Rapid Solid-State Precursor Synthesis of Materials

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Precursor reactions based on metathetical (exchange) pathways have been found to be an effective synthetic route for the preparation of a large number of materials. These solid-solid reactions are extremely rapid (typically less than 1 second) and often can be initiated at or near room temperature. They are potentially useful for controlling product particle size and for preparing high-quality cationic or anionic solid solutions. The frequently self-propagating and sometimes explosive behavior exhibited by these reactions can be attributed to the large amount of heat they release. As a consequence, thermodynamic considerations can be used to help select the best set of precursors as judged from reaction enthalpies. The factors that influence these reactions are illustrated by a discussion of MoS_2, ZrN, $MoSi_2$, and GaAs, examples of the many compounds accessible by this synthetic route.

DIRECT SOLID-SOLID REACTIONS [FOR EXAMPLE, Ti(s) + C(s) → TiC(s)] are often complicated by the need for long reaction times at elevated temperatures. Such kinetic constraints can usually be attributed to a limited amount of intimate contact between solid reactants and to long diffusion path lengths. An ongoing goal of synthetic solid-state chemistry is to minimize these effects through the rational design of alternative preparative routes.

One effective strategy, originally developed in the Soviet Union, is known as self-propagating high-temperature synthesis (SHS) (*1–4*). This is a direct reaction between the elements in which a compressed powder mixture is ignited to initiate a self-sustaining exothermic reaction. These combustion processes are usually over in a few seconds and can reach temperatures of thousands of degrees Celsius. The keys to this approach are: (i) intimate contact between finely divided reagents and (ii) a highly exothermic reaction. The first maximizes contact between reagents and minimizes diffusion path lengths, and the second provides a high "internal" heat source to further aid diffusion processes. Many materials have been produced by the SHS method, including borides, carbides, nitrides, and silicides. The maximum temperature possible for a given reaction can be calculated on the basis of thermodynamics of an adiabatic process (*5, 6*). Applying this concept, metal borides could reach temperatures from 1800 K (for MoB_2) to 3370 K (for TaB_2), metal nitrides 2900 K (AlN) to 4900 K (TiN or ZrN), metal carbides 1000 K (WC) to 3900 K (HfC), and metal silicides 1900 K ($MoSi_2$) to 3340 K (Nb_5Si_3) (*7*). When the adiabatic temperature exceeds ~1800 K a self-propagating reaction can occur after initiation (*8*). Below this temperature the reactants need preheating before initiating the combustion reaction.

The advantages of the SHS method lie in the potential energy and cost savings over conventional synthetic routes. High-purity products are possible because of the volatilization of contaminants. High cooling rates can result in reactive products that can be readily sintered (*8*). Additionally, pressure can be applied to improve product density (*9*). Disadvantages of the SHS method include acquiring starting elements in finely divided form, incomplete conversion to products, and the need for further processing.

Another synthetic approach involves the use of precursors. These reagents are more reactive than the elements and can offer access to gas-phase and solution pathways, as well as to improved solid-state routes. Predominant among precursor methods are those based on the decomposition of "single-source" precursors. Typical examples include the pyrolysis of the gas-phase precursor $[(CH_3)_2Al(NH_2)]_3$ to produce aluminum nitride (*10*) and the decomposition of the solid-state precursors $(NH_4)_2M(CrO_4)_2 \cdot nX$ (M = Mg, Ni, Cu, or Zn; $n = 6$ for X = H_2O and $n = 2$ for X = NH_3) to produce important mixed metal spinels, MCr_2O_4 (*11*). This approach has the obvious advantage of atomic-scale mixing. Single-displacement reactions are also common precursor routes. Here two reactants come together, with at least one in the gas phase, to provide a more dynamic reaction interface. Examples include the formation of ZrN from the metal hydride and nitrogen gas (*12*) and the synthesis of gallium arsenide in hydrogen from $AsCl_3$ and gallium metal (*13*).

