Solvothermal syntheses of Cu₃P via reactions of amorphous red phosphorus with a variety of copper sources

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Abstract

Polycrystalline Cu_3P was successfully prepared under a wide variety of solvothermal conditions. The reaction of red phosphorus with several copper sources (copper metal, copper (I) iodide, copper (I) chloride and copper (II) chloride) at 150–200 °C for 1–2 days in water produced Cu_3P. Products were examined with powder X-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy. Thermal analyses and optical spectroscopy were also performed. A detailed list of reaction conditions, products and impurity phases (where applicable) are reported.
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1. Introduction

Copper (I) phosphide has attracted attention due to its existent and potential technological properties. This complex material, see Fig. 1, enhances the sintering behavior of 316 L stainless steel [1] and acts as a reinforcing agent in high speed steel (HSS) composite materials [2]. More recently, copper (I) phosphide has gathered attention as a potential negative electrode material in lithium batteries because of its good cyclability and reversible capacity [3].

Traditionally, transition metal phosphides such as Cu_3P have been prepared via inconvenient routes that are not practical for industrial scale preparation, such as high temperature solid-state synthesis in sealed ampoules [4] and metathesis reactions using Na_3P, a hazardous reagent [5]. Within the past decade, solvothermal synthesis has been demonstrated to be a successful method for the facile preparation of main

group and transition metal pnictide (pnicogen = Group 15 element) materials [6–8]. Nanocrystalline Cu_3P has been previously prepared by the reaction of yellow phosphorus and copper (II) chloride dihydrate in ethylenediamine (en) solvothermally at 80–140 °C for 12 h [7] and in a dilute ammonia liquor at 140 °C for 10 h [8]. In both cases it was proposed that the chelating solvent and the yellow phosphorus play a very important role in the formation of Cu_3P. Specifically, it was suggested that the yellow phosphorus reacts with hydroxide groups, generated in the basic en or ammonia solution from the hydrated metal salts, to produce phosphate ions and the reducing equivalents necessary to reduce the Cu^{2+} to Cu^{1+}. The resultant Cu^{1+} ions react directly with the yellow phosphorus as they are generated to form the metal phosphide. The role of the N-donor ligand is to control this reaction by coordinating copper ions, resulting in their slow release, and the subsequent generation of a nanocrystalline material. It was also reported that reactions performed with red phosphorus or in aqueous solution did not yield complete reactions [8].

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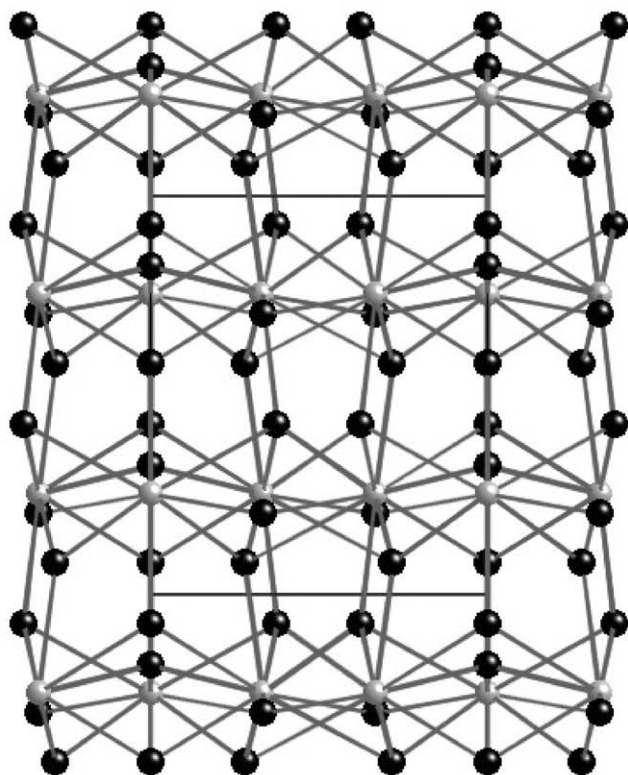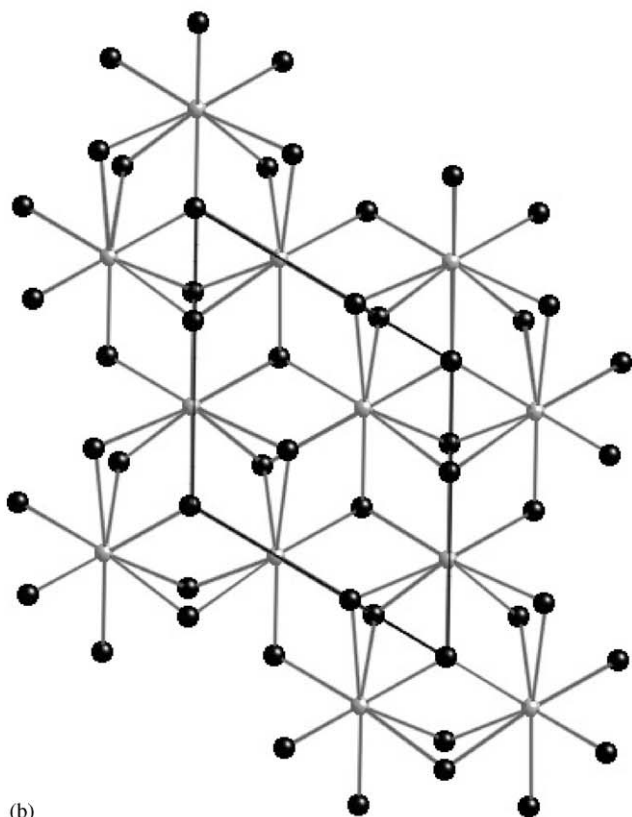
The initial goal of our solvothermal reactions was to find a set of conditions under which to produce copper pnictide halides via a soft chemical route. We thought that under conditions different than those utilized for Cu_3P we might be able to form $Cu_aP_bX_c$ (X = halide) type materials, which show promise as copper ion-conductors [9]. To our surprise, we obtained Cu_3P in each case, regardless of the conditions employed. This finding compelled us to re-examine the conditions necessary to synthesize Cu_3P solvothermally.

