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Title.

First Copper(II) Phase $M'_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$ and Analogous $M' = Co^{II}, Ni^{II}$ and Zn^{II} Materials Obtained by Microwave Assisted Synthesis.

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Abstract.

$M'_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$ materials are obtained by a mild microwave assisted reaction ($M' = Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}$), which permitted to obtain the first copper(II) bimetallic phase. All these materials have a lower energy GAP and antiferromagnetic interactions with lower values of the Weiss constant, than that of the pristine phase $MnPS_3$.

Main text.

The lamellar MPS_3 phases, prepared around the seventies by Hahn and Klingler, and Nitsche and Wild^{1,2} have been investigated over the past years due to their unusual reactivity and the numerous properties of both the pristine and intercalated phases.³ Among these, the magnetic properties of the MPS_3 layered compounds have been the subject of several publications.⁴⁻¹⁰ Specifically for the $MnPS_3$ layered material both intra and interlayer interactions are antiferromagnetic (AF);^{11,12} the intralayer ordering taking place below a critical temperature of 78 K.¹³ However, when guest monocations (G^+ such as potassium, cobaltocinium or pyridinium) are introduced into the interlamellar space, the intercalation compound $[G]_{2x}Mn_{(1-x)}PS_3$,^{14,15} acquires a spontaneous magnetization. This magnetization has been explained by the fact that vacancies are created in the lamellae, these being necessary to maintain the charge balance of the composite.¹⁶ The created vacancies form an ordered superstructure which modifies the AF interactions that are present in the lamellar structure of the pristine MPS_3 system.¹⁵⁻¹⁸ The order of the vacancies was demonstrated by neutron diffraction.^{15,17}

Some bimetallic $M^{II}(x)M^{II}(1-x)PS_3$ phases have also been prepared by the ceramic synthetic method, and magnetically characterized. Mainly the pristine $FePS_3$, $MnPS_3$, and the corresponding bimetallic phases, $Mn_xZn_{1-x}PS_3$, $Fe_xMn_{1-x}PS_3$, $Fe_xNi_{1-x}PS_3$ and $Fe_xCd_{1-x}PS_3$ have been reported in the literature.¹⁹⁻²³ The $M'_{2x}Mn_{1-x}PS_3$ systems ($M' = Ag^I$ or Cu^I) have also been reported but in this specific system M' is a monovalent cation. The $Cu_{0.26}Mn_{0.87}PS_3$ compound has been fully characterized by XRD and EXAFS; disorder existing in this solid.²⁴ Another copper(I) bimetallic compound which has been reported in the literature is $Cu_{0.5}Cr_{0.5}PS_3$.²⁵ The structure of this bimetallic compound derives from that of $FePS_3$, but the CrS_6 octahedra are smaller and the CuS_6 larger than those of FeS_6 . To the best of our knowledge, bimetallic phases containing Cu^{II} have not been reported to date. Furthermore, in the case of bimetallic phases obtained by the ceramic method, the different metal ions that replace the Mn^{II} ions are randomly distributed in the phase, as was established by Chandrasekharan and Vasudevan²⁰ and confirmed by Goossens and Hicks²³.