Not so common among the precursor methods are those based on metathetical (exchange) reaction pathways. This approach, though necessarily requiring the use of two precursors, can be done in the liquid, gas, or solid state. Chianelli and Dines (*14*) have carried out a series of investigations on the synthesis of transition-metal dichalcogenides in solution. Transition-metal chlorides were found to react with lithium sulfide in nonaqueous solvents to produce metal disulfides (MS_2, M = Ti, Zr, Hf, and V) and lithium chloride (Eq. 1):

$$MCl_4 + 2\,Li_2S \rightarrow MS_2 + 4\,LiCl \qquad (1)$$

The resulting metal dichalcogenides are typically amorphous but can be crystallized on heating (to ≥400°C). Gas-phase metathesis reactions are exemplified by the synthesis of silicon nitride from silicon tetrachloride and ammonia (Eq. 2) (*15*):

$$3\,SiCl_4 + 4\,NH_3 \rightarrow Si_3N_4 + 12\,HCl \qquad (2)$$

Relatively few examples of solid-state metathesis reactions are known. Hilpert and Wille (*16*) reported the preparation of mixed

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metal ferrites at moderate temperatures (400° to 500°C) by the reaction:

$$MCl_2 + Li_2Fe_2O_4 \rightarrow MFe_2O_4 + 2\,LiCl \quad (3)$$

Similar methods have been used for the synthesis of chromites (*17*).

The limited number of investigations into solid-state metathesis reactions suggested to us the need to explore this approach as a viable precursor method. We have found these reactions to be an extremely powerful synthetic route; these reactions can self-initiate at room temperature, internally produce enough heat to be self-sustaining, and yield crystalline products in seconds. We have applied this approach to a broad range of compounds, including transition-metal, main-group, rare-earth, and alkaline-earth chalcogenides (O, S, Se, and Te) (*18–23*) and pnictides (N, P, As, and Sb) (*24, 25*), as well as selected carbides and silicides. Many of these compounds are important refractory, electronic, magnetic, and catalytic materials. Two significant features, not typically seen in other precursor methods, are the facile control of crystallinity and the ability to prepare both cationic and anionic solid solutions (*21, 26*).

Synthesis of Molybdenum Disulfide

Metathesis reactions allow the preparation of pure materials in seconds. Typical syntheses are carried out with metal-halide and alkali-metal main-group precursors. These reagents are ground separately and combined. Reactions are usually initiated in one of three ways; self-initiation on light mixing or grinding, local heating with a hot filament, or low-temperature heating in an evacuated sealed vessel. The particular method used depends on the activation energy and facility of the reaction. [Warning: Solid-state metathesis reactions can be quite exothermic, and in a sealed system, potentially explosive due to high gas pressures (*22, 23*). Ideal gas law calculations should be carried out before any reaction is performed.] After reaction, the product mixture contains both the desired material and an alkali-metal halide salt by-product; the latter is simply washed away with an appropriate solvent.

Molybdenum disulfide, an important lubricant, catalyst, and battery cathode material, is readily prepared by a metathetical pathway (*20*). Although many precursor pairs are possible, $MoCl_5$ and Na_2S have been found to be the most effective (Eq. 4):

$$MoCl_5 + 5/2\,Na_2S \rightarrow MoS_2 + 5\,NaCl + 1/2\,S \quad (4)$$

This reaction is carried out in a helium-filled drybox and self-initiates on light mixing at room temperature. The series of photographs in Fig. 1, obtained with a high-speed movie camera, show the evolution of the reaction process as carried out in an agate mortar. After a short induction period (~30 s), an intense white flash of light is observed along with a small mushroom cloud of volatilized sulfur by-product. The time from initiation to the peak of the reaction is less than 0.5 s. The final two frames (>0.5 s elapsed time) show the cooling down of the dark product mixture. Yellow elemental sulfur can be seen deposited away from the product. The pure, crystalline MoS_2 is isolated by washing the product with methanol to remove any unreacted $MoCl_5$ and water to remove sodium chloride and any unreacted Na_2S. Excess sulfur can be removed with chloroform or carbon disulfide, although this is often not necessary because it essentially all boils away during the reaction. The percent yield for the reaction is typically 80% of theoretical. The x-ray powder-diffraction pattern of the MoS_2 sample made from precursors in seconds (Fig. 2B) can be compared to one made from the elements in 5 days at 900°C (Fig. 2A). Both of the samples exhibit a high degree of crystallinity. Thermogravimetric analysis (TGA) of the MoS_2 metathesis reaction product in hydrogen at 1000°C showed the sulfur content to be within 0.1% of the theoretical value.