Here we report a wide variety of solvothermal conditions under which Cu_3P can be produced, including the optimal conditions for preparing pure-phase material. Our work shows that red phosphorus is sufficiently active to be employed in lieu of yellow phosphorus in the solvothermal preparation of Cu_3P. Furthermore, ethylenediamine or ammonia can be substituted by H_2O as a cleaner and cheaper solvent to successfully synthesize Cu_3P. We also report the optical spectra and thermal analyses of several samples of Cu_3P that we obtained.

2. Experimental

2.1. Reagents

The chemicals in this work were used as obtained: (i) copper metal powder, −625 mesh, 99.9% Alfa–Aesar, Ward Hill, MA; (ii) copper (I) iodide, 99.999%, Aldrich, Milwaukee, WI; (iii) copper (I) chloride 99% Acros, Morris Plains, NJ; (iv) copper (II) chloride 99% anhydrous, Acros, Morris Plains, NJ and (v) red phosphorus amorphous powder, 100 mesh, EM Science, Gibbstown, NJ.

2.2. Synthesis

2.2.1. General synthetic procedure

Red phosphorus powder and a copper source were weighed in appropriate amounts and loaded into a 23 mL Teflon cup. No more than 13 mL of solvent or mixture of solvents was added to the cup. The Teflon cup was capped and then placed inside a stainless steel Parr acid digestion bomb. The bomb was inserted into an oven already at the reaction temperature, 150–200 °C, allowed to stay there for a time period of 1–2 days and subsequently removed from the oven and allowed to cool to room temperature. The resulting product was filtered by vacuum suction and washed with distilled H_2O and ether. In one example of an ideal synthesis, 0.15 g red phosphorus (4.8 mmol) was combined with 0.479 g CuCl (4.8 mmol) in 13 mL of deionized H_2O and heated at 200 °C for 24 h.

(a)

(b)

Fig. 1. Crystal structure of Cu_3P projected down the a-axis showing layers of phosphorus trigonal prisms stacked in the c-direction (a) and the structure of one such layer viewed down the c-axis (b). Phosphorus atoms are shown as gray spheres while the black spheres represent copper atoms.

2.3. Physical measurements

2.3.1. Powder X-ray diffraction

Powder X-ray diffraction patterns were collected with a Rigaku RU 200 B rotating anode X-ray diffractometer operating at 40 kV and 150 mA and using graphite monochromatized $CuK\alpha$ radiation. Samples were ground with mortar and pestle and deposited onto a glass slide coated with a thin layer of Vaseline. Data were collected from $10°$ to $70°$ 2θ. Phases were identified using the search match capabilities of the JADE program along with the ICDD (International Center for Diffraction Data) powder diffraction file (PDF) database.

