Solid State Metathesis Reaction For Metal Borides, Silicides, Pnictides and Chalcogenides: Ionic or Elemental Pathways

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1 Introduction

A key focal point in inorganic and materials chemistry is the development of new routes to materials The conventional 'heat and beat' approach, which has been utilised since antiquity, requires starting materials (precursors) to be heated in a fire or oven followed by grinding and further reheating until the desired phase is produced This method works extremely well and forms the basis for most of the ceramics industry New approaches that aim to alleviate the time and energy costs involved in conventional preparations include sol–gel and hydrothermal synthesis,[1] molecular precursors and self propagating high temperature synthesis (SHS)[2] Some of these methods aim to reduce the external energy input for the reaction by introducing mixing of the required elements on the atomic scale, and thereby overcoming the solid-state diffusion barrier

This review will concentrate on a modification of the SHS process, termed a solid state metathesis reaction or SSM[2] It will first address in sections 1 1 – 1 5 the general features of SSM reactions initiation conditions, product purity, effect of diluents and thermal profiles It will then discuss in sections 2 1 – 2 5 the range of materials obtained from metathesis reactions borides, silicides, pnictides and chalcogenides Finally the evidence collated from sections 2 1 – 2 5 will be interpreted in terms of a reaction mechanism in section 3 Future directions and conclusions will be summarised in section 4

Table 1 SHS and SSM reaction parameters

Parameter	SHS	SSM
Typical combustion temperature, $T_c/°C$	1400—4000	700—1400
Velocity route, V_c/cm s⁻¹	0 1—10	0 1—10
Initiation power, P/cal cm² s⁻¹	10—100	10—100
Initiation duration, t/s	0 5—5	0 5—5

SHS and SSM reactions have a number of features in common (Table 1) Energy for the SHS process comes from the inbuilt chemical energy of the reaction and relies on outside energy only for initiation The process is very rapid and reaches temperatures in the range 1000—4000 °C in a matter of seconds, cooling rates are dependent on reaction size – with larger scale reactions being better

Ivan Parkin (born Portsmouth 1965) obtained his BSc (1986) and PhD (1989) from Imperial College His thesis entitled "Metalla Sulfur/Selenium Nitrogen Heterocycles Reactions in Liquid Ammonia" was obtained under the guidance of J D Woollins He then spent two years at Indiana University with M H Chisholm FRS on a NATO Fellowship before taking up a lectureship at the Open University Since 1993 he has been a lecturer at University College London He has widespread research interests from SSM, SHS reactions, and CVD to solid state chemistry especially frustrated magnetism
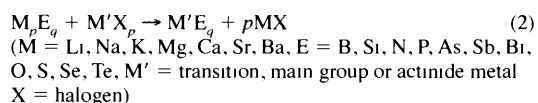
insulated against heat loss, however, compared to the 'heat and beat' approach, cooling rates are rapid SHS processes can be used to make a range of materials, although control of the temperature and formation of specific phases can be difficult In a typical SHS reaction, a fuel source and an oxidiser are required and the reaction is normally of a reduction–oxidation type This is exemplified by the well known thermite reaction (1), which has commercial application for the formation of welds (railway tracks) and in metallurgical separation[3]
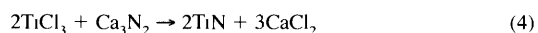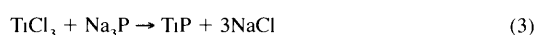
$$Fe_2O_3 + Al \rightarrow Fe + Al_2O_3 \tag{1}$$

In this reaction iron is the oxidising agent and aluminium the fuel source The ΔH_{rxn} is −850 kJ mol⁻¹ per mole of Al and the maximum adiabatic combustion temperature (T_{ad}) reached is in excess of 3000 °C[4] It has been found empirically that SHS reactions will proceed with a propagation wave, spreading out from a point of ignition, if the calculated T_{ad} is greater than 1530 °C[1]

Solid-state metathesis reactions are a variant of the SHS process, reactions are just as rapid, energy for the process comes from the reaction enthalpy, and as will be highlighted in this review, a range of materials can be obtained In a solid-state metathesis reaction an alkali metal or alkaline earth metal pnictide, chalcogenide, silicide or boride is reacted with a metal halide [reaction (2)]

$$M_pE_q + M'X_p \rightarrow M'E_q + pMX \tag{2}$$
(M = Li, Na, K, Mg, Ca, Sr, Ba, E = B, Si, N, P, As, Sb, Bi, O, S, Se, Te, M' = transition, main group or actinide metal X = halogen)

Three specific examples of these reactions are given below [reactions (3—5)]

$$TiCl_3 + Na_3P \rightarrow TiP + 3NaCl \tag{3}$$
$$2TiCl_3 + Ca_3N_2 \rightarrow 2TiN + 3CaCl_2 \tag{4}$$
$$TiCl_4 + 2Li_2O \rightarrow TiO_2 + 4LiCl \tag{5}$$

The driving force is the co-formation of alkali or alkaline earth metal halide, which accounts for up to 90% of the reaction enthalpy Co-formation of a salt also has important consequences for the maximum reaction temperature and hence the phases of material obtained It should be pointed out that removal of co-produced salt is relatively straightforward and involves trituration with an appropriate solvent, such as water, tetrahydrofuran or acetone

