THE SYNTHESIS OF MONOCLINIC ZINC DIPHOSPHIDE SINGLE CRYSTALS

Thomas Andrew Mowles
(M. S. thesis)

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THE SYNTHESIS OF MONOCLINIC ZINC DISPHOSPHIDE SINGLE CRYSTALS

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PREFACE

Humanity is turning to the sun for continually renewing energy. Solar photovoltaic systems must be developed to compliment other energy sources. The problems of extracting electricity from sunshine are both economic and physical. Materials comprising the system must be readily available in quantities sufficient for addressing the problem on a global scale. And they must be formed into a high efficiency structure by a cheap, large area, controlled process. The behavior of the absorbing material is the essence of the high efficiency cell. A cell will cost more than the material cost of this layer. The volume of material required depend upon its absorption property. Two types of useful absorption occur. "Direct gap" semiconductors absorb the solar spectrum in less than a micrometer. "Indirect gap" semiconductors require 10 to 100 times that thickness. No cheap and abundant direct gap semiconductors were being evaluated for solar photovoltaic application. The purpose of this research has been aimed at filling this void so that solar electric power becomes available to all of humanity.

THE SYNTHESIS OF MONOCLINIC ZINC DIPHOSPHIDE SINGLE CRYSTALS

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ABSTRACT

Monoclinic zinc diphosphide is a cheap, plentiful, direct-gap semiconductor with an optimum transition energy for solar absorption. Single crystals were grown from the vapor to be evaluated as a new photovoltaic material. Monoclinic and tetragonal crystal formed within evacuated quartz ampules that were charged with zinc and excess phosphorous and heated in a temperature gradient to give phosphorous pressures from 0.07 to 8.5 atmospheres. The monoclinic form melts incongruently near 990°C. The tetragonal form is metastable; its growth is enhanced by impurities but retarded by high phosphorous pressures. The mechanism of the synthesis indicates that a tightly-controlled vapor deposition is possible and that high-quality thin films should form at temperatures from 950 to 990°C at pressures below 10 atmospheres.

By a modification of the technique, sesquizinc phosphide single crystals were grown for comparison.

I. INTRODUCTION

Phosphorous and zinc are inherently cheap and abundant. But little has been known of the zinc/phosphorous system until recently when high pressure/high temperature synthesis equipment has become available.

Grey-black single crystals of sesquizinc phosphide (Zn_3P_2) were first synthesized by M. V. Stackelberg and R. Paulus¹ in 1935. This material is rather well known. It is currently being evaluated for solar photo-voltaic material. In this same paper, Stackelberg and Paulus synthesized single crystals of red zinc diphosphide having a tetragonal crystal symmetry ($\text{ZnP}_2\text{-T}$). This material is currently being synthesized for devices relying on non-linear optical absorption properties.³ It has a 2.22 eV indirect absorption⁴ and is thus of no use for photo-voltaic cell applications.

Crystals of black zinc diphosphide having a monoclinic symmetry ($\text{ZnP}_2\text{-M}$) were first synthesized by I. J. Hegyi, E. E. Loebner, E. W. Poor, Jr., and J. G. White⁵ at RCA in 1962. They determined that $\text{ZnP}_2\text{-M}$ had a direct optical absorption at a 1.33 and 1.37 (Birefringent). These values are very close to the optimum for solar absorption.⁶ Such a match is a necessary requirement for a cell of the highest level of efficiency. Crystals were subsequently prepared by M. Rubenstein and P. J. Dean at Westinghouse⁴ and also B. Ray and P. Burnet at the University of Dundee⁷ in 1969. Current synthesis is primarily by L. A. Bitjutskaya and associates at Voronezh State University, USSR.⁸

Thin films about 1 micron thick have been made to improve silicon MIS devices.⁹ Both zinc diphosphides are naturally p-type.^{4,5} $\text{ZnP}_2\text{-T}$ has been grown n-type by doping with Selenium.¹⁰ Thus $\text{ZnP}_2\text{-M}$ could possibly be used for homojunction solar cells.

Unfortunately, little is known of the zinc/phosphorous system and the nature of the phase relations of the zinc diphosphides. The most recent information is in still-to-be-translated Russian journals. The key properties of $\text{ZnP}_2\text{-M}$ that have been measured are shown in Table I.

There are several gaps in the understanding of these materials. It is not clear whether $\text{ZnP}_2\text{-M}$ melts congruently. Berak¹¹ reports congruent melting at 1040°C and eutectic formation with Zn_3P_2 at 980°C at 55 at.% phosphorous. Bitjutsкая⁸ reports a peritectic reaction at 980°C with a liquidus at 1036 to 1058°C (at 40 to 15 atmospheres respectively). Rubenstein⁴ reports congruent melting at $992 \pm 1^\circ\text{C}$. Ray⁷ reports gradual decomposition above 700°C without melting.

The relationship between the two diphosphides is also unclear. Berak¹¹ reports that $\text{ZnP}_2\text{-T}$ transforms to $\text{ZnP}_2\text{-M}$ irreversibly at 990°C and they do not form a solid solution. Bitjutsкая⁸ reports that: $\text{ZnP}_2\text{-T}$ is not formed from the melt; heating for several hours at 930°C and a pressure of 5 to 15 atmospheres will convert $\text{ZnP}_2\text{-T}$ to $\text{ZnP}_2\text{-M}$; and $\text{ZnP}_2\text{-T}$ is a metastable phase. Sirota¹⁴ reports that $\text{ZnP}_2\text{-T}$ transforms reversibly to a black monoclinic form at 107°C and then irreversibly to $\text{ZnP}_2\text{-M}$ at 990°C. Sirota¹⁹ also reports that $\text{ZnP}_2\text{-T}$ has a stoichiometry of $\text{ZnP}_{2.1}$.

There has been no direct measurement of the decomposition temperature of the diphosphides nor is there any information on the synthesis mechanism whereby deposition may be controlled.

Based on the necessity of developing new materials for economic photo-voltaic conversion and the lack of information on this promising material, it was decided to learn to synthesize $\text{ZnP}_2\text{-M}$ to provide samples for further evaluation. The initial aims were to synthesize large enough single crystals for $\text{ZnP}_2\text{-M}$ from the pure elements to permit study of its thermal and atmospheric stability and to compare its properties to the Zn_3P_2 phase which is better known.

This report details the accomplishment of these objectives.

The data in this report encompasses 19 process runs. The identification number of the runs and the target condition or special objective of each is shown in Table II.

II. SYNTHESIS

A. Method

Vapor deposition techniques were used due to lower pressure required, ease of control, and greater application to eventual thin film growth.

Hegyi⁵ formed his crystals from the vapor in evacuated ampules placed in a three-zone furnace. The lowest temperature zone, containing excess phosphorous, was controlled from 460-510°C. This maintained a phosphorous pressure of from 3 to 10 atmospheres. The highest temperature zone contained zinc, which was held between 1000 and 1050°C. In the middle zone, at a temperature from 700 to 850°C, a deposit of primarily $\text{ZnP}_2\text{-M}$ with some $\text{ZnP}_2\text{-T}$ was formed.

