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Solid state metathesis routes to metal nitrides; use of strontium and barium nitrides as reagents and dilution effects

Shahbano Ali, Marco D. Aguas, Andrew L. Hector, Geoff Henshaw and Ivan P. Parkin*

Department of Chemistry, Christopher Ingold Laboratory, 20 Gordon Street,
London WC1H OAJ, U.K.

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Abstract—Bulk thermal or filament initiated reactions of mixed powders of transition metal chlorides and Sr_2N and Ba_3N_2 produce transition metal nitrides (TiN, ZrN, HfN, VN, V_2N) in good yield. The products were characterised by X-ray powder diffraction, SEM/EDAX, FT-IR, microelemental analysis and imaging XPS. The affect of diluting the reaction by the addition of LiCl was used to lower reaction temperatures and in the case of WCl_4 and Li_3N produced WN. Reaction propagation was investigated by using various mixtures of nitriding reagent (Li_3N, Mg_3N_2, Ca_3N_2), this was correlated with $T_{ad,s}$ the maximum adiabatic combustion temperature for salt formation only. © 1997 Elsevier Science Ltd

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Transition metal nitrides play a major role in determining the properties and performance of many materials [1]. Compounds such as TiN, ZrN and (Ti, Zr)N are all used as hard wear resistant coatings, cermet cutting tools and precipitates in micro-alloyed HSLA steels. They have also been utilised as catalysts, diffusion barriers, fracture tougheners in ceramics and solar control coatings [2].

Metal nitrides have been synthesised by a variety of routes including arc-deposition, high temperature combination of elements or element hydrides, MOCVD and MBE [3]. Most of these preparative routes require high temperature furnaces and prolonged time periods with total exclusion of oxygen and moisture and often produce non-stoichiometric nitrides with significant metal and carbon impurities [4]. Self-propagating High-temperature Synthesis (SHS) has been developed for the formation of metal nitrides by direct combination of the elements [5]. In this process the energy for the formation of the nitrides comes from the exothermic reaction enthalpy. The reaction is initiated either by a filament at a point source or by heating of the bulk material. In both cases the reaction is propagated by a synthesis wave that travels through the bulk solid.

An adaptation of the SHS technique termed a Solid State Metathesis reaction (SSM) has been developed for nitrides and a range of other materials, eq. (1) [6].

$$ME_q + M'X_p \rightarrow MX_p + M'E_q \qquad (1)$$

[M = Li, Na, Mg, Ca; E = N, P, As, Sb, O, Se, Te; M′ = transition, main group or lanthanide metal; X = halide].

The driving force for SSM reactions is the lattice energy of the co-produced salt which accounts for up to 90% of the reaction enthalpy. The reactions are typified by rapid heating (1s), generating temperatures up to 1400°C, followed by rapid cooling (*ca* 20s, depending on reaction scale). Overall SSM and SHS reactions share common features and terms such as propagation velocity, adiabatic reaction temperature (T_{ad}) and reaction exothermicity [5]. One important difference is that the coproduced salt in the SSM reaction acts as an internal heat break, absorbing reaction energy and often limiting T_{ad} to the salts boiling point. As illustrated in eq. (1) the SSM reactions have enabled synthesis of metal nitrides [7], oxides [8], sulfides [9], selenides [10], phosphides [11] and arsenides [12].

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* Author to whom correspondence should be addressed.

Previous nitrogen sources in SSM reactions include lithium nitride, sodium azide, and calcium and magnesium nitride [7]. The metal nitrides produced vary in phase and stoichiometry dependant on the nature of the nitriding agent. For example, reaction of VCl_3 with Li_3N produces a mixture of two nitrides VN and V_2N whilst reaction with Mg_3N_2 produces exclusively VN [13]. Typically the use of an azide increases the degree of nitridation of the products but decreases the product crystallinity.

