Self-Propagating Metathesis Routes to Metastable Group 4 Phosphides

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Group 4 phosphides, which are typically prepared at high temperatures (>800 °C) over several days, are synthesized in self-propagating metathesis (exchange) reactions in seconds. These reactions produce cubic forms of zirconium phosphide (ZrP) and hafnium phosphide (HfP) which are normally made at temperatures greater than 1425 °C and 1600 °C, respectively. To test whether the high temperatures reached in the metathesis reactions are responsible for the formation of the cubic phases, inert salts are added to lower the maximum reaction temperatures. The lower temperature reactions still result in cubic phosphides, although smaller crystallites form. Further experiments with phosphorus addition indicate that the phosphorus content is not responsible for cubic phase formation. Templating is ruled out using lattice mismatched KCl and hexagonal ZnS as additives. Therefore, the direct synthesis of the high-temperature cubic phase in metathesis reactions appears to be caused by nucleation of the metastable cubic form that is then trapped by rapid cooling. Heating the cubic phase of either ZrP or HfP to 1000 °C for 18 h, or carrying out metathesis reactions in sealed ampules at 1000 °C, results only in the hexagonal phase.

Introduction

The group 4 phosphides are known for their hardness and chemical inertness even at elevated temperatures.[1−6] When zirconium phosphide (ZrP) and hafnium phosphide (HfP) are heated above 1425 °C and 1600 °C, respectively, they each undergo a hexagonal (h) to cubic (c) phase transition as demonstrated by Irani and Gingerich.[7] This transition may involve loss of phosphorus.[7] Hexagonal ZrP and HfP are isostructural with h-TiP, each having a superstructure of NiAs that can be thought of as interpenetrating slabs of NaCl-like (ABC) and NiAs-like (BCB) sandwiches.[8] Cubic ZrP and HfP possess NaCl-type lattices. To observe the cubic phase, hexagonal metal phosphide samples are heated above their transition temperatures and then quenched to room temperature.[7]

Other researchers have synthesized group 4 phosphides by a variety of methods including reactions of metals with phosphorus,[9,10] metals or metal halides with Ca_3P_2,[3] metals with PH_3,[4,5,10,11] and $ZrCl_4$ with PCl_3,[6] or reduction of metal oxides with aluminum in the presence of phosphorus and iodine.[12] These synthetic methods have three points in common: (1) they require high temperatures, usually greater than 800 °C; (2) they generally need long reaction times of several days; and (3) the extensive heating at elevated temperatures ensures that only the thermodynamic, hexagonal phase is obtained. Other methods must be used to synthesize the cubic phase. Motojima et al. have shown that the presence of Au, Pd, or Pt in gas-phase reactions of $ZrCl_4$ and PCl_3 helps to control nucleation and yields whiskers of c-ZrP.[13]

Solid-state metathesis reactions are capable of producing in seconds materials that normally take days to form from the elements.[14−20] Metal halides and alkali metal chalcogenides or pnictides react to form metal chalcogenides or pnictides and an alkali metal halide salt that is easily washed away with alcohol or water. The reaction, depending on the system, is initiated by either stirring the reactants together or igniting them using a resistively heated wire. The self-propagating reaction that ensues can reach its peak temperature in less than 1 s, and then it rapidly cools.[14] This paper reports the application of solid-state metathesis reactions using sodium phosphide (Na_3P) and metal tetrahalides ($ZrCl_4$ or $HfCl_4$) to produce the high-temperature cubic phase of ZrP or HfP in seconds. An earlier survey of metathesis reactions conducted in sealed tubes produced phosphides, indicating that cubic ZrP and HfP could form, but did not explain why.[20] In this paper we examine the process leading to high-temperature metastable cubic ZrP and HfP formation.

Experimental Section

Starting Materials. All handling of air-sensitive elements and compounds was carried out in a helium-filled drybox (Vacuum Atmospheres) with a drytrain (Mo-40), which kept the oxygen and

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(20) Hector, A. L.; Parkin, I. P. *J. Mater. Chem.* **1994**, *4*, 229.