Rubenstein⁴ synthesized single crystals in a two-zone furnace. The phosphorous excess was loaded in the lower temperature zone at 350°C yielding a vapor pressure of approximately 230 mmHg and the zinc was loaded in the other zone at a temperature of 850°C. In the temperature gradient between the zone at 750-775°C, a similar ZnP_2 deposit was formed.

Ray and Burnet⁷ simplified the process by loading both the zinc and phosphorous in the same end. The temperature of this zone was held at 500°C for 1 hr prior to raising to the final temperature of 950°C. This constant temperature procedure served the purpose of distilling the excess phosphorous into the lower temperature zone. This zone was then raised to 510°C for the final synthesis giving a 10 atmosphere phosphorous pressure.

These synthesis techniques were further simplified by eliminating the 1 hr when this was found to be unnecessary and by

using gradient of one furnace zone to approximate a two zone furnace. The length of the ampule was adjusted so that its end intercepts the furnace profile at a desired low temperature while the hot end was located near the center of the zone.

In Fig. 1 a typical furnace profile was compared to a typical ampule, both before and after processing. The temperatures shown were tabulated in Table V.

B. Equipment

A 1 in. inside diameter Marshall furnace was used. The 18 in. long furnace had 7 of its original 10 zones intact. The center zone temperature ranged from 840 to 1075°C but was typically used from 1000 to 1050°C. The zone center temperature could be raised from room temperature to 1000°C in 3 hr. The maximum furnace temperature was 1100°C.

The synthesis takes place within evacuated quartz ampules. The low purity ampules were of 1 mm wall thickness with a 13 mm inside diameter and were 18 to 23 cm long (depending on the final phosphorous pressure desired). The ampules were constructed from stock quartz tubing to the experiment specifications and should be safe to a phosphorous pressure equivalent to a phosphorous temperature in excess of 550°C.

For high purity runs the ampules were redesigned to incorporate a 1 cm inside diameter by 1 mm quartz liner that extended to within a centimeter of the low temperature tip. This design also incorporated a quartz ball and socket joint so that atmosphere could be excluded from the ampules during preparation (see Fig. 2).

C. Preparation

1. Low Purity Runs

Red phosphorous powder, 100 mesh, 99+% (ROC/RIC P102), was used as starting material in the low purity runs. This phosphorous had the violet color associated with low purity red phosphorous. This material was first exposed to the atmosphere just prior to loading the first ampules. The phosphorous gained weight while it was on the scales during the weighing process. During the 6 month span of low purity ampule loading, there was an increase in the hazy white/tan deposits left in the source end of the ampules. Zinc powder, 100 mesh, 99.999% (UMC) was also loaded. This zinc had been exposed to the atmosphere for several years prior to use. After weighing and loading, the ampules were shaken on a powder shaker. It was not possible to shake all of the phosphorous powder into the ampule because of the adhesion of the powder to the quartz. Often, an additional amount of phosphorous was added to insure the presence of a condensed phase. The ampules were then evacuated with a mechanical pump for 1 hr to approximately 50 torr. Care was taken to prevent the loss of phosphorous into the pumping line when the pumping valve was first opened. An oxy/acetylene torch was used to seal the ampules which were flame annealed for 1 min and then water-quenched. The standard charge was 1.75 grams of phosphorous and 1.75 grams of zinc. This should produce 1 cubic centimeter of zinc diphosphide crystals. Run L8, having a double charge and run L1, having a half charge, deposited with equal success. The actual ampule loading is shown in Table III.

2. High Purity Runs

Red phosphorous chunks, 99.999% (Gallard-Schlesinger A3407) were used for starting material in the high purity syntheses. Five grams came sealed in quartz under an argon atmosphere. This ampule was opened in dry argon atmosphere. The chunks were crushed with a clean tungsten carbide anvil and screened through a clean 8 mesh sieve. Zinc rod, 99.999% (UMC) was filed to a powder with a clean file in the argon box. Filings from the surface were discarded. The ampules had been cleaned and acid etched during construction and came wrapped in clean paper. Equal weights of phosphorous and zinc were weighed and loaded in a dry argon atmosphere. A standard charge was two grams, although one had less (Run H3). There was virtually complete powder transfer with no clinging noticeable. Each ampule was then sealed with a high vacuum stopcock. This entire unit was removed from the argon box and attached directly to the diffusion pump system. The ampules were evacuated for over 4 hr, pulling the vacuum down to greater than 10^{-5} torr. There was no loss of material during the evacuation because the stopcock opened very slowly. The ampules were sealed in the same manner as the low purity runs. A sealed run (H3) is shown on the right of Fig. 2. The ampule loadings are shown in Table III.

D. Processing

The ampule was washed with soap and water and the powder was shaken into the "hot" end. The ampules were located in the furnace between pieces of quartz tubing of the same diameter as the ampule and cut to a premeasured length. The position was recorded with an accuracy of a millimeter. The ampule and the locators were slipped

into a 60 cm x 16 mm inside diameter quartz tube. The zone-center temperature was controlled and monitored with a chromel/alumel thermocouple that was externally attached to the locating tube at the center of the zone. This thermocouple degraded and was broken several times throughout the course of the experiment.

The ampule was placed in the support tube and its position was recorded. This unit was carefully inserted in the furnace. Another chromel/alumel thermocouple was located above the unit and adjacent to the low temperature end.

In some runs a presynthesis phosphorous distillation was incorporated in the process. The zone center temperature was raised, in 30 min to about 400°C, and held there for 1 hr before driving the furnace to its final temperature. The ampule was held at this temperature for about a day. The low temperature thermocouple was used to measure the temperature gradient along the furnace. This is probably accurate to within 5°. Then furnace power was cut and within 30 min the temperature dropped to below 500°C. Most runs were processed without this step by heating, in 3 hr, directly to the final temperature.

Run H4 was shut off in midrun, the temperature gradient was from 175 to 750°C. The run was removed, examined and then completely reprocessed. Run L4 was reprocessed, without opening, as run L5 due to a very poor yield during the original processing. Run L6 was completely reprocessed after a thermocouple broke during the first processing (see Table IV).

E. Post-Treatment

While cooling down in the furnace, white phosphorous condensed on the ampule walls as translucent droplets or haze. The color of these droplets change in time by the crystallization of red dendrites. Since the process of opening the ampule dislodged the larger crystals, visual examination was performed before opening. All ampules were opened in a dry argon atmosphere. Low purity runs were opened with a diamond saw blade powered by a hand held motor. The high purity runs were opened by fracturing along a scratch made with a carbide tool. The liner and the hand technique gave better results by preventing quartz contamination of the deposit.

The white phosphorous was dissolved in carbon disulfide which was poured through a filter to save any free crystals. Any CS₂ residue was removed by dissolution in absolute ethanol followed by acetone to promote drying. The crystals were then exposed to the air without further processing.

A scribing tool was used to vibrate the deposit out of the ampule intact.

III. ANALYSIS

A. Visual Examination

1. General

The appearance of the ampules after processing is shown in Fig. 3. Each ampule was given a thorough examination with a 7x to 30x binocular microscope. This was used to determine the location of the primary phases as distinguished by color and morphology. $\text{ZnP}_2\text{-M}$ was black, $\text{ZnP}_2\text{-T}$ was red and Zn_3P_2 dark grey/silver. Phosphorous was from dark red/violet to scarlet to orange. This identification was confirmed by X-ray powder diffraction.

