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Liberation of Pnicogen Chains from $Cu_2P_{1.8}As_{1.2}I_2$: Synthesis and Characterization of a New Allotrope of P–As

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Removal of CuI from $Cu_2P_{1.8}As_{1.2}I_2$ results in a novel P–As allotrope. Although the product is X-ray amorphous, lattice fringes are observed in the transmission electron micrographs with spacings reflecting the diameter of the linear pnicogen polymer in $Cu_2P_{1.8}As_{1.2}I_2$, suggesting the pnicogen chains remain intact upon loss of CuI. The straight needles present in $Cu_2P_{1.8}As_{1.2}I_2$ appear to be kinked in the P–As phase due to lattice mismatch between the liberated polymers, ultrasonic treatment, or a combination of these effects. This new P–As modification is semiconducting with a band gap of 1.05 eV.

Mixed P/As phases isostructural to white phosphorus (P_4) and the three crystalline allotropes of black phosphorus are well established and form over an extensive composition range.[1,2] However, P/As phases that adopt the structure of the polymeric amorphous red phosphorus phases, or the crystalline 1-D violet allotrope (Hittorf's phosphorus), are rare.[3] CuI has proven to be an effective matrix for crystallization of novel 1-D tubular phosphorus polymers, which are close cousins to Hittorf's phosphorus. Examples include (in the nomenclature proposed by Böcker and Häser)[4] the $([P8]P4(4)[\,])^0$ chains in $Cu_2P_3I_2$,[5] the $([P10]P2[\,])^0$ chains of CuP_4I,[6] and the $([P12(4)]P2[\,])^0$ chains of CuP_7I.[7] We have found that CuI is also effective at stabilizing P/As solid solutions and have reported a series of compounds $Cu_2P_{3-x}As_xI_2$, $x < 1.65$,[8,9] which are isostructural to $Cu_2P_3I_2$. Here we report the effective "liberation" of the formally neutral polypnicogen chain in $Cu_2P_{1.8}As_{1.2}I_2$ to create a new P–As phase, and the resultant structure and optical properties.

The approach described herein is based on the results from Ag^+ ion-exchange reactions performed on $Cu_2P_{1.8}As_{1.2}I_2$ to prepare the corresponding Ag analogue.[10] Reactions in aqueous solutions with $AgNO_3$ invariably produced elemental silver as a byproduct, along with $Ag_2P_{1.8}As_{1.2}I_2$. However, Möller and Jeitschko reported that addition of KCN permitted facile exchange of Cu^+ by Ag^+ in $Cu_2P_3I_2$ without silver deposition, and proposed that the reaction proceeds according to eq 1.[5] Our attempts to employ excess KCN with $Cu_2P_{1.8}As_{1.2}I_2$ did produce a material with Ag incorporation, according to energy dispersive spectroscopy (EDS), but it was X-ray amorphous.[10]

$$Cu_2P_3I_2 + 2AgNO_3 + 8KCN \rightarrow Ag_2P_3I_2 + 2K_3[Cu(CN)_4] + 2KNO_3 \quad (1)$$

We surmise several possible explanations for these observations: KCN may attack the compounds, perhaps even cyanating them, eventually causing a complete structural collapse, or the KCN may solubilize the Cu^+ and I^-, leaving the polypnicogen polymer intact, as described in eq 2. To discern between these alternatives, we have performed a detailed study on the reaction between KCN and $Cu_2P_{1.8}As_{1.2}I_2$.

$$Cu_2P_{1.8}As_{1.2}I_2 + 8KCN \rightarrow 3P/As + 2K_3[Cu(CN)_4] + 2KI \quad (2)$$

Crystals of $Cu_2P_{1.8}As_{1.2}I_2$ were synthesized according to the literature procedure,[8] ground, and stirred in 1−10 wt % solutions of aqueous KCN for 2−6 h at room temperature. The product (**1**) was then suction filtered, washed several times with distilled water, and permitted to air-dry.