Thermodynamic Considerations

A conscious exploitation of thermodynamics has greatly contributed to the success of these metathesis reactions. By designing reactions in which the formation of by-products is extremely favorable, we are able to direct the formation of the

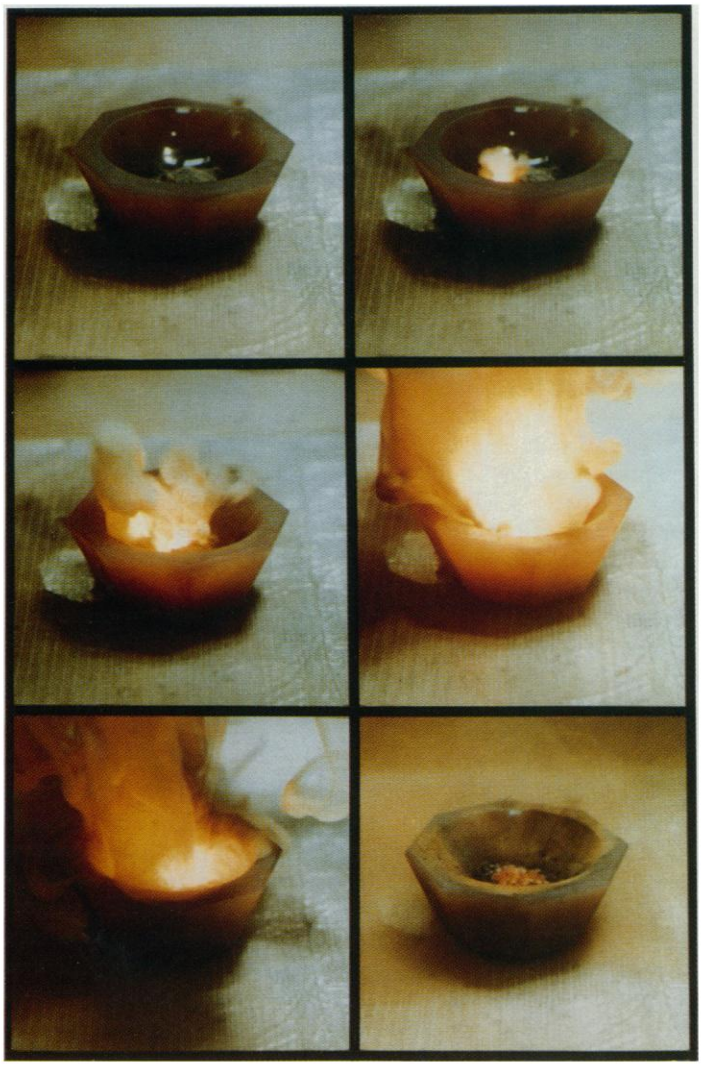


Fig. 1. The exothermic reaction between $MoCl_5$ and Na_2S in an inert helium atmosphere yields crystalline MoS_2 within seconds. After mixing the reactants together in an agate mortar, an induction period ensues before the reaction spontaneously ignites. The first frame shown (upper left) is after an ~30-s induction period, and the subsequent frames (moving left to right and down) are 0.06, 0.12, 0.31, 0.88, and 3.44 s after frame one. [Photographs by Richard Mantonya]

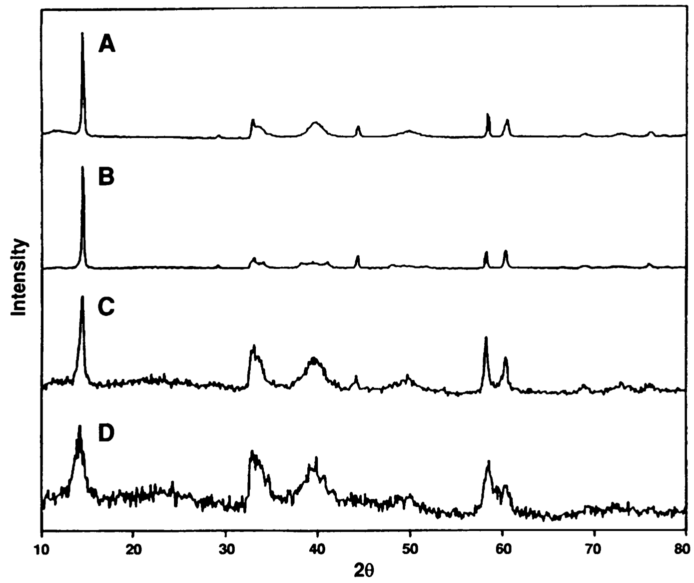
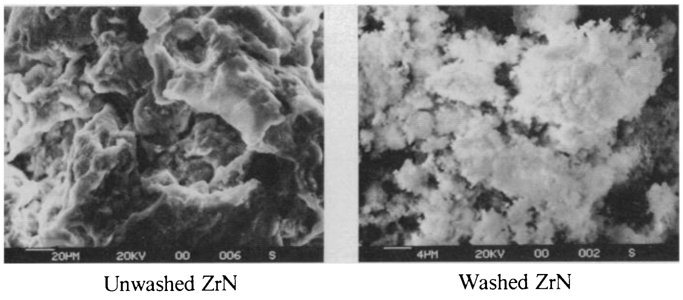