2.3.2. Scanning electron microscopy and energy dispersive spectroscopy

Samples were mounted onto an adhesive carbon tab that was attached to an aluminum specimen stub and examined using a Hitachi S-2400 Scanning Electron Microscope operating at 25 keV. Energy dispersive spectroscopy was performed using an EDAX unit with an active area of $10\,mm^2$, and data were analyzed using the Genesis Spectrum V. 2.5 software package by EDAX INC. Data were collected with an accumulation time of 60 s.

2.3.3. Differential thermal analysis (DTA)

Thermal analyses were performed using a Shimadzu DTA50 Thermal Analyzer. Samples were sealed in small carbon coated fused silica ampoules. Alumina was used as a reference material. The difference in μV between the sample and the reference was measured as a function of temperature up to $1100\,°C$. The sample and reference were heated and cooled at a rate of $10\,°C/min$. Multiple heating and cooling cycles were performed.

2.3.4. Optical spectroscopy

Optical diffuse reflectance measurements were measured on a Cary 5000 double-beam double-monochromator spectrophotometer equipped with the praying mantis attachment and operating from 2500 to 200 nm. The samples and a $BaSO_4$ 100% reflectance standard were prepared by grinding the material to a fine powder and loading it into the sample holder. The reflectance versus wavelength data were used to estimate the band gap by converting reflectance to absorption data [10].

3. Results and discussion

3.1. Synthesis

Three key factors have been previously proposed in the synthesis of Cu_3P [7,8]. First, an N-donor ligand such as ethylenediamine or ammonia plays a crucial role in the formation of the Cu_3P material obtained; second, yellow phosphorus is very active under solvothermal conditions, acting both as a reducing agent and a reactant; and third, an enormous amount of excess phosphorus is needed to ensure a complete reaction and generate pure phase product. Our investigation shows that none of these "key factors" pointed out by Qian and coworkers are necessary to synthesize Cu_3P.

Our initial experiments were conducted using yellow phosphorus, the most volatile and reactive form of phosphorus; however, we quickly determined that yellow phosphorus was not practical to work with and resulted in a number of phosphate byproducts. Amorphous red phosphorus is much less reactive than yellow phosphorus under normal conditions, but this makes it safer and easier to handle in air. It is well known that many starting materials that are unreactive or insoluble under normal conditions can react or become solubilized under solvothermal conditions. Indeed, we have demonstrated that red phosphorus can react with a number of copper sources solvothermally to form Cu_3P.

Tables 1–3 list 23 of approximately 60 different reactions that we performed, which yielded Cu_3P as the major product or as a pure phase material. We successfully determined the right conditions under which copper metal, copper (I) iodide, copper (I) chloride and copper (II) chloride react with red

Table 1
Summary of solvothermal reactions performed at $150\,°C$ for 24 h using en or en/H_2O mixtures

Copper source	Ratio of copper source	Ratio of red phosphorus	% en	Result of powder X-ray diffraction
CuCl	3	1	100	$Cu_3P + Cu$
CuCl	3	1	50	$Cu_3P + Cu$
CuCl	3	1	2.5	$Cu_3P + Cu$
CuCl	3	1	2	$Cu_3P + Cu + CuCl$
CuCl	3	1	1	$Cu_3P + CuCl$
$CuCl_2$	3	1	100	$Cu_3P + Cu$

Table 2
Comparison of solvothermal reactions performed at $150\,°C$ and $200\,°C$ in H_2O for 24 h

Copper source	Ratio of copper source	Ratio of red phosphorus	Reaction temperature (°C)	Result of powder X-ray diffraction
CuI	1	5	150	$Cu_3P + CuI$
CuI	1	5	200	Cu_3P
CuCl	1	1	150	$Cu_3P + CuCl$
CuCl	1	1	200	Cu_3P

Table 3
Summary of solvothermal reactions performed at 200 °C in H_2O for 24 h using several copper sources (*a* designates a prominent amorphous background)