Compound **1** is a dark powder, similar in appearance to $Cu_2P_{1.8}As_{1.2}I_2$, but less dense. As evidenced by light microscopy as well as by scanning electron microscopy (SEM), the needle crystal morphology characteristic of $Cu_2P_{1.8}As_{1.2}I_2$

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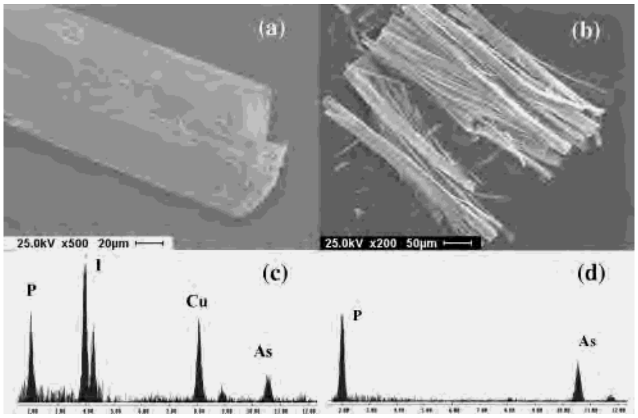

Figure 1. SEM micrographs of (a) a needle crystal of $Cu_2P_{1.8}As_{1.2}I_2$ and (b) the product obtained after reacting $Cu_2P_{1.8}As_{1.2}I_2$ in aqueous KCN. EDS spectra of $Cu_2P_{1.8}As_{1.2}I_2$ (c) before and (d) after the KCN reaction.

is retained in **1**, although there is obvious fraying (Figure 1).[11] From EDS, it can be seen that this fraying is accompanied by the loss of Cu and I in the materials, while the relative P/As peak intensities remain approximately the same. Since the needle axis corresponds to the propagation direction of the pnicogen polymers in these materials, the fraying can be simply interpreted as a disassociation of polymeric chains upon dissolution of the CuI "glue" in the KCN solution. X-ray powder diffraction measurements of **1** show that the consequence of this CuI stripping is the loss of order, resulting in an amorphous product (Supporting Information).[12]

The optical reflectance spectrum (converted to absorption) of **1** reveals only a subtle change in the physical properties of the material upon KCN treatment (Figure 2).[13] A decreased energy gap (1.05 eV) with a more diffuse onset is observed in **1**, relative to $Cu_2P_{1.8}As_{1.2}I_2$. However, since the band gap in the parent compound (1.20 eV) is attributed largely to the defective CuI lattice,[8] the difference cannot a priori be assigned to a chemical change or a loss of order in the polypnicogen chains. Accordingly, we turned to transmission electron microscopy to determine if any local ordering could be detected in **1**. For comparison, the $Cu_2P_{1.8}As_{1.2}I_2$ parent material was also analyzed.[14]

High-resolution TEM micrographs of $Cu_2P_{1.8}As_{1.2}I_2$ reveal the presence of lattice fringes propagating along the [101] needle direction with a line spacing of 9.7 Å (Figure 3a). This corresponds very closely to the distance between two parallel pnicogen chains in the crystal structure of $Cu_2P_{1.8}As_{1.2}I_2$, or to the $(\bar{1},1,0)/(0,1,\bar{1})$ set of planes (9.6 Å, Figure 3b).[8] Hence, each "line" observed in the TEM image can be correlated to a single P/As chain in the parent structure.

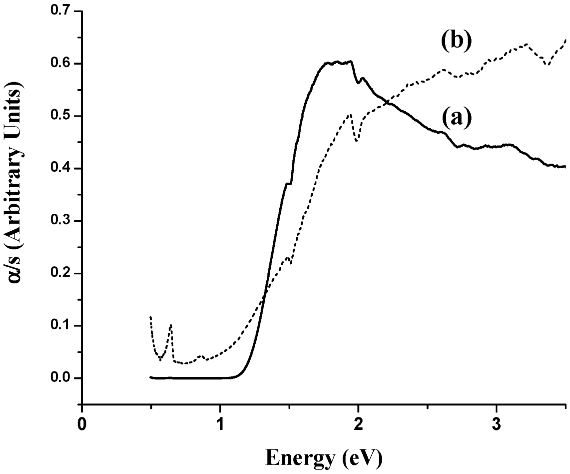

Figure 2. Optical diffuse reflectance spectra of (a) $Cu_2P_{1.8}As_{1.2}I_2$ and (b) **1**. Note: The discontinuity at 1.5 eV is due to a change in detector.