1.1 Maximum Reaction Temperature

The maximum adiabatic reaction temperature, T_{ad}, for a solid state metathesis reaction can be determined by calculation of the reaction enthalpy using Hess' law and correlating this with the heat capacities of the reagents and products[5] It is found that despite large reaction enthalpies, T_{ad} normally correlates with the boiling point of the co-produced salt, thus limiting the maximum reaction temperature (1400 °C for LiCl co-production) In practice, although the reactions are relatively fast, some heat losses do occur to the surroundings Salt mediation and thereby lower maximum reaction temperature for SSM compared to SHS reactions implies that a different range of materials are accessible
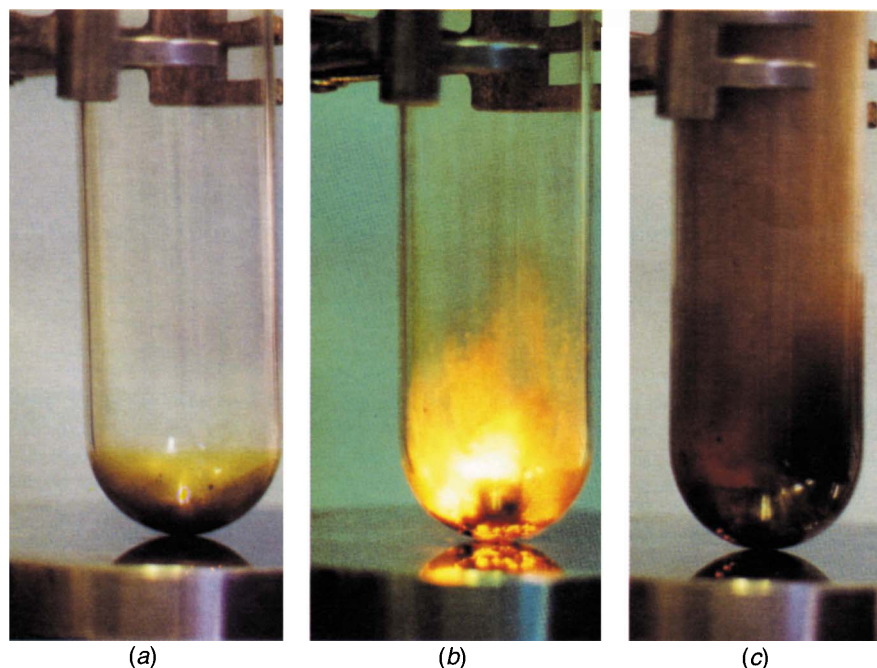
Figure 1 Photographs of the reaction of lithium nitride and titanium tetrachloride (a) before addition of Li$_3$N, (b) 1 s after addition, (c) 3 s after addition
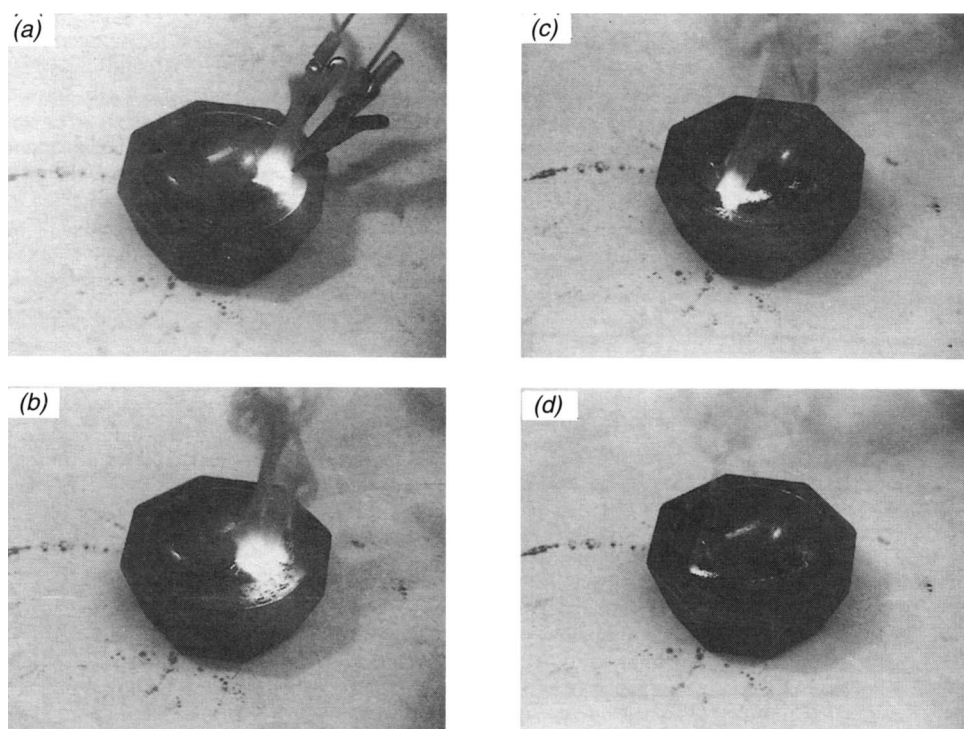

Figure 2 Photographs of the filament initiated reaction of VCl$_3$ with a mixture of 1 Ca$_3$N, —2Mg$_3$N$_2$ after (a) 0 7, (b) 1 4, (c) 3 5, (d) 4 9 s
(Reproduced with permission from *Chem Mater*, 1995, 7, 1728[11])

1.2 Initiation of the Reactions

SSM reactions require some energy input to initiate the reaction In some cases this may come from addition of reagents at room temperature [6] Grinding reagents together,[7] touching reagents with a heated filament,[8] heating of the bulk sample in a furnace[9] and heat from a chemical reaction such as partial hydrolysis (addition of a drop of water) have all proved successful in starting the reaction In many cases initiation is accompanied by a brief thermal flash of 2—3 s duration Initiation is dependent on the ease by which the solid state diffusion barrier is overcome and consequently is related to reagent melting points Addition of lithium nitride to titanium tetrachloride (liquid) at room temperature produces a spontaneous reaction on mixing (Fig 1) For low melting point solids the energy supplied by grinding of the reagents is often suf-

ficient to initiate reaction, for example, reaction of GaCl$_3$ with Na$_3$P to form GaP[7]

The two most common ways to start an SSM reaction are filament initiation (often in a sealed bomb type reactor) and oven heating in a sealed evacuated glass ampoule Filament initiation is propagated by the passage of a synthesis wave through the solid compact[8] (Fig 2) In some instances a reaction can be initiated at the tip of the filament but fails to proceed through the whole of the solid [10][11] The alternative way to initiate the reaction is to heat bulk material in a sealed ampoule, in many of these cases a thermal flash occurs indicating a fast SSM reaction In others, notably the less exother mic reactions, such as formation of metal oxides, no thermal flash is produced and heating at 500—800 °C for 2—12 h is sufficient to drive the reaction Care must be exercised with any SSM reaction
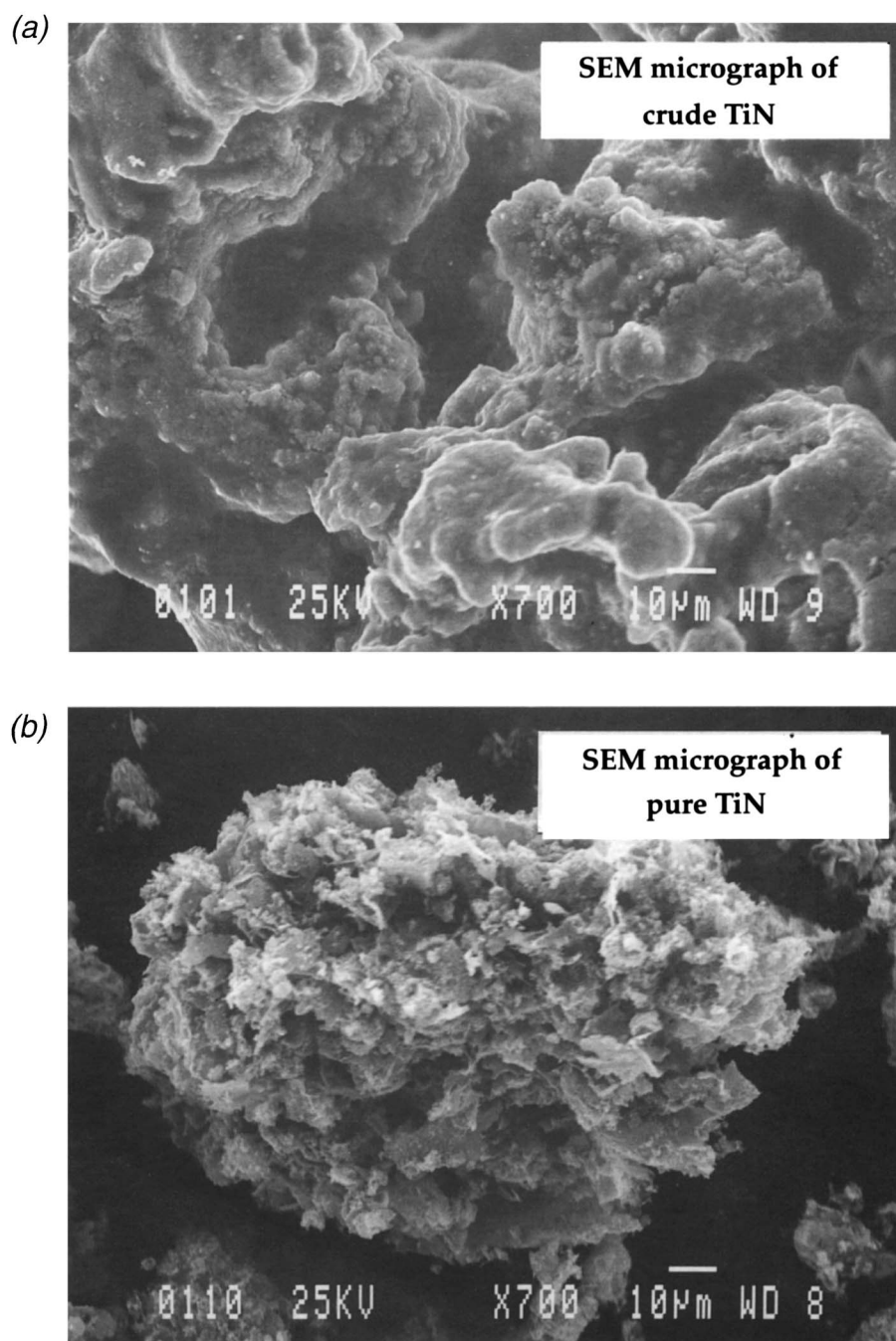
Figure 3 SEM micrograph of the product from the reaction of $TiCl_3$ and Li_3N: (a) before and (b) after trituration with water.