We herein report the synthesis and characterization of the first copper(II) bimetallic system, $Cu_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$ a green solid obtained from $K_{0.4}Mn_{0.8}PS_3 \cdot H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$. The potassium intercalated phase is made to react with the copper(II) salt, assisted by microwave radiation, reaction that produces the migration of the transition metal ions into the vacancies in the layers. This same procedure permits to obtain the new hetero-metallic materials, $Co_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$, $Ni_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$ and $Zn_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$, with an ordered distribution of the secondary metal ions (Fig. 1.). These bimetallic phases are interesting to study since they are obtained from the same potassium precursor, $K_{0.4}Mn_{0.8}PS_3 \cdot H_2O$, where all potassium ions, located in the van der Waals gap,¹⁶ are removed by the insertion of the transition metal ions into the vacancies. This fact permits to obtain bimetallic phases with the same composition and with the secondary metal ions in ordered positions, as is the case of the vacancies of $K_{0.4}Mn_{0.8}PS_3 \cdot H_2O$.^{15,17} Due to the similarity of the radii of the octahedral Zn^{II} , Cu^{II} , Ni^{II} and Co^{II} ions ($r_{Zn} = 88$; $r_{Cu} = 87$; $r_{Ni} = 83$; $r_{Co} = 89$ pm²⁶) with that of the intralayer Mn^{II} ones ($r_{Mn} = 83$ pm), the added transition metal ions do not remain in the interlamellar space when replacing the potassium ions ($r_K = 152$ pm), but occupy the existing vacancies in the $K_{0.4}Mn_{0.8}PS_3 \cdot H_2O$ layers. The stoichiometry of the novel cation-mixed phases was verified by atomic absorption analyses, and the percentages of the transition metal ions are given as supplementary information. (Table S1). Thus, ordered bimetallic compounds can be obtained by the microwave synthetic route which requires only a few minutes as compared to the ceramic method which is time consuming.

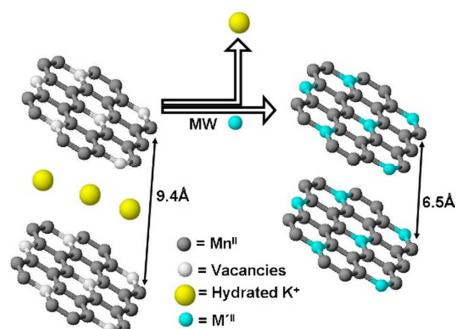


Fig. 1: Scheme of $K_{0.4}Mn_{0.8}PS_3 \cdot H_2O$ (left) and bimetallic $M'_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$ phases (right). Water molecules, sulphur and phosphorus atoms have been omitted for clarity.

The migration of the divalent transition metal ions into the existing vacancies in the layered $K_{0.4}Mn_{0.8}PS_3 \cdot H_2O$ was also verified using FTIR data (Fig.S1). The absorption bands at 557 and 608 cm^{-1} ascribed to the vibration of the PS_3 groups of $K_{0.4}Mn_{0.8}PS_3 \cdot H_2O$ are replaced by the unique absorption band at 575 cm^{-1} as observed for the pristine MPS_3 phase.²⁷ This modification in the number and position of the PS_3 vibrations can be related to the fact that the vacancies in the lamellae present in the potassium intercalated compound are filled by the transition metal ions. The characteristics of the FTIR spectrum of the pristine phase are retained in the spectra of the mixed cation phases. Thus, it is possible to assess that the strength of the interaction in the P-S and P-P bonds in the bimetallic phases is similar to that in MPS_3 .

The X-ray powder diffractograms show that the interlayer distance of all the bimetallic phases has a similar value as that of the pristine $MnPS_3$ phase (Fig.S2). The 00/ lines of the X-ray diffraction pattern for the pristine $MnPS_3$ phase are sharper as compared with the bimetallic phases indicating that the crystallinity is decreased for the bimetallic species. The cell parameters of the studied phases have been refined from the whole powder pattern fitting (patternmatching). Plots and refined parameters are given as supplementary material (Fig. S3a to S3e; Table S2). Using the 2θ value of the 001 reflection, the interlamellar distances of all the layered phases were calculated to be around 6.5 \AA , a value similar to that of the pristine $MnPS_3$ phase. Thus, the interlayer distance of 9.4 \AA observed in the potassium precursor $K_{0.4}Mn_{0.8}PS_3 \cdot H_2O$, due to the presence of the hydrated potassium ions in the interlayer space is reduced to 6.5 \AA by the migration of the transition metal ions into the existing vacancies in the layers. This cation exchange produces the elimination of the counterbalancing potassium ions as also evidenced by SEM-EDX analyses (Fig.S4a to S4e).