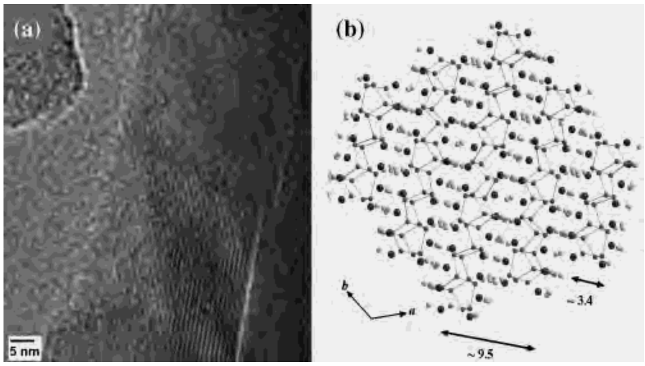

Figure 3. (a) TEM image of a sample of $Cu_2P_{1.8}As_{1.2}I_2$. (b) The corresponding structure showing the polypnicogen chains and inter- and intrachain dimensions. The dark spheres linked by bonds represent P/As; the large black spheres, I; and the small pale spheres, Cu.

A similar investigation of **1** also reveals a series of closely spaced lines, suggesting the presence of at least some degree of order. Unlike the parent phase, these lines appear to "curl" around a compact center, generating structures similar in appearance to tree-rings (Figure 4). The spacing between these lines ranges from 3.6 to 4.1 Å, representing a contraction relative to the spacing in $Cu_2P_{1.8}As_{1.2}I_2$, as would be expected if the Cu^+ and I^- ions were no longer propping the chains apart. Moreover, this distance correlates nicely with the diameter of a single P/As mixed pnicogen tube (3.4−3.5 Å). Thus, the patterns of lines observed in the TEM micrographs of **1** can be attributed to the 1-D polymers drawing closer together upon CuI stripping. The fact that some degree of order is retained after KCN treatment is also evident in the electron diffraction pattern, in which a series of well-defined spots are observed (Figure 4a, inset). The first set of spots corresponds to a *d* spacing of 1.8 Å, exactly half the lattice spacing obtained from the image (Figure 4a, 3.6 Å).

The "curling" phenomena noted in the TEM micrographs of **1** may be due to several factors. Considering pure phosphorus chains only, a number of structures have been

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(11) SEM/EDS data were acquired on a Hitachi S-2400 scanning electron microscope with an associated EDAX unit. Samples were placed on adhesive carbon tabs on Al stubs for the measurement.

(12) X-ray powder diffraction was conducted using a Rigaku D-Max RU 200B with rotating anode operating at 40 kV, 100 mA (Cu Kα). Samples were dusted onto double sticky tape.

(13) (a) Optical diffuse reflectance measurements were conducted on a Shimadzu model UV-3101PC double-beam, double-monochromator spectrophotometer equipped with an integrating sphere, using $BaSO_4$ as a 100% reflectance sample. The reflectance data were converted to absorption data for optical band gap determination.[13b] (b) Wendlandt, W. W.; Hecht, H. G. *Reflectance Spectroscopy*; Interscience Publishers: New York, 1966.

(14) TEM data were acquired on a JEOL 2010F in the bright field mode. Solid $Cu_2P_{1.8}As_{1.2}I_2$ or **1** was ultrasonically dispersed in acetone and deposited onto copper grids coated with amorphous carbon.

