Reviews

Synthesis of Refractory Ceramics via Rapid Metathesis Reactions between Solid-State Precursors

Edward G. Gillan[1] and Richard B. Kaner*

Department of Chemistry and Biochemistry and the Solid State Science Center, University of California, Los Angeles, California 90095-1569

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Chemical exchange (metathesis) reactions are used in many syntheses of important solids. While metathesis reactions in the liquid and gas phase are well-known, metathesis reactions from solid-state precursors have received much less attention. This review details work on the synthesis of refractory ceramics via rapid metathesis reactions between solid metal halides and alkali (or alkaline earth) metal main group compounds (e.g., Li_3N or MgB_2). The discussion includes thermodynamic considerations in choosing appropriate precursor couples. Through a careful choice of precursors, rapid, highly exothermic reactions can reach high temperatures (>1000 °C) on very short time scales (<1 s). The products are often crystalline and single phase with crystallite sizes varying from tens of angstroms to a few microns, depending on the refractory nature of the material and the reaction conditions (i.e., scale and the use of inert additives). The utility of this metathesis route is demonstrated by metal nitride, boron nitride, and metal boride systems. Additionally, metastable cubic zirconium oxide and phosphide phases are mentioned. Since these reactions can be considered pseudoadiabatic, maximum reaction temperatures (T_{ad}) can be calculated using thermodynamic relationships. The calculated T_{ad}'s agree well with experimental measurements carried out using in situ thermocouples. Calculating the value of T_{ad} at an intermediate point in a reaction (for salt and element formation only) is found to be a useful tool in predicting reaction propagation. Self-propagating reactions generally occur after localized initiation when the intermediate T_{ad} value is greater than the melting point of the byproduct salt.

Introduction and Background

Synthesis of Solid Compounds. Solid-state synthesis has traditionally involved high-temperature reactions between elements as represented in eq 1 and/or

$$A + B \rightarrow AB \qquad (1)$$

metal-containing compounds to yield crystalline, homogeneous products.[2] Since the starting materials frequently have high melting points and low vapor pressures, overcoming diffusion barriers is an important consideration. The rate of reaction between two solids is directly related to the surface contact between grains of each solid and slow solid-state diffusion often results in long reaction times.[3] Various means have been used to increase diffusion rates in solid−solid reactions, including the use of high reaction temperatures (>1000 °C), high surface area starting materials (achieved through grinding, ball milling, or precipitation) and extreme conditions such as arc melting.[4] Performing solid-state reactions in molten fluxes or high-temperature solvents (e.g., Bi, Sn, halide salts, or alkali metals) is another method which has served to increase the diffusion and reactivity of solids.[5] Over the past few decades processes have been developed which involve rapid reactions between elements. This general route, known as self-propagating high-temperature synthesis (SHS), uses the fact that fine elemental powders can be ignited to produce a combustion-like reaction if the heat of formation of the product is sufficiently exothermic.[6] In recent years this approach has resulted in a wide variety of ceramics and alloys including elemental solid−solid (e.g., TaC, TiB_2, NiTi, and Al_3Ti)[7] and solid−

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(1) Current address: Department of Chemistry, Rice University, Houston, TX 77005.

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gas (e.g., TiN and NbN)[8] reactions.

In the past two decades the increasing demand for solid materials (e.g., ceramics, refractories, intermetallics, and semiconductors) with a wide range of controllable properties (e.g., phase, composition, and structure) and morphologies (e.g., nanocrystals, thin films, or porous solids) has led to an explosion of materials-based chemical research.[4,9,10] One well-developed synthetic method is the controlled hydrolysis of metal alkoxides (sol−gel) to form porous, often transparent, oxide glasses with a range of useful and controllable properties.[11,12] Another example of precursor-based synthesis involves the use of organic/inorganic polymers to form non-oxide ceramic films or powders when decomposed at high temperatures. These include the commercially successful polycarbosilane family of polymers, $(Si_xC_yH_z)_n$, which are precursors to SiC,[13] and more recently, polymeric precursors to Si_3N_4,[14] BN,[15] and ceramic composites.[16] Reactive organometallic precursors have also been decomposed under relatively facile conditions to deposit metal films,[17] GaAs,[18] nanocrystalline GaP,[19] and InP,[20] insulating metal nitride films (M_3N_4 where M = Zr or Hf),[21] and metastable cubic GaS.[22]

Exchange Reactions in Materials Synthesis. In one aspect or another, all chemical syntheses involve some form of bond rearrangements. Traditionally, reactions in which only one of the precursors gives up one of its constituents to another precursor (generally AB + C → A + BC) are known as single-displacement reactions, while reactions with both precursors exchanging components are called double displacement or double-decomposition reactions:

$$AB + CD \rightarrow AC + BD \quad (2)$$

Many of the syntheses of solid-state materials proceed via decomposition or exchange (metathesis) processes. For example, aqueous reactions such as metal oxide precipitations from a solution of metal (M) ions (often from a dissolved nitrate or carbonate salt)[23] are ultimately metathesis-like processes and exhibit intimate mixing of reactive species:

$$M(NO_3)_x(aq) + xNaOH(aq) \rightarrow MO_{x/2} + xNaNO_3(aq) + x/2H_2O \quad (3)$$

Sol−gel reactions forming silica glasses similarly proceed via an exchange of a hydroxide group of water with an alkoxide group on the silicon alkoxide:[11]

$$Si(OR)_4 + 4H_2O \rightarrow Si(OH)_4 + 4ROH \quad (4)$$

A subsequent loss of water leads to the silica (SiO_2) product. Solution metathetical reactions producing non-oxides are also known in which metal halides react with alkali compounds to form chalcogenides[24] and pnictides:[25]

$$TiCl_4 + 2Li_2S \rightarrow TiS_2 + 4LiCl \text{ (in THF)} \quad (5)$$

$$GaCl_3 + Na_3P \rightarrow GaP + 3NaCl \text{ (in diglyme)} \quad (6)$$

These solution-phase metathesis reactions exhibit characteristically small diffusion barriers limited primarily by bond rearrangements. The resulting precipitate from reactions of this type is often amorphous or nanocrystalline, although high-temperature sintering will generally produce a crystalline product.

There are numerous examples of vapor phase reactions which involve the exchange of atoms or molecular fragments forming metal pnictides[26] and nitrides:[21,27]

$$GaCl_3 + AsH_3 \rightarrow GaAs + 3HCl \quad (7)$$

$$3M(NR_2)_4 + 4NH_3 \rightarrow M_3N_4 + 12HNR_2 \quad (8)$$

$$MCl_x + x/3NH_3 \rightarrow MN + xHCl + \frac{(x-3)}{6}N_2 \quad (9)$$

The formation of metal nitrides by high temperatures from solid metal oxides and ammonia also serve as examples of metathesis reactions:

$$MO_{3y/2} + yNH_3 \rightarrow MN_y + 3y/2H_2O \quad (10)$$

Recent mixed metal nitride reactions[28,29] follow this reaction path, although other side products (e.g., N_2) are formed if the metal is reduced during this process.