in a sealed container as large, potentially explosive, gas pressures may be built up.

1.3 Product Formation

The solid formed in SSM reactions is a composite of salt and product. Some salt – especially lithium chloride – will sublime during the course of the reaction; however, the morphology of the particles is consistent with formation of agglomerates of crystallites with a surface covering of the salt. Trituration of the material with water, tetrahydrofuran or methanol has been utilised to remove the adherent salt completely (to < 0.01%). Trituration can alter the nature of the material, especially with solvent-sensitive products.[9] A typical SEM micrograph before and after trituration is shown in Fig. 3. Energy-dispersive X-ray analysis (EDXA) has proved to be a good technique for the analysis of the surface (top 1—5 μm) elemental composition. Fig. 4 shows the EDXA trace before and after trituration indicating ready removal of the co-produced salt. It

is not always possible to determine crystallite size from SEM data. An average crystallite size is obtainable from the linewidths of the X-ray powder diffraction patterns via the Scherrer equation.[9] These indicate crystallite sizes typically in the range 300—700 Å. Crystallite sizes are remarkable considering the short timescales of the reactions (2—3 s) and are due to high reaction temperatures, in some cases possibly helped by the co-formed alkali metal halide.[12] Reaction scale and enthalpy are important factors in determining the crystallite sizes, with larger scale, high-temperature reactions favouring larger crystallites.

1.4 Reaction Thermal Profile.

The maximum temperature reached in SSM reactions has been determined by optical pyrometry and by direct thermocouple measurements.[13] Direct measurements involve placing a thermocouple at the centre of a mix of powders and recording the reaction temperature with time. The trace obtained (Fig. 5) is similar to the
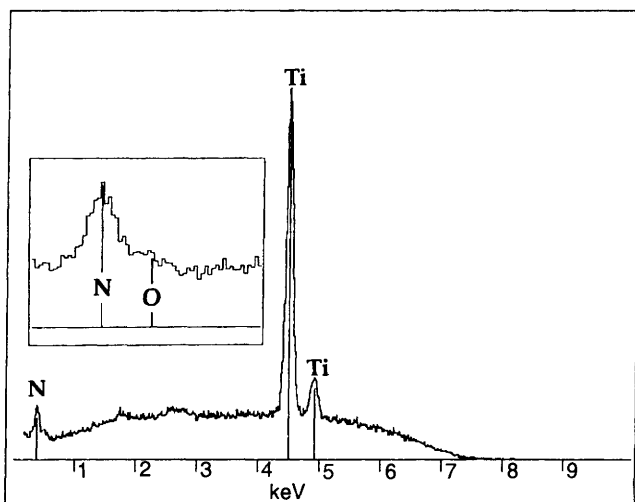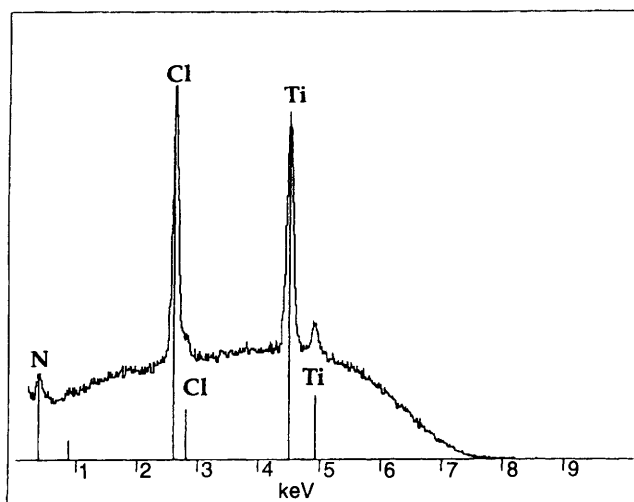
Figure 4 EDAX trace from the reaction of $TiCl_4$ and Li_3N (*a*) before tri turation (*b*) after trituration with water
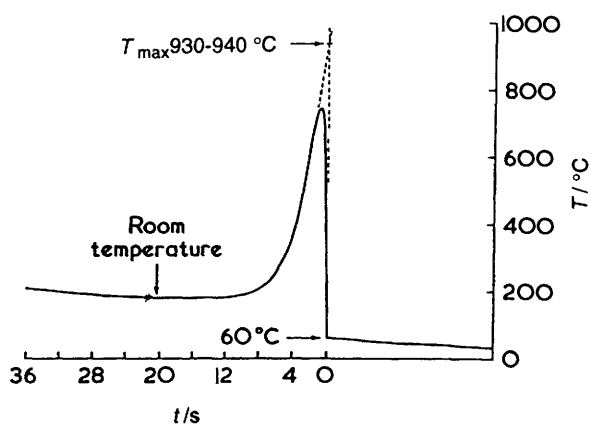

Figure 5 Thermocouple trace from the reaction of $HfCl_4$ and Na_3P

thermal explosion mode observed in SHS reactions, in that the reaction is rapid A 0 5 g scale reaction reaches its maximum tem perature after *ca* 0 5 s and cools to room temperature in *ca* 12—20 s This rapid heating and cooling leads to high concentrations of defects in the material and should make it readily sinterable Optical pyrometry assesses reaction temperature by means of the colour of the thermal flash associated with the reaction This often varies from a yellow–white (1400 °C) to a red–orange flash (800 —1000 °C), it works best for reactions that are most exothermic Use of differential scanning calorimetry (DSC) enables heat flows
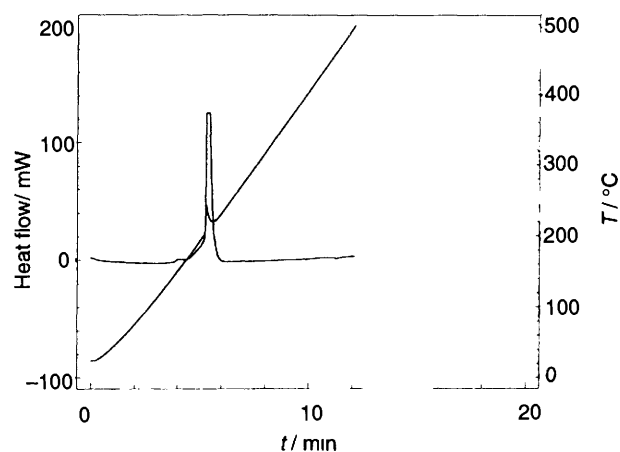