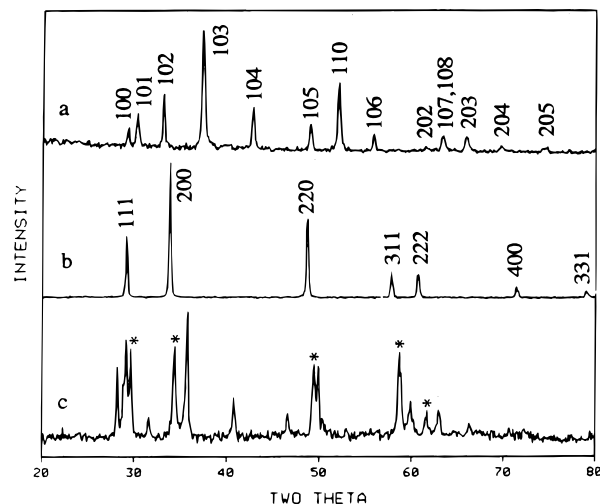**Table 1.** Summary of Group 4 Phosphide Metathesis Reactions

reactants	reaction conditions	products	X-ray diffraction figure
TiI$_4$ + $^4/_3$ Na$_3$P	ignited	h-TiP	1a
ZrCl$_4$ + $^4/_3$ Na$_3$P	ignited	c-ZrP	1b
HfCl$_4$ + $^4/_3$ Na$_3$P	ignited	c-HfP + h-HfP	1c
ZrCl$_4$ + $^4/_3$ Na$_3$P	ignited	c-ZrP	2a
ZrCl$_4$ + $^4/_3$ Na$_3$P + 3 mol equiv NaCl	ignited	c-ZrP	2b
ZrCl$_4$ + $^4/_3$ Na$_3$P + 6 mol equiv NaCl	ignited	c-ZrP	2c
ZrCl$_4$ + $^4/_3$ Na$_3$P + 3 mol equiv KCl	ignited	c-ZrP	
ZrCl$_4$ + $^4/_3$ Na$_3$P + 3 mol equiv ZnS	ignited	c-ZrP	
ZrCl$_4$ + $^4/_3$ Li$_3$P + 6 mol equiv NaCl	ignited	c-ZrP	
TiI$_4$ + $^4/_3$ Na$_3$P	1000 °C, 18 h	h-TiP	3a
ZrCl$_4$ + $^4/_3$ Li$_3$P	1000 °C, 18 h	h-ZrP	3b
HfCl$_4$ + $^4/_3$ Na$_3$P	1000 °C, 18 h	h-HfP	3c
HfCl$_4$ + $^4/_3$ Na$_3$P	stirred	HfCl$_4$ + Na$_3$P	4a
HfCl$_4$ + $^4/_3$ Na$_3$P	ground	amorphous	4b
HfCl$_4$ + $^4/_3$ Na$_3$P	stirred, ignited	c-HfP + h-HfP	4c
HfCl$_4$ + $^4/_3$ Na$_3$P	ground, ignited	c-HfP + trace h-HfP	4d

moisture contents to <1 ppm. Na$_3$P was synthesized by reacting a 3:1 ratio of sodium and phosphorus in an evacuated Pyrex tube that was heated for 30 min at 170 °C, 30 min at 350 °C, and 5 h at 480 °C. Li$_3$P was synthesized by combining lithium and phosphorus in a tantalum boat inside an evacuated Pyrex tube. The tube was then placed in a furnace set at 150 °C and the temperature was raised to 350 °C over a period of 5 h, followed by a final heating at 400 °C for 4 h. KCl (Aldrich, 99.99+%), NaCl (Fisher, certified ACS), and ZnS (Johnson Matthey, 99.999%) were used as received. Reagent grade TiI$_4$ (Alfa, 99%), TiCl$_3$ (Fluka, >97%), ZrCl$_4$ (Aldrich, 99.9%), and HfCl$_4$ (Johnson Matthey, 99%) were purified using vapor transport in a 300 °C to room-temperature gradient. This purification allowed separation of the tetrahalide from lower halides and oxyhalides as described by Schäfer.[21]

Metathesis Reactions. Sodium phosphide and the appropriate metal halide, salt-balanced on a molar scale, were each ground separately with a mortar and pestle and then either stirred or ground together before reaction. Ignition reactions were carried out in a stainless steel reaction vessel (50-mm height, 48-mm o.d., 35-mm i.d.)[19] typically using 0.5 g of total starting reagents. When red phosphorus was added to the reaction it was ground in with the Na$_3$P. Half of the NaCl (or KCl or ZnS) added as a heat sink was ground with the Na$_3$P and half with the metal halide. A resistively heated Nichrome wire was used to initiate the reactions. Sealed-tube reactions were run in evacuated quartz tubes for 18 h at 1000 °C using 1.0 g of starting reagents and 2.0 g of NaCl as an inert additive to prevent ignition of the reactants. Products of all reactions were washed with methanol, water, and ethyl ether before being dried under dynamic vacuum for at least 1 h.