The SSM reaction mechanism has been formulated as either a reduction to the elements followed by recombination, or by a direct ionic metathesis [13]. Evidence for either route has been gathered from end product analysis. Some pointers are clear, reactions of lanthanide halides and a nitride source tend to prefer the ionic metathesis reaction (intermediates of the form Ln_2NCl_3 isolated) [13]. Reaction of transition metal halides and lithium nitride have evidence for both reductive recombination and ionic metathesis depending on reaction scale and mode of initiation. Progress has also been made in determining reaction propagation in the filament mode. Kaner [14,15] has shown that the ease of an SSM reaction spreading out from a point source and encompassing the bulk material can empirically be equated with $T_{ad,s}$ the adiabatic combustion temperature for salt formation only (i.e. the ΔH_r of $Li_3N+MCl_3 \rightarrow 3LiCl+M+N$). The reaction propagates only if $T_{ad,s}$ is greater than the melting point of the coproduced salt. Some evidence has been gathered to corroborate this theory [13].

In this paper we explore two new routes to transition metal nitrides by using Ba_3N_2 and Sr_2N as nitride sources, investigate the role of dilution on SSM reactions and correlate $T_{ad,s}$, with a number of empirical measurements.

EXPERIMENTAL

All reagents were handled under a nitrogen atmosphere using either a glove box or Schlenk line techniques. Glass ampoules (borosilicate or quartz glass typically 2 mm thick with an internal diameter of 15 cm^3) were annealed prior to use and thoroughly dried, either by baking in a furnace at 450°C for six hours or by flame drying under vacuum. Anhydrous transition metal halides, lithium nitride, calcium nitride and magnesium nitride were obtained from Strem Chemicals or Aldrich Chemical Co. and used as supplied. Barium and strontium nitride were prepared by reaction of nitrogen with the alkaline earth element in molten sodium at elevated temperature by the group of Dr Barker, Nottingham University. The barium and strontium nitrides were typically crystalline (1–2 mm crystals) and were checked by microanalysis (Sr_2N calc. N = 7.14%, found N = 7.10%; Ba_3N_2 calc. N = 6.37%, obs. 6.02%). Methanol was dried over 3 Å molecular sieves and degassed with nitrogen prior to use. Infra-red spectra were recorded on a Nicolet 205 (KBr) using KBr discs. X-ray powder diffraction (XRD) measurements were performed on a Siemens D5000 Diffractometer using germanium monochromated $CuK_{\alpha 1}$ (λ = 1.5406 Å) radiation. Patterns were indexed using the TREOR program. Magnetic moment measurements were determined on a Johnson Matthey balance and SEM profiles on a Jeol JSM820 instrument using a Kevex program for EDAX analysis. X-ray photoelectron spectroscopy (XPS) was performed on a pressed disc of sample with a VG ESCALAB 220i XL using focused (300 μm spot) monochromatised Al K_α radiation at a pass energy of 20 eV. Scans were acquired with steps of 50 MeV. The binding energies were referenced to an adventitious C 1s peak at 284.4 eV. Microanalysis was performed by the departmental service by combustion with tin powder. A Lenton Thermal Designs programmable tube furnace or a resistive electric filament was used to initiate the reactions. The filament reactions were initiated by a resistive nicrome wire heater at *ca* 800–900°C in an agate mortar under a dinitrogen or argon atmosphere within a Saffron Scientific Glove Box. DSC experiments were performed using a Shimadzu DSC 50 Thermoanalyser using Perkin–Elmer high pressure stainless steel cells with gold seals. Scans were measured from 20–500°C at a heating rate of 10°C/min.

Preparation of metal nitrides (*thermal initiation at* 550–850°C)

Anhydrous metal chloride MCl_n (1.0 mmol) and Ba_3N_2 (n/6 mmol) or Sr_2N (n/4 mmol) were ground together in an agate pestle and mortar in a nitrogen or argon filled glove box and then placed in a quartz or pyrex ampoule which was evacuated and sealed. The ampoule was placed in an oven at 250–550°C for between 1 min and 10 h and allowed to cool to room temperature for typically 1–2 h. The ampoule contained a fused black solid which was opened in air and triturated with methanol (20 ml) and water (20 ml) and dried *in vacuo* to yield a metal nitride (typically, 0.80 mmol, 60–80%). The solids were identified by XRD (Table 1), SEM/EDAX, FT-IR, magnetic moment measurements and microanalyses. HfN (from reaction of Sr_2N and $HfCl_4$) calc 7.28% obs 7.04%.