After identifying the phase, their position in the ampule was carefully measured using a steel rule. This position was compared to the final furnace temperature profile to give the temperature limits of each phase. This data is shown in Table V.

Then the appearance of the deposits in each ampule were described. General descriptions of the phosphorous, the $\text{ZnP}_2\text{-M}$ product, the $\text{ZnP}_2\text{-T}$ byproduct and the source deposit are given in following sections.

The ampules were then opened and the product deposits were removed. Typical low purity deposits process to 1 and 3 atmospheres are shown in Figs. 4 and 5, respectively.

The deposits were reexamined with the microscope to describe the morphology of the crystalline deposits more accurately. A description of the typical morphologies of the product from low purity and high purity runs are given in following sections.

2. Phosphorous Deposit

In all normally processed runs, there was a deposit of a solid phase that covered the lowest temperature surfaces of the ampule. This deposit was colored red of various hues from dark to brilliant. X-ray powder diffraction has shown this to be red phosphorous.

This phase extended to temperatures well above the minimum temperature in the ampule. It showed definite color variations and some distinctly visible colored interfaces. An orange band was observed several times in the higher temperature region.

If the deposit was heated above about 350°C the phase was tightly adherent to the quartz. If process below this temperature the deposit easily flakes off as a unit.

In the low purity runs, the region between the phosphorous and product deposits formed many colored phases which did not always occur regularly. Since these phases did not appear in the high purity runs, they will not be described. Because these phases overlapped both deposits, locating the phase boundaries was more difficult.

3. Product Deposit

The main deposit was in the form of a black polycrystalline mass that formed on the top side of the ampule. This side was cooler because the control thermocouple lay along this surface. The mass had two main sections. On the inside of the ampule was a microcrystalline coating. A forest of large crystals had grown this coating. Both sections share the same temperature range. The single crystals deposited with various morphologies at different temperatures and pressures. All deposits have a definite upper temperature limit.

The morphology of the edge near this limit is of two kinds. Often there were well formed crystals right to the edge of the deposit (Fig. 5), but sometimes the edge was severely decomposed (Fig. 4). In this severely pitted and channeled region there were no crystals. The color was silver-grey. There was distinct interface between the two regions. In most deposits there was a definite lower temperature where the large crystals stop. The rather thick coating thinned markedly and the deposit often cracks off as a unit at this point. The deposit is actually continuous down into the phosphorous region, but the amount and quality of the crystals decreased rapidly past this lower limit.

4. Byproduct Deposit

In each run there was at least one crystal having a transparent red appearance. These were quite striking and could be distinguished easily against the black deposit. There was never more than a few isolated crystals in any run. These were randomly distributed in the high purity runs. In the low purity runs, these crystals also grew in well defined regions, which appeared to be associated with impurity phases. A high temperature limit to the crystals was not observed below 925°C. The number of these crystal was always very small (below 5% red) but the amount of ZnP_2 -T material can become a significant part of the deposit (25% red). Both diphosphides formed single crystals but only black coatings were observed.

5. Source Deposits

In the highest temperature region of the ampule several different deposits have been observed:

a. Grey Mass. Mid-process examination of H4 showed a grey porous mass having the same location as the original powder charge but more homogeneous. This is low temperature Zn_3P_2 .

b. Grey Plug. In H1 there was a porous grey that occupied a limited temperature range away from the end of the ampule. This is a Zn_3P_2 mass; the higher temperature section was evaporated through the plug. This plug did not restrict gas flow but was continuous across the diameter of the ampule.

c. Black Mass. These deposits were found in those runs (L2, L4) which had a very low yield of deposited crystals. The mass has the same location as the original powder but with a more uniform density and without the sloping edge of a spilled powder. Although the mass was very porous, a sharp blow with the anvil was necessary to fracture it. This is low temperature $\text{ZnP}_2\text{-M}$ that was synthesized without deposition.

d. Black Plug. This occurred frequently (L5, L6, H5). The plug had a very limited stability range. It was usually less than 10° wide at a temperature of at least 990°C but less than 1015°C . This plug completely obstructed the diffusion of gases down the ampule (see Fig. 4, run H5). The surface had a crystalline structure and did not show signs of having been melted. The lack of porosity, however, implies some liquidlike behavior. Powder diffraction shows that this is primarily $\text{ZnP}_2\text{-M}$ with some Zn_3P_2 peaks.

e. Drop(s). This occurred frequently (L9, H2, H4). There may be one large or a few small drops. These were almost spherical with a dendritic surface appearance as if solidified from a liquid. One

drop was observed to be contiguous with the remnants of a black plug as if it has been in the process of melting. This drop was moved before its temperature could be determined. Since this deposit was not found below 1030°C, its melting point must be between 1015 and 1030°C.

f. Nothing. This was found in runs having the highest yield of deposited material. In low purity runs (L1, L3), a white/tan hazy residue was left. In the high purity run (H3), the ampules were visually clean.

g. Trapped Mass. This was observed when the tip was not the highest temperature in the ampule (L7, L8). The material that collected at the tip was very irregularly structured. The mass appeared to have liquid but there were large internal voids some of which were lined with red residue. Some runs with this type of deposit cracked the ampule on cooling.

6. Low Purity Crystals

The typical morphology of the low purity runs is best represented by run L5. The crystals in this run and run L4 had the clearest morphologies and the best perfection. Both of these runs were processed at one atmosphere. And both were processed from initial low yield runs and thus were prenucleated. The description is supplemented as needed with morphologies observed in other runs.

At 650°C, small hair-like needles were found. These were typically 1 mm long.

At 700°C, two-dimensional blade-like crystals were found. These often had parallel striations running the length of the blade, as

if several needles had aligned irregularly side-by-side. Figure 5 has a good picture of a striated blade. A few transparent greenish blades were seen but most blades were opaque.

At 750°C, rods were found to form. These were from 2 to 8 mm in length but seldom more than 2 mm in diameter. They have a distorted hexagonal cross-section. The end of the crystals nearer the substrate were often irregularly striated parallel to the axis. The free end usually was well perfected and had well developed facets (Fig. 5). These ends may be truncated on a slight angle to the axis, or chisel pointed, or chiselled in three directions, or hollow. The hollow area never ran completely through the crystals. The surfaces of the crystals were smooth when observed with a scanning electron microscope. The corners were sharp with regular symmetry. Figure 4 shows the end structures of several large rods.

At 800°C, equiaxed polyhedrons were found. The most massive crystals were of this type. Some crystals (run L9) had maximum dimensions to 5 mm.

Over 850°C, the size and number of large crystals starts to decline. The polycrystalline coating on the quartz starts to thicken. The scanning microscope shows the surface of the coating to be irregular and rather rough with numerous small protruding crystals. There were fewer protrusions at the higher temperatures. The maximum substrate temperature in these runs was 950°C.

7. High Purity Crystals

There were some distinct differences in crystal morphology between high purity runs and low purity runs deposited under similar conditions.

No hairlike deposits were observed. The blades were larger and very few had striated surfaces. Platelets were formed at about 725°C throughout the pressure range. A few platelets were observed in only one low purity run (at 6.8 atmospheres). The platelets were extremely thin and completely opaque. The surfaces were mirror smooth. The high purity crystals were generally of smaller size and larger number though this may be due to the size reduction necessitated by the linear.