Figure 6 DSC trace from the reaction of $TiCl_4$ and Li_3N *y* axis heat flow in mW *x* axis time in minutes temperature can be extrapolated from the diagonal line
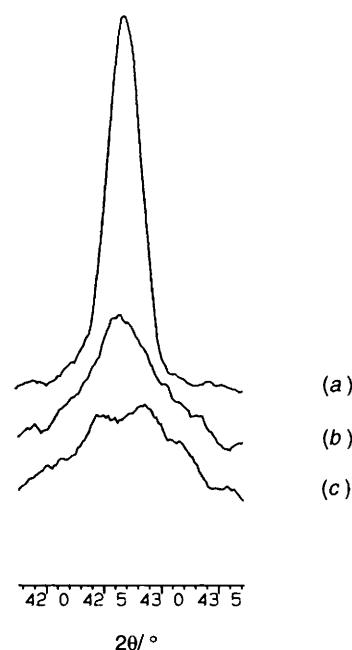

Figure 7 X Ray powder diffraction of the TiN (2 0 0) line (*a*) no added LiCl (*b*) with 200 mg of LiCl (*c*) with 400 mg of LiCl (reaction scale 100 mg of Li_3N)

associated with the reaction to be monitored (Fig 6) In most SSM reactions, a very sharp exotherm is observed corresponding to initiation and propagation In some SSM studies the reactions show a small but reproducible exotherm prior to the main reaction [14]

1.5 The Effect of Diluents

Reaction of anhydrous metal halides and alkali metal or alkaline earth metal pnictides and chalcogenides can be modified by the addition of an inert heat sink Addition of lithium chloride to a reaction mixture of $TiCl_4$ and Li_3N reduces the crystallite size of the product, TiN (Fig 7) The diluent can absorb some of the reaction enthalpy and also increase the path length for diffusion of reacting components, thereby reducing overall reaction temperature and product crystallinity [15] Ease of initiation can also be modified by use of a diluent, *i e* reaction of $MoCl_5$ and Li_3N is initiated at room tem perature on mixing the components but requires heating to *ca* 120 °C in the presence of 1000 mol% of LiCl [16] One interesting case of a dilution experiment modifying the reaction is that of WCl_4 and Li_3N In the absence of dilution, only tungsten metal was observed, whilst on subsequent dilution significant amounts of WN are detected in the product by XPS (Fig 8) The lower overall reaction
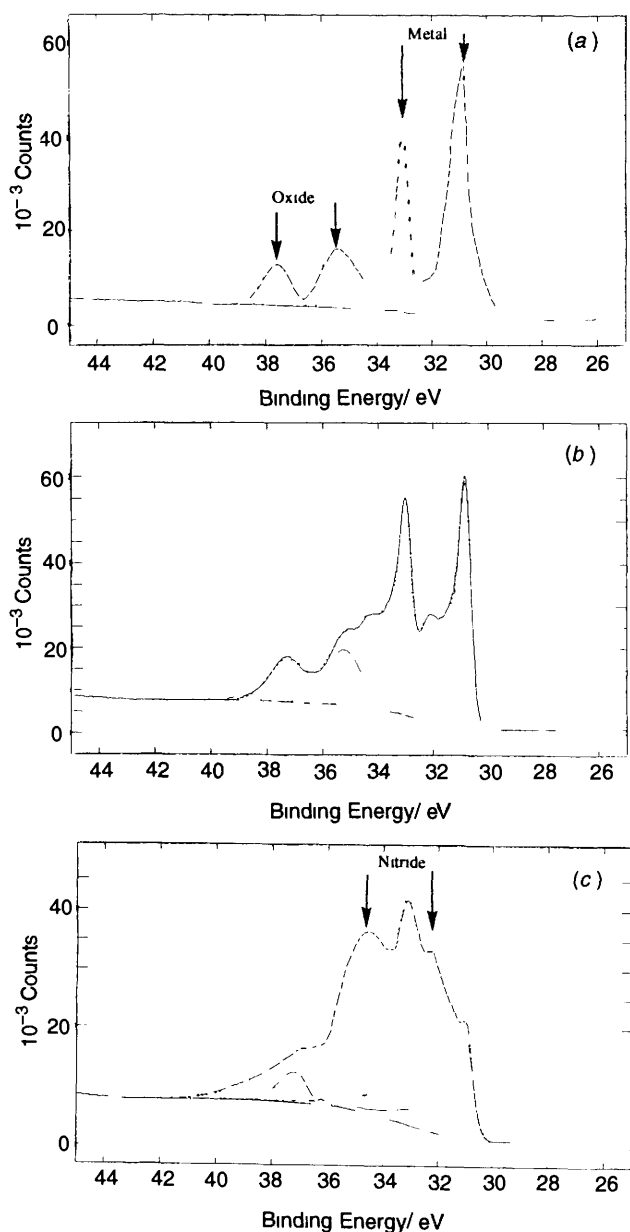
would be expected (confirmed by the experiments) to thermally decompose to the metal and dinitrogen This phenomenon has been called the 'chromium enigma ' For group 3 and 4 metals a single phase of binary nitride, MN, is formed in the reaction, whilst for group 5 metals a mixture of MN and M_2N is formed For chromium a mix of CrN and Cr_2N is produced and for manganese, metal and a trace of Mn_4N are obtained Isolated phases conform to the most thermally stable metal nitride and in no instances have nitrogen-rich phases, such as M_3N_4 (M = Hf, Zr) or Ta_3N_5, been observed Instead an amount of nitrogen gas was also produced |reaction (6)| [9] Changing the nitriding agent from lithium nitride to calcium or magnesium nitride does not affect the phases of material produced, except that single phases of VN and V_2N [12] have been isolated

$$3HfCl_4 + 4Li_3N \rightarrow 3HfN + 12LiCl + 1/2N_2 \qquad (6)$$
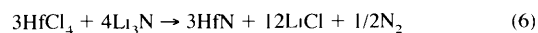
Oven-initiated reactions of sodium azide and anhydrous transition metal halides also produce metal nitrides in good yield, with the same products as from comparable Li_3N reactions [16] A comparison by X-ray powder diffraction (Fig 9) reveals broader lines and hence less crystallinity for the NaN_3 reactions The increased amount of N_2 produced with NaN_3 |reaction (7)| tends to spread the product rather than forming a fused mass as in the Li_3N reactions, thus cooling is more rapid and a less crystalline material is obtained It is also interesting to note that the degree of nitridation for small-scale reactions (ca 0 5 g) that are oven-initiated in sealed ampoules is not increased by using sodium azide Contrastingly, Kaner et al [15] have found that filament-initiated reactions conducted in a modified bomb calorimeter on a larger scale (ca 5 g) do lead to better product nitridation For example, reactions that form a mixture of Ta_2N and TaN with Li_3N can be forced to form a single phase of product, TaN, by employing NaN_3 Presumably in a sealed bomb reactor, very high nitrogen pressures can be generated using NaN_3 that favour increased product nitridation [15]

$$HfCl_4 + 4NaN_3 \rightarrow HfN + 4NaCl + 11/2N_2 \qquad (7)$$
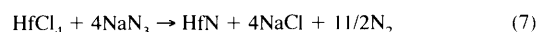
The reaction of lithium nitride and anhydrous lanthanide and actinide chlorides in sealed ampoules produces metal nitrides in good yields [15] These reactions proceed with a thermal flash and require heating to ca 400 °C to induce initiation The lanthanide nitride phases produced were consistent with the formation of LnN_x $(x = 0—0 1)$