Copper source	Ratio of copper source	Ratio of red phosphorus	Result of powder X-ray diffraction
Cu metal	1	1	$Cu_3P + Cu$
Cu metal	1	8	$Cu_3P + Cu$
Cu metal	1	10	$Cu_3P + Cu$
Cu metal	1[a]	10[a]	Cu_3P
CuI	1	1	$Cu_3P + CuI$
CuI	1	2	$Cu_3P + CuI$
CuI	1	5	Cu_3P
CuCl	2.8	1	$Cu_3P + CuCl$
CuCl	2	1	$Cu_3P + CuCl$
CuCl	1	1	Cu_3P
CuCl	1	1.5	$Cu_3P + a$
$CuCl_2$	1	4	$Cu_3P + CuCl$
$CuCl_2$	1	4.5	Cu_3P
$CuCl_2$	1	5	Cu_3P
$CuCl_2$	1	8	$Cu_3P + a$

[a] Ingredients were ground together before being placed in the bomb.
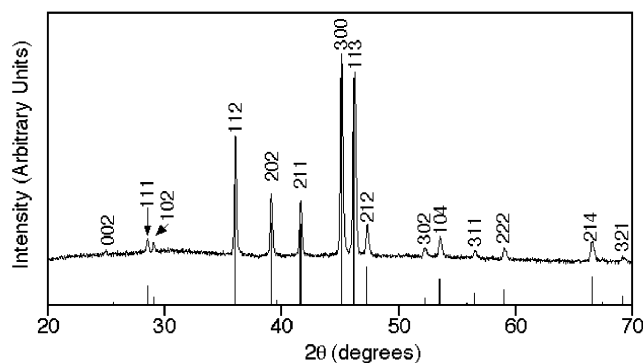

Fig. 2. Powder X-ray diffraction pattern of Cu_3P (CuCl + red P, 1:1 molar ratio, 200 °C, 24 h) versus that obtained from the powder diffraction file (line diagram: PDF # 71-2261).

phosphorus in H_2O to produce pure phase Cu_3P. Therefore, en or ammonia does not play a crucial role in the synthesis of Cu_3P. Ironically, although we performed some reactions in en and en/H_2O mixtures at 150 °C, we never obtained pure Cu_3P under those conditions (Table 1). The fact that H_2O is a suitable solvent to make Cu_3P is a significant finding since it is much more industrially practical to produce Cu_3P in H_2O because it is easier and safer to work with, as well as significantly less costly.

The critical factors in the synthesis of phase-pure Cu_3P in water are temperature, stoichiometry and precursor identity. Byproducts are obtained for reactions conducted at 150 °C, whereas pure phase Cu_3P can be obtained at 200 °C (Table 2) once the appropriate stoichiometries have been determined for the various precursors. This is consistent with a lower reactivity for red phosphorus relative to yellow.

Reactions in which en makes up $\geqslant 2\%$ of the solvent mixture always produce metallic copper as a byproduct (Table 1). Indeed, en is used as a reducing agent in electrolysis copper plating baths, so this is not a surprise [11]. This led us to test whether copper metal could be used directly as the copper source in these solvothermal reactions.

The reaction of copper metal with red phosphorus in a 1:10 molar ratio heated at 200 °C for 1 day in H_2O produced pure Cu_3P (Table 3). The powder X-ray diffraction pattern did not show the presence of any other product. However, complete reaction requires grinding of the precursors to create an active surface area. The EDS spectrum showed only copper and phosphorus in the product. If less than ten equivalents of phosphorus is used, copper metal is found in the powder X-ray diffraction pattern. For example, if we performed a similar reaction with a 1:8 molar ratio of starting materials, we obtained peaks for both Cu_3P and copper metal in the powder X-ray diffraction pattern. However, if this resulting material is then placed in a bomb with additional phosphorus (0.064 g of product $(Cu_3P + Cu) + 0.09$ g of phosphorus) and heated again to 200 °C for 1 day, a pure material can be obtained. Several ratios of Cu:P were attempted, see Table 3, with the 1:1 reaction having the most copper metal impurity.

The reaction of copper iodide and red phosphorus in a 1:5 molar ratio heated at 200 °C for 1 day in H_2O also produced Cu_3P in pure form (Table 3). The powder X-ray diffraction pattern of the product showed peaks for Cu_3P and no residual CuI was observed. EDS analysis gave a semiquantitative composition of $Cu_{2.87}P$. If the ratio of CuI:P is changed to 1:1 or 1:2 at 200 °C, the powder X-ray diffraction pattern shows Cu_3P plus a large amount of unreacted CuI.