The solid reflectance UV-visible spectra of the bimetallic lamellar phases are compared with that of the potassium precursor $K_{0.4}Mn_{0.8}PS_3 \cdot H_2O$ and that of the pristine phase $MnPS_3$ (Fig. S5). While $K_{0.4}Mn_{0.8}PS_3 \cdot H_2O$ has an energy gap at 2.65 eV , all the obtained bimetallic phases

$M'_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$ ($M' = Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}$) are characterized by an absorption edge at lower energies (Table 1); the effect of the Co^{II} and Ni^{II} ions on the absorption edge being the largest, while that of the Zn^{II} and Cu^{II} the lowest. The shift in the energy GAP of these bimetallic phases has to be correlated with the data given in the literature for the pristine phases.^{5,28-30}

Table 1: Energy GAP values.

Phase	Energy GAP (eV)	Ref
ZnPS ₃	3.40	[5]
NiPS ₃	1.60	[5]
CoPS ₃	1.40	[28]
MnPS ₃	2.50	[29]
K _{0.4} Mn _{0.8} PS ₃ ·H ₂ O	2.65	[29]
Co _{0.2} Mn _{0.8} PS ₃ ·0.25H ₂ O	1.57	This work
Ni _{0.2} Mn _{0.8} PS ₃ ·0.25H ₂ O	1.61	This work
Cu _{0.2} Mn _{0.8} PS ₃ ·0.25H ₂ O	2.46	This work
Zn _{0.2} Mn _{0.8} PS ₃ ·0.25H ₂ O	2.47	This work

The band structure for several MPS₃ phases has been widely studied and a detailed description of the electronic structure responsible for the absorption edge is now available.³¹⁻³⁴ In conclusion, it has been assessed that the partially filled 3d orbitals must be responsible for the electron acceptor capability of the corresponding phase.⁴ Calculations done by Mercier et al. have shown that the pristine Mn^{II} phase is expected to have the highest absorption edge as compared with Fe^{II} and Co^{II}, while for the Ni^{II} phase an increase in energy of the absorption edge is expected.³¹ Therefore the observed shift in the absorption edge of the bimetallic phases can be attributed to the influence of the added transition metal ions, each secondary ion having a different 3d configuration from that of Mn^{II}.

The bimetallic phases also show a different magnetic behaviour as compared to that of the MnPS₃ phase.¹² Figure 2a shows the temperature dependence of χ^{-1} for all the studied phases. The calculated Weiss constants values are all negative, lower than that for the corresponding MnPS₃ phase. The variation of the values of the Weiss constant of the bimetallic compounds, as compared to that obtained for the pristine phase suggests that the antiferromagnetic interactions in the bimetallic phases are attenuated ($\theta = -255$ K for MnPS₃; $\theta = -123$ K for Co_{0.2}Mn_{0.8}PS₃·0.25H₂O; $\theta = -160$ K for Ni_{0.2}Mn_{0.8}PS₃·0.25H₂O; $\theta = -154$ K for Cu_{0.2}Mn_{0.8}PS₃·0.25H₂O and $\theta = -149$ K for Zn_{0.2}Mn_{0.8}PS₃·0.25H₂O). In addition, in the χ^{-1} (T) curves of the bimetallic phases it is not possible to observe the minimum around 120 K, typical of the intralayer antiferromagnetism due to the coupling of the Mn^{II} ions present in MnPS₃. Moreover, the interlayer antiferromagnetism shown by the second minimum at 12.5 K in the pristine phase is not evident in all the bimetallic phases. In contrast, the curves corresponding to the temperature dependence of χT show a change in the slope in the low temperature range (10 to 20 K). While for the MnPS₃ phase this variation is observed at 12.5 K, for the bimetallic phases the temperature is