B. X-Ray Powder Diffraction

Several samples were selected for X-ray powder diffraction analysis to confirm the visual identify of the phases. Three samples of $\text{ZnP}_2\text{-M}$ were selected: A large number of midsize crystals (L5), an entire deposit (L9) and a black porous deposit (L2). A large number of red $\text{ZnP}_2\text{-T}$ crystals were collected from L5 and L6. The entire deposit (SQL) was selected to verify the synthesis of sesquizinc phosphide.

These samples were ground to powder. A freshly cleaned mineral anvil was used to fracture the larger specimen. Chunks were ground to a fine powder with an agate mortar and pestle. The powder was pressed with the edge of a glass slide into the indentation of a plastic powder-sample-holder. This was held horizontal and stationary while an X-ray powder spectrum was taken using a Picker diffractometer. Copper, K alpha, radiation was used at 40 keV and 14 ma. The two degrees per minute scan was recorded on a chart at 2 in. per minute. The detector used a crystal monochromator. A scale of 1000 counts per sec was used except to resolve some of the small peaks or if secondary

phases were present. The spectra thus collected were tabulated for peaks that were easily discernable about 10% of scale intensity.

For comparison with reference information the spectra were further filtered. The relative intensities were normalized to the intensity of the primary peak as given by reference. Peaks less than about 10% relative intensity were omitted. The remaining dozen or so peaks were used for identification. For $\text{ZnP}_2\text{-M}$ the three spectra were almost identical. These were merged into a typical spectra by averaging the angular location of the peak. Adjustment was never more than 0.2° (in two theta).

Reference spectra came from two sources. Spectra of all three phases found in the 1972 International Centre for Diffraction Data file. Spectra of the Diphosphides are also given by Rubenstein and Dean,⁴ through there were several discrepancies, the main peaks are virtually identical. In Table VI, the reference spectrum was compared with the experimental spectra for $\text{ZnP}_2\text{-M}$. Table VII is the same presentation for $\text{ZnP}_2\text{-T}$, and a Table VIII for Zn_3P_2 .

IV. DISCUSSION

A. Introduction

The X-ray powder diffraction spectra of the primary phases was an excellent agreement with reference spectra (see Tables VI, VII and VIII).

The phase location information in Table V was used to propose a synthesis mechanism based upon the stability of the phases in the ampule. This mechanism will permit a controllable process for vapor deposition of $\text{ZnP}_2\text{-M}$. The implications of the mechanism on the synthesis conditions will be discussed. Then, observations of the nature and relations between the primary phases on the synthesis of $\text{ZnP}_2\text{-M}$ will be presented.

The reliability of phase location information is limited. The deposit could have been formed at any time during the run. During the heatup (to the final conditions), the pressure, temperature and the deposition rates simultaneously varied. Plugs which formed in some ampules may have formed and decomposed at the conditions of the source changed. The conditions in the ampules as derived from the temperature profile should be considered to represent the equilibrium annealing rather than deposition conditions.

B. Phase Stability in Ampules

1. Phosphorous

The stoichiometric excess of phosphorous in the ampules forms a reservoir which establishes a constant chemical potential of phosphorous. The phosphorous pressure depends on the temperature and the crystal form of the red phosphorous. The crystal form depends on the thermal

history of the deposit.¹⁵ The form and color of red phosphorous prepared by heating white phosphorous to different temperatures is given in Table IX. These changes in the crystal forms of red phosphorous are irreversible.

Phosphorous V will not be form in the reservoir at the conditions used herein. Phosphorous IV would form in runs over 475°C. In the lowest temperature runs, the reservoir would contain phosphorous I. The Pressure in the ampules will be asymptotic to the vapor pressure of these crystal forms. The pressure over phosphorous I is:¹⁶

$$\text{Log } P \text{ (Atm)} = -4296/^{\circ}\text{K} + 6.404 \quad \text{from } 320 \text{ to } 500^{\circ}\text{C} \quad .$$

The pressure over phosphorous IV is:¹⁶

$$\text{Log } P \text{ (Atm)} = -6070/^{\circ}\text{K} + 8.67 \quad \text{from } 380 \text{ to } 560^{\circ}\text{C} \quad .$$

These curves are shown in Fig. 6. The vapor pressure near 475°C is intermediary between these curves. The ampule pressures determined this way are included in Table 5.

Lower pressure red phosphorous phases deposit within the ampule due to the equilibrium between the reservoir and the ampule walls at temperatures above the minimum. This explains the distinct multi-colored "red" phases seen at the lowest temperatures.

2. Zinc Diphosphide

Zinc diphosphide is known to decompose by the reaction:¹⁷

Evaluation of the equilibrium constant for this reaction will yield

the temperature at which zinc diphosphide decomposed under any phosphorous vapor pressure. Jordan¹⁷ estimated this to be:

$$T(^{\circ}\text{K}) = -14029.7/(\log(P(\text{Atm})) - 12.06) \quad .$$

This curve was extrapolated and plotted in Fig. 7 and gives the decomposition temperature at a fixed pressure, the vapor deposition temperature at a fixed pressure and the phosphorous stabilizing pressure required at a fixed temperature.

Bitjutskaya⁸ reports that the peritectic reaction temperature was independent of pressure from 10 to 40 atm. This is also shown in the figure. The pressure necessary to prevent decomposition increases sharply at the reaction temperature.

In several of the deposits (L1, L7, H1, H4), a sharp interface between the phosphides was observed. This was due to the decomposition at the edge of the deposit when the temperature increased following deposition. These points represent equilibrium decomposition conditions and are in general agreement with expectations.

The minimum and maximum temperatures of the ampule are compared in Fig. 8. The line at the left represents the limiting case of one temperature synthesis. The minimum temperature determines the phosphorous pressure which in turn determines the decomposition temperature. Solution of the equations for phosphorous I and zinc diphosphide pressures gives the stability limits for the phosphides in a two zone furnace. Zinc diphosphide is stable to the left of this line shown in the figure.

3. Sesquizinc Phosphide

Sesquizinc phosphide sublimes when heated according to the reaction:¹⁸

The equilibrium constant of the reaction is known:¹⁸

$$\log K(\text{torr}^{7/2}) = -31750/^\circ\text{K} + 33.81$$

from 617 to 857°C, where:

$$K = p_{\text{Zn}}^3 p_{\text{P}_4}^{1/2} \quad .$$

The phosphide evaporates in an environment of constant chemical potential of phosphorous. The equilibrium constant can be solved for the equilibrium zinc sublimation pressure given the phosphorous pressure and the temperature. The effect of the reservoir is to reduce the zinc sublimation pressure at lower temperatures and to increase it at the higher temperatures.

The sesquizinc phosphide evaporates in an ampule containing phosphorous in excess of zinc diphosphide stoichiometry. Any zinc lost to the sesquizinc phosphide will incorporate into the zinc diphosphide deposit if the zinc is free to move to a region of zinc diphosphide stability.

C. Mechanism of Synthesis

1. Distillation

At a temperature of 400 to 450°C, phosphorous was observed to distill away from the powder charge (H4). The phosphorous distills to the lowest temperature in the ampule and establishes the phosphorous

reservoir. The pressure is maintained by several crystal forms as the lowest temperature is raised.

