity at room temperature and activation energy of $Ag_xFe_{1-x}PS_3$.

x	σ(295K)[Scm^{-1}]	Ea[eV]
0.00	9.0×10^{-5}	0.40
0.10	2.8×10^{-2}	0.19
0.20	4.6×10^{-2}	0.16
0.30	9.1×10^{-2}	0.15
0.40	3.7×10^{-2}	0.18
0.50	5.7×10^{-2}	0.19

From results of X-ray diffraction, $Mn_{1-x}Zn_xPS_3$ have the same layered structures as $MnPS_3$, $ZnPS_3$, and the d values of (*001*) plane were 6.51~6.47Å. The infrared absorption and Raman spectra both show vibrational modes of P_2S_6 cluster. In the Raman spectra, however, the band of $T'_{xy}(PS_3)$mode was 247cm^{-1} ($x \leq 0.4$), 254cm^{-1} ($x \geq 0.6$) and this band was not found at x=0.5. In the ultraviolet-visible-near infrared absorption spectra, the bands of the d-d transition of Mn were observed at 1.95eV ($^6A_{1g}$-$^4T_{1g}$) and 2.38eV($^6A_{1g}$-$^4T_{2g}$). Absorbance of these bands decreased with substitution by Zn^{2+} ion.

Their resistivities at room temperature were 2.0×10^{10}~$2.5\times10^{12}\Omega$cm, and their activation energy Ea were 0.12~0.22eV. Both of them increased with substitution by Zn^{2+} ion.

From these results, an exchange reaction between Zn^{2+} and Mn^{2+} proceeds, but mixed valency does not appear at metal sites in $Mn_{1-x}Zn_xPS_3$. Since metal 3d orbitals are deeper than P or S 3p orbital for MnPS3, ZnPS3, their bandgaps between the conduction band and the valence band are a difference between the phosphate 3p* and 3p. The bandgap of $ZnPS_3$ is slightly wider than $MnPS_3$. If the band structures of $Mn_{1-x}Zn_xPS_3$ are expressed as superimpose of those of $MnPS_3$ and $ZnPS_3$, this bandgap increases with substitution by Zn^{2+} ion. It is concluded that the metal 3d electrons of $Mn_{1-x}Zn_xPS_3$ do not contribute to the electrical conductivity, but the P, S 3p orbitals do.

In the reactions of $Mn_{1-x}Zn_xPS_3$ with 2,2'-Bipyridyl, new intercalation compounds were obtained for $Mn_{1-x}Zn_xPS_3$ ($0.0 \leq x \leq 0.9$), except for $Zn_{1.0}PS_3$. The color of these intercalation compounds changed from green to redbrown or yellowgreen. The d values on (*001*) plane changed from 6.5Å to 15.7Å. This increased interlayer space, 9.2Å, is bigger than the thickness of 2,2'-Bipyridyl molecules. The model for tris-complex of Mn^{2+} ion and 2,2'-Bipyridyl has the shortest length of planes of about 9.4Å which is very close to the interlayer space. In the infrared absorption spectra (FIG 1), the band, 574cm^{-1}, which was assigned to the vibrational modes of P_2S_6 cluster *V*d(PS_3) mode, splitted into three bands, 609, 592 and 557cm^{-1}, with increasing the values of Mn/Zn. This suggests elimination of Mn^{2+} ions from the host lattices. The infrared absorption and Raman spectra of bipyridyl species in the interlayers were very close to those of tris-complex of Mn and bipyridyl. In ultraviolet-visible-near infrared absorption spectra (FIG 2), a new peak appearing at 2.3eV was assigned to the d-d transition of tris-complex of Mn and bipyridyl.

From these results, it is concluded that Mn^2+ ion and 2,2'-Bipyridyl formed a tris-complex in the interlayer of $Mn_{1-x}Zn_xPS_3$ ($0.0 \leq x \leq 0.9$). In this intercalation reaction, Mn^{2+} ion forms tris-complex, but Zn^{2+} ion does not. Since the color of solution does not change during intercalation reaction, the tris-complex is more stable in the interlayer space than in the solution.

Their resistivities at room temperature were smaller by about one order of magnitude than that of host crystals. XPS spectra of 2,2'-bipy-$MnPS_3$ crystals showed that there existed in mixed valency not in the metal site, but in the P_2S_6 cluster. During the intercalation reaction, some vacancies are generated by extraction of Mn^{2+} ions from the host lattices. These vacancies increase mixed valency in the P_2S_6 cluster, so resistivities of these materials become smaller. The tris-complexes in the interlayer do not contribute to the conductivity. 1,10-Phenanthroline, of which structure is similar to 2,2'-Bipyridyl and is known to a stronger ligand, intercalated into $Mn_{1-x}Zn_xPS_3$. A new intercalation compound was obtained only x=0.0. Other crystals were broken into small pieces. An ultraviolet-visible-near infrared absorption spectrum of this new intercalation compound, 1,10-phen-$Mn_{1.0}PS_3$, was very closed to that of 2,2'-bipy-$Mn_{1.0}PS_3$: a new peak appears at 2.3eV. So it was concluded that Mn^{2+} ion and 1,10-Phenanthroline formed tris-complex in the interlayer of host crystal, similarly as 2,2'-bipy- $Mn_{1-x}Zn_xPS_3$.