Although one might expect similar reactivity for CuCl as that found for CuI, CuCl has proved far more reactive. The reaction of copper (I) chloride and red phosphorus in a 1:1 ratio heated in a bomb to 200 °C for 1 day in H_2O produced pure Cu_3P (Fig. 2, Table 3). If the ratio of CuCl is increased, large peaks indicative of CuCl are observed in the powder X-ray diffraction pattern. However, this product can be washed with dimethylsulfoxide (50 mL, three times with stirring) to obtain a phase pure powder diffraction pattern for Cu_3P. If the ratio of P is increased we see an amorphous presence in the powder X-ray diffraction pattern and an excess of phosphorus in the EDS spectrum (Table 3). Thus, the optimal amount of phosphorus needed to produce phase-pure Cu_3P is considerably less for CuCl

(3 equivalents of phosphorus) than for CuI (15 equivalents of phosphorus).

For the reaction of copper (II) chloride plus red phosphorus in H_2O at 200 °C the best ratio is 1:5, similar to the case of CuI. Increased copper (II) chloride amounts produced CuCl as a byproduct, whereas increased amounts of phosphorous resulted in a significant amorphous background in the powder diffraction pattern, which we attribute to red phosphorus.

While our results show that an excess of phosphorus is always necessary to form pure Cu_3P, the excess is not nearly as much as was reported by Qian and coworkers. Their reactions required 22 mol of phosphorus (66 equivalents) for every 1 mol of $CuCl_2 \cdot 2H_2O$ while our *greatest* excess of phosphorus was 10 mol (30 equivalents) for every 1 mol of copper metal. The reaction of copper (I) chloride with red phosphorus requires the *least* amount of excess phosphorus, only two additional equivalents (i.e. Cu:P 1:1). The finding that less phosphorus can be used than originally proposed makes the formation of Cu_3P under solvothermal conditions much more atom efficient. Additionally, despite being less reactive, red phosphorus can be employed successfully in lieu of yellow phosphorus.

3.2. Structure and X-ray diffraction

Cu_3P is a very interesting material since both its composition and structure have been the center of some controversy. The structure of Cu_3P was originally proposed to be a member of the anti-LaF_3 structure-type, along with many alkali metal pnictide 3:1 phases, crystallizing in space group $P\bar{3}C$ [12,13]. The structure was later solved in space group $P\bar{3}m$ [14]. Finally, in 1972 Olofsson proposed that the space group $P6_3cm$ was correct [15]. Indeed, we calculated the powder X-ray diffraction pattern based on the $P\bar{3}C$ model and that of the $P6_3cm$ model to find that there were no differences in the number of observed peaks and little difference in intensities. Our diffraction data fits with the Olofsson model and therefore that is the structure we based our indexing upon (Fig. 2).

The structure of Cu_3P contains both P and Cu with high coordination numbers. Each P atom is surrounded by eleven Cu atoms. The coordination sphere is quite distorted but can be best described as a trigonal prism with additional capping atoms on each of the three rectangular faces and the two triangular faces. The trigonal prisms are connected in the *ab*-plane to form "layers" that stack along the *c*-axis (Fig. 1). The coordination of Cu is also irregular. Each Cu has either three or four phosphorus atoms as neighbors with distorted trigonal pyramidal and tetrahedral coordination spheres, respectively. In addition, each Cu atom has nine Cu neighbors.

It has been reported that Cu_3P has a moderate range of homogeneity that can depend on the synthetic conditions used. In a study undertaken by Olofsson it was demonstrated that at 700 °C the homogeneity range lies approximately between $Cu_{2.82}P$ and $Cu_{2.73}P$. It was also found that by changing the reaction temperature from 400 to 800 to 850 °C a change in lattice parameters can be observed, where at higher temperature smaller lattice parameters were obtained, suggesting a larger extent of Cu vacancies. Our experiments also show that Cu_3P displays a homogeneity range, since we obtained slightly different ratios of Cu:P for nearly every sample obtained, while the powder diffraction patterns looked nearly identical. Under all solvothermal conditions essayed, a slightly copper deficient material was obtained, as determined by EDS, which could be attributed to either intrinsic defect formation in the copper phosphide materials as postulated by Olofsson, or to the presence of amorphous phosphorus.