Many well-known industrial solid-state reactions are driven by exchange processes; for example, carbothermic

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and aluminothermic routes to metal formation:[30]

$$MO_{2x} + xC \rightarrow M + xCO_2 \qquad (11)$$

$$MO_{3x} + 2xAl \rightarrow M + xAl_2O_3 \qquad (12)$$

Both routes rely on the production of very stable byproducts to drive the single-displacement reactions to completion. Sometimes only a short external initiation is needed, such as igniting a magnesium ribbon in an aluminothermic reaction. Another industrial route for producing pure metals provides a particularly interesting example of a single-displacement reaction. The Kroll process[2a,30] involves reacting a metal halide and an alkaline earth metal (usually magnesium). An exothermic reaction occurs at elevated temperatures (>900 °C) between the metal halide and molten magnesium. The overall reaction is

$$MX_n + n/2Mg \rightarrow M + n/2MgX_2 \qquad (13)$$

where X is a halide (F, Cl, Br, or I). The heat of formation of the salt ranges from −269 kcal/mol (MgF_2) to −87 kcal/mol (MgI_2) and drives the reaction to the right. Conveniently, the byproduct salt is simply washed away with water, leaving the pure metal behind. This is a common industrial process for the purification of metals since the starting metal halides often originate from the halogenation of crude metal ore.

There are relatively few examples of solid-state metathesis reactions which form salt byproducts, with a few notable exceptions. In 1902, Guntz et al.[31] were performing experiments on the reactivity of Li_3N, which was synthesized soon after Li was first isolated. They reported that late transition-metal halides (e.g., $FeCl_3$ or $CuCl_2$) react with Li_3N in an "incandescent" manner when the mixtures are heated in an oven to 500 °C:

$$3CuCl_2 + 2Li_3N \rightarrow \text{"}Cu_3N\text{"} + 6LiCl + 1/2N_2 \qquad (14)$$

At the time the products were not fully identified, but there were indications of metals and metal nitrides. Interestingly, the authors attributed the exothermic nature of the reactions to the fact that a very thermodynamically stable salt (LiCl) was also formed. Thirty years later Hilpert and Wille were experimenting on synthetic routes to mixed-metal oxides, specifically ferrites (MFe_2O_4),[32] and found that by combining metal halides with mixed-metal oxides (e.g., $Li_2Fe_2O_4$) and heating the mixture in a furnace at 500 °C, they could produce relatively pure mixed-metal oxides:

$$MnCl_2 + Li_2Fe_2O_4 \rightarrow MnFe_2O_4 + 2LiCl \qquad (15)$$

The lithium halide byproduct was easily removed with water. Recent survey work on similar sealed-tube metathesis reactions by Parkin and others have shown that a wide range of oxides,[33,34] nitrides,[35] pnictides,[36] and chalcogenides[37] can be formed by this method. There are also reports of a modified Kroll-type process which produces rare-earth alloys.[38]

Solid-State Metathesis Routes

General Properties. Over the past few years our research has focused on the development of solid-state metathesis (SSM) reactions motivated by the desire to provide an alternate, rapid route to important solid-state compounds.[39] This combustion-like synthetic technique rapidly produces **crystalline** compounds without continuous external heating. Reactions occur between solid metal halides and alkali or alkaline-earth main-group compounds. The reactive solids generally initiate rapid self-propagating reactions upon mixing, grinding, or brief contact with a heated filament. The precursors are selected such that the resulting reaction is highly exothermic. This allows the reaction to produce enough heat to enter a self-sustaining mode and to rapidly reach temperatures generally greater than 1000 °C. The products of this synthetic route typically have small crystallite sizes as a consequence of the very short reaction times (<1 s). The desired product is easily separated from the salt byproducts and any unreacted starting materials by washing with alcohol and/or water. By a careful choice of precursors, it is possible to synthesize well-mixed solid solutions and, occasionally, metastable phases. Over the past five years our group has reported on rapid SSM reactions that form crystalline NiS_2,[40] MoS_2,[41] GaAs and other III−V (13−15) semiconductors,[42] in addition to successful syntheses of transition-metal phosphides,[43] oxides,[44]

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and other metal alloys (e.g., aluminides and silicides).[44b,45] Reactions forming mixed-metal solid solutions (e.g., $Mo_xW_{1-x}S_2$),[46] as well as metal mixed-anion solid solutions (e.g., MoS_xSe_{2-x}[47] and GdP_xAs_{1-x}[48]) have been achieved. Recent results on refractory metal nitride,[49] boron nitride,[50] and metal boride[51] systems are detailed below.

Selection of SSM Precursors. The general reaction of a metal halide with an alkali-metal main-group compound may be written as

$$MX_n + n/mA_mL \rightarrow ML_y + nAX + (n/m - y)L \quad (16)$$

where M is a metal, X is a halide, A is an alkali metal, and L is a main-group element. Since there is no excess alkali metal or halogen on the product side of the equation, this is considered a salt-balanced SSM reaction. In general, reactions are performed with this type of molar balancing. When alkaline-earth compounds are used instead of alkali metal compounds, eq 16 is modified to

$$MX_n + n/2mA_mL \rightarrow ML_y + nAX_2 + (n/2m - y)L \quad (17)$$

Equations 16 and 17 assume that the main-group element (L) will be present in excess. This is only strictly true when high oxidation state metal halides are used such that $n \geq m$ (or $n \geq 2m$ for the alkaline-earth systems) and the binary product ML_y has $y \approx 1$. These conditions are readily achieved since there are a wide variety of solid transition-metal and main-group halides in oxidation states of three or greater and alkali (or alkaline-earth) metal main-group compounds usually exist with at most three metals per main-group element. The desire to use high-oxidation-state metal halides is aided by the fact that many are readily available or easily synthesized in the laboratory.

One of the primary driving forces behind the design of successful rapid SSM reactions is a careful consideration of thermodynamics; thus it is necessary to determine how different choices of halogen and alkali or alkaline-earth metal will affect the overall enthalpy released in an SSM reaction. The contribution of product formation to the overall heat of reaction (ΔH_{rxn}) varies greatly depending on such factors as product structure, type of bonding, and lattice energy, all of which factor into the product's heat of formation (ΔH_f). The inorganic solids studied so far provide between about 10 and 80 kcal/mol of enthalpy. The real driving force for SSM reactions comes from the formation of very thermodynamically stable alkali or alkaline-earth halides, since 2 or more moles of salt (ΔH_f from −60 to −150 kcal/mol) are produced along with each mole of product. In general, for a given alkali metal, the heat of formation of its halide salt decreases as one moves down the column from fluorine to iodine. For example, lithium halide salts have ΔH_f values ranging from −147 (LiF) to −65 (LiI) kcal/mol. The contributions of the product and the main-group precursor to the ΔH_{rxn} remain constant while the halide (X) is varied within a given reaction system. A closer examination of eqs 16 and 17 shows that it is sufficient to simply consider the reaction of the metal halide with an alkali ($MX_y + yA \rightarrow yAX + M$) or alkaline earth metal ($MX_y + y/2A \rightarrow y/2AX_2 + M$) when one is interested in the influence of the halide on the overall ΔH_{rxn}.