2. Reaction

The zinc reacts readily at low temperatures with phosphorous. Sesquizinc phosphide has been formed at 440°C.¹ The diphosphide should form near the same temperature if the phosphorous pressure is sufficient. Diphosphides were deposited from the vapor below 650°C (see Appendix A).

This reaction occurs at the zinc site because zinc gas is not formed when the diphosphide decomposes and the sesquizinc phosphide does not sublime rapidly below about 750°C. The sesquizinc phosphide mass in run H4 had negligible evaporation at 750°C for a short time. In the sesquizinc phosphide synthesis runs the deposit occurred from 700 to 800°C.

3. Heating

The heating/cooling conditions for run H4 is shown in Fig. 9. The theoretical and empirical stability limits for the diphosphide are also shown. The source is seen to heat in the region of diphosphide instability. This fact was confirmed by mid-process examination. The source cools in the region of diphosphide stability. This hysteresis is necessary for the vapor deposition.

This curve was similar for all the runs. Only the final conditions of the other runs were presented in the figure.

Runs that were to the right of the stability line gave good yields of deposited crystals. The runs that were farthest from the line had the best deposited yield. The runs that were closest to the line had the best crystal quality.

Runs that were to the left of the stability line had no, or very little, crystal deposition. The black porous mass deposits that form in the source was pure $\text{ZnP}_2\text{-M}$. Thus $\text{ZnP}_2\text{-M}$ was synthesized but not evaporated.

The properties of the stability line may be illustrated with runs L4 and L5. L4 was processed at about 400 to 800°C for 65 hr without any deposited yield. L5 had a good yield of excellent crystals when processed to about 400 to 1000°C for 17 hr. The deposition temperature of about 925°C was near the expected value.

The final temperature conditions that were used in previous vapor synthesis are also shown on the figure. The present synthesis repeats and extends the pressure range of earlier synthesis. It was not possible to get crystalline yield from the approximate conditions of Rubenstein.⁴ Duplication of Ray's⁷ exact conditions were not attempted. Hegyi's⁵ results were duplicated.

A source temperature of 1100°C will be necessary for good crystalline yields at a processing pressure of 10 atm, i.e., during thin film vapor deposition.

4. Decomposition

Any sesquizinc phosphide formed will sublime at a zinc sublimation pressure dependent on the reservoir pressure and source temperature. The flux of zinc to the deposition and hence the rate of crystal growth depend on this pressure.

The sublimation of sesquizinc phosphide at reasonable pressures is critical to the vapor deposition of the diphosphide. Most transition metals form an extremely stable lower phosphide. These metals cannot

be evaporated within quartz ampules in the presence of phosphorous. Thus the reservoir permits the deposit of zinc diphosphide while preventing the evaporation of most important impurities.

5. Diffusion

Any zinc gas formed at the sources diffuses through the phosphorous vapor to the deposition site.

The equilibrium zinc sublimation pressure of zinc diphosphide is negligible if the decomposition is prevented by a sufficient phosphorous pressure. Thus the diffusional flux to the deposit is controlled by the zinc sublimation pressure of the source alone. Adjustment of the system geometry may be used to give diffusion-, orifice- or kinetically-limited fluxes.

The diffusion of zinc away from the source maintains the nonequilibrium conditions at the source.

The diffusion is strongly influenced by the temperature gradient. If the source end was cooler than the hottest place in the ampule, the zinc diffuses to this end. The zinc is trapped by the gradient and cannot diffuse to the deposition. The zinc deposits in the end as sesquizinc phosphide when the equilibrium concentration is reached. This trapped deposit reduces the yield and can fracture the ampule on cooling.

6. Vapor Deposition

Zinc atoms arriving at a surface with a temperature below the decomposition temperature will be incorporated into the deposit by reaction with phosphorous from the surrounding reservoir.

The mobility of the atoms on the surface depends on the temperature of the surface. The ratio of atoms that are incorporated to those that reevaporated is dependent upon the difference between the substrate and decomposition temperatures.

The morphology of the deposit also depends on the flux of zinc arriving at the surface, the reactivity of the substrate and its thermal conductivity.

7. Cooling

The substrate must be cooled before the phosphorous pressure is reduced. This prevents the full or partial decomposition of the crystals to sesquizinc phosphide.

In this one zone gradient synthesis, the hottest parts cooled the fastest. Thus the temperature was reduced before the pressure. Since the crystals were in the stable diphosphide region when the cooling began, there was no decomposition on cooling.

The effect of cooling on the source is to stabilize it. If the source is evaporating in a marginally unstable condition, it enters into the diphosphide stable region at a high temperature. The source could be transformed before cooling. If the source was highly unstable, then the stable region will be entered at a low temperature and the source will not transform on cooling.

D. Implications of Mechanism

1. Process Control

The process can be controlled by using three different temperature zones that can be independently controlled. Assume that there is

complete control of the system geometry. Each zone affects the deposition differently.

a. Low Temperature Zone. The lowest temperature controls the phosphorous pressure in the ampule.* This sets the thermodynamic decomposition temperature of zinc diphosphide. The temperature is approximately the deposition temperature. The temperature of this zone may be varied to adjust the deposition temperature over a wide range.

b. Middle Temperature Zone. The temperature of this zone controls the substrate temperature. This must be below the decomposition temperature if deposition is to occur. The difference in the temperature is a measure of the thermodynamic stability of the growing interface. This stability affects the vapor/solid exchange conditions during growth. The absolute temperature of the substrate determines the mobility of the atoms on the surface and the reaction of the components. The morphology of the deposit is strongly influenced by the substrate temperature.

c. High Temperature Zone. The highest temperature controls the sublimation of the source. At a fixed pressure, this zone controls the flux of zinc to the substrate. With suitable geometry, the flux can be adjusted over a wide range.

These three zone temperatures can be adjusted to fix the substrate temperature, the thermodynamic stability of the substrate and the

*This is essentially the total pressure of the system and thus sets the mechanical constraints on the equipment.

zinc flux independently. These parameter control the deposition process and hence the deposit morphology. The growth conditions can be shifted over a wide range and can be optimized at any useful substrate temperature.

2. Thin Film Conditions

As the temperature of the substrate is raised near the decomposition point, there will come a point where a film rather than extended crystals will form.

Hegyi⁵ deposited crystals to a temperature of 850°C. At temperatures above 900°C there was a marked thickening of the coating on the quartz. Scanning micrographs showed a irregular surface. These runs had deposits to 950°C. Equiaxed crystals were observed to 950°C but the size of these crystals was very small. A temperature in excess of 950°C will probably give good thin films.

If zinc diphosphide melt congruently then the process can be taken up to the melting point (1040°C). If zinc diphosphide melts incongruently, this process is limited to 990°C. This is 95% of the "melting" temperature which should be good for thin films.

Thin film deposition is expected to occur between 950 and 990°C with commensurate pressure of 5 to 10 amp. Choice of a favorable substrate might reduce this substantially.

3. Low Pressure Synthesis

By reducing the phosphorous pressure, the vapor deposition temperature is lowered.