3.3. Physical properties

Optical diffuse reflectance measurements were performed for powdered samples of Cu_3P. Analyses of several Cu_3P products obtained from different reaction conditions all showed an optical absorption edge of approximately 0.8 eV, indicating that Cu_3P is a relatively narrow gap semiconductor, consistent with the black color of the material (Fig. 3).

Differential thermal analyses were performed for several samples of Cu_3P obtained under different reaction conditions. The expected thermal behavior was obtained for a sample obtained from the reaction of CuI and P in a 1:5 molar ratio heated to 200 °C for 1 day in H_2O to yield a material of stoichiometry $Cu_{2.87}P$ (Fig. 4). The DTA diagram shows an endothermic peak
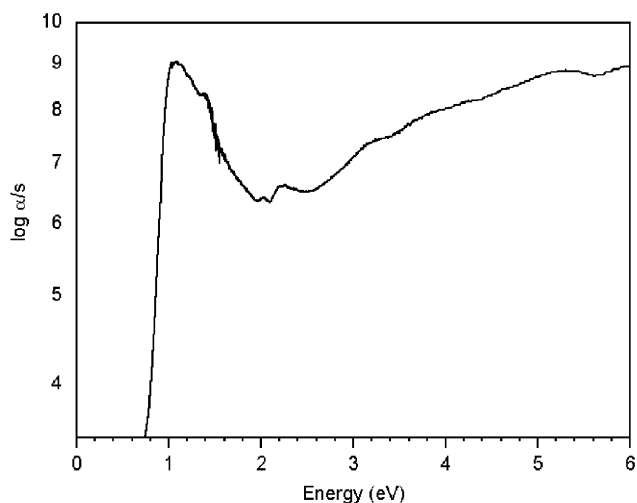

Fig. 3. Optical diffuse reflectance spectrum converted to absorption for a powdered sample of Cu_3P (CuCl + red P, 1:1 molar ratio, 200 °C, 24 h).
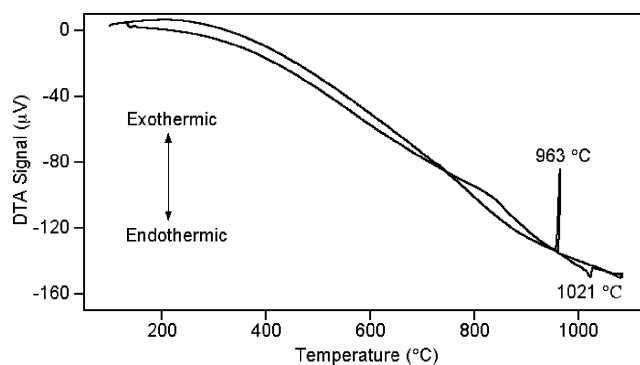
Fig. 4. DTA diagram (10 °C/min heating and cooling) obtained for Cu_3P (CuI + red P, 1:5 molar ratio, 200 °C, 24 h).

stoichiometric proportions, we have shown the solvothermal synthesis of Cu_3P to be much easier, safer and more efficient than originally proposed.

at ~ 1021 °C upon heating, corresponding to a melting point, and an exothermic peak at ~ 963 °C upon cooling, indicative of a recrystallization. These results are in close agreement with the melting point of 1022 °C reported by Ugai and coworkers [16]. This suggests that the low copper content is a function of intrinsic defects, rather than the presence of amorphous phosphorus, since the latter would be expected to reduce the melting point. However, several other samples which appeared to be pure from the analysis of powder X-ray diffraction data, energy dispersive spectra and optical diffuse reflectance measurements gave slightly different thermal analysis diagrams, resulting in a shift of up to 10 °C in the melting/recrystallization curve. Furthermore, the thermal analysis diagrams show a subtle exothermic peak occurring slightly above 800 °C that we cannot assign to a specific thermal event. The differences between samples and extra thermal events may be due to small impurities, the formation of eutectics and/or reactions such as $Cu_3P + P \rightarrow CuP_2$.

4. Conclusion

We have shown that a variety of starting materials can be used to prepare Cu_3P as a bulk, microcrystalline pure phase material. Most importantly, we have removed the prejudice that highly reactive yellow phosphorus must be used for the solvothermal preparation of Cu_3P and that an *N*-donor coordinating solvent plays a key role in this synthesis. By making Cu_3P using a copper source, red phosphorus and H_2O in closer to

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