Fig. 2. Normalized x-ray powder diffraction patterns of MoS_2: (**A**) from the elements heated to 900°C for 5 days; (**B**) from the metathesis reaction of a $MoCl_5$ and Na_2S mixture; (**C**) from a mixture as in (B) with 4 mol of NaCl added per mole of $MoCl_5$; and (**D**) from a mixture as in (B) with 16 mol of NaCl added per mole of $MoCl_5$. X-ray patterns were collected on a diffractometer equipped with Ni-filtered Cu Kα radiation in increments of 0.05° 2θ at 5 s per step.

desired phase. Also, by maximizing the heat generated in these processes the reactions can become self-propagating. By-products are usually chosen to be alkali-metal halides. The formation of these salts is thermodynamically very favored and acts as a very effective driving force. Consequently, the exothermicity of the reactions is so great that the heat released is enough to actually melt the halide salt by-product. Melt formation is thought to contribute to the self-propagating nature of these reactions; the molten salt forms a solution in which the reactants can more easily diffuse. If the diffusion and reaction rates of the precursors are very fast, a "chain" reaction can ensue and the overall process, short in duration (often <1 s), can be quite vigorous. Evidence for salt formation is shown in Fig. 3. Unwashed products from the reaction $ZrCl_4$ and Li_3N to form ZrN show the smooth continuous surfaces expected for an alkali halide (LiCl) melt. The washed sample contains submicrometer size particles of x-ray–pure cubic ZrN.

The amount of heat released in these metathesis reactions can be quantified by a straightforward consideration of thermodynamics. In the MoS_2 system, for example, the heat of reaction (ΔH_{rxn}) calculated from Hess's law is −213 kcal/mol (*27*). This is consistent with bomb calorimetry experiments that yield −174 ± 5 kcal/mol, considering the product yield was 80%. The magnitude of the heat released in this type of reaction is comparable to the heats of reaction for the thermite reaction ($Al + 1/2\ Fe_2O_3 \rightarrow 1/2\ Al_2O_3 + Fe$, $\Delta H_{rxn} = -102$ kcal/mol) and for the combustion of low molecular weight hydrocarbons, such as methane ($\Delta H_{rxn} = -210$ kcal/mol) (*28*).

An estimate of the maximum temperature of a particular reaction can be made from a consideration of the calculated ΔH_{rxn}, heat capacities, heats of fusion (ΔH_{fus}), and heats of vaporization (ΔH_{vap}) of the products (*29*). The rapidity of these reactions makes reasonable the assumption that they are psuedo-adiabatic. In Fig. 4A, a plot of enthalpy (heat) versus temperature illustrates where heat is consumed for the products from the reaction of $MoCl_5$ and Na_2S; specifically, 1 mol of MoS_2, 5 mol of NaCl, and 1/2 mol of elemental sulfur (Eq. 4). In this process, heat is consumed by the products during phase transitions as well as by simply raising the temperature of the materials. The phase transitions for the melting of sulfur (388 K), boiling of sulfur (882 K), melting of NaCl (1074 K), and boiling of NaCl (1686 K) are seen as plateaus. Enough heat is produced in this process (−213 kcal/mol, as indicated by the vertical line in Fig. 4) to reach a maximum temperature of 1686 K, the boiling point of NaCl. Insufficient heat is produced, however, to completely volatilize all of the NaCl present. Optical pyrometry (*20*) determined that the minimum temperature reached by this reaction is ~1400 K. This value limits the actual maximum temperature to a range of 1400 to 1700 K.



Unwashed ZrN

Washed ZrN

Fig. 3. Scanning electron micrographs of the ZrN reaction products before and after washing.