Table 1. ΔH_{rxn} Values for ZrX_4 and NbX_5 Reacted with Alkali (A) and Alkaline-Earth Metals[a]

(a) $ZrX_4 + 4A \rightarrow 4AX + Zr$

(b) $ZrX_4 + 2Mg \rightarrow 4MgX_2 + Zr$

(c) $NbX_5 + 5A \rightarrow 5AX + Nb$

(d) $NbX_5 + 2.5Mg \rightarrow 2.5MgX_2 + Nb$

X	LiX^(a)^	NaX^(a)^	MgX_2^(b)^	LiX^(c)^	NaX^(c)^	MgX_2^(d)^
F	−132	−94	**−81**	**−303**	−256	**−238**
Cl	**−156**	−159	−72	−298	**−301**	−193
Br	−154	**−163**	−69	−286	−298	−180
I	−143	−160	−59	−258	−279	−153

[a] All values are in kcal and the most exothermic systems in each column are in bold. Thermodynamic data are taken from ref 52.

The effect of varying the halide on SSM reactions can be illustrated using standard thermodynamic values[52] for the examples of zirconium tetrahalides and niobium pentahalides as shown in Table 1. It is valid only to compare enthalpy values within a given column because the ΔH_f of the alkali or alkaline-earth main-group precursor (e.g., Li_3N, Na_2O, Na_2S, or MgB_2) must be included in order to compare values between columns. Table 1 demonstrates that a strongly exothermic reaction can occur regardless of which halide is chosen and that the energy released in an SSM reaction generally increases significantly as more moles of byproduct salt are produced (compare columns 1 and 2 to 3 or columns 4 and 5 to 6). Table 1 also shows that reactions with magnesium produce less enthalpy than their alkali-metal counterparts. Of course if the alkali or alkaline-earth main-group precursor is unusually stable and the product has either a small negative or positive ΔH_f, the overall ΔH_{rxn} in a specific system could, in theory, be positive, although very few examples of this situation have been encountered thus far.

Reaction Characteristics. Previous SSM syntheses have shown that while an exothermic reaction can be designed on paper, one must consider the stability of each precursor in order to obtain a successful self-propagating reaction. Since both precursors are initially solids, one or both of them must undergo a phase change at some point during the reaction in order to circumvent the slow process of solid−solid diffusion. Empirical studies support the basic idea that an SSM reaction initiates near the point where one of the precursors decomposes or changes phase (i.e., melting or sublimation).[39e,40,49] Reactions involving a precursor with an

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Table 2. SSM Reaction Speeds and Temperatures[a]

reaction	reaction time[b] (ms)	measured temp (°C)	theoretical T_{ad} (°C)
$MoCl_5 + 5/2Na_2S$	300[c]	~1050[c]	1413
$ZrCl_4 + 4/3Li_3N$	650	1370	1382
$ZrCl_4 + 2Na_2O$	830	1090	1413
$TiCl_3 + 3LiAl$	260	1300	1350

[a] Measurements of speed and temperature were made with an in situ thermocouple unless otherwise noted. [b] Taken as the time interval from reaction initiation to the maximum reaction temperature. [c] Reaction time and temperature were approximated using high-speed video and an optical pyrometer, respectively.

appreciable room-temperature vapor pressure (e.g., $MoCl_5$) can self-initiate and enter a rapid propagation mode without any external initiation.[41] In most cases, however, the onset of rapid SSM reactions is controlled by local initiation with a heated nichrome filament ($T \approx 850$ °C) which causes phase changes in one or both precursors, resulting in a fast exothermic reaction.

While SSM reactions were initially performed in open mortars in an inert atmosphere drybox, small (45 mL) stainless steel reactors with screw tops, similar in form and function to oxygen bomb calorimeters, are now used in order to provide better control and safety during SSM syntheses.[53] The speed and high temperatures reached in these systems have been examined by optical pyrometry,[41] high-speed video,[39b] and recently in situ thermocouples.[49] Table 2 shows a comparison of experimental results and calculated theoretical maximum reaction temperatures. The theoretical adiabatic temperature (T_{ad}) is calculated from standard thermodynamic data (i.e., heat capacities and heats of transition)[7c,52,54] based on two assumptions: (a) the SSM reactions are so rapid that all of the energy produced is used to heat the products and (b) the reactions go to completion as given by eqs 16 and 17. The reasonable agreement between experiment and theory implies that the most rapid SSM reactions proceed in a high-yield, pseudoadiabatic, combustion-like manner. While in situ temperature measurements currently provide the best way to monitor reaction temperatures, deviations from theoretical values are not surprising since chemical yields can range from 50 to >90% depending on the reaction scale. For example, MoS_2 and ZrN reactions producing the temperatures in Table 2 had yields of about 80% and 90%, respectively (see Figure 1). Additionally, measurements with the in situ thermocouple did not take into account any effects of heat losses to the container and thermocouple/recorder response time. A pictorial representation of a rapid SSM reaction forming ZrN is shown in Figure 2. A physical mixture of finely divided $ZrCl_4$ (white) and Li_3N (black) is ignited with a heated filament and the ZrN product (black dots) grows in a molten LiCl flux (white), while the reaction front containing reactive species moves quickly through the sample.

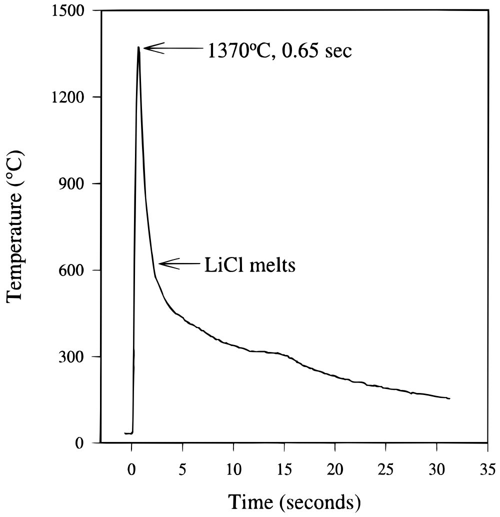

Figure 1. In situ temperature measurement of the reaction $ZrCl_4 + 4/3Li_3N$ by direct recording of a 0.1 mm chromel–alumel thermocouple inserted into the reaction mixture.