Good quality single crystals have been synthesized at near atmospheric pressures. Thus there is no need of high pressure equipment

to synthesize single crystals of high perfection. And vapor deposition was successful at pressures less than 0.1 atm and less than 700°C.

At pressures below 1 atm, the phosphorous can be diluted in an inert gas. Then pressure containment will not be needed and the phosphorous pressure can be adjusted by dilution as well as by adjustment of the reservoir temperature. Fine tuning becomes possible. Stackelburg¹ made red ZnP_2 at 780°C in an open tube.

It is unlikely that thin films could be made at sub-atmospheric pressure.

4. Diphosphide Evaporation

The excess of phosphorous is necessary to prevent the formation of sesquizinc phosphide.

To test this, two ampules were loaded with zinc diphosphide to exact stoichiometry. On processing normally the ZnP_2 -M was almost completely converted to Zn_3P_2 and ZnP_2 -T (see Appendix B).

This means that the diphosphide must be in a phosphorous atmosphere whenever the processing requires heating to high temperature. Ray noticed decomposition starting at 700°C.⁷ It is estimated that processing over 600°C will require phosphorous protection. Vacuum formation of thin films will not be possible.

E. Diphosphide Phase Relations

The diphosphides do not form a solid solution with each other.¹¹ It was never noticed that red and black crystals comingled. No crystals of intermediate properties were observed. Both crystal forms were clearly faceted and though they intersected, they did not share a common boundary.

$\text{ZnP}_2\text{-M}$ grows epitaxially on $\text{ZnP}_2\text{-T}$.⁵ This was observed though the monoclinic crystal was never very large. Needles of $\text{ZnP}_2\text{-M}$ were seen growing epitaxially on a $\text{ZnP}_2\text{-T}$ crystal in a regular geometric array. The growth of $\text{ZnP}_2\text{-T}$ on ZnP_2M crystals was never observed. Black "amorphous" deposits were observed. These have a globular nature as if the facetting that produces the edges and surfaces was suspended. One black rod was found that was well facettted at one end and globular at the other without any change in the color or appearance of the material. This morphology was seen in deposits made at low temperature and high deposition rate. The transition of this morphology to a well facettted red crystal was observed.

There was a generally uniform number ratio of the red to black crystals (about 5% red), but the volume ratio varied widely (up to 25% red). The mass of red crystals was largest in the impure low pressure runs. The black form is definitely the most stable form, but both form nuclei to temperatures in excess of 900°C. The rate of growth of the red form is retarded by pressure and impurities.

Red crystals cannot be formed from the melt.⁸ Red crystals convert irreversibly to black crystals if heated in excess of 930°C.¹⁴

The monoclinic zinc diphosphide is the more stable, preferentially-nucleating phase. There will be no red phase formed during thin film growth at temperatures above about 900°C. And any red phase that forms under any conditions can be converted to the black form by subsequent heat treatment to 930°C.

F. Phosphide Phase Relations

The morphology of the source end residue depends on the source conditions and the cooling conditions. At the lower temperatures, the source will be a grey porous mass. As the temperature rises, the mass evaporates leaving a grey porous "plug." At a high enough temperature an impermeable black plug is formed. The black plug was not seen below 990°C. The plug has obviously prevented deposition in run H5 (see Fig. 3). This means that the plug existed at the source condition and was not an artifact of the cooling condition. The change in porosity indicates melting. Since the plug shape does not change there must be a solid component of the plug. At a temperature between 1015 and 1030°C, the plug melts giving a drop deposit that does not obstruct the flow. This temperature is too low for the melting of the sesquizing phosphide (1193°C¹¹). X-ray powder examination of the plug showed it to be $\text{ZnP}_2\text{-M}$ with a little Zn_3P_2 .

These changes in source morphology can best be explained by a peritectic reaction very near 990°C. This gives a viscous liquid $\text{ZnP}_2/\text{solid Zn}_3\text{P}_2$ phase that completely melts near 1025°C. This quenches to $\text{ZnP}_2\text{-M} + \text{Zn}_3\text{P}_2$ on cooling.

The synthesis of $\text{ZnP}_2\text{-M}$ will not be possible from the melt under equilibrium conditions. The perfection required for photovoltaic use will require near-equilibrium synthesis. Clearly melt synthesis will not be useful in forming device structures.

G. Sesquizinc Phosphide Synthesis

With slight modification, the process described above can be used to synthesize single crystals of sesquizinc phosphide. By changing the stoichiometry of the loading to Zn_3P_2 , or slightly zinc excess, the same process yields sesquizinc phosphide without any contaminating diphosphide (see Appendix C).

The ampules were processed normally, but without the phosphorous reservoir: the source sublimates with equilibrium vapor pressures, sesquizinc phosphide deposits by condensation from the equilibrium vapor, and no zinc diphosphide will be formed.

Single crystal prepared in this manner were of sufficient size and perfection to be used for comparison with the diphosphide single crystals.

V. SUMMARY

1. Monoclinic zinc diphosphide single crystals have been synthesized in phosphorous pressure from 0.07 to 8.5 atm, which duplicated and extended the range studied by previous investigators.

2. A synthesis mechanism has been proposed that is based on the known behavior of the phases and is the foundation of a process control technique.

3. Conditions for the stability and the vapor deposition of monoclinic zinc diphosphide have been presented.

4. Sesquizinc phosphide was formed as a grey porous mass in the region of diphosphide instability if the temperature was below 750°C.

5. Monoclinic zinc diphosphide was formed below atmospheric pressure as a black porous mass in the region of diphosphide stability at a temperatures below 990°C.

6. Monoclinic zinc diphosphide single crystals have been formed from the vapor at atmospheric pressure in the form of platelets at 725°C, or rods at 775°C, or massive crystals at 825°C.

7. High quality thin film should form at 950 to 990°C at a pressure below 10 atm.

8. Tetragonal zinc diphosphide is metastable and does not form along with the black porous mass, forms from low pressure vapors in small amounts, does not form from the melt and should not form at the thin film growth conditions.

9. The presence of impurities greatly facilitates the growth of tetragonal zinc diphosphide.

10. Monoclinic zinc diphosphide has a peritectic reaction about 990°C and thus cannot be formed directly from the melt.

11. Monoclinic zinc diphosphide requires a stabilizing phosphorous pressure if it is heated over 600°C during processing so vacuum evaporation to form thin films is not possible.

12. Sesquizinc phosphide single crystals were formed in ampules loaded to that stoichiometry and evaporated above 800°C.

13. Monoclinic zinc diphosphide can be formed from the vapor at sub-atmospheric pressures to a temperature of almost 850°C.

VI. CONCLUSION

High purity single crystals of monoclinic zinc diphosphide have been grown from the vapor.

The mechanism of the vapor deposition of this material is understood.

The vapor deposition of thin films suitable from solar photovoltaic energy conversion appears to be possible.

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APPENDIX A. LOW TEMPERATURE SOURCE

Ampule SLT was loaded to the normal phosphorous excess stoichiometry (Zn:0.94 gm/P:0.96 gm). The source of the zinc was an approximately 2 mm wide strip cut from a 1 mil sheet. The ampule was located in a temperature gradient of 345 to 1025°C and held for 23 hr.

The entire strip, right down to its minimum temperature of 650°C, and evaporated completely. This was converted to a normal looking deposit.