Preparation of metal nitrides via *filament initiation*

The reaction of various nitride sources (Li_3N, Sr_2N, Ba_3N_2, Mg_3N_2 and Ca_3N_2) and transition metal halides were investigated by touching a mixed pre-ground powder with a filament from a resistive heater. The products were washed with methanol and water, dried *in vacuo* and analysed by SEM/EDAX, FT-IR and X-ray powder diffraction.

Table 1. X-ray powder diffraction data

Reagents	Colour of product	Phase observed	Observed[a] a value/Å	Literature a value/Å
$Ba_3N_2+TiCl_3$	Black	TiN	4.240 (3)	4.244
$Ba_3N_2+ZrCl_4$	Black	ZrN	4.571 (3)	4.577
$Ba_3N_2+HfCl_4$	Black	HfN	4.510 (3)	4.518
$Sr_2N+TiCl_3$	Black	TiN	4.238 (3)	4.244
Sr_2N+VCl_3	Black	VN, (V_2N)[b]	4.128 (3)	4.139
$Sr_2N+ZrCl_4$	Black	ZrN	4.572 (3)	4.577
$Sr_2N+HfCl_4$	Black	HfN	4.512 (3)	4.518

[a] Literature values are for nitrides of stoichiometry $MN_{1.0}$[16]. The lower a values observed are consistent with formation of $MN_{0.9}$. Note for some nitrides the phase observed as MN can have a compositional range from $MN_{1.0}$ to $MN_{0.5}$ and still have the same cubic pattern with slight modification of the a-parameter.

[b] Minor phase observed.

Dilution experiments

The reactions were carried out by filament initiation as above except that the reagents were mixed with a measured quantity of lithium chloride (typically 5 and 10 mol equivalents of LiCl). The products were triturated with methanol and water prior to analysis and pressed into a disc prior to measurement. XPS analysis showed only metal, nitrogen and oxygen (along with a small amount of carbon) in the sample and no residual lithium or chlorine.

Caution. Reactions involving self propagating reactions have been known to be very exothermic and on occasions produce large amounts of dinitrogen gas. As such if the reactions are contained within a small ampoule an explosion can occur. It is recommended that all reactions are carried out behind a blast proof safety screen.

RESULTS AND DISCUSSION

Reaction of Sr_2N *and* Ba_3N_2 *with metal halides; bulk thermal initiation*

The reactions of strontium nitride and barium nitride with lanthanide and transition metal chlorides ($TiCl_3$, $ZrCl_4$, $HfCl_4$, VCl_3) were investigated both by bulk thermal initiation in an evacuated ampoule at 250–500°C and by point source propagation. The black powders formed from the bulk thermal studies were purified by washing with methanol or water to remove the coproduced MCl_2 (M = Sr, Ba). The FT-IR spectra of the black powders showed only a broad band centred at 450 cm^{-1} assignable to M–N vibrations. SEM micrographs of the initial pre-triturated powder showed a relatively homogeneous coating of strontium or barium chloride; this coating was removed on trituration to reveal micron sized aggregates of particles with sharp features. Step EDAX analysis showed the presence of metal, nitrogen and smaller amounts of strontium or barium and chlorine in the untriturated material. The strontium/barium and chlorine was usually reduced to below EDAX detection limits (1–2%) on trituration.

The X-ray powder diffraction patterns (Table 1) of the powders after trituration showed a single phase of material cubic MN (M = Ti, Zr, Hf) and VN (with *ca* 10% V_2N) [16]. Prior to trituration, peaks due to the coproduced strontium or barium chloride were observed. The magnetic moments of the metal nitrides were consistent with previous work [9]. The phases of material produced in the reaction were invariably the thermodynamically most stable nitride and corresponded with similar studies using calcium (Ca_3N_2) or magnesium (Mg_3N_2) as the nitride source [13]. Transition metal nitrides are known to be non-stoichiometric with cubic phases spanning a compositional range from *ca* MN to $MN_{0.50}$ [2]. The a lattice parameter of the cubic phase can be used to measure the degree of nitridation [16], in the reactions studied with Ba_3N_2 and Sr_2N and anhydrous metal chlorides this indicates nitridations in the range $MN_{0.80}$–$MN_{0.96}$.