*CAUTION! Unreacted Na$_3$P reacts violently with water and can ignite methanol.*

Characterization. Powder X-ray diffraction patterns were taken using a Crystal Logic diffractometer with Ni-filtered Cu Kα radiation. X-ray patterns were scanned with 0.1° 2θ steps at 2 s/step. Lattice constants were calculated using linear regression on patterns taken with 0.02° 2θ steps. Line-broadening analysis was performed on the (200), (220), and (311) peaks of ZrP using the Scherrer equation[22] to calculate the average crystallite size. Silicon was used as an internal standard for both lattice-constant and line-broadening studies. Polypropylene film was used to cover air-sensitive X-ray samples.

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Figure 1. Powder X-ray diffraction patterns of ignition metathesis reactions between Na$_3$P and TiI$_4$, ZrCl$_4$, or HfCl$_4$ forming (a) h-TiP, (b) c-ZrP, and (c) c-HfP + h-HfP, respectively. The Miller indices for h-TiP and c-ZrP are given in (a) and (b), respectively, and * = c-HfP in (c).

Results

Solid-state metathesis reactions forming group 4 phosphides were ignited with a hot wire or carried out in sealed quartz tubes. These reactions follow the form shown in Eq 1 where M = Ti, Zr, or Hf and X = halogen.

$$MX_4 + {}^4/_3 Na_3P \rightarrow MP + 4NaX + {}^1/_3P \quad (1)$$
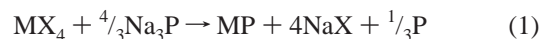
Both the Na$_3$P and the metal halide starting reagent are solids. Ignition with a hot wire initiates a fast, self-propagating reaction which is followed by rapid cooling over several minutes. A summary of the group 4 phosphide metathesis reactions carried out in this study is presented in Table 1.

TiI$_4$, ZrCl$_4$, and HfCl$_4$ were reacted with Na$_3$P in ignition reactions forming h-TiP, c-ZrP, and a mixture of c-HfP and h-HfP, respectively (Figure 1). Adding 3 and 6 mol equiv (approximately 0.5 and 1 wt equiv) respectively, of NaCl to the ZrP ignition reactions caused line broadening in the X-ray patterns, but the resulting products were still c-ZrP (Figure 2). Using the Scherrer equation,[22] the ZrP crystallite size was calculated to be 760 Å for the regular ignition reaction (Figure 2a), 250 Å when 3 mol of NaCl was added (Figure 2b), and 140 Å when 6 mol of NaCl was added to the reaction (Figure 2c). The addition of either 3 mol of KCl or 3 mol of ZnS to the reaction between ZrCl$_4$ and Na$_3$P still resulted in formation of c-ZrP exclusively. The average crystallite size was calculated to be 320 Å with KCl addition and 290 Å with ZnS addition. Reactions between Li$_3$P and ZrCl$_4$ also led only to cubic ZrP.