In the infrared absorption spectra, $Mn_{1-x}Zn_xPS_3$ ($0.1 \leq x \leq 1.0$) in contact with 1,10-Phenanthroline show very similar bands to the tris-complex of Mn^{2+} ion and phenanthroline, and the bands assigned to the vibrational mode of P_2S_6 cluster disappeared. So in this intercalation, the elimination reaction Mn^{2+} and Zn^{2+} from the host lattice gives formation of the tris-complexes. Since these complexes are not stable in the interlayer, they dissolve immediately into the solution. Then these crystals were broken into pieces. This view is supported by the color change of solution to yellow: the color of Mn and/or Zn- phenanthroline complexes is yellow. As to the difference between results of x=0.0 and $x \geq 0.1$, the existence of Zn^{2+} ion is very important to intercalation reaction.

Accordingly, in the case of 2,2'-Bipyridyl intercalation into $Mn_{1-x}Zn_xPS_3$, the important factor is Mn^{2+} ion. In the case of 1,10-Phenanthroline intercalation into $Mn_{1-x}Zn_xPS_3$, the important factors are both Mn^{2+} ion and Zn^{2+} ion.

The resistivity of 1,10-phen-$Mn_{1.0}PS_3$ crystal at room temperature was smaller by about two orders of magnitude than that of host crystal (TABLE II). This increase is due to the vacancy-induced mixed valency in the P_2S_6 cluster as mentioned in 2,2'-bipy- $Mn_{1.0}PS_3$ system.

TABLE II (001) spacing d and electrical resistivity ρ

sample	d / Å	ρ / Ωcm
$Mn_{1.0}PS_3$	6.51	2.0×10^{10}
2,2'-bipy- $Mn_{1.0}PS_3$	15.66	1.7×10^{9}
1,10-phen- $Mn_{1.0}PS_3$	15.38	4.7×10^{8}

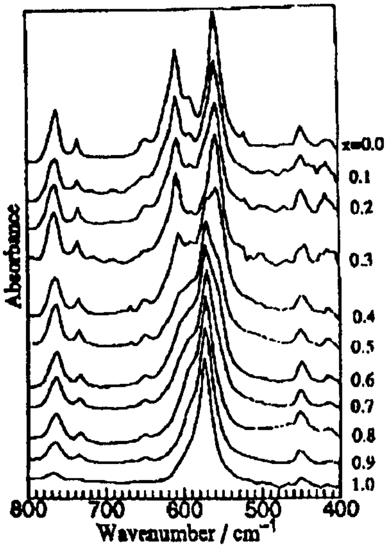

FIGURE 1 Infrared absorption spectra of 2,2'-bipy-$Mn_{1-x}Zn_xPS_3$.

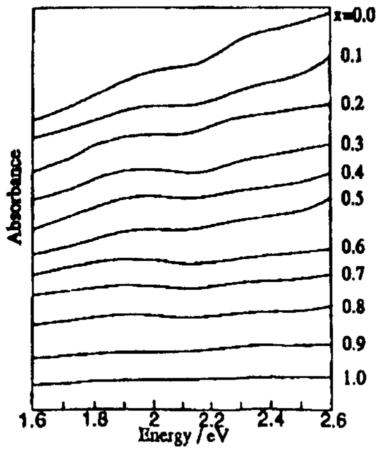

FIGURE 2 Ultraviolet-visible-near infrared absorption spectra of 2, 2'-bipy-$Mn_{1-x}Zn_xPS_3$.

References

[1] K. Ichimura and M. Sano, *Chem. Letters,* 787–790 (1988).
[2] K. Ichimura and M. Sano, *Synth. Met.,* **45,** 203–211 (1991).
[3] K. Ichimura, et al., *Materials Sci. Forum,* **91–93,** 505–510 (1992).
[4] T. Miyazaki, et al., *J. Phys. Chem. Solids,* **54**(9), 1023–1026 (1993).
[5] S. Matsuzaki, et al., *Synth. Met.,* **64,** 39–42 (1994).
[6] T. Miyazaki, et al., *Solid State Commun.,* **85**(11), 949–951 (1993).
[7] T. Miyazaki, et al., *Chem. Phys.,* **201,** 539–546 (1995).