Similar synthetic methods can be used to prepare other transition-metal dichalcogenides. Layered sulfides (*20, 21*), such as WS_2, NbS_2, and TaS_2, are accessible with the halide precursors WCl_6, $NbCl_5$, and $TaCl_5$, respectively. Layered selenides (*20, 21*) can be synthesized from metal halides with the precursor Na_2Se. Three-dimensional network sulfides (pyrite structure) (*19*) of late transition metals like NiS_2 are best prepared from a high-oxidation-state fluoride precursor like K_2NiF_6.

Particle Size Control

One of the important features of this synthetic method is its use in the control of particle (crystallite) size. Fine-grain, high-surface-area materials are especially important in ceramics processing. Refractory materials can be processed to form more dense, and potentially fully dense, ceramics from small submicrometer particles (*30*). Further use of small particles is seen in the area of catalysis. High-surface-area catalysts offer more active sites for a given weight of material.

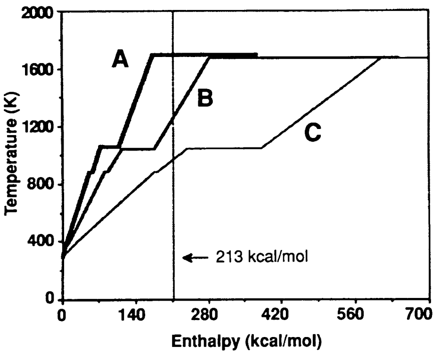


Fig. 4. Plot of enthalpy versus temperature as calculated for the products from the reaction of $MoCl_5$ and Na_2S: (**A**) with no salt added; (**B**) in the presence of 4 mol of NaCl per mole of $MoCl_5$; and (**C**) in the presence of 16 mol of NaCl per mole of $MoCl_5$. The value for the heat released in the reaction (213 kcal/mol) is indicated by the vertical line.

Table 1. Particle size control through the addition of NaCl. All values were obtained from the (002) reflection and were calculated relative to MoS_2 prepared from the elements at 900°C.

$MoCl_5$:NaCl (molar basis)	Particle size (Å)
1:0	450
1:4	180
1:16	80

The particle size of the products from a metathesis reaction are easily controlled through the addition of an inert additive. In the case of MoS_2, NaCl is used as the additive. Although any inert material could have been used, an alkali-metal salt like NaCl can potentially assist in the reaction when it melts at high temperature and can be easily removed after the reaction. In Fig. 2, C and D, are shown the x-ray powder-diffraction patterns of MoS_2 samples synthesized in the presence of 4 mol of NaCl per mole of $MoCl_5$, and 16 mol of NaCl per mole of $MoCl_5$, respectively. The diffraction peaks broaden with increasing amounts of NaCl. The reduction in particle size can be related to the peak broadening through the use of the Scherrer and Warren equations (*31*). The estimated particle size for the MoS_2 samples are presented in Table 1. The average size of MoS_2 crystallites can be lowered into the nanocrystalline range.

The addition of salt to these reactions serves to lower the overall reaction temperature. The effects of the addition of salt on the estimated maximum temperature for the MoS_2 reaction are seen in Fig. 4B (4 mol of NaCl to 1 mol of $MoCl_5$) and Fig. 4C (16 mol of NaCl to 1 mol of $MoCl_5$). As would be expected, the additional salt shifts the curves to the right, which results in a lowering of the estimated maximum temperature to ~1250 K for the 4:1 (NaCl:$MoCl_5$) sample and to ~950 K for the 16:1 (NaCl:$MoCl_5$) sample. The lower temperature correlates with lower crystallinity.

Solid Solutions

Another important feature of these precursor reactions is that they can be readily extended to the preparation of high-quality solid solutions. Such materials are important for the fine tuning of properties intermediate between two isostructural compounds. The band gap of a set of semiconductors (AY and BY in $A_{1-x}B_xY$), for instance, can be varied continuously over the range $0 \leq x \leq 1$ as a function of x. The metathesis route offers a diverse set of precursors with an advantage over other methods in that both mixed anion and mixed cation reagents are readily accessible. We have successfully prepared mixed anion solid solutions (*21, 25, 26*) such as $Mo(S,Se)_2$, $W(S,Se)_2$, Gd(P,As), Sm(P,As), and Ga(P,As) from the precursors $Na_2(S,Se)$ and $Na_3(P,As)$. These precursors are solid solutions themselves and can easily be prepared from ammonia solutions [$Na_2(S,Se)$] or by direct reaction between the elements [$Na_3(P,As)$]. Precursors do not have to be solid solutions to be successful. Cationic solid solution compounds of $(Mo,W)S_2$ were readily prepared from the cocrystallized mixed molecular precursor ($MoCl_5 \cdot WCl_6$).