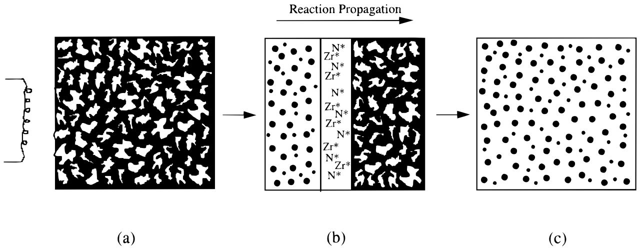

Figure 2. Pictorial representation of a rapid self-propagating reaction forming ZrN showing (a) a physical mixture of $ZrCl_4$ (white) and Li_3N (black), (b) a moving reaction front containing transient zirconium and nitrogen species (ions and/or elements) which yields ZrN (black dots) in a molten LiCl flux (white), and (c) ZrN particles growing and crystallizing in the rapidly cooling flux.

The first three reactions in Table 2 have T_{ad} values which equal the boiling points of their byproduct salts, NaCl and LiCl. This demonstrates another characteristic feature of most SSM reactions: the theoretical maximum temperature is usually limited to the boiling point of the byproduct salt because it comprises the bulk of the reaction product. In cases where the product melts at lower temperatures, the T_{ad} can be below the salt's boiling point. Such is the case for the fourth reaction in Table 2 where the Al_3Ti product melts at 1350 °C. In general, ignited SSM reactions reach and maintain their high temperatures for less than a second or two after which the reaction is essentially over and the products cool quickly (~30 s for 5 mmol reactions) to near room temperature.

The above characteristics and reaction criteria have been used to produce a wide variety of successful rapid SSM reactions. In the following sections a few ceramic systems are described to illustrate this synthetic route. In the course of this work some systems were found which seem to defy the above, empirically based reaction requirements. This has lead to an improved thermodynamic interpretation of rapid SSM propagation which is presented in the section SSM Reaction Propagation.

Ceramic Synthesis via SSM Reactions

Refractory materials have attracted interest due to their high melting points, oxidative resistance, and high strength. Small particle size products are particularly desirable to the ceramics community since the sinterability of a high-temperature ceramic can often be improved when the particle or crystallite size is de-

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creased to the submicron level.[9,55] In some cases the physical properties also change as the crystallite size varies.[56] As described earlier, conventional syntheses are usually slow, energy intensive processes, and many approaches to refractory materials proceed via amorphous intermediates which must be annealed at high temperatures to achieve crystalline compounds (e.g., precipitation, sol−gel, and polymeric routes), while others suffer from the problem of insoluble impurities remaining in the product if reactions are incomplete (e.g., SHS and carbothermic reactions). SSM routes could provide advantages over traditional ceramic synthetic methods because of their rapid reaction rates, little need for external energy input or manipulation of high pressures of gas, and direct production of fine, crystalline powders. The following describes SSM reactions on selected refractory ceramic systems including transition-metal nitrides, boron nitride, and transition-metal borides, as well as metastable zirconium oxide and zirconium phosphide phases.

Transition-Metal Nitrides. The rapid synthesis of crystalline transition-metal nitrides is readily accomplished by the reaction of high oxidation-state metal halides with alkali metal nitriding agents, namely, Li_3N and NaN_3.[49] A balanced reaction using metal halides (MX_n, $n \geq 3$) with lithium nitride to produce metal mononitrides may be written as

$$MX_n + n/3Li_3N \rightarrow MN + nLiX + (n/3 - 1)/2N_2 \quad (18)$$

When Li_3N is reacted with lower valent metal halides ($n < 3$) or when nitrogen-rich phases are formed, the balanced equation will include the production of excess metal instead of nitrogen gas. If sodium azide is substituted for lithium nitride, the reaction becomes

$$MX_n + nNaN_3 \rightarrow MN + nNaX + (3n - 1)/2N_2 \quad (19)$$

While sodium azide may appear to be the more favorable choice as a nitrogen precursor owing to the large excess of nitrogen gas produced when it is used (eq 19), other factors including precursor stability and decomposition processes must also be considered. Both of the nitrogen precursors provide the necessary alkali metal component for salt formation and nitrogen for metal nitride formation, but Li_3N (mp ≈ 810 °C) remains intact in the hot reaction zone (where temperatures rapidly exceed 1000 °C) for much longer than NaN_3 (dec ≈365 °C). The products from reactions using only NaN_3 show evidence of significant elemental sodium and small amounts of metal (e.g., Zr) along with the metal nitrides. This indicates that NaN_3, which decomposes rapidly to sodium and nitrogen gas,[57] does not fully react with the metal halide before the reaction ends. The presence of elemental transition-metal suggests that either the metal halide breaks down to elements prior to reacting or the sodium metal (from NaN_3 decomposition) reduces the metal halide in a Kroll-type process.

Table 3. Powder X-ray Diffraction Results for the SSM Synthesis of Group 4 Nitrides

product	precursors[a]	lattice parameter[b] (Å)	crystallite size[c] (Å)
TiN	$TiI_4 + 4/3Li_3N$	4.24	170
ZrN	$ZrCl_4 + 4/3Li_3N$	4.57	210
HfN	$HfCl_4 + 4/3Li_3N$	4.51	180

[a] Small scale reactions with 4 mmol of the metal halide. [b] All crystallize in the NaCl (F_{m3m}) structure. [c] Calculated from XRD peak broadening.

In general, high oxidation-state metal chlorides provide sufficient volatility and reactivity to result in rapid, exothermic reactions with lithium nitride or sodium azide. In the case of TiN, $TiCl_3$ and TiI_4 were both utilized as successful precursors ($TiCl_4$ is a liquid). Table 3 shows product characteristics from the reaction of group 4 tetrahalides with Li_3N; the lattice parameters agree with published values.[58,59] In each case the reactions are exothermic enough to generate rapid, self-propagating reactions.

Some SSM nitride reactions with Li_3N produce significant amounts of subnitride phases (M_2N, M = Nb or Ta) or partially nitrided transition metal (e.g., 10% N in Ti) even though the balanced equation (eq 18) indicates that a small amount of excess nitrogen gas should be produced.[49] In these cases, the partial substitution of Li_3N by NaN_3 reduces the amount of under-nitrided material in favor of the stoichiometric cubic mononitride. It appears that the most important action of sodium azide is as a solid source of a large excess of nitrogen gas. As an example, the reaction of $TiCl_3$ with Li_3N produces no excess nitrogen gas so the pressure due to N_2 in the closed stainless steel reaction vessel is expected to be zero, and the product is found to contain significant amounts of titanium metal. However, when a third of an equivalent of Li_3N is replaced with 1 equiv of NaN_3 in a reaction using 20 mmol of $TiCl_3$, the vessel's nitrogen pressure at the maximum reaction temperature is calculated to be greater than 80 atm. This increase in "nitrogen concentration" is sufficient to produce a single-phase TiN product. A similar situation occurs in the synthesis of NbN and TaN, where M_2N secondary phases are eliminated by the partial use of NaN_3 as a nitrogen source. The results of a selection of these mixed Li_3N/NaN_3 reactions are listed in Table 4, in which the lattice parameters agree with published values.[58,60,61] For comparison, conventional nitride synthesis involves heating the elements in a nitrogen atmosphere and requires high temperatures and pressures ($T > 1200$ °C; $P > 20$ atm) to produce cubic mononitrides.[62,63] Since the pressures calculated in Table 4 assume a sealed reactor which is