No reaction were observed between lanthanide chloride and either strontium or barium nitride in sealed ampoule reactions at 450–500°C. This correlates with previous reactions between calcium and magnesium nitride and lanthanide halides where reactions could only be made to go albeit slowly at 900°C [13]. Lithium nitride does react with lanthanide chloride at 400°C in a sealed ampoule inducing in some cases a thermal flash and formation of lanthanide nitride [7].

Point source initiation

The reactions between various nitriding agents and metal chlorides were investigated in the point source propagation mode. Lithium nitride and transition metal chlorides reacted to form a binary nitride of formulation M_xN_y and lithium chloride eq. (2). The phases of materials produced were in line with bulk thermal studies. Other nitride sources such as Ba_3N_2 and Sr_2N could also be made to react with early transition metal halides in the propagation mode [eqs (3) and (4)]. Reactions of the latter transition metal chlorides and lithium nitride produced the metal and dinitrogen [eq. (5)].

$$MCl_n + Li_3N \rightarrow MN + LiCl \quad (M = Ti, Zr, Hf) \quad (2)$$

$$MCl_n + n/6Ba_3N_2 \rightarrow MN + BaCl_2 \quad (M = Ti, Zr, Hf) \quad (3)$$

$$MX_n + n/4Sr_2N \rightarrow MN + SrCl_2 \quad (M = Ti, V, Zr, Hf) \quad (4)$$

$$MCl_n + Li_3N \rightarrow M + N_2 + LiCl$$
$$(M = Mo, W, Mn, Fe, Co, Ni, Cu). \quad (5)$$

Reactions of anhydrous lanthanide chlorides and lithium nitride only worked very slowly in the propagation mode for $EuCl_3$ and $YbCl_3$ and not for Ln = Gd, Tb, Ho, Er, Y and La. The other nitride sources (Ba_3N_2, Sr_2N, Ca_3N_2) would not support a propagation wave, however some reaction did occur at the tip of the filament. Interestingly $LaCl_3$ (m.p. 873°C) would not support a propagation wave but reaction of LaI_3 (m.p. 761°C) did with equimolar amounts of Li_3N. The fact that $EuCl_3$ and $YbCl_3$ did support a propagation wave could be related to their lower reduction potentials than the other lanathanides. As such this could tie in with a reductive recombination mechanism. However detailed speculation based on these results is not warranted and does not correlate with previous bulk thermal studies [7]. In all of the propagation mode reactions the degree of reagent mixing and filament temperature was crucial. Ease of reaction was affected by the particle size and filament temperature; better grinding of the reagents helping to facilitate propagation, so to did a filament temperature above 800°C. Reactions that could not be initiated despite thorough grinding can be directly related to thermodynamic considerations [15] (i.e. the reaction is endothermic or weakly exothermic).

Kaner has shown that ease of propagation in the filament mode initiation can be related to $T_{ad,s}$ the adiabatic reaction temperature for salt formation only and the melting point of the coproduced halide [15] ($T_{ad,s}$ was calculated by equating the reaction enthalpy for $MCl_3 + Li_3N \rightarrow LiCl + M + N$, to the integrated heat capacity, taking into account any heats of fusion or evaporation). If $T_{ad,s}$ is greater than the melting point of the coproduced salt then the reaction will propagate, if less then the reaction fails to propagate. Here we have found that reaction of Mg_3N_2 and $TiCl_3$ fails to propagate and has a calculated $T_{ad,s}$ value of 80°C ($\Delta H_{ad,s} = -3$ kJ mol^{-1}), whilst reaction of Li_3N and $TiCl_3$ has a $T_{ad,s}$ value of 1343°C ($\Delta H_{ad,s} = -340$ kJ mol^{-1}) and the reaction proceeds rapidly in the filament mode. Taking a mix of 1 Li_3N to 1 Mg_3N_2 with $TiCl_3$ has a $T_{ad,s}$ value of 670°C (m.p. of LiCl = 617°C) and the reaction just propagates, lower than this ratio and the reaction fails to propagate.