Metal halides were also reacted with Na$_3$P in sealed tubes at 1000 °C for 18 h producing only crystalline hexagonal products: h-TiP, h-ZrP, and h-HfP (Figure 3). In addition, when c-ZrP from an ignition reaction was heated in a sealed quartz tube for 18 h at 1000 °C, X-ray diffraction showed that it had converted completely to h-ZrP.
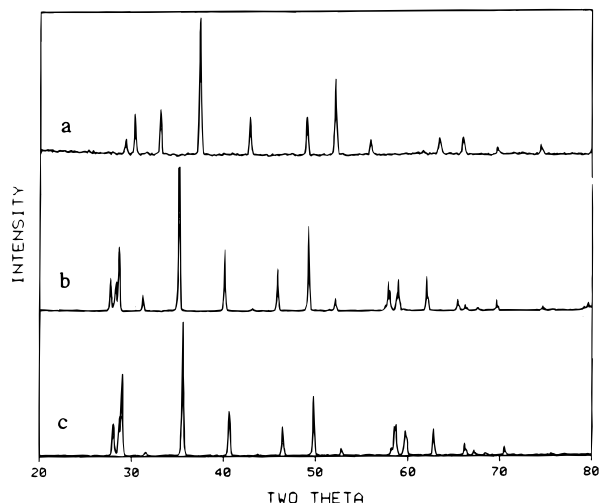
The reagent mixture preparation affects the products formed in a reaction (Figure 4). The X-ray pattern of crystalline HfCl$_4$ and Na$_3$P stirred together is shown in Figure 4a (note: no reaction has taken place). Grinding HfCl$_4$ and Na$_3$P together leads to a loss in crystallinity (Figure 4b). Running an HfP ignition reaction after the reagents were stirred together, after being ground individually, formed an approximately equal
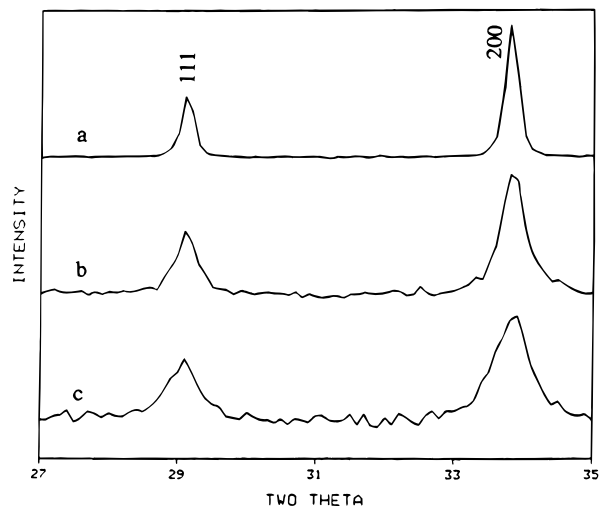
Figure 2. Expanded powder X-ray diffraction patterns of the (111) and (200) peaks of c-ZrP formed in ignition metathesis reactions with the addition of (a) no NaCl, (b) 3 mol equiv of NaCl (∼0.5 wt equiv), and (c) 6 mol equiv of NaCl (∼1 wt equiv) to the starting reactants.
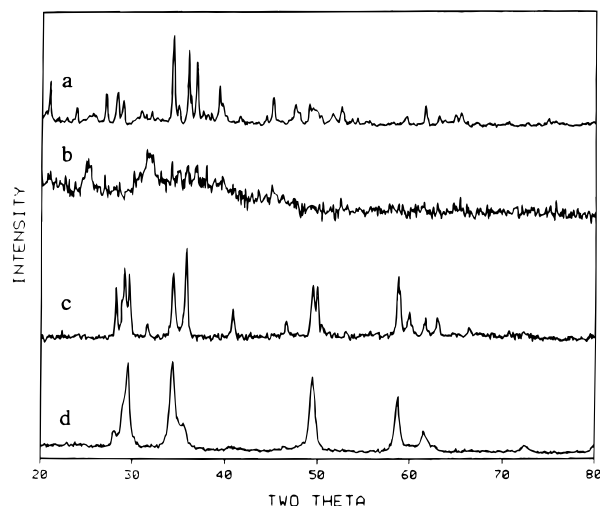

Figure 3. Powder X-ray diffraction patterns of sealed-tube metathesis reactions forming (a) h-TiP, (b) h-ZrP, and (c) h-HfP.

Figure 4. Powder X-ray diffraction patterns of HfCl₄ and Na₃P (a) stirred together, (b) ground together, (c) stirred together and ignited, and (d) ground together and ignited.

Table 2. Selected Group 4 Phosphide Lattice Parameters

product	lattice constant (Å)	literature values (Å)
ignited h-TiP	$a = 3.498(1)$, $c = 11.70(1)$	$a = 3.499(1)$, $c = 11.700(6)$[8]
ignited c-ZrP	$a = 5.275(1)$	$a = 5.27$[23]
ignited h-HfP	$a = 3.651(2)$, $c = 12.38(2)$	$a = 3.650$, $c = 12.37$[24]
ignited c-HfP	$a = 5.213(2)$	
sealed tube h-TiP	$a = 3.501(1)$, $c = 11.69(1)$	$a = 3.499(1)$, $c = 11.700(6)$[8]
sealed tube h-ZrP	$a = 3.691(1)$, $c = 12.55(1)$	$a = 3.677$, $c = 12.52$[23]
sealed tube h-HfP	$a = 3.650(4)$, $c = 12.39(2)$	$a = 3.650$, $c = 12.37$[24]

tography of an ignition reaction forming MoS_2 from $MoCl_5$ and Na_2S has shown that the peak temperature of a reaction can be reached in approximately one-third of a second, followed by rapid cooling of the products.[14] It is likely that the analogous short reaction times and rapid cooling are responsible for quenching the phosphide reactions, thus preserving the cubic phase. Sealed tube metathesis reactions carried out at 550 °C for 4 h also produce the metastable cubic phase.[20] This is likely to be due to the reaction igniting to create the cubic phase and the temperature (550 °C) and time (4 h) being insufficient to cause conversion to the thermodynamically stable hexagonal form.