Figure 8 Tungsten 4f region of the X ray photoelectron spectra for products of WCl_4 and Li_3N with increasing dilution (a) undiluted, (b) with 300 mg of LiCl added, (c) with 600 mg of LiCl added All reactions on a scale of 50 mg of Li_3N

temperature obtained by using a diluent enables the thermally sensitive tungsten nitride (decomp 650 °C) to be isolated

2 Preparation of Materials

2.1 Metal Nitrides

A range of transition metal, lanthanide, actinide and main group nitrides have been made by solid-state metathesis reactions (Table 2) Starting materials have included Li_3N, Mg_2N_3, Ca_2N_3 or NaN_3 as nitrogen sources

Reactions with lithium nitride have been the most extensively studied [9,15] Reaction of anhydrous transition metal halides with lithium nitride produces either transition metal nitride or elemental metal Thermal stability of the metal nitride determines the nature of the product Early transition metal nitrides, MN (M = Ti, Zr, Hf, V, Nb, Ta, Cr), all have decomposition points above 1900 °C, well above the maximum temperature in the reaction (1400 °C) and hence nitrides can be obtained [17] Later transition metal nitrides (groups 7—12) have decomposition points below 1000 °C Hence, even if a transition metal nitride were formed in these cases, it
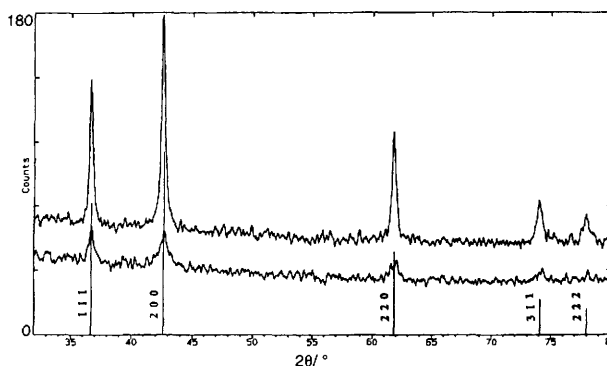

Figure 9 Top trace X ray powder diffraction pattern from the reaction of Li_3N and $TiCl_3$ Bottom trace X ray powder diffraction pattern of the material from the reaction of NaN_3 and $TiCl_3$ (on the same scale as the top trace) Stick pattern is the standard pattern for TiN, Osbornite synthesis (Reproduced with permission from *Polyhedron*, 1995, **14**, 913[16])

Solid-state metathesis reactions yielding metal nitrides can be adapted to form solid solutions of mixed metal nitrides, providing there is some degree of lattice matching between the individual nitride phases For example, solid solutions of Ti_xV_xN $(x + y = 1)$ could be obtained[6] (Fig 10) Similarly, making nitride solid solutions of lanthanides was possible if the lanthanides had similar ionic radii but it was difficult if that ionic radii were dissimilar— despite all lanthanide nitrides having a cubic lattice It was found

Table 2 Materials isolated from solid state metathesis reactions. Where two phases are indicated the first listed phase was the most abundant, phases shown in brackets were present at less than 10% Data are included for both filament- and ampoule-initiated reactions

Metal chacogenide/ pnictide / Metal halide	Li₃N⁹ ¹⁵	Na₃N¹⁵	Ca₃N₂¹¹	Na₃P⁸ ¹⁸	Na₃As¹⁸	Na₃Sb¹⁸	Na₃Bi¹⁸	Li₂O²⁰ ²¹	Na₂S²³ ²⁴ ²⁶	Li₂Se²⁶	Li₂Te²⁶	Mg₂Si²⁹	Mg₃B₂¹⁰
TiCl₃	TiN	TiN	TiN	TiP	TiAs	TiSb₂, TiSb	Ti, Bi	TiO₂	—ᵃ	—	—	TiSi₂	—
TiCl₄	TiN	—	—	TiP	TiAs	TiSb	Bi	TiO₂ |Li₂TiO₃|	TiS₂ᵇ	—	—	Ti₅Si₃	—
ZrCl₄	ZrN	ZrN	—	ZrP	ZrAs	—	Zr, Bi	ZrO₂	ZrS₂ᵇ	—	—	ZrSi₂ Zr₂Si	ZrB₂
HfCl₄	HfN	HfN	HfN	HfP	HfAs	—	—	HfO₂	HfS₂ᵇ	—	—	HfSi₂ Hf₂Si	HfB₂
VCl₃	VN,|V₂N|	VN,V₂N	VN,|V₂N|	VP,|VP₂|	VAs |VAs₂|	—	—	VO₂ |Li₃VO₄|	VS₂ᵇ	—	—	—	VB₂
VCl₄	VN	—	—	VP	VAs	—	Bi	—	—	—	—	—	—
NbCl₅	NbN, |Nb₂N|	—	—	NbP	NbAs, NbAs₂	NbSb₂	—	LiNbO₃	NbS₂ᵇ	—	—	NbSi₂, Nb₅Si₃	—
TaCl₅	TaN, |Ta₂N|	TaN, Ta₂N	Ta₂N,TaN	TaP	TaAs, |TaAs₂|	TaSb₂, |Ta₅Sb₄|	Ta,Bi	LiTaO₃	TaS₂ᵇ	—	—	Ta₅Si₃	—
CrCl₂	Cr₂N,Cr	—	—	CrP, |Cr₁₂P₇|	—	—	—	—	—	—	—	—	—
CrCl₃	Cr,Cr₂N	Cr,Cr₂N	—	—	CrAs	—	—	Cr₂O₃	—	—	—	—	—
MoCl₃	Mo	Mo, |Mo₂N|	Mo	MoP	Mo₅As₄, MoAs	—	—	MoO₂	MoS₂,MoS	—	—	—	—
MoCl₅	—	—	—	—	—	—	—	—	MoS₂,MoS	MoSe₂, Seᶜ	Mo₃Te₄ᶜ, MoTe,Teᵈ	—	—
WCl₄	W	W, |W₂N|	W	WP	WAs₂	W,Sb	—	WO₂	WS₂ᵉ	WSe₂,Seᶜ	WTe₂ᶜ	W,WSi₂,— W₅Si₃	
MnCl₂	Mn₄N, Mn	Mn₄N, Mn	Mn₄N	—	—	—	—	MnO	—	—	—	—	—
FeCl₃	Fe	Fe	—	FeP	—	FeSb₂, |FeSb|,|Sb|	—	Fe₃O₄ᶠ |Fe₂O₃|	—	—	—	FeSi	—
CoCl₂	Co	—	—	CoP	CoAs, Co₂As	CoSb, |CoSb₂|	Co,Bi	CoO	—	—	—	—	—
NiCl₂	Ni	—	—	Ni₂P	Ni₁₁As₈, Ni₅As₂	NiSb, NiSb₂	Ni,Bi	NiO	NiS₂ᵍ	—	—	Ni,Si, Ni₃₁Si₁₂	—
CuCl₂ʰ	Cu—	—	—	—	Cu₃As, Cu	—	—	Cu₂O	—	—	—	—	—
ZnCl₂	Zn	—	—	Zn₃P₂	Zn₃As₂	Zn₄Sb₃	—	ZnO	ZnS	ZnSe	ZnTe	Zn,Si	—
CdCl₂	Cd	—	—	—	—	—	—	CdO	CdS	CdSe	CdTe	—	—
HgCl₂	Hg	—	—	—	—	Hg,Sb	—	HgO	HgS	HgSe	HgTe	—	—
LnCl₃ⁱ	LnN	LnN	LnN	LnP	LnAs	LnSbᵏ	LaBi	Ln₂O₃	NaLnS₂	—	—	LnSi₂, LnB |Ln₅Si₃|	
AcCl₃ʲ	AcN, Ac₃N₄, Ac₂N₃	—	—	Ac₃P₄, AcP	Ac₃As₄	Ac₃Sb₄	—	AcO₂	AcS₂	AcSe₂	AcTe₂	—	—
AlI₃	AlN	—	—	AlP	AlAs,|Al|	AlSb	—	—	—	—	—	—	—
GaX₃	Ga	—	—	GaP	GaAs	GaSb,Sb	—	LiGaO₂	Ga₂S₃ⁱ	Ga₂Se₃ⁱ	Ga₂Te₃ⁱ	—	—
InCl₃	In	—	—	InP	InAs	InSb,In	—	In₂O₃	In₂S₃	In₂Se₃	In₂Te₃	—	—
SnI₄	Sn	—	—	—	—	—	—	SnO₂	SnS₂	SnSe₂	—	—	—
PbCl₂	Pb	—	—	—	—	—	—	Pb₂O₂Cl	PbS	PbSe	PbTe	—	—