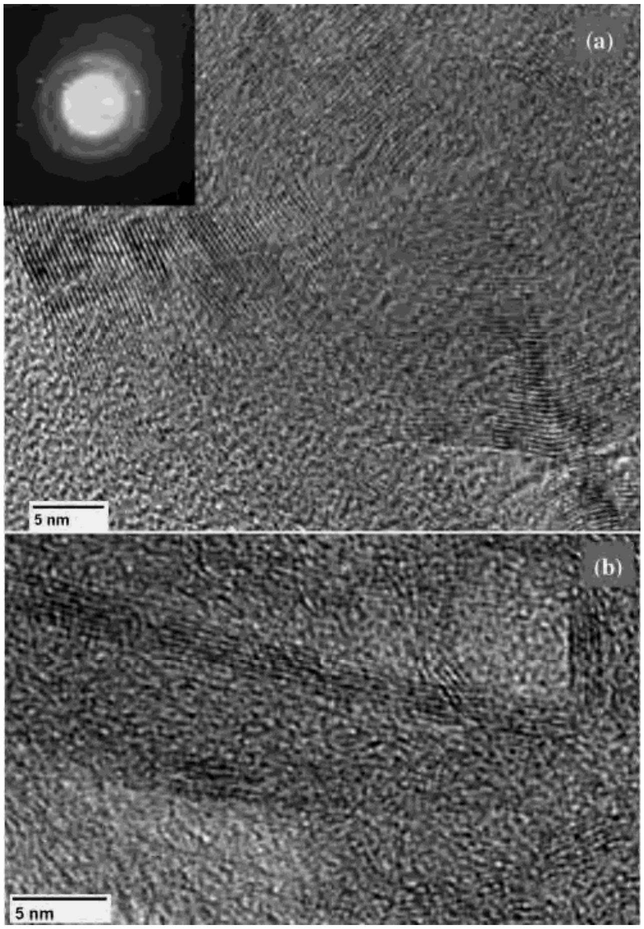

Figure 4. TEM images of sonicated **1** illustrating the lattice lines (3.6−4.1 Å) and (a) the curling of the polypnicogen chains to form tree-ring-like structures; (b) the kinking at the ends of the frayed polypnicogen needles. The inset of part a shows a corresponding electron micrograph.

computed to be stable but have never been crystallized as pure phosphorus allotropes.[4] For example, the neutral infinite 1-D $([P10]P2[])^0$ spirals in $(CuI)_3P_{12}$ are reported to have the highest calculated stability among the CuI stabilized neutral phosphorus phases, with a stability comparable to that of Hittorf's phosphorus. However, computational studies indicate that the helical shape of the polymer results in difficulties associated with packing, which may be the reason it is not known as a pure crystalline allotrope.[4] Similarly, the consequences of stripping CuI in our mixed pnicogen solid solution may be to produce polypnicogen chains that cannot pack together in an ordered manner over a long range (hundreds of nanometers) as required to produce a stable crystal. Over a short range, regions of order are observed, suggesting the mismatch between interacting polymeric chains is small. However, at medium range (∼10 nm) the mismatch begins to add up, resulting in a kinking, or folding over of the rods. This folding is clearly evident in Figure 4b, where a rodlike structure has developed a loop at the end.

Alternatively, the "curling" may be a consequence of the ultrasonic treatment used to disperse **1** for TEM sample preparation. Indeed, the "curling" or "scrolling" of layered phases upon ultrasonic treatment is well documented,[15,16] and this may be a similar phenomenon. However, similar treatment of $Cu_2P_{1.8}As_{1.2}I_2$ does not result in curling, suggesting that the removal of CuI has, at minimum, compromised the robustness of the P/As chain structure.

Thus, although the X-ray diffraction data suggests disorder on the atomic scale (i.e., amorphous product or glass formation), the 1-D character of the polypnicogen chains does not change upon treatment of $Cu_2P_{1.8}As_{1.2}I_2$ with KCN. Although we cannot rule out cross-linking between the chains, cyanation of the chains does not appear to be occurring; chemical analysis of **1** reveals less than 0.5% of the sample mass is due to combined C and N.[17] Finally, this strategy of CuI stripping would appear to be quite general, as a recent paper reporting a similar method for liberating phosphorus chains from $Cu_2P_3I_2$ and CuP_4I appeared while this manuscript was under review.[18]

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Supporting Information Available: Powder X-ray diffraction data for P−As. This material is available free of charge via the Internet at http://pubs.acs.org.

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