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Table 4. SSM Reactions Using Both Li_3N and NaN_3

product	precursors[a]	lattice parameter[b] (Å)	crystallite size[d] (Å)	nitrogen pressure[e] (atm)
TiN	$TiCl_3 + {}^2/_3Li_3N + NaN_3$	4.24	490	83
NbN	$NbCl_5 + {}^2/_3Li_3N + 3NaN_3$	4.39	440	269
TaN	$TaCl_5 + {}^1/_3Li_3N + 4NaN_3$	4.32[c]	340	36

[a] The TaN reaction was performed with 2 mmol of metal halide, while the others were done on a 20 mmol scale. [b] The nitrides form in the cubic NaCl (F_{m3m}) structure. [c] A hexagonal TaN phase is also present with $a = 5.19$ Å, $c = 2.91$ Å. [d] Calculated from XRD peak broadening. [e] Calculated from the ideal gas law at $T = 1700$ K.

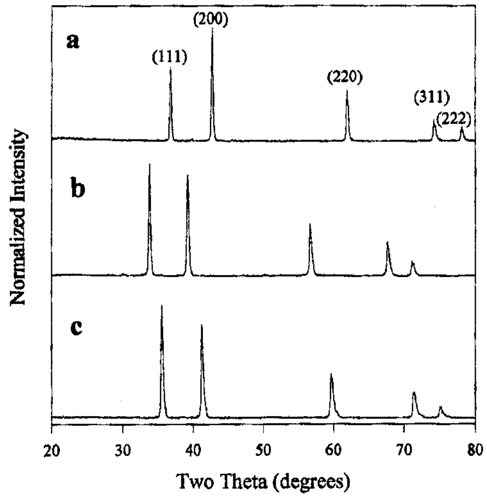

Figure 3. Powder X-ray diffraction results for rapid SSM nitride reactions forming (a) TiN from $TiCl_3 + 2/3Li_3N + NaN_3$, (b) ZrN from $ZrCl_4 + Li_3N$, and (c) NbN from $NbCl_5 + 2/3Li_3N + 3NaN_3$. The Miller indices (*hkl*) for cubic TiN are labeled.

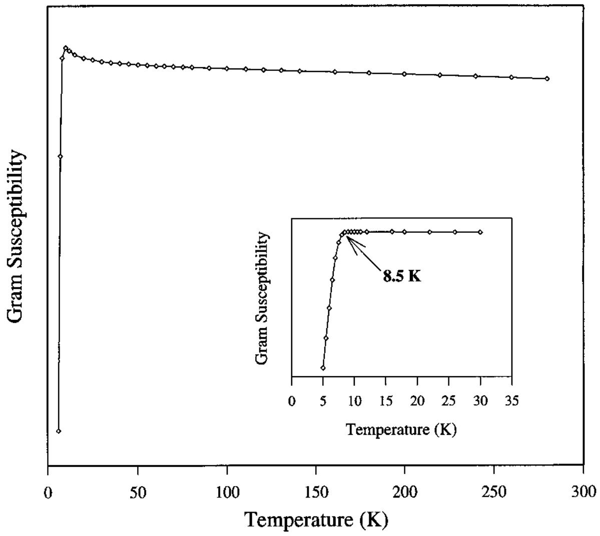

Figure 4. Magnetic susceptibility results for crystalline ZrN from the rapid SSM reaction between $ZrCl_4$ and Li_3N. The inset shows a more detailed scan around the diamagnetic, superconducting transition at 8.5 K.

not strictly true here, the actual pressures are likely lower than those calculated. In contrast to the above TiN reactions, when $TiCl_3$ and Li_3N were heated to 400 °C in a sealed ampule, there was no XRD evidence for titanium in the product.[35b] Possibly this synthetic approach allows the precursors to prereact to a greater extent than is allowed by room-temperature-initiated methods, leading to more efficient nitridation.

The average crystallite sizes of the cubic nitrides are understandably small owing to short reaction times which limit crystal growth. Additionally, refractory transition-metal nitrides have high melting points (2000−3000 °C) which limit their degree of crystallization at the reaction temperature. The reaction scale also influences the degree of crystallinity of the final product, likely because the increased amount of heat generated from larger reactions slows the cooling of the products in the stainless steel reactor. Figure 3 shows a selection of powder X-ray diffraction (XRD) results on large-scale nitride products.

Some cubic transition-metal nitrides are known to become superconducting at low temperatures. The superconducting transition temperature (T_c) is quite sensitive to variations in nitride stoichiometry.[62,64] Nitrogen vacancies of as little as 10% can result in a complete suppression of the transition. Analyses of ZrN and NbN SSM products show superconducting transitions characteristic of nearly stoichiometric phases. Figure 4 shows a characteristic magnetic susceptibility result for ZrN produced via SSM synthesis. The T_c of 8.5 K corresponds to an approximate composition of $ZrN_{0.96}$.[64]

Boron Nitride. The synthesis of crystalline BN provided a particularly challenging synthetic problem since there are few solid boron halide precursors. The logical choice appears to be BI_3 since it is a low melting solid (mp = 50 °C). The balanced reaction using this precursor with Li_3N is

$$BI_3 + Li_3N \rightarrow BN + 3LiI \qquad (20)$$

Unfortunately, this reaction does not propagate; instead BI_3 sublimes out of the reaction mixture when a hot filament is applied. Apparently the sublimation of BI_3 is preferable to reaction with Li_3N at low temperatures and pressures. A search for more reactive boron halides led to the use of complex fluoride salts of the general form ABF_4 where A = Li, Na, or K. These salts decompose to BF_3 and AF at temperatures from 200 to 550 °C.[65] Reactions of these precursors with Li_3N or NaN_3 have the general form

$$ABF_4 + Li_3N \rightarrow BN + AF + 3LiF \qquad (21)$$

$$ABF_4 + 3NaN_3 \rightarrow BN + AF + 3NaF + 4N_2 \qquad (22)$$

SSM reactions performed according to eqs 21 and 22 all proceed in a rapid, propagating manner except for the $LiBF_4/NaN_3$ couple, which contains precursors with very low decomposition temperatures.[50] The BN products from the above reactions consist of crystalline turbostratic boron nitride. This disordered hexagonal form is comparable to BN material resulting from polymeric precursors (e.g., the thermal decomposition

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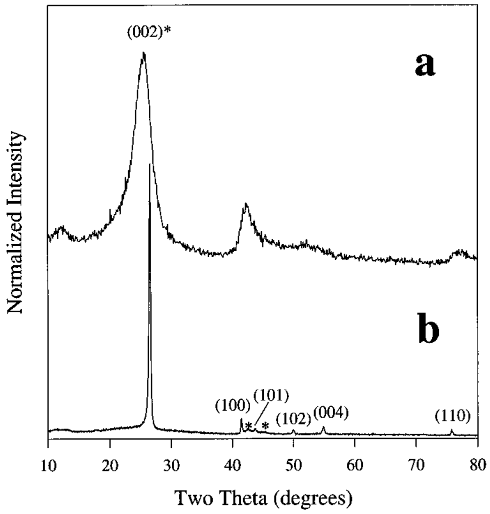

Figure 5. Powder X-ray diffraction of boron nitride from (a) the decomposition of polyborazine at ca. 950 °C and (b) the rapid SSM reaction of $LiBF_4 + 0.8Li_3N + 0.6NaN_3$. The hexagonal BN peaks are labeled with (*hkl*) values, while the rhombohedral phase is marked by asterisks.

