

RAPID, LOW ENERGY SYNTHESIS OF LANTHANIDE NITRIDES

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Abstract—Thermal initiation (400°C) of the reaction between lithium nitride and anhydrous lanthanide halides produces lanthanide nitrides LnN (Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb) *via* a rapid exothermic solid state metathesis reaction. Mixed lanthanide nitrides LnLn'N (LnLn' = PrNd; DyHo; TbDy) are made by reaction of ground powders of LnCl₃ with Li₃N. The lanthanide nitrides were characterized by X-ray powder diffraction, scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDXA), FTIR, magnetic moment measurement and microanalysis.

Metal nitrides are refractory, durable, ceramic materials that are used industrially as hardness/reflectance coatings, catalysts, abrasives and semi/super conductors.^{1,2} They are made conventionally by direct combination of the elements or by reaction of ammonia with anhydrous metal halides.^{3,4} Both routes require temperatures in excess of 900°C and prolonged annealing to produce a crystalline material.

Recently a resurgence of interest in novel synthetic strategies to new and existing metal nitrides have been developed using so called "advanced materials" wherein formation of a pre-ceramic material at low synthesis temperatures is encouraged by facile intramolecular or ammonia initiated bimolecular decomposition reactions.^{5,6} Such reactions, involving a single source precursor, often suffer from incorporation of carbon and oxygen into the nitride film or powder from competitive degradation pathways.7 Dual source reactions involving ammonia and metal amides have proven useful for both the MOCVD deposition of nitride films and for bulk solid production. The introduction of extra nitrogen from the ammonia may stimulate decomposition intramolecularly. although pure metal nitrides are difficult to isolate using this approach because of competing side reactions which incorporate other elements into the product, particularly carbon.⁶

A new approach to the synthesis of transitionmetal sulphides has been initiated recently by Kaner *et al.*⁸ Wherein reaction of an alkali metal sulphide with a metal halide induces a spontaneous exothermic solid state metathesis reaction, yielding an alkali metal salt and the desired metal sulphide.⁹ Similar reactivity has also been reported for the formation of gallium arsenide and phosphide¹⁰ and tetrasulphur tetranitride.¹¹

Lanthanide nitrides can often be non-stoichiometric in nitrogen¹² or occluded metal with the physical properties determined by the degree of nitrogen vacancy.¹³ Lanthanide nitrides LnN possess the NaCl type (Fm3m) structure.¹³ A solventless preparation of lanthanide nitrides involving ammonlysis of homoleptic lanthanide bistrimethylsilylamide derivatives has allowed synthesis temperatures approaching 250°C but require prolonged annealing at 570–880°C to produce a crystalline product.¹⁴ We report here the use of lithium nitride in the formation of lanthanide nitrides *via* solid state metathesis reactions.

EXPERIMENTAL

Tetrahydrofuran (THF) was distilled from Na/benzophenone and stored over 4 Å molecular sieves prior to use. All reagents were handled under nitrogen using either a glove box or Schlenk line techniques. Glass ampoules made of thick walled borosilicate or quartz glass were annealed prior to use and thoroughly dried, either, by baking in a fur-

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nace at 450°C for 6 h or by flame drying under vacuum. Anhydrous lanthanide halides and lithium nitride were obtained from Strem chemicals and used as supplied. Infra-red spectra were obtained on a Nicolet 205 (CsI) using KBr and CsI pellets. Xray powder diffraction (XRD) measurements were performed on a Siemens Diffractometer D5000 using Cu- K_{α} ($\lambda = 1.5418$ Å) radiation; magnetic moment measurements on a Johnson Matthey balance and SEM profiles on an Jeol JSM820 instrument using a Kevex program¹⁵ for EDXA analysis. Gas chromatograph (G.C.) analyses were performed on a Pye Unicam 204 with 5 Å sieves column using a thermal conductivity detector with helium carrier gas.

Nitrogen microanalyses were performed by Medac Ltd using fierce condition combustion analysis (1400°C) and at the Open University using Kjedahl nitrogen analysis.¹⁶ A Lenton Thermal Designs programmable tube furnace or an industrial microwave oven (750W, 2.45 GHz) was used to initiate the reaction of Li₃N and lanthanide halides.

Preparation of lanthanide nitrides

The same general procedure was adopted for the preparation of all the lanthanide nitrides (Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb), illustrated below for dysprosium nitride.