The solid solutions produced by metathesis reactions are of high quality in that the mixed ions (for example, A and B in $A_{1-x}B_xY$) are evenly dispersed throughout the lattice. This can be seen in the compound $Mo_{1-x}W_xS_2$ ($0 \leq x \leq 1$) by an analysis of alloys formed from the reduction of these compounds in hydrogen. Figure 5, A to E, shows the high angle reflection (123) of alloys prepared from a physical mixture of Mo and W metal heated to 1000°C for 6 days, $Mo_{0.5}W_{0.5}S_2$ prepared from the elements at 1000°C over a 4-day, 2-week, and 4-week period, and $Mo_{0.5}W_{0.5}S_2$ prepared through a metathesis reaction, respectively. The $Mo_{0.5}W_{0.5}S_2$ solid solution prepared in seconds from precursors is at least comparable in quality to materials made from the elements after an extensive heating regimen.

Ceramic Materials

A large part of our research effort has been directed toward the synthesis of high-temperature ceramics. These materials, including nitrides, carbides, and silicides, often display high melting points (>2000 K) coupled with technologically important properties (such as hardness, chemical resistance, and metallic conductivity). When prepared by direct reaction between the elements, syntheses typically require long heating times at temperatures greater than 1500 K (*32*). The SHS reactions have been useful in the synthesis of these materials, but in some instances self-sustaining reactions cannot be initiated at room temperature (*4*).

Zirconium nitride and molybdenum disilicide are two of the many refractory materials synthesized by solid-state metathesis reactions. Zirconium nitride (melting point ~3300 K) is readily prepared by an exchange reaction between $ZrCl_4$ and Li_3N (Fig. 3 and Eq. 5):

$$ZrCl_4 + 4/3\ Li_3N \rightarrow ZrN + 4\ LiCl + 1/6\ N_2 \qquad (5)$$

In this case, yields as high as 90% can be achieved with millimolar quantities of reagents. Molybdenum silicide, because of its high melting point (~2200 K), electrical conductivity, and high resistance to oxidation and corrosion, is an especially desirable refractory material. This compound is commonly used as a heating element in furnaces operated at temperatures up to 2000 K or more in air. It can be prepared from the precursors $MoCl_5$ and Mg_2Si in an especially vigorous reaction. The heat of reaction (−253 kcal per mole of

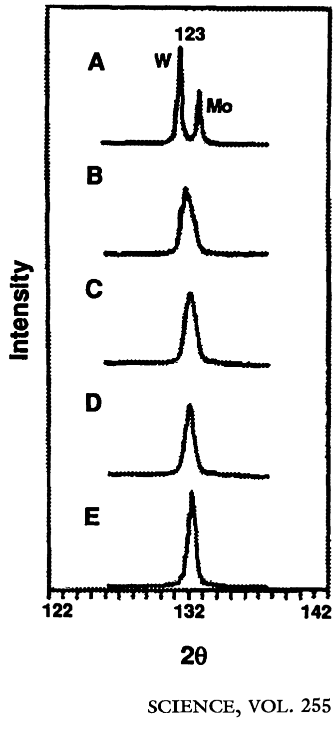


Fig. 5. X-ray powder diffraction patterns of: (**A**) Mo and W heated at 1000°C for 6 days; (**B** to **E**) alloys resulting from the reduction of the indicated compounds with H_2 at 920° to 950°C for 24 to 30 hours: (B) $Mo_{0.5}W_{0.5}S_2$ prepared from the elements heated at 1000°C for 4 days; (C) $Mo_{0.5}W_{0.5}S_2$ from the elements heated at 1000°C for 2 weeks; (D) $Mo_{0.5}W_{0.5}S_2$ from the elements heated at 1000°C for 4 weeks; and (E) $(Mo,W)S_2$ from the reaction of $MoCl_5 \cdot WCl_6$ and Na_2S.