ⁱ No data available ʰ Solution phase metathesis   Na₂Se or Na₂Te used ⁱ Reaction dependent on conditions ᵉ WCl₆ ᶠ With Na₂O₂ only Fe₂O₃ formed ᵏ K₂NiF₆ and Na₂S₂ ʰ Note CuO formed by Na₂O₂ or KO₂ with CuCl or CuCl₂   Ln = Y, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm ⁱ Ac²ⁱ = Th, U ᵏ For Ln = Yb, Eu, Eu₃Sb₃ and Yb₅Sb₄ found ⁱ Li₂S, Li₂Se or Li₂Te used
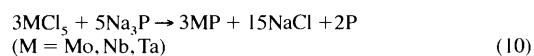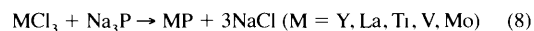
difficult to form solid solutions where the individual nitrides had different crystalline modifications ⁶ ⁹ Thorough premixing of the reagents was also found to be important in forming solid solutions and was best achieved by using miscible liquid metal halides

2.2 Metal Phosphides, Arsenides and Stibides¹⁷

Reaction of anhydrous transition metal halides and Na₃E (E = P, As, Sb) produces a range of metal phosphides, arsenides and stibides¹⁸ (Table 2).

Metal phosphide reactions all involved some reduction of the transition metal and formation of some elemental phosphorus In

most cases a single phase of metal phosphide was formed with no traces of elemental transition metal [reactions (8)—(10)]

$$MCl_3 + Na_3P \rightarrow MP + 3NaCl \ (M = Y, La, Ti, V, Mo) \quad (8)$$

$$3MCl_4 + 4Na_3P \rightarrow 3MP + 12NaCl + P \ (M = Zr, Hf, W) \quad (9)$$

$$3MCl_5 + 5Na_3P \rightarrow 3MP + 15NaCl + 2P$$
$$(M = Mo, Nb, Ta) \quad (10)$$

Reactions were typically conducted in heated sealed ampoules at 500 °C, however, for the more volatile metal halides, TaCl₅, NbCl₅ and MoCl₅, the reaction was found to be initiated on light grinding
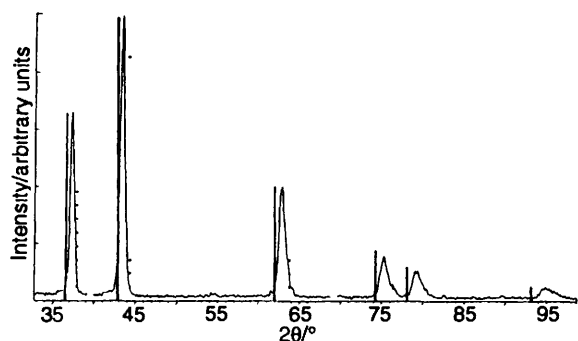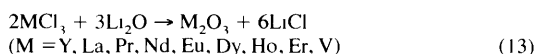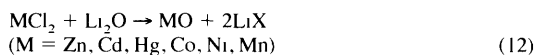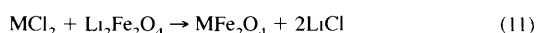
Figure 10 X Ray powder diffraction pattern of Ti_xV_yN formed from the reaction of $xTiCl_4$ and $yVCl_4$ with Li_3N Standard patterns for TiN (—) and VN (   )

with Na_3P and did not require thermal assistance A similar pattern of products and initiation on mixing was found for reactions involving Na_3As, with MAs the most common phase [18] For reactions with Na_3Sb initiation was less facile and MSb_2, transition metal and antimony were the major products Reaction of transition metal halides and sodium bismuthide did not form a single binary metal bismuthide, only metal and bismuth The reactivity of sodium pnictides with transition metal halides thus alters on progressing down the pnictogen group, with formation of the elements more likely and metal pnictide phases less likely with the heavier congeners

Lanthanide halides readily react with Na_3E (E = P, As, Sb) at 500 °C in sealed glass ampoules to form LnE in good yield [18] A range of solid solutions, from mixed lanthanide compounds $LnLn'E$ (Ln, Ln' = lanthanides, E = P, As, Sb) through to lanthanide mixed pnictides LnEE' (EE' = PAs, PSb, AsSb) could also be formed in good yields Reactions of some main group halides with sodium phosphide were often spontaneous on mixing the powders and enabled formation of high purity GaP and InP[8]

2.3 Metal Oxides[17]

Solid-state metathesis reactions have been utilised for the formation of metal oxides One of the first examples was by Heppert and Wille in the preparation of mixed metal ferrites by the reaction of metal halides and lithium ferrite[19] |reaction (11)| Recently reactions have concentrated on use of Li_2O, Na_2O_2, Na_2O and KO$_2$ with transition metal and lanthanide metal halides[20] (Table 2) Most reactions have been studied in sealed evacuated ampoules and heated in an oven In these reactions a thermal flash has not been observed In some instances, notably the filament-initiated reactions of Na_2O_2 with CuF, the reaction will proceed in the propagation mode with a synthesis wave of velocity 3 mm s^{-1} [21] Both filament-initiated and oven-initiated reactions afforded products which were normally single phase metal oxides Products are quite predictable in that the metal maintains its oxidation state throughout |reactions (12)—(14)|

$$MCl_2 + Li_2Fe_2O_4 \rightarrow MFe_2O_4 + 2LiCl \qquad (11)$$

$$MCl_2 + Li_2O \rightarrow MO + 2LiX$$
$$(M = Zn, Cd, Hg, Co, Ni, Mn) \qquad (12)$$

$$2MCl_3 + 3Li_2O \rightarrow M_2O_3 + 6LiCl$$
$$(M = Y, La, Pr, Nd, Eu, Dy, Ho, Er, V) \qquad (13)$$

$$MCl_4 + 2Li_2O \rightarrow MO_2 + 4LiCl (M = Zr, Hf, W) \qquad (14)$$

In all the reactions (12)—(14) lithium was not observed to be incorporated in the product after trituration Reactions which involved tantalum and niobium, however, generated the technologically important ferroelectric materials $LiNbO_3$ and $LiTaO_3$ Other reactions involving vanadium and titanium starting materials, especially when using $TiCl_4$ and VCl_4, produced minor phases such as Li_2TiO_3 and Li_3VO_4 in addition to the expected TiO_2 and VO_2