Thermal studies

The initiation and maximum reaction temperatures (T_{max}) reached in the reaction of Li_3N and MCl_n were determined by thermocouple measurements. Initiation temperatures for reactions of Li_3N and metal halides were commonly found to be in the region of 300–400°C. This is below the decomposition temperatures of the chlorides and lithium nitride and so must correspond to the temperature at which solid state diffusion is rapid enough to support self propagation [13]. Heating occurs very rapidly and mixtures return to the furnace temperature within about 30 s. Maximum self generated reaction temperatures were normally measured as 900–1100°C. The theoretical maximum temperatures in these reactions, the adiabatic temperature $T_{ad} = 1383$°C, the boiling point of LiCl since the heat of vaporisation of LiCl (151 kJ mol^{-1}) takes up all the excess energy. The difference between theoretical and experimentally determined temperatures may be attributed to expulsion of material from around the thermocouple. (Note; T_{ad} and $T_{ad,s}$ are different, T_{ad} takes into account the heat of formation of the metal nitride.)

Differential scanning calorimetry for the reaction of zirconium chloride with lithium nitride is shown in Fig. 1. This reaction shows a complex but reproducible series of exotherms in the temperature region 200–500°C. SHS reactions typically proceed in thermal explosion mode with the DSC showing a single sharp peak. Clearly the processes occurring in the metathesis reactions are more complicated. The DSC traces do not match the thermocouple measurements for SSM reactions (on a much larger scale) which show a single exotherm. The small scale of the DSC experiments could allow the separation of two distinct reaction steps which are not observed with the thermocouple because the volume of reagents is sufficient to allow the reaction to propagate.

Dilution experiments

Previous work has shown that addition of LiCl to a reaction of Li_3N and $TiCl_3$ reduces the overall maximum reaction temperature and reduces the crystallinity of TiN produced [17]. A dividing line in

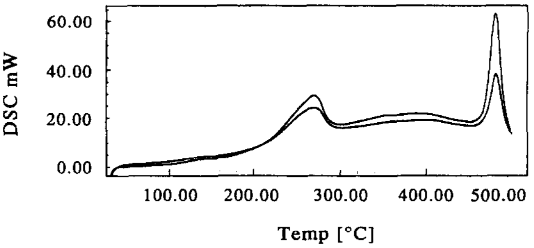

Fig. 1. DSC trace for the reaction of zirconium chloride and lithium nitride (upper and lower traces are for different reaction scales).