Lithium nitride (0.1 g, 2.85 mmol) and anhydrous dysprosium chloride (0.76 g, 2.85 mmol) were carefully ground together under an atmosphere of nitro-

gen and placed in a thick walled glass ampoule. The ampoule was sealed in vacuo, the contents thoroughly mixed using a whirlimixer and placed in a tube furnace at 400°C. After approximately 1 min; a red glow eminated from the ampoule for 2-3 sec in which time the ampoule walls were coated in a white solid and the main body of material was contained in a fused homogeneous black lump. The ampoule was removed from the oven, allowed to cool to room temperature and broken open under a nitrogen atmosphere. The black material was triturated with THF (2×20 ml) and dried in vacuo. The identity of the black solid was confirmed by Xray powder diffraction, microanalysis, FTIR, magnetic moment measurement and SEM/EDAX, as reported in Table 1 for DyN. Ceramic yields of lanthanide nitrides were typically greater than 90%.

Microanalysis (combustion) Found: N, 6.5; Calc. for ErN: N, 7.7; Found: N, 5.5; Calc. for TbN: N, 7.9; Found: N, 7.5; Calc. for SmN; N, 8.5. Lithium was present at less than 0.1% and C and H levels were less than 0.25% in the LnN powders by microanalysis.

The reaction of lithium nitride with anhydrous lanthanide halides in sealed ampoules *in vacuo* were also initiated by heating in a microwave oven for a variable induction period between 1 and 10 min. The formation of a white solid on the ampoule walls and a fused black solid was also apparent when using microwave induction. The physical properties of the materials prepared in the microwave oven where initiation occured were identical to that of those prepared by conventional oven initiation.

Table 1. Observed lattice parameter a and magnetic moment measurements for lanthanide nitride made by low temperature reaction of Li₃N and LnCl₃

Lanthanide nitride	Crystallite size ¹⁹ (Å)	Lattice parameter a (Å) (ESD ± 0.01 Å)	Ref <i>a</i> parameter ¹⁷ (Å)	μ_{exp} (BM)	$\mu_{\rm ref}^{18}$ (BM)	$\mu_{cal} (Ln^{3+})^{14}$ (BM)
YN	200	4.89	4.89			
LaN	200	5.33	5.30			
PrN	320	5.15	5.15	3.6	3.57	3.58
NdN	300	5.14	5.14	3.7	3.65-4.0	3.62
SmN	250	5.03	5.04	1.4	1.60	0.85
EuN	350	5.01	5.01	4.1	0–5	0
GdN	350	4.98	4.99			
TbN	250	4.94	4.93	9.6	9.5-10.0	9.72
DyN	250	4.91	4.91	10.4	10.5-10.6	10.6
HoN	250	4.87	4.87			
ErN	200	4.84	4.84	9.4	9.2–9.4	9.5
YbN	250	4.78	4.78	4.4	5.1	4.54

 $\lambda = 1.5418$ Å (measurements at room temperature 291 K). Crystallite size based on the Scherrer equation,¹⁹ all LnN adopt a NaCl type lattice, $\mu_{exp} =$ experimentally observed magnetic moment; $\mu_{ref} =$ literature value for magnetic moment; $\mu_{eal} =$ theoretical value for the magnetic moment based on Ln³⁺.

Mixed lanthanide nitride preparation

The same procedure as outlined for lanthanide nitrides was used to make the mixed lanthanide species, except equal molar quantities of the preground lanthanide chlorides and lithium nitride were combined in the glass ampoules and evacuated prior to initiation.

Detection of evolved gases from the reactions of anhydrous lanthanide halide with Li_3N were performed in evacuated glass ampoules with sealable teflon taps and an adaptor suitable for GC analysis. After the reaction had been initiated by the conventional oven technique and allowed to cool to room temperature, the ampoule was opened to an argon line for 2–3 sec to equalise pressure and a sample of the gas above the solid was analysed by G.C. This showed a peak assignable only to that of argon.

The reaction of lithium nitride with lanthanide halides is extremely exothermic and over many runs some ampoules cracked during the reaction. The use of safety screens around the oven is essential. Combining hydrated lanthanide halides with lithium nitride can lead to a spontaneous reaction with the formation of some lanthanide oxide without external initiation. Such a reaction is highly dangerous and seemingly uncontrollable.