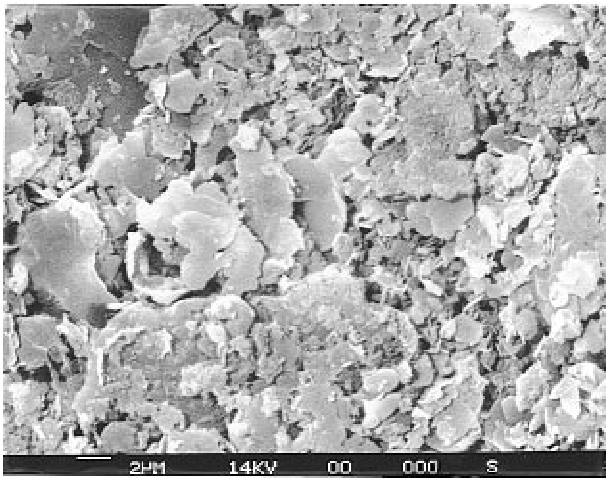

Figure 6. Scanning electron micrograph of crystalline boron nitride powder from the rapid SSM reaction of $LiBF_4 + 0.8Li_3N + 0.6NaN_3$.

of polyborazine $(B_3N_3H_4)_n$ shown in Figure 5a).[66] The crystallinity, homogeneity, and yield all improve as the reaction scale increases. A significant improvement in the crystallinity of BN is found when a combination of Li_3N and NaN_3 is used as the nitrogen source. The powder X-ray diffraction results of $LiBF_4$ reacted with a mixture of these precursors is shown in Figure 5b. The crystalline phase consists of a mixture of ordered hexagonal (55%) and rhombohedral (45%) phases. The crystalline boron nitride (Figure 5b) has average crystallite sizes in the *a* and *c* directions of 1200 and 300 Å, respectively, and a density (2.25 g/cm^3) that is approximately equivalent to fully dense BN (2.27 g/cm^3). Scanning electron microscopy reveals a platelike microscopic structure evident in the product powder which is consistent with the preferential stacking of BN hexagonal layers (see Figure 6).

The improved crystallinity of the boron nitride produced with the mixed Li_3N/NaN_3 system may be due to several factors which increase the longevity of the molten flux in which the BN product grows. The reaction produces a mixture of by-product alkali metal fluorides, LiF (mp 848 °C) and NaF (mp 992 °C), which may form a low melting eutectic flux, e.g., 40 at. % LiF in NaF melts at about 650 °C.[67] The formation of such an eutectic would allow the BN crystallites to remain in a molten salt medium for a longer period of time, enabling increased crystallization. Additionally, the excess nitrogen gas from sodium azide should retard Li_3N decomposition and allow it to participate in the melt. Finally, it is significant that along with the improved crystallinity there is a component of rhombohedral BN in the XRD pattern in Figure 5b. This form of BN has been shown to convert readily to metastable, cubic BN,[68] the second hardest material known (after diamond), and experiments with the above SSM reactions performed under high external pressures are in progress.

Metastable Oxide and Phosphide Phases. Since SSM reactions reach high temperatures, they generally produce thermodynamically stable phases. However, there are a number of cases that demonstrate how the short-lived nature of these systems can result in quenched high-temperature, metastable phases. In the metal nitrides described above, high-temperature and high-pressure cubic phases of NbN and TaN were synthesized which persist when heated for extended periods. There are two specific metal oxide and metal phosphide systems where metastable high-temperature cubic phases are synthesized; specifically MO_2[44] and MP[43] where M is zirconium or hafnium. The as-synthesized cubic products transform on prolonged heating to their room-temperature monoclinic oxide and hexagonal phosphide phases. The following balanced reactions are rapidly initiated with a heated filament:

$$MCl_4 + 2Na_2O \rightarrow MO_2 + 4NaCl \qquad (23)$$

$$MCl_4 + 4/3Na_3P \rightarrow MP + 4NaCl + 1/3P \qquad (24)$$

The cubic ZrP product showed no dependence on the nature of the byproduct salt or the phase of inert additives (cubic or hexagonal salts). Cooling the ZrP reaction down through the use of an inert additive only serves to produce a less-crystalline cubic product. Work is continuing on understanding how these metastable phases form in rapid SSM reactions. Recent experiments by Chen and Dorhout[37c] demonstrate that carefully controlled low temperature (300−800 °C) metathesis reactions in sealed tubes can produce metastable phases (e.g., α-LaS_2). Either annealing of the metastable phases or carrying out the reactions at elevated temperature leads to the thermodynamically stable phase.

Transition-Metal Borides. A wide variety of layered transition-metal diborides are produced from SSM reactions performed in a rapid, self-propagating mode or heated in evacuated silica ampules.[51] The required reaction mode varies with the metal halide used. In these reactions an alkaline-earth boride, MgB_2, is used as the boron source. This boron precursor was chosen

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Table 5. Self-Propagating SSM Reactions with Metal Chlorides and MgB_2

product	metal chloride	lattice parameters $(a/c)^a$	ΔH_{rxn} (kcal) $(T_{ad})^b$
VB_2	VCl_3	3.00 Å/3.07 Å	−86.9 (1329 °C)
NbB_2	$NbCl_5$	3.11 Å/3.31 Å	−197.8 (1418 °C)
TaB_2	$TaCl_5$	3.08 Å/3.27 Å	−172.9 (1418 °C)
$CrB_2{}^c$	$CrCl_2$	2.97 Å/3.06 Å	−59.3 (1255 °C)

[a] All diborides form hexagonal, layered structures (*P*6/*mmm*). [b] Calculated for the formation of 1 mol of MB_2. [c] The product also contains some CrB.