If reactions of Li_2O and MCl_n are carried out in air, then the degree of lithium incorporation becomes significantly greater, such that Li_xMO_4 (M = V, Nb, Ta) and Li_2MO_3 (M = Ti, Zr, Hf) are
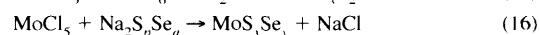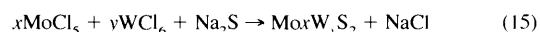
formed exclusively In the latter cases, it is difficult to determine if the process is a direct metathesis or a partial oxidation in air followed by lithium incorporation [22]

Thermal studies by DSC for formation of metal oxides from Li_2O and MCl_n show a single exotherm around 290—340 °C dependent on the sample [14] The exotherm is of 5 minutes duration and is thus atypical of a fast metathesis reaction, but correlates well with the predicted reaction enthalpy Formation of mixed metal solid solutions using Li_2O have had only limited success, probably as the reaction is not very exothermic

Wide-scale application of metathesis routes to metal oxides is unlikely in preference to the number of other methods available for their synthesis, especially as the reactions have no obvious advantage over more traditional routes It could prove useful for those instances where an aerobic environment or use of a large heat source is not possible Additionally, SSM reactions have been found to produce materials with high surface areas

2.4 Metal Sulfides, Selenides and Tellurides

Solid-state metathesis reactions used to form metal chalcogenides have concentrated primarily on formation of sulfide materials A range of transition metal,[23] lanthanide,[24] actinide[25] and main group metal sulfides[26] have been synthesised from the reaction of sodium sulfide (Na_2S) with anhydrous metal halides (Table 2) Reactions can be thermally initiated inside a sealed ampoule or by the propagation mode by means of a heated filament The most active area of this research by R B Kaner et al has been directed to the preparation of MS_2 (M = Mo, W) materials, layered dichalcogenides, which have important applications as lubricants and cathode materials [23] A range of mixed metal disulfides |reaction (15)| and metal dichalcogenides |reaction (16)| have also been formed from analogous reactions

$$xMoCl_5 + yWCl_6 + Na_2S \rightarrow Mo_xW_yS_2 + NaCl \qquad (15)$$

$$MoCl_5 + Na_2S_pSe_q \rightarrow MoS_xSe_y + NaCl \qquad (16)$$

One of the most notable features of filament-initiated reactions which produce metal mixed dichalcogenides (MS_xSe_y) is that the stoichiometry of the product does not reflect that of the starting materials, with enhancement of the more volatile sulfur relative to selenium in the product Filament-initiated reactions to form $MoTe_2$ and WTe_2 proved unsuccessful, however, the reaction could be thermally driven by heating in an evacuated quartz tube at 1000 °C for 7 days These findings have important consequences for determining the reaction mechanism
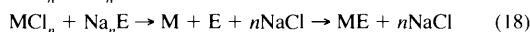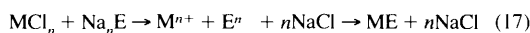
Reactions of lanthanide halides with sodium sulfide in some cases have formed metal sulfides, Ln_2S_3, as well as $NaLnS_2$ These reactions have been hampered somewhat by oxygen contamination [24]

2.5 Metal Borides and Silicides

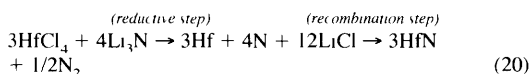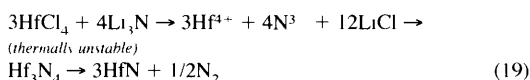Solid-state metathesis reactions have been used to form a range of transition metal and lanthanide borides and silicides [10 29] Silicide reactions (from Mg_2Si and MCl_n) produce a range of phases from MSi_2 to M_2Si They cannot be initiated by a heated filament and have required oven thermolysis at 800—900 °C for 2—24 h Products are often contaminated with the elements and can be directly related to the thermodynamically most stable phase Indeed, in this case, the reactions offer little advantage over conventional synthesis by direct combination of elemental powders Metal boride reactions (Mg_3B_2 and MCl_n) can be initiated in the filament mode [10]

3 Reaction Mechanism

Two extreme mechanistic pathways for solid-state metathesis reactions have been proposed a direct ionic metathesis |reaction (17)| and a reductive recombination route |reaction (18) | In direct ionic metathesis the reaction intermediates are ions, that interdiffuse in the 'NaCl' melt In a reductive recombination pathway the components are reduced to the elements followed by recombination promoted by the high reaction temperatures

$$MCl_n + Na_nE \rightarrow M^{n+} + E^n + nNaCl \rightarrow ME + nNaCl \quad (17)$$

$$MCl_n + Na_nE \rightarrow M + E + nNaCl \rightarrow ME + nNaCl \quad (18)$$

The actual mechanism could be intermediate between the two extremes The initially formed product could further decompose as a result of thermal instability, this is illustrated by the formation of HfN from $HfCl_4$ and Li_3N as shown via an ionic route (19) and an elemental route (20)

$$3HfCl_4 + 4Li_3N \rightarrow 3Hf^{4+} + 4N^3 + 12LiCl \rightarrow$$

(thermally unstable)

$$Hf_3N_4 \rightarrow 3HfN + 1/2N_2 \quad (19)$$

(reductive step)   (recombination step)

$$3HfCl_4 + 4Li_3N \rightarrow 3Hf + 4N + 12LiCl \rightarrow 3HfN$$
$$+ 1/2N_2 \quad (20)$$

The speed of fast metathesis reactions, which are over in ca 2—10 s, makes it difficult to study the reaction directly and isolate intermediates Mechanistic discussions have been built up from end-product analysis In no reactions involving the lanthanide halides with lithium nitride, sodium phosphide, arsenide and antimonide has any elemental metal been detected in the product If the reaction were to proceed by an elemental pathway of reduction followed by recombination it would be expected that some elemental metal would be detected Further, the lanthanide ions are stable (E° = $-2\,778$ V vs Pt) in the presence of a strong reducing agent (E^3) indicating that an ionic pathway is probably preferred [8]

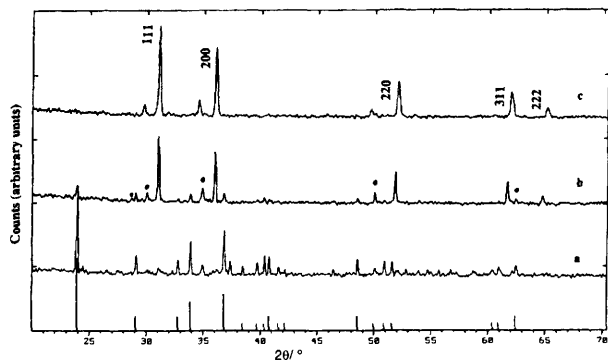**Figure 11** X Ray powder diffraction patterns of the crude products of reactions of (a) $GdCl_3$ with Mg_3N_2 heated for 2 h at 500 °C, (b) $GdCl_3$ with Mg_3N_2 heated at 900 °C, (c) $TbCl_3$ with Mg_3N_2 heated at 900 °C Stick pattern represents Gd_3Cl_3N, bold circles represent $MgCl_2$, indexed lines for LnN