The process by which these high-temperature cubic phases form is a question that needs to be addressed. Four possible explanations are considered. First and simplest, these reactions could be exothermic enough to reach the high temperatures at which the phase transition occurs. Second, the short reaction times in which the ignition reactions take place may prevent sufficient phosphorus from diffusing into the zirconium, thereby forming a phosphorus deficient cubic compound.[7] Third, the byproduct salt could assist in the crystallization of the cubic phases via templating. Finally, the conditions present in the ignition reaction may cause the cubic phase to nucleate first, followed by rapid quenching of the system. These four possibilities were investigated to determine which most likely causes the formation of metastable c-ZrP and c-HfP.

Using the calculated heat of reaction, heat capacities, heats of fusion, and heats of vaporization of the products, a theoretical maximum reaction temperature can, in principle, be calculated

mixture of c-HfP and h-HfP (Figure 4c). However, if the reagents were *ground* together in a mortar and pestle after individual grinding, an ignition reaction then formed mainly c-HfP with only a trace amount of h-HfP (Figure 4d).

A summary of all of the metathesis reactions performed is provided in Table 1. Most products were found, by X-ray diffraction, to be pure crystalline phosphides, and their lattice constants were in good agreement with values published in the literature,[8,24,25] as presented in Table 2.

Discussion

As with other literature syntheses of group 4 phosphides, sealed-tube metathesis reactions run at 1000 °C produce only the low-temperature hexagonal phase as expected (Figure 3). However, ignition reactions can form the cubic phase due to the manner in which these reactions take place (Figure 1). These highly exothermic reactions are very rapid. High-speed pho-

(23) Schäfer, H. *Acta Chem. Scand.* **1954**, *8*, 226.

(24) Jeitschko, N. *Monatsh. Chem.* **1962**, *93*, 1107.

(25) Unfortunately, an exact calculation could not be performed for the reactions given in eq 1 because no thermodynamic data are available for TiP, ZrP, or HfP.

for any metathesis reaction.[14] Reactions involving group 4 halides are typically predicted to reach the boiling point of the salt produced in the reaction.[25] In this case, the boiling point of the byproduct salt, NaCl, is 1413 °C.[26] This is very close to the phase transition temperature reported for ZrP, which is 1425 °C. To see if the maximum reaction temperature causes the formation of the cubic phase, NaCl was added to the system as a heat sink. Results of the salt additions are shown in Figure 2. Energy given off in the reaction now has to heat both the products and the heat sink, thereby lowering the maximum temperature reached in the reaction.[14] Because there is now less heat present to sinter the ZrP crystallites to larger sizes, the ZrP X-ray peaks have broadened. Note, however, that the product is still c-ZrP. Therefore, it can be concluded that the maximum reaction temperature is not responsible for the formation of the cubic phase.

Because cubic phase formation is not due to the maximum temperature, phosphorus deficiency was investigated next. Irani and Gingerich showed that their c-ZrP was relatively stable on heating in the absence of phosphorus, but converted to h-ZrP upon heating in the presence of phosphorus. This suggested that ignition metathesis reactions might not allow for sufficient diffusion of phosphorus to the zirconium resulting in cubic ZrP. However, when 0.25 g of red phosphorus was added to a 0.5 g ZrP ignition reaction, only c-ZrP was produced. Adding the extra phosphorus should alleviate the problem of insufficient phosphorus diffusion in the reaction, if it exists. In the presence of sufficient phosphorus the system still nucleates the high-temperature cubic phase. It can be concluded that, although phosphorus deficiency may be associated with c-ZrP, it is not responsible for its formation in metathesis reactions.