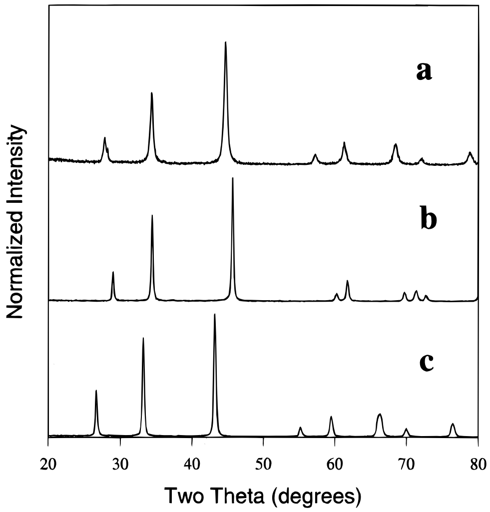


Figure 7. Powder X-ray diffraction of single-phase, crystalline metal diborides (a) TiB_2 from $TiCl_3 + 2/3MgB_2$ heated at 850 °C for 18 h, (b) VB_2 from the rapid initiated reaction of $VCl_3 + 3/2MgB_2$, and (c) NbB_2 from the rapid initiated reaction of $NbCl_5 + 5/2MgB_2$.

because there are no easily obtainable alkali-metal borides with high metal-to-boron ratios. The balanced reaction is

$$MCl_n + n/2MgB_2 \rightarrow MB_2 + n/2MgCl_2 + (n - 2)B \quad (25)$$

where $n \geq 2$. Generally group 5 and 6 chlorides lead to rapid self-propagating reactions while their group 4 counterparts ($TiCl_3$, $ZrCl_4$, and $HfCl_4$) require prolonged external heating (>650 °C) in evacuated silica tubes to produce a complete reaction. Several self-propagating boride systems are illustrated in Table 5; listed lattice parameters agree with published values.[59] The layered metal boride products are crystalline (see Figure 7) and structurally related to the boron precursor MgB_2, which has a similar hexagonal layered structure with a larger *c* spacing (3.52 Å) than the transition-metal diborides. Thermodynamic calculations predict that the self-propagating reactions are quite exothermic and should reach high temperatures, approaching the boiling point of the byproduct salt, $MgCl_2$ (bp 1418 °C). Additionally, reactions with intimate mixtures of metal halides were found to result in mixed-metal solid-solution diborides:

$$(Nb,Ta)Cl_5 + 5/2MgB_2 \rightarrow (Nb,Ta)B_2 + 5/2MgCl_2 + 3B \quad (26)$$

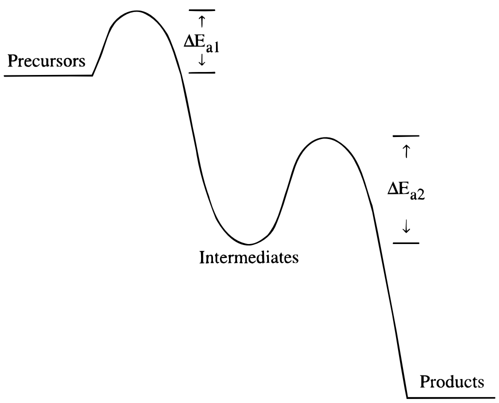
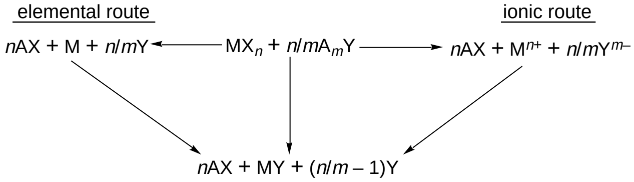


Figure 8. Reaction profile for an SSM reaction with an intermediate step before product formation.

Scheme 1



Coupling a nonpropagating boride reaction ($TiCl_3 + MgB_2$) with a self-propagating metal nitride reaction ($TiCl_3 + NaN_3$) produces a rapid self-propagating composite reaction resulting in an intimate mixture of the metal nitride and boride:

$$2TiCl_3 + 3/2MgB_2 + 3NaN_3 \rightarrow TiB_2 + TiN + 3/2MgCl_2 + 3NaCl + B + 4N_2 \quad (27)$$

Equation 27 shows that a "nonpropagating" reaction can be converted to a self-propagating mode with added energy, supplied in this case from a second chemical reaction. Table 6 shows results from reactions which could *not* be ignited with a hot filament. These precursor mixtures were heated at 850 °C for 18 h to allow for complete reaction, although reactions occur at temperatures as low as 650 °C. The crystalline layered diboride products have the same structure as those mentioned above (see Figure 7a). From Table 6 it is not clear why the listed reactions should be nonpropagating since they are as exothermic as the self-propagating reaction couples in Table 5 and should reach comparable temperatures. The volatility of the metal halides is also equivalent or superior to those which result in self-propagating reactions (e.g., $CrCl_2$ melts at 815 °C, while $ZrCl_4$ sublimes by 335 °C). Clearly there are other factors to consider in these systems. These results have lead to a more careful analysis of the reaction mechanism which is presented next.

SSM Reaction Propagation

Rapid SSM reactions have been postulated to proceed via ionic or elemental intermediates or through a combination of both. The rapidity of these self-propagating systems has thus far inhibited any direct detection of intermediates, but the nature of the reaction products in various systems have suggested primarily either ionic[39e,48] or elemental routes.[42b,47,49] The general ideas for each of these reaction pathways are presented in Scheme 1.

A generic reaction profile for an SSM reaction may be thought to have a set of energy barriers with an

Table 6. Nonpropagating SSM Reactions Using MgB_2 To Form Metal Borides

product	metal halide	ΔH_{rxn} (kcal/mol)	T_{ad} (°C)
TiB_2	$TiCl_3$	−113.5	1418
ZrB_2	$ZrCl_4$	−105.6	1024
HfB_2	$HfCl_4$	−106.2	1031

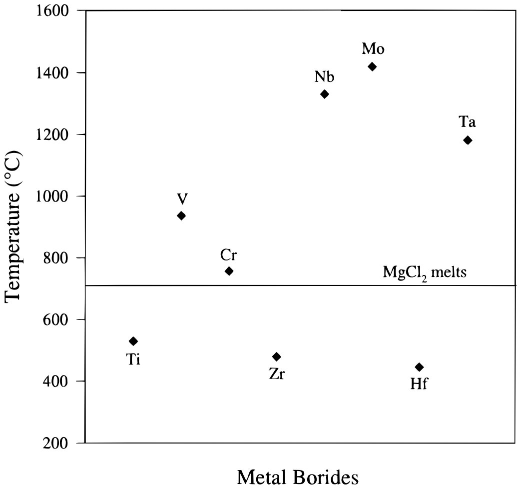


Figure 9. Plot of calculated $T_{ad,s}$ values for a variety of metal diboride SSM reactions using $MCl_x + x/2MgB_2 \rightarrow x/2MgCl_2 + M + xB$.

intermediate state somewhere between them (Figure 8). In ignited self-propagating SSM reactions the first activation barrier (E_{a1}) is crossed with the aid of the heated filament. This barrier likely contains important components including precursor bond and lattice energies. If one assumes that salt formation occurs first, then the intermediate state would consist of the byproduct salt plus ions or elements. The second barrier (E_{a2}) should contain a diffusion component which will depend on the mobility, state (i.e., solid, liquid, or gas) and reactivity of the species present. To have a rapidly self-propagating system, the overall reaction must be vigorous enough so these activation barriers are readily surmounted.