RESULTS AND DISCUSSION

The solid state reaction of anhydrous lanthanide chloride with lithium nitride is extremely rapid and exothermic producing crystalline lanthanide nitrides in good yield eq. 1.

$$Li_3N + LnCl_3 \rightarrow LnN + 3LiCl$$
 (1)

(Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb)

The only products detected from the reaction (Xray powder diffraction)¹⁷ were LnN and LiCl, the latter of which was removed by THF trituration to leave phase pure LnN (Table 1). A representative powder pattern for NdN is shown in Fig. 1. Both the THF washings and the white solid that coated the ampoule walls was identified as lithium chloride by X-ray powder diffraction, EDXA analysis (just chlorine present) and lithium flame test. The EDXA elemental step analysis of the lanthanide nitride (after THF trituration) showed no chlorine (or oxygen, 3% detection limit) remaining in the product. No nitrogen was detected from the sealed ampoule reactions by G.C. analysis.

Nitrogen microanalysis of the lanthanide nitrides revealed a stoichiometry of $LnN_{1-x}(x = 0.1-0.2)$ analogous to previous studies using molecular pre-



Fig. 1. Upper trace; X-ray powder diffraction pattern for the reaction of NdCl₃ and Li₃N after thf trituration lower trace standard NdN pattern.¹⁷

cursor routes.¹⁴ Combustion analysis invariably gives low levels of nitrogen because lanthanide nitrides are refactory materials (m.p.t. > 1400°C). Kjedahl microanalysis¹⁶ gave nitrogen levels higher than that of the combustion analysis; however an insoluble residue was present, so the formulation SmN_{0.9} should be taken as a lower limit to the amount of nitrogen. Microanalysis indicated lithium was present at less than 0.1% in the triturated LnN powders.

The FT-IR spectra of the triturated lanthanide nitride showed only a broad band at 450 cm^{-1} , probably due to Ln-N stretching vibration. Magnetic moment measurements¹⁸ showed values typical of lanthanide nitrides indicating that the metal was in the expected Ln^{3+} oxidation state (Table 1). SEM analysis of the pre-triturated material showed a smooth surface profile due to LiCl coatings; washing with tetrahydrofuran removed this coating and sharp edges due to small (micron sized) particles of lanthanide nitride were observed. From the Scherrer equation,¹⁹ based on the X-ray powder diffraction line width the LnN (Fm3m) crystallite size is in the range 200-350 Å. The crystallite size determined by XRD is smaller than the particle size determined by SEM indicating that the paticles are agglomerates.

The washed lanthanide nitrides slowly oxidize in air to Ln_2O_3 ; the EDXA analysis shows an increase in the intensity of the oxygen peak resulting from exposure to air. The non-triturated material rapidly absorbs moisture from the air due to the presence of LiCl, with consequent loss of crystallinity for the nitride and rapid formation of the oxides. Lanthanide nitrides made by corresponding high temperature reactions are also moisture sensitive, decomposing to the metal oxide and ammonia on prolonged exposure to air.^{14,16}

Hess' law calculations²⁰ indicates that the reaction of lanthanide chloride and lithium nitride is exothermic with $\Delta H_{\rm f} = -300$ kJ mol⁻¹. Similar values would be expected for the $\Delta H_{\rm f}$ of the other lanthanide nitrides because of the isostructural nature of the products.

The reactions of LnCl₃ with Li₃N required initiation by an external heat source either by microwave or conventional oven heating. Grinding the reagents together at room temperature did not initiate a reaction unlike the work of Kaner to produce transition metal sulphides.⁸ After a variable induction period of a few seconds to 10 min in either oven, the reaction initiated and the ampoule glowed red for a few seconds during which time a white solid was sublimed onto the ampoule walls and the bulk product was fused in a black mass. It is apparent that a certain initiation temperature is required because ampoules heated to 250 or 300°C in the conventional oven showed no reactivity even after an hour. It is likely that a critical temperature is required to overcome the solid state diffusion barrier and allow a localized reaction to spread through the whole material. An initiation temperature of 400°C, as commonly used in these experiments, does not correspond to the decomposition/melting points of either LiCl (613°C) or Li₃N (550°C).¹⁶ The crystallinity of the lanthanide nitrides are comparable with conventional synthesis temperatures of 850°C for many hours.¹⁶ Optical pyrometry of associated solid state metathesis reactions to form GaP and GaAs, from gallium trichloride and sodium phosphide, indicate temperatures in excess of 750°C are generated.⁹ The short reaction time (once initiated) and observation of sublimed material on the ampoule walls indicates that the reaction is exothermic and self energetic. The main bulk of the solid is in the form of a fused lump which is consistent with a molten reaction core. The co-formation of lithium chloride may be advantageous in inducing a crystalline product. Molecular precursor routes to lanthanide nitrides have found that judicious addition of lithium chloride or lithium amide to the pre-reacted material allowed significantly lower lanthanide nitride crystallization temperatures (275–500°C).¹⁴