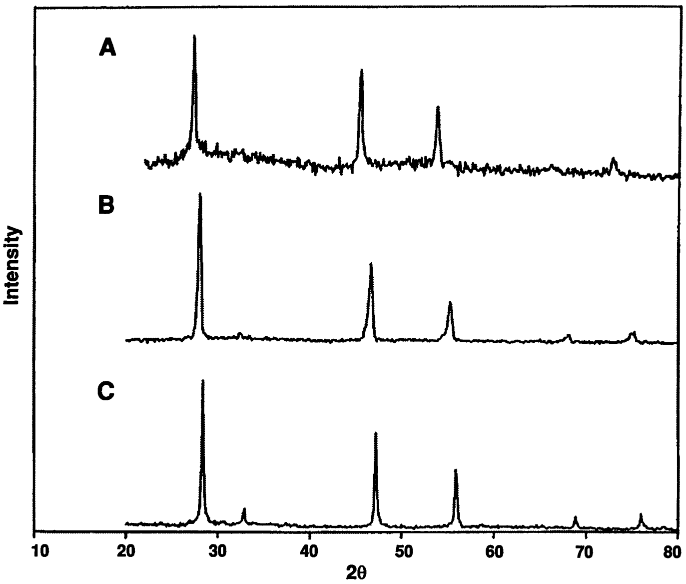


Fig. 6. Normalized x-ray diffraction patterns of (**A**) GaAs, (**B**) Ga(P,As), and (**C**) GaP, prepared from the reaction of GaI_3 and Na_3As, $Na_3(P,As)$, and Na_3P, respectively.

$MoCl_5$) is even more exothermic than the formation of MoS_2; here the estimated maximum temperature is found to exceed 2290 K, well above the boiling point of $MgCl_2$. The exothermicity of this reaction exceeds that of a comparable SHS reaction. Also, this reaction initiates near room temperature, whereas the SHS system must be preheated before initiation (*4*).

Electronic Materials

Metathesis reactions can be effective in the synthesis of important electronic materials. Semiconductors, insulators, metals, and low-temperature superconductors have all been prepared by solid-state precursor reactions. One significant area is the preparation of III–V semiconductors. Compounds such as GaAs and GaP can be prepared readily by reaction of GaI_3 with Na_3As and Na_3P, respectively (*24*).

An especially important feature to electronic materials, as stated above, is the ability to prepare solid solutions over a complete range of composition. Solid solution semiconductors, for example, are important for optoelectronic devices (*33*). In this work, we have prepared solid solutions of GaP and GaAs. These materials, $GaP_{1-x}As_x$, can be prepared over the complete range of composition $0 \leq x \leq 1$ and follow Vegard's law. The x-ray powder diffraction pattern of Ga(P,As) is shown in Fig. 6, along with GaP and GaAs. The peak positions clearly shift to lower 2θ (larger *d*-values) as the larger arsenic anion is substituted for phosphorus. Note that alkali-metal impurities could potentially effect semiconducting properties.

General Considerations

Solid-state metathesis reactions offer a rapid method for synthesizing an extensive range of materials. The resplendence of this method is its vast range of potential precursors. The combination of any metal-halide and alkali-metal main group, or as seen in the case of $MoSi_2$, an alkaline-earth main group (Mg_2Si), can be considered once suitable thermodynamic criteria have been met. These criteria, however, do not always require reactions to be extremely exothermic; we have found that even mildly exothermic reactions [such as $CuF_2 + Na_2O_2 \rightarrow CuO + 2NaF + 1/2\ O_2$, $\Delta H_{rxn} \approx -61$ kcal/mol (*18*)] can be successful. A further appeal of these reactions is the ease in which solid materials can be handled. Solids, like Na_2S and Na_3P, are much more manageable than the respective toxic gases, H_2S and PH_3.

The full scope of this synthetic approach has yet to be determined. We are presently directing our efforts toward a more basic understanding of the reaction mechanisms and a development of this method for the synthesis of novel compounds. Recently we have synthesized the high-temperature (>1700 K) form of ZrP directly from $ZrCl_4$ and Na_3P. The use of this precursor route to access metastable phases could be significant in the development of new materials.

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29. All thermochemical values and melting and boiling points were obtained from (*27*) with the exception of the boiling point of NaCl, which was obtained from (*28*). Melting points and boiling points were rounded off to the nearest 100 K to simplify calculations. The melting point of MoS_2 was assumed to be $>>1700$ K. Its melting point, reported to be 2023 K under 1 atm S_2(g), can be lowered as much as 350 K at lower S_2(g) pressures. Because in the reaction 0.5 mol of sulfur are produced for every mole of MoS_2, the assumption appears to be reasonable.
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