Run SLT showed that evaporation of zinc phosphide was complete at less than 650°C. The deposit produced was indistinguishable from a high temperature source. Thus the deposition depends primarily on the temperature of the deposit.

APPENDIX B. SUBLIMATION OF ZINC DIPHOSPHIDE

Ampule SRP was sealed containing 3.14 gms of black porous $\text{ZnP}_2\text{-M}$ that had been synthesized but not redeposited in run L2. This was processed normally to a temperature gradient of 460 to 1015°C for 13 hr.

Ampule SRC was sealed containing 0.66 gms of $\text{ZnP}_2\text{-M}$ single crystals that had been synthesized in run L6. This was processed to a final gradient from 365 to 1010°C for 22 hr.

Both ampules showed similar deposits. These were annular and without large crystals. The deposit was primarily silver-grey interspersed with numerous red crystals. There were several black crystals. The ratios of red to black phase was very large. The deposit was tightly adherent and could not be removed from the ampule without fracturing the substrate. Instead of the normal phosphorous deposit, the ampule end was coated with a reflective material with an unusual rainbow coloration. This is probably zinc metal.

A substantial amount of the diphosphide decomposes before equilibrium is established in the ampule. The degree of decomposition depends on the free volume in the ampule.¹¹ When decomposing the diphosphide crystal form is tetragonal. Berak¹¹ has reported the association of tetragonal sesquizinc phosphide with tetragonal zinc diphosphide. This association permits better packing of the deposit.

APPENDIX C. SESQUIZINC PHOSPHIDE SYNTHESIS

Ampule SQL was loaded with 3.46 gms of zinc and 1.10 gms of phosphorous. This is sufficient for 1 cubic centimeter of Zn_2P_2 with no excess components. This run was held for 1 hr at 420°C and then raised to a final gradient of 418 to 970°C for 20 hr.

Ampule SQH was loaded with 2.37 gms of zinc and 0.75 gms of phosphorous. This is a stoichiometry with a slight zinc excess. Since the furnace shut down at some point in the run when the thermocouple broke, no furnace profile could be taken.

These deposits were distinctly different from the phosphorous excess runs (see Fig. 10). These had thick annular coatings with a number of large crystals in the interior space. The deposit in SQL was between 675 and 790°C .

Crystals formed near the lower temperature were long rods that increased in size as the temperature increased. The largest crystals were about $1/2$ mm in diameter and up to 3 mm long. These had an approximately hexagonal cross-section. The color of the crystals was a strikingly iridescent silver. Scanning microscopy revealed that the surface was formed of crystallites of various sizes where each had well-developed facets that protruded from the surface. The rods may not be single crystals.

Crystals formed at the higher temperatures were rectangular parallelopipeds having sharp but irregular edges with numerous surface steps running parallel to each other. These single crystals were colored a dark steel grey.

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Table I. Monoclinic zinc diphosphide properties.

Name: Zinc Diphosphide

Formula: ZnP_2

Molecular weight: 127.37 gms/mole

Color: Black

Crystalline form:⁵ Monoclinic (C_{2h}^5 , P_{21}/c)

$a = 8.85 \pm 0.02$ angstroms

$b = 7.29 \pm 0.02$ angstroms

$c = 7.56 \pm 0.02$ angstroms

$\beta = 102.3 \pm 0.2$ degrees

$z = 8$ molecules/unit cell

Density:⁵ 3.47 measured
3.55 calculated

Melting point 700°C gradual decomposition⁷
980°C peritectic reaction⁸
992 $\pm$ 1°C congruently⁴
1040°C incongruently¹¹

Microhardness:¹¹ 517

Coefficient of linear expansion:¹⁴ $2.60 \times 10^{-6}/^\circ\text{C}$

Energy gap:⁵ 1.33 eV (E parallel c) by direct transition
1.37 eV (E perpendicular c) by direct transition

Carrier type:¹² Acceptor, as grown

Carrier concentrations:¹² 5×10^{14} to $6 \times 10^{15}/\text{cm}^3$

Carrier mobility:¹² 20 cm^2/Vsec

Room temperature resistivity:⁵ 10 ohm-cm

Thermopower:⁴ 230 microvolts/ $^\circ\text{K}$

Thermodynamic properties:¹⁴ $-\Delta H^{298} = 122.9 \pm 5.5$ kJ/mole ZnP_2
 $-\Delta S^{298} = -15.2 \pm 6.4$ J/mole degree

Table II. Run identification key.

Run	Conditions/Objective
Low Purity:	
L1	$T_{\min} = 300^{\circ}\text{C}/T_{\max} = 1050^{\circ}\text{C}$
L2	350/850 (Duplicates Rubenstein ⁴)
L3	350/1025
L4	400/800
L5	400/1000
L6	400/1025
L7	400/1075
L8	450/1050
L9	450/1050
High Purity:	
H1	360/1025
H2	440/1025
H3	460/1025 (Hegyi; ⁵ lower unit)
H4	490/1025
H5	515/1025 (Hegyi; ⁵ upper limit) (approximates Ray ⁷)
Special Runs	
SQL	Low purity sesquizinc phosphide
SQH	High purity sesquizinc phosphide
SLT	Low temperature synthesis
SRP	Diphosphide evaporation (mass load)
SRC	Diphosphide evaporation (crystal load)

Table III. Ampule loading.

Run	Zinc Grams	Phos Grams	Remarks
Low Purity:			
L1	0.90	0.91	Half load
L2	1.78	1.78	
L3	1.78	1.78	
L4	1.80	1.80	
L5	1.80	1.80	L4 reprocessed
L6	1.80	1.80	
L7	1.79	1.81	
L8	1.79	1.80	
L9	3.59	3.50	Double Load
High Purity:			
H1	1.0	1.0+	
H2	1.0	1.0+	
H3	0.5	0.5+	Half load
H4	1.0	1.0+	
H5	1.0	1.0+	

Table IV. Furnace processing data.

Run	Nominal Conditions	PHOS	HOLD		SYNTHESIS		
		Temp. °C	Time Hrs	Temp. °C	Time Hrs	Temp. Edge °C	Temp. End °C
L1	300/1050	295	---	---	20	1050	1060
L2	350/850	355	1	420	24	840	845
L3	350/1025	369	1.5	420	22	1020	1025
L4	400/800	412	2.5	500	65	800	812
L5	400/1000	412	---	---	17	990	1015
L6	400/1025	414+	---	---	17+	1000+	1035+
L7	400/1075	410	---	---	18	1075	1070
L8	450/1050	465	---	---	23	1065	1060
L9	450/1050	460	1	420	29	1045	1045
H1	350/1025	362	---	---	15	1020	1025
H2	450/1025	443	---	---	18	1040	1045
H3	450/1025	458	---	---	21	1040	1045
H4	500/1025	489	---	---	19	1035	1045
H5	525/1025	513	---	---	9	1000	1020

Table V. Phase location table.