ca. 14 K. Thus, the magnetic ordering is obtained at a slightly higher temperature for all the bimetallic phases once the vacancies of the potassium precursor are filled by the transition metal ions (Fig. 2b). The ferromagnetic behaviour at low temperatures, due to the presence of the vacancies in the potassium precursor $K_{0.4}Mn_{0.8}PS_3 \cdot H_2O$, is absent in all the obtained bimetallic phases. In addition, the $Zn_{0.2}Mn_{0.8}PS_3$ phase obtained by ceramic method and reported by Chandrasekharan and Vasudevan²⁰ presents a shift in the T_N value as compared to $MnPS_3$ phase. The pristine phase has a Néel temperature of 78 K, while the value for $Zn_{0.2}Mn_{0.8}PS_3$ is 54 K. However, this shift was not observed in our $Zn_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$, permitting to infer that the order of the Zn^{II} and Mn^{II} ions is different to that of the phase obtained by ceramic method. For the magnetic properties of randomly organized bimetallic systems it is important to define the percolation threshold ($p_c = 0.7$ for $MnPS_3$), which is the minimum of Mn^{II} ions necessary for the antiferromagnetic coupling to be observed; lower Mn^{II} concentrations produced a paramagnetic behaviour.^{20,22,23} Since we cannot define a percolation threshold for the studied bimetallic phases, the absence of the T_N in our data for $Zn_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$ is supported, giving evidence for the order of the inserted ions. These observations are clearly in favour for the migration mechanism of the divalent transition metal cations into the existing vacancies of the layered starting material $K_{0.4}Mn_{0.8}PS_3 \cdot H_2O$.

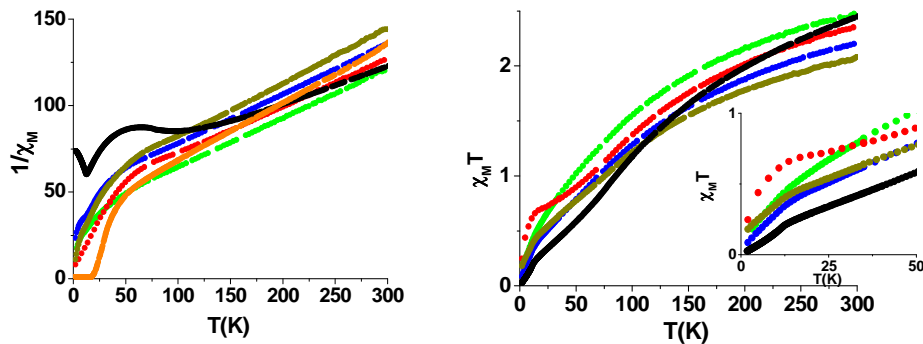


Fig. 2: Temperature dependence of reciprocal molar susceptibility (2a-left) and Temperature dependence of the molar susceptibility temperature product data (2b-right) of $MnPS_3$ (◆), $K_{0.4}Mn_{0.8}PS_3 \cdot H_2O$ (▲), $Co_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$ (●), $Ni_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$ (●), $Cu_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$ (●) and $Zn_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$ (●).

In conclusion, a remarkable feature is that this microwave assisted method permits to obtain an ordered bimetallic copper(II) lamellar thiophosphate phase. On the other hand, it is important to stress that the traditional high temperature ceramic method does not permit to prepare this material; always yielding copper(I) phases. This low energy and low time consuming method allows to obtain ordered bimetallic transition metal ion phases, as evidenced by the spectroscopic and magnetic properties. The authors acknowledge the financial support of FONDECYT Project 1120001, Financiamiento Basal (CEDENNA) FB0807. This work was done under the Chilean-French International Collaboration program (LIA-MIF 836) (CNRS/CONICYT). The authors also acknowledge T. Guizouarn (Université de Rennes 1, France) for the magnetic measurements. PF thanks CONICYT for the doctoral and thesis support 21110612 grants.

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