

Properties of NiPS₃ and ZnPS₃ prepared at Ambient Temperature

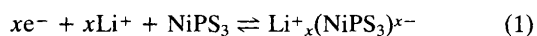
Peter J. S. Foot^{*a} and Brian A. Nevett^b

^a School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, U.K.

^b School of Physical Sciences, Brighton Polytechnic, Brighton BN2 4GJ, U.K.

Ni^{II}PS₃ and Zn^{II}PS₃ have been prepared in new amorphous forms which show high reactivity in chemical or electrochemical insertion.

Divalent metal phosphorus trisulphides, especially NiPS₃, are promising cathodes for high energy secondary lithium cells.^{1,2} Their formulae can be written as M_{2/3}(P₂)_{1/3}S₂ and their layered structure is then comparable to that of CdCl₂. Quasi-octahedral vacancies between alternate pairs of sulphur planes are occupied by M²⁺ ions and P₂ pairs, while the others are empty and can act as intercalation sites.² The lithiation of NiPS₃ may be represented as the redox process in equation (1), where 0 ≤ x ≤ 1.5.^{1,3} The extra electrons in NiPS₃ occupy the vacant Ni(3d) orbitals; hence reaction (1) cannot occur for d¹⁰ systems.



In contrast, the reactions of MnPS₃ with cobalticinium iodide⁴ or CdPS₃ with alkylamines⁵ for example, occur by a substitution–intercalation process in which some host cations are lost in exchange for the intercalant ions. This occurs because Cd²⁺ and Mn²⁺ (d¹⁰ and d⁵) have no crystal-field stabilisation and are somewhat labile.⁴

Crystalline MPS₃ compounds are synthesised at high temperature,⁶ but we have previously described a method of preparation at close to room temperature.⁷ This has now been used to make amorphous and highly reactive forms of MPS₃ (M = Ni, Fe, Co, Cd, Zn, Ba, and Pb), but we shall only compare NiPS₃ and ZnPS₃ here. The preparation⁷ used the reaction (2) of M²⁺ salts with sodium hexathiohypodiphos-

phate in aqueous solution. (The sodium salt was prepared from Na_2S and PCl_3 as described by Fälius.⁸)



In a useful modification, colloidal NiPS_3 was obtained by slowly passing aqueous $\text{Na}_4\text{P}_2\text{S}_6 \cdot 6\text{H}_2\text{O}$ (25 g dm^{-3}) through an ion-exchange column (Dowex 50W-X6) saturated with Ni^{2+} ions. The deep-red eluate contained negatively charged particles estimated by osmometry to comprise 67 NiPS_3 units, and hence to be only about 2.4 nm in diameter. The visible-near-i.r. spectrum of the colloid showed the same absorptions as crystalline NiPS_3 .⁹ On standing, the suspension became a thixotropic gel.

Amorphous NiPS_3 was precipitated from the colloid by adding an equal volume of propan-2-ol; when washed with acetone and dried *in vacuo* it had the composition $\text{NiP}_{0.992}\text{S}_{2.87}$ and gave the same i.r. spectrum as crystalline NiPS_3 ,¹⁰ though with broader bands. A high reactivity was shown by the solid in rapidly absorbing 0.5 moles of NH_3 gas, which does not react with crystalline NiPS_3 .⁵ This process caused its electronic conductivity to increase by 10^4 times (to $10^{-2} \text{ S cm}^{-1}$) and to become n-type, indicating that electronic charge was donated to the host by the ammonia, as in other NiPS_3 intercalates.^{3,5,9}

Powder X-ray diffraction examination of precipitated NiPS_3 showed only a diffuse peak corresponding to the 001 line in the crystalline compound. Partial annealing occurred after 3 h *in vacuo* at temperatures from 150 to 500 °C, but full crystallinity required 18 h at 560 °C. Diffuse patterns seen at lower temperatures are not simply due to microcrystallinity, and are probably associated with stacking faults and cationic disorder.¹¹

We have tested both annealed and un-annealed amorphous NiPS_3 as lithium intercalation cathodes, using LiClO_4 in propylene carbonate as an electrolyte.¹² Samples annealed at 350 °C showed particularly good kinetic reversibility, which does not appear to correlate with any increase in the B.E.T. (Brunauer-Emmett-Teller) surface area on annealing, and so is probably due to faster diffusion of Li^+ ions. Reaction with 2 moles of lithium was observed, at an average potential of 2.2 V vs. Li/Li^+ , giving a significantly higher energy-density than for crystalline NiPS_3 .

Despite its reactivity, the relatively covalent NiPS_3 showed no tendency toward ion-exchange of the kind shown by MnPS_3 .⁴ However, amorphous ZnPS_3 , prepared by the method of ref. 7, rapidly lost Zn^{2+} ions (d^{10}) in exchange for K^+ in aqueous KCl , to form $\text{K}_{0.30}\text{Zn}_{0.85}\text{PS}_3$. Similar stoichiometry was obtained even if a solution containing a large cation such as $\text{Bu}^n_4^+$ was used. The reaction times were fast (minutes), and in principle organometallic cations with catalytic activity could also be rapidly incorporated into amorphous ZnPS_3 . Like NiPS_3 , pure ZnPS_3 is X-ray amorphous when precipitated, but it readily anneals at only 300 °C to give a product with the same diffraction pattern as crystalline ZnPS_3 . Since the structure and dimensions are nearly the same as for NiPS_3 ,⁶ we conclude that the much higher lability of Zn^{2+} allows cationic disorder to disperse more easily.¹¹

Further work on structural and electronic properties of amorphous MPS_3 will be reported, and tests on lithium-amorphous NiPS_3 cells are underway at A.E.R.E. Harwell.¹²

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