The initiation of some of the reactions by microwave heating appears fortuitous because the microwave source was not tunable and relied on the commercial excitation frequency (2.45 GHz). However metal halides are known to absorb microwave energy to various degrees this is reflected in the varying induction periods for the reaction depending on which lanthanide halide was used.²¹ The use of microwaves to initiate these reactions has no clear advantages over the initiation of the reaction by means of a conventional oven. Indeed not all of the reactions initiated, even after 10 min of microwave irradiation.

The initiation temperature and similar conventional oven induction times were observed for all the reactions of lanthanide halides and Li_3N studied. No deviation in reactivity was observed for either YbCl₃ or EuCl₃, which have the possibility for reduction to a stable M^{2+} oxidation state. Reaction of InCl₃ or GaCl₃ with Li_3N under similar conditions was found to undergo reduction to the metal with simultaneous formation of nitrogen.

Combination of equimolar quantities of $LaCl_3$ and $ErCl_3$ with lithium nitride in an ampoule followed by mixing and thermal initiation does not lead to the formation of a mixed nitride $La_x Er_y N_z$ but to the individual LaN and ErN lattices, (and some crystalline LiCl) Fig. 2. However when lan-



Fig. 2. Upper trace, X-ray powder diffraction pattern for the reaction of LaCl₃ and ErCl₃ with Li₃N (before trituration); lower trace, standard LaN and ErN patterns.¹⁷ The asterixed peaks are due to crystalline LiCl co-produced in the reaction.

thanides of similar ionic radii are reacted in this manner, a broadened XRD pattern between that expected for the individual lanthanides nitrides is observed. This indicates the possibility of making mixed lanthanide nitrides in a stoichiometrically controlled fashion. In the latter case, the scale of the reaction is crucial with the larger scale producing better intermixing of the lanthanide elements, consistent with better solid state diffusion and higher reaction temperatures. The EDXA



Fig. 3. Upper trace expansion of X-ray powder diffraction pattern of mixed DyHoErTbN₄ obtained form the reaction of Li₃N and equimolar quantities of DyCl₃, HoCl₃, ErCl₃, TbCl₃ (before trituration), patterns for Gadolinium nitride GdN (···), Terbium nitride TbN (—), Dysprosium nitride DyN (---) and Holmium nitride HoN (·-·-).¹⁷ *indicates LiCl co-product.

elemental step analysis and SEM profile of the mixed lanthanide nitrides $Ln_x Ln_y' N (Ln, Ln' = Pr,$ Nd; DyHo; TbDy) were uniform across the surface, whilst the magnetic moment of the mixed lanthanide nitrides were intermediate between the values for the individual lanthanide nitrides (TbDyN; $\mu = 10.0$ BM, TbN $\mu = 9.6$ BM; DyN $\mu = 10.4$ BM). Lanthanide elements with similar ionic radii will have a lower barrier to solid state diffusion and hence a mixed lanthanide nitride lattice or solid solution (as predicted by Vegards law²²) is more likely. The broadening of the XRD pattern for the mixed lanthanide nitrides reactions could also be due to localized changes in composition. This is the case for reaction of equimolar quantities of GdCl₃, TbCl₃, DyCl₃ and HoCl₃ with Li₃N where a solid solution nitride is formed. The diffraction lines of the mixed species Gd_{0.25}Tb_{0.25}Dy_{0.25}Ho_{0.25}N $(\mathbf{a} = 4.925\text{\AA})$ are broad and between those of the binary compounds GdN, TbN, DyN and HoN (a = 4.877 - 4.976 Å) Fig. 3.

CONCLUSION

Reaction of lithium nitride with anhydrous lanthanide halides produces crystalline lanthanide nitrides and lithium chloride *via* a rapid exothermic solid state metathesis reaction. The reaction requires initiation *via* a conventional or microwave oven but is self sustaining. All of the lanthanide halides in this study rapidly produced crystalline materials on reaction with Li₃N. The easy removal of impurities (LiCl) and lack of oxygen or carbon contamination in the product compared to molecular precursor routes, illustrates the growing applicability of solid state routes to materials.

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