Run	Phosphorous			Deposit			Source			
	TOC Min	Pres Atm	TOC Red	TOC Prod	TOC Int	TOC Lim	TOC Low	TOC Max	* Form	# Yield
L1	295	0.07	400	540	690	740	-	-	F	E
L2	355	0.35	420	620	-	740a	840	840	C	N
L3	369	0.52	440	735	-	860	-	-	F	E
L4	412	1.3	-	-----No Exam-----			800	812	C	N
L5	412	1.3	475	725	-	930	990	995	D	G
L6	414	1.3	-	---No Profile---			1000	1015	D	G
L7	410	1.2	485	830	925	970	1070	1075	G	G
L8	465	3.7	615?	775	-	945	1060	1065	G	G
L9	460	3.5	485	805	-	950	1030	1040	E	G
H1	362	0.44	445	840	900	915	1015	1020	B	E
H2	443	2.6	495	850	-	945	1035	1040	E	G
H3	458	3.5	510	790	-	875	-	-	F	E
H4m	175	-	-	-----No Yield-----			700	775	A	N
H4	489	5.2	545	790	950	970	1035	1040	E	G
H5	513	8.5	575	860	-	910	1010	1015	D	P

*Source morphology:

A = Grey porous mass

B = Grey porous plug

C = Black porous mass

D = Black plug

E = Drop

F = Nothing

G = Trapped deposit

Crystalline yield:

E = Excellent

G = Good

P = Poor

N = None

Table VI. X-ray identification of monoclinic zinc diphosphide.

Monoclinic $P2_1/c$			$a_0 = 8.85 \text{ \AA}$ $b_0 = 7.29 \text{ \AA}$ $c_0 = 7.56 \text{ \AA}$ $\beta = 102.3^\circ$				
-----Reference #24-1463-----			-----Experiment-----				
hkl	I/I ₀	d lit	d	2 θ aver	L2	L9	L5
100	vw, 4	8.64					
110	w, 10	5.56	5.60	15.8	--	--	37
210	s, 28	3.72	3.70	24.0	35	54	91
120	vs, 75	3.36	3.35	26.6	56	88	58/84
11 $\bar{2}$, 012	w, 29	3.29	3.26	27.3	21	17	23
102, 12 $\bar{1}$, 20 $\bar{2}$	vs, 100	3.16	3.15	28.3	100	100	100
220	s, 27	2.79	2.78	32.2	36	61	104
			2.55	35.2	14	19	
212, $\bar{3}$ 12	m, 11	2.41	2.40	37.4	17	19	35
130	m, 10	2.34	2.34	38.5	18	20	52d
222, $\bar{3}$ 22	m, 23	2.09	2.09	43.3	36	33	65
132, $\bar{2}$ 32	m, 12	1.93	1.92	47.3	16	19	17
$\bar{1}$ 04	m, 25	1.89	1.88	48.3	18	19	20
420, 330, 33 $\bar{1}$	m, --	1.86	1.86	49.1	10	15	34
332, 422	s, 38	1.80	1.80	50.7	--	--	63
			1.78	51.2	--	--	26
			1.76	51.9	--	--	18
141, 402	m, 15	1.72	1.71	53.4	--	--	50
			1.68	54.5	--	--	20d
			1.64	56.2	--	--	19
123, $\bar{3}$ 24	--, 10	1.57	1.56	59.0	--	--	38
424, 624, 541	m, --	1.205					

Table VII. Identification of tetragonal zinc diphosphide.

Tetragonal P_4Z_{12}			$a_o = 5.07 \text{ \AA}$ $c_o = 18.55 \text{ \AA}$		
-----Reference #24-1464-----			-----Experiment-----		
hkl	I/I _o	d lit	d	2θ	I/I _o
			4.67	19.0	11
111	--,25	3.52	3.54	25.1	17
104	vs,87	3.42	3.45	25.8	83
112	vs,100	3.34	3.37	26.4	92.5
113	--,9	3.10			
105	--,10	2.99			
114	s,45	2.84	2.86	31.3	30
201	m,15	2.51			
116	m,17	2.35	2.35	38.2	19
008	--,9	2.32	2.32	38.7	22
204	--,15	2.23	2.23	40.4	23
122	s,51	2.20	2.21	40.8	33
108	m diff,--	2.11			
124	m,--	2.03			
125	m,20	1.95	1.95	46.5	23
126	s,36	1.83	1.83	49.7	32
222	m,18	1.76	1.76	51.8	13
208	m,17	1.71	1.71	53.4	21
1110	m,12	1.65	1.65	55.7	21
			1.61	57.3	17
130	m,27	1.60	1.60	57.4	17
304	m,25	1.59	1.59	57.9	19
			1.55	59.7	16
2210	m,--	1.29			

Table VIII. Identification of sesquizinc phosphide (Zn_3P_2).

Tetragonal $P4_2/nmc$			$a_0 = 8.113 \text{ \AA}$ $c_0 = 11.47 \text{ \AA}$		
-----Reference #22-1021-----			-----Experiment -----		
hkl	I/I ₀	d lit	dcalc	2	I/I ₀
102	4	4.64	4.67	19.0	8
201	8	3.82	3.83	23.2	11
211	20	3.46	3.46	25.7	23
202	30	3.29	3.31	26.9	33
212	15	3.07	3.07	29.1	31
202,004	50	2.85	2.86	31.2	47
203	30	2.76	2.78	32.2	50
213,301	70	2.63	2.63	34.1	24
302	15	2.45	2.44	36.8	18
303	4	2.19	2.20	41.0	11
224,400	1000	2.02	2.03	44.7	O.S.
242	2	1.74			
404	6	1.64	1.65	55.7	8
			1.56	59.3	8
			1.49	62.4	10
			1.45	64.0	8

Table IX. Phase conversion in red phosphorous.¹⁵

Temp., °C	Time, hrs	Color	Crystal Form
400	17.5	Violet-Red	I
450	20	Dark Red	II or III
475	17	-	IV
510	4	Bright Orange	IV
555	48	Red	IV
560	17	Red	IV
540	715	Red	V
575	18	-	V
585	20	-	V

FIGURE CAPTIONS

Fig. 1. Furnace temperature profile.

Fig. 2. High purity ampules before processing.

Fig. 3. High purity ampules after processing.

(a) Run H1 showing a grey plug deposit.

(b) Run H2 showing fracturing of the deposit.

(c) Run H4 showing source drops.

(d) Run H5 showing a black plug.

Fig. 4. Deposit from Run L7.

(a) Decomposed edge.

(b) Flat-ended rod.

(c) Chisel-ended rod.

(d) Large tetragonal crystal.

Fig. 5. Deposit from Run L8.

(a) Equiaxed crystalline edge.

(b) Striated platelets.

(c) Irregular rods.

Fig. 6. Vapor pressure of red phosphorous.

Fig. 7. Decomposition pressure of zinc diphosphide.

Fig. 8. Zinc diphosphide stability region.

Fig. 9. Ampule heating conditions.

Fig. 10. Effect of stoichiometry on the morphology of the deposit.

(a) Run SQH (zinc excess) showing an annular deposit.

(b) Run H4 (phosphorous excess) with same processing.

XBL 785-5096

Fig. 1

XBB 782-1413

Fig. 2

XBB 782-1409A

Fig. 3

XBE 782-1407A

Fig. 4

XBB 782-1405A

Fig. 5

XBL785-5100

Fig. 6

XBL 785-5099

Fig. 7

XBL 785-5098

Fig. 8

XBL 785-5097

Fig. 9

XBB 782-1413

Fig. 10