(Reproduced with permission from Chem Mater, 1995, 7, 1728[11])

Reaction of lanthanide halides with magnesium and calcium nitride produces lanthanide nitrides after heating at 900 °C for 1 h If the reaction is stopped prior to completion then it is possible to isolate intermediates of the form Ln_2Cl_3N (Fig 11), further heating of the mix sequentially lowers the Ln_2Cl_3N concentration and increases the amount of LnN Detection of such intermediates strongly suggests an ionic mechanism Contrastingly, for transition metal nitride reactions, using Li_3N and NaN_3 as an alternative nitrogen source and conducting the experiments in a bomb type container, significantly extra nitridation is introduced for the azide reaction This is to be expected if the reaction proceeds via a reductive recombination pathway because of the increased nitrogen pressures generated by the azide [reactions (6) and (7)] It is also worth noting that in filament-initiated transition metal nitride reactions some residual metal (ca 1%) is often found in the product, whilst for ampoule reactions in an oven, a negligible amount of metal is detected This is probably because the oven reactions are somewhat self-annealed and hence do not cool to room temperature as quickly Detection of metal powders in the product does point to a reductive recombination pathway for the transition metal nitride reactions, however, one caveat is that the metal halide precursor does not thermally decompose before it reacts For example, $TiCl_3$ is known to disproportionate at

elevated temperatures to $TiCl_2$ and $TiCl_4$ (500 °C), and the $TiCl_2$ to disproportionate further to Ti metal and $TiCl_4$ on additional heating It may be that these decomposition events lead to the traces of metal observed in the reaction and that the process is properly considered as an ionic metathesis

Reactions to form metal silicides, antimonides, bismuthides and tellurides always seem to proceed by a reductive recombination pathway, elemental metal and element are observed in high concentrations and the phases of material formed are determined by thermodynamics Further, reactions are thermally driven (12—24 h, at 800 °C) and do not proceed by a thermal flash Reactions of MCl_n and $Na_2(S_xSe_x)$ formed $M(S_{x+y}\,Se_y)_2$ (M = Mo, W, $x+y = 1$) in good yield The products normally showed a measurable enhancement of the content of the more volatile sulfur compared to selenium and compositional gradients Both of these facts are best explained by a reductive recombination pathway
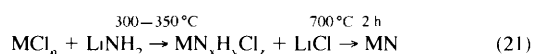
Solid-state metathesis reactions can thus be thought of as proceeding via either a reductive recombination pathway or an ionic metathesis route or both Some points are clear—lanthanide halides prefer the ionic metathesis route, whilst transition metal halides can prefer either, sodium salts of the heavier pnictides and chalcogenides (Sb, Bi, Te) and magnesium silicide seem to follow a reductive recombination pathway exclusively A full and detailed understanding of the reaction mechanism will require some sort of in situ probe to monitor the reaction, for fast metathesis reactions this is obviously very difficult as the process is complete in only a few seconds One experiment that has been tried is addition of a different powdered elemental metal to a reaction mixture to note if that element has become involved in the reaction Incorporation would favour a reductive recombination pathway

Analysis of reaction enthalpy and correlation with the melting point of the coproduced salt has allowed reaction propagation to be determined in the filament-initiated mode Molten co-produced salt is important in breaking down the solid-state diffusion barrier If the reaction enthalpy is not sufficient to melt the salt then spread of the reaction to intervening layers would be impeded and propagation would fail Propagation occurs when the calculated adiabatic temperature for the reaction, $T_{ad\,s}$, is sufficient to melt a fraction of the coproduced salt [10] It was found that reaction of VCl_3 with Mg_3N_2 Has a $T_{ad\,s}$ of 78 °C and no propagation occurred, reaction of VCl_3 and Ca_3N_2 has a $T_{ad\,s}$ of 1338 °C and propagation was rapid, whilst a mixture of 2/3 Mg_3N_2— 1/3 Ca_3N_2 with VCl_3 had a calculated $T_{ad\,s}$ of 714 °C, the melting point of $MgCl_2$, and the reaction just propagated (Fig 2) [11]

4 New Directions in Metathesis Reactions

One of the most interesting new directions in solid-state metathesis reactions has been shown by Wells and co-workers [27] They performed reactions in the presence of a solvent in which the alkali metal pnictide had limited solubility, and the metal halide ($GaCl_3$, $InCl_3$) was soluble and coordinated by a range of different solvent and co-ligating molecules The metathesis reaction proceeded in much the same way as in the solid state, except that reactions required 2—12 h at reflux and, most importantly, products GaP, InP and GaAs were nanoparticulate with a relatively narrow size distributions The size of the nanoparticles could be altered simply by changing the solvent or co-ligating molecules Nanoparticles have a very large surface area to size ratio and can show quantum confinement effects that could be utilised in a new generation of electronic devices

It has also been possible to develop new reactions that are intermediate between solid-state metathesis and a molecular precursor approach to ceramics Reaction of anhydrous metal halides and lithium amide at 300—350 °C induced a reaction with a thermal flash [28] This produced a material that was rich in nitrogen and after gentle thermolysis produced a metal nitride [reaction (21)]

$$MCl_n + LiNH_2 \xrightarrow{300-350\,°C} MN_xH_yCl_z + LiCl \xrightarrow{700\,°C\ 2\,h} MN \quad (21)$$

These reactions are less exothermic than those of lithium nitride, and nitrogen-rich phases such as Ta_3N_5 have been isolated, as well as thermally sensitive phases such as Zn_3N_2

Solid-state metathesis reactions have also been extended to the synthesis of electroceramic materials such as barium titinate, from the reaction of barium peroxide and $TiCl_3$ Further work has also allowed the formation of metal borides, main group nitrides, e g BN, and composite materials such as BN/TiN [17]

Products of SSM reactions are usually very pure with little chemical contamination from the walls of the reaction vessel, as reactions are fast compared to traditional ceramic techniques The inbuilt heat brake afforded by the co-produced alkali metal halide regulates the maximum reaction temperature and allows for isolation of phases not accessible from conventional SHS reactions SSM reactions can also be initiated by means of a heated filament, which means that access to high-temperature furnaces is not required, this should prove useful for small laboratory-scale preparations of binary ceramic materials

The SSM reactions are important not only because of the speed of the reaction but because they can engender metastable products of unusual microstructure A full and detailed investigation of the product microstructure has not so far been achieved and scope for extensive TEM work exists Average crystallite size has been determined by the Scherrer equation but a detailed analysis including size distributions and domain structure has yet to be achieved Particulate morphologies have been hinted at by SEM which normally reveals agglomerates of crystallites In this context the work of Wells, in both determining microstructure by high resolution TEM and in manipulating crystallite size by use of a solvent heat sink, is particularly noteworthy [27]

In some cases SSM reactions can provide access to new phases of materials and to better purity than conventional methods For example, the reactions of $TaCl_5$ with Li_3N and NaN_3 produce the metastable high-temperature cubic phase TaN rather than the expected hexagonal TaN Traditionally cubic TaN requires high nitrogen pressures (20—160 atm), long time periods and temperatures in excess of 1600 °C for it to form The reactions also have future potential to make composite materials by reactions with layers of different composition

Solid state metathesis reactions offer an alternative, relatively straightforward and in some cases advantageous synthetic route to a vast range of inorganic ceramic materials

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