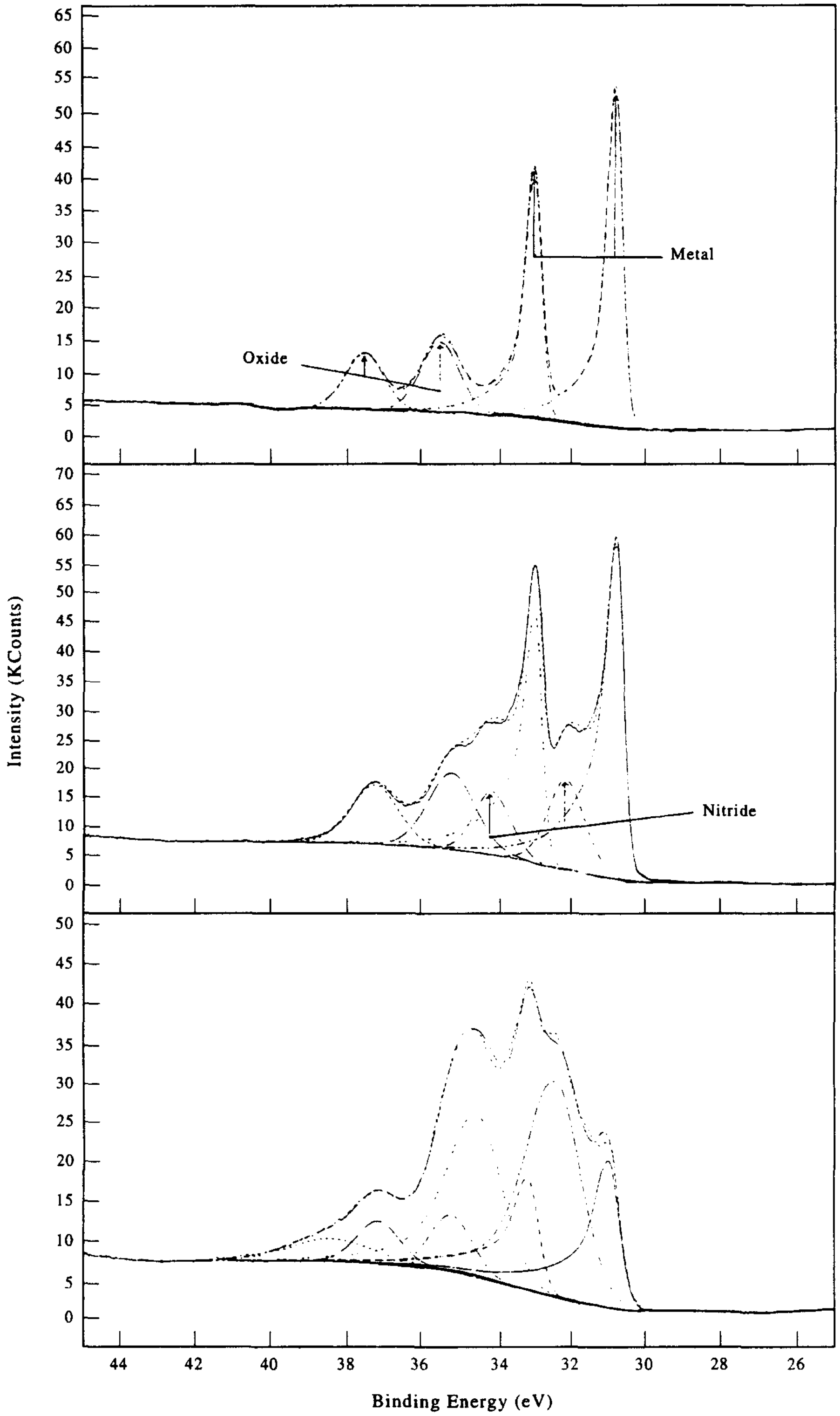

Fig. 2. W4f region of the X-ray photoelectron spectra for products of WCl_4 and Li_3N with increasing dilution; (top) undiluted, (middle) with 300 mg of LiCl added, (bottom) with 600 mg of LiCl added. All reactions on a scale of 50 mg of Li_3N.

nitride formation reactions has been observed at the chromium group. Reaction of $CrCl_3$ and Li_3N produces Cr_2N whilst reaction of tungsten tetrachloride with lithium nitride produced only tungsten metal, as analysed by XRD. This is because tungsten nitrides are thermally unstable, decomposing at 650°C (WN) and 790° (W_2N). Diluting the reaction of WCl_4 and Li_3N with LiCl progressively increases the degree of nitridation presumably because the reaction temperature is reduced. The products were poorly crystalline and characterised by XPS. Figure 2 shows the XPS data for three samples. With no added LiCl, tungsten metal and tungsten oxide are the only peaks in the W 4f region [18]. The oxide may be attributed to surface oxidation since subsequent argon ion etching reduced the oxide peak intensity relative to the metal. Addition of 300 mg of LiCl causes some nitride to be produced and the ratio of tungsten metal : tungsten nitride is 1 : 0.48. Addition of 600 mg of LiCl increases the amount of nitride and the ratio of metal : nitride is 1 : 2.22. The peaks in the nitride region are also asymmetric, indicating metallic character and supporting their assignment as nitride [18]. The tungsten nitride produced by the lower temperature metathesis reaction was of insufficient crystallinity to be studied by XRD. However the XPS data suggests that it is possible to form nitrides for the later transition metals providing the reaction temperatures can be lowered to below the nitride decomposition point. This data may shed some light onto the mechanism of the solid state metathesis reaction. The ionic metathesis mechanism could be seen to be effective at lower temperatures (600–700°C).

CONCLUSIONS

Reaction of strontrium and barium nitride with anhydrous transition metal chlorides offers a facile route to early transition metal nitrides. The reactions of Li_3N and transition metal halides have initiation temperatures between 300 and 400°C and generate maximum reaction temperatures in excess of 1000°C. Dilution with lithium chloride reduces reaction voracity, results in smaller particle and crystallite sizes and in some cases increases product nitridation.

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