A third possibility is that the byproduct salt is assisting in the crystallization of the cubic phase via templating. Because there is only a 6.6% lattice mismatch between the lattice parameters of the byproduct salt NaCl ($a = 5.64$ Å)[26] and the product c-ZrP ($a = 5.27$ Å)[14] and the requirement for some epitaxial growth is a mismatch of $\leq 15\%$, templating is a possibility.[27] When Li_3P is substituted for Na_3P to produce the byproduct salt LiCl ($a = 5.14$ Å),[13] the result is still cubic ZrP; this is consistent because the lattice mismatch is only 2.5%. To further test the templating hypothesis, the salt KCl ($a = 6.29$ Å)[13] was added to the reaction. KCl has a 16% lattice mismatch with c-ZrP and would therefore not be expected to assist in the crystallization of the cubic phase. The reaction still yielded only cubic ZrP. As a further test, hexagonal ZnS was added to the $ZrCl_4/Na_3P$ reaction. Hexagonal ZnS would certainly not be expected to help form the cubic phase and might reasonably be expected to assist in the formation of the hexagonal phase. Interestingly, cubic ZrP was still the exclusive phosphide phase and the crystallite size decreased to 290 Å as may be expected for an inert additive. Hence, templating of the cubic phase can be ruled out.

It can be concluded that the high-temperature phases are most likely nucleating first and retained due to the rapid quenching of the system because neither maximum reaction temperature, phosphorus deficiency, nor a templating effect is responsible for cubic phase formation. Further evidence to support this conclusion comes from the HfP system when the reaction conditions are varied. If HfP and Na_3P are ground separately,

then stirred together and ignited, approximately equal amounts of c-HfP and h-HfP are observed in the product (Figure 4c). However, if the starting materials are ground separately, then *ground* vigorously together and ignited, the product is almost exclusively c-HfP (Figure 4d). The explanation for these results becomes clearer upon closer examination of the reactants before ignition. An X-ray pattern taken of the reactants just after stirring shows only peaks for $HfCl_4$ and Na_3P (Figure 4a). But the pattern of the reactants ground together is different in two obvious ways (Figure 4b). First, the diffraction peaks of the reactants are greatly reduced in intensity if not altogether eliminated. Second, two diffraction peaks emerge at ∼26° and ∼32° 2θ that can be assigned to the (111) and (200) lines of NaCl. From these two observations it can be concluded that the starting material lattices begin breaking down and the product salt, NaCl, starts to form. The formation of NaCl during the grinding stage lowers the amount of heat given off during ignition by forming some product ahead of time. Less heat given off with the ignition reaction means that the product is heated less and quenched sooner. This is why more c-HfP is observed and the diffraction peaks are broadened when the precursors are ground separately and then ground vigorously together and ignited.

The compound TiP has been predicted to undergo a hexagonal to cubic transition at a lower temperature than ZrP (1425 °C) does.[7] This study does not support this prediction. Both ignition and sealed tube metathesis reactions between TiI_4 and Na_3P form only h-TiP. No evidence was found in any of the TiP reactions that a phase transition takes place in this system. Additionally, a reaction between $TiCl_3$ and Na_3P produced exclusively hexagonal TiP, thereby ruling out a templating effect between the byproduct salt NaCl and cubic TiP.

Conclusions

Solid-state metathesis reactions can be used to rapidly synthesize metastable cubic phases of transition-metal phosphides. In contrast, sealed tube reactions between metal halides and sodium phosphide, at 1000 °C, lead exclusively to the low-temperature hexagonal phase. Salts were added to lower the maximum reaction temperatures to check whether the high temperatures reached in the rapid metathesis reactions were responsible for cubic phase formation. The lower temperatures produced by salt addition resulted in lower crystallinity, but still produced only the cubic phase. Because phosphorus deficiency can lead to cubic phases, excess phosphorus was added to the ignited metathesis reactions; however, the result was still exclusively the cubic phase. To test a possible templating effect, compounds with lattice mismatches greater than the 6.6% mismatch of NaCl were added to the metathesis reactions. The addition of KCl with a 16% lattice mismatch still resulted in cubic ZrP. Even the addition of hexagonal ZnS led only to cubic ZrP formation, essentially ruling out a templating effect. Hence, it appears most likely that the high-temperature cubic phases of ZrP and HfP are nucleated first and then quenched rapidly before the cubic phase can convert to the low-temperature hexagonal phase.

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(27) West, A. R. *Solid-State Chemistry and Its Applications*; John Wiley and Sons: New York, 1984.