Since the elemental path appears to operate in many SSM systems,[42,47,49] we will consider it in more detail. Additionally, since on a molar basis the bulk of the intermediates will be salt (AX), it is useful to consider how adiabatic reaction temperatures calculated for the intermediate step correlate with the propagating nature of SSM reactions. As an illustrative example, consider the group 4 boride reactions at this "intermediate" step in the reaction which produces only elements and salt:

$$MCl_n + n/2MgB_2 \rightarrow M + nB + n/2MgCl_2 \quad (28)$$

The heat of reaction for this process ($\Delta H_{rxn,s}$) is simply the overall ΔH_{rxn} for the full reaction less the heat of formation of MB_2. The theoretical adiabatic reaction temperature is then defined as $T_{ad,s}$. A plot of calculated $T_{ad,s}$ values versus a variety of metal borides (self-propagating and nonpropagating systems) is shown in Figure 9. There is a region between 530 and 760 °C where the reaction changes from a nonpropagating to a self-propagating mode.

To more closely bracket this barrier, additional experiments were carried out involving the addition of $MgCl_2$ as a heat sink to a self-propagating reaction forming TaB_2:

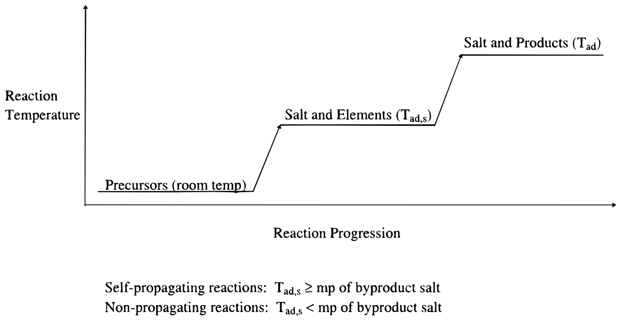


Figure 10. Reaction temperature as a function of reaction progression illustrating the propagation criteria.

$$TaCl_5 + 5/2MgB_2 + xMgCl_2 \rightarrow TaB_2 + (5/2 + x)MgCl_2 + 3B \quad (29)$$

The effect of these additions is to lower the $T_{ad,s}$ since the amount of heat generated is unchanged but the number of moles of salt which must be heated is larger. As a result, values of $x \geq 2.5$ cause $T_{ad,s}$ to drop to 714 °C, which is the melting point of $MgCl_2$, and the reaction is no longer self-propagating. In addition, material clumped around the hot filament was identified as poorly crystalline tantalum metal. On the basis of the above observations, a general thermodynamic concept emerges relating SSM self-propagation to the temperature reached by an intermediate state described by salt and element formation (see Figure 10). If the temperature at this point is high enough to melt the byproduct salt, the mobility of all species in the reaction is increased and subsequent reaction can rapidly occur. If, on the other hand, the salt forms as a solid, then it will prove to be a formidable barrier to a self-propagating reaction. Note however that the addition of salt to "cool" the reaction between $MoCl_5$ and Na_2S still results in a difficulty self-propagating reaction even when $T_{ad,s}$ is below the melting point of NaCl, possibly because the salt is only mixed on a macroscopic level and $MoCl_5$ has a high vapor pressure.[39b]

It is useful to consider other SSM reactions (besides metal borides) using this new idea to determine whether or not it is more generally applicable. In the metal nitride system, the reaction between $ZrCl_4$ and Li_3N is self-propagating but, surprisingly, reactions between $ZrCl_4$ and Mg_3N_2 are not, even though the overall heat released (ΔH_{rxn}) in both reactions is sufficient to raise the products to high temperatures (see T_{ad} values in Table 7). In a related case, there is also no self-propagation in the reaction of GdI_3 (mp 930 °C) and Li_3N. In the above reactions, while the overall T_{ad} values are all high, the $T_{ad,s}$ values vary widely (see Table 7). The only reaction which is predicted to be self-propagating according to the idea illustrated in Figure 10 is the $ZrCl_4/Li_3N$ couple, in agreement with experimental observations. The reaction with Mg_3N_2 represents an extreme case since it is actually endothermic by 1.4 kcal upon reaching the intermediate step which produces only salt and elements. The reaction to form NiAl also fails to reach an intermediate temperature higher than the byproduct salt's melting point and does not self-propagate. In many nonpropagating reactions the metal halide often sublimes out of the reaction mixture as it comes in contact with the heated filament. A recent independent verification of the utility of $T_{ad,s}$ in predicting reaction self-propagation is shown by

Table 7. Predictive Ability of the Adiabatic Temperature on Ignited SSM Reactions

precursors[a]	T_{ad} (°C)	$T_{ad,s}$ (°C)	prediction	experimental
$ZrCl_4/Li_3N$	1408	1186	self-propagating	rapid propagation
$ZrCl_4/Mg_3N_2$	1515	25	nonpropagating	no propagation
GdI_3/Li_3N	1140	139	nonpropagating	no propagation
AlF_3/Mg_2Ni	1263	750	nonpropagating	no propagation

[a] The byproduct melting points are LiCl, 610 °C; $MgCl_2$, 714 °C; LiI, 469 °C; MgF_2, 1263 °C.

Hector and Parkin[69] who found that metal nitride metathesis reactions using Mg_3N_2 are generally nonpropagating, while reactions with Ca_3N_2 are self-propagating and mixtures of the two nitrides produce slowly propagating reactions. Their calculations for the vanadium nitride system show that $T_{ad,s}$ must at least equal the melting point of the salt byproduct in order for the reaction to self-propagate, in general agreement with the discussion above. It will be interesting to determine how far this thermodynamic approach can be extended in a priori predictions of precursor reactivities in new SSM systems.

Conclusions

The utility of SSM reactions in the synthesis of refractory ceramics has been described through the examples of the synthesis of transition-metal nitrides, boron nitride, and transition-metal borides. Rapid self-propagating reactions have been designed such that crystalline, single-phase materials are produced in seconds without any external heating. These rapid reactions generally reach high temperatures and produce a molten salt flux which lasts for only a few seconds. These SSM systems are so fast that they are pseudoadiabatic in nature and theoretically calculated maximum reaction temperatures (T_{ad}) are close to experimentally measured values. Some precursor couples do not produce self-propagating reactions even when the components are volatile and the overall reaction is quite exothermic. To better explain these seeming anomalies, a criterion is presented which relates $T_{ad,s}$ (the temperature for salt formation only) to the melting point of the byproduct halide salt as an indication of whether or not a particular precursor couple will enter a rapid self-propagating mode after localized initiation. Generally it is found that self-propagating reactions occur if $T_{ad,s}$ is greater than the melting point of the byproduct salt, strongly suggesting that a molten medium is crucial for rapid, unassisted reaction propagation to occur in SSM systems.

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