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Preparation of Lanthanide Nitrides via Ammonolysis of Molten $\{(Me_3Si)_2N\}_3Ln$: Onset of Crystallization Catalyzed by $LiNH_2$ and LiCl

The recent resurgence of materials[1] and solid-state chemistry[2-4] has prompted interest in new methodologies[5-8] for the preparation of refractory metal oxides, carbides, and nitrides.[9] Conventional syntheses of ceramics require combining the appropriate elements at very high temperatures for long periods, in order to attain diffusion rates sufficient to produce a homogeneous material. One alternative involves the use of molecular precursors that contain or can be converted to an intimate mixture of the desired elements. Advantages of such methods include lower processing temperatures and the generation of metastable (i.e., kinetic) phases that are inaccessible via standard procedures that inevitably lead to thermodynamic products.[10]

Rare-earth metal nitrides are conventionally synthesized[11-13] as black powders from nitrogenolysis or ammonolysis of the metal or metal hydride at temperatures near 1000 °C. The nitrides possess a rock salt structure (*Fm*3*m*), display substantial conductivity, and are frequently nonstoichiometric in nitrogen or contain occluded metal.[14] Their magnetic, electronic, and conductivity[15] properties appear to be dictated by numerous nitrogen-site vacancies,[16] and thus measurements of the intrinsic properties of stoichiometric LnN are difficult to achieve. Reported herein is a versatile method for the preparation of lanthanide nitrides involving the ammonolysis[10,17] of molten molecular precursors.

Precursor Synthesis. The precursors used in this study are three-coordinate amido complexes, $\{(Me_3Si)_2N\}_3Ln$ (Ln = Y, La, Pr, Nd, Sm, Eu, Yb), initially prepared by Bradley et al.[18] according to eq 1. The literature procedure was slightly modified,[19]

$$LnCl_3 + 3LiN(SiMe_3)_2 \xrightarrow[-3LiCl]{THF} \{(Me_3Si)_2N\}_3Ln \qquad (1)$$

leading to increased yields (75–90%), and the series was expanded to include Tb and Er. Importantly, these compounds melt in the range 150–180 °C without decomposition. Care was taken to rid the tris(amides) of trace amounts of THF in order to ensure minimal oxide contamination. Sublimation served as the final purification step, yet small amounts (1–3 mol %) of $LiN(SiMe_3)_2$ remained in certain cases (Ln = Pr, Nd, Er), and proved critical to low-temperature nitride formation.

LnN_{1-x} Synthesis. Scheme I illustrates the two-stage process utilized in the synthesis of LnN_{1-x}.[20] Under dinitrogen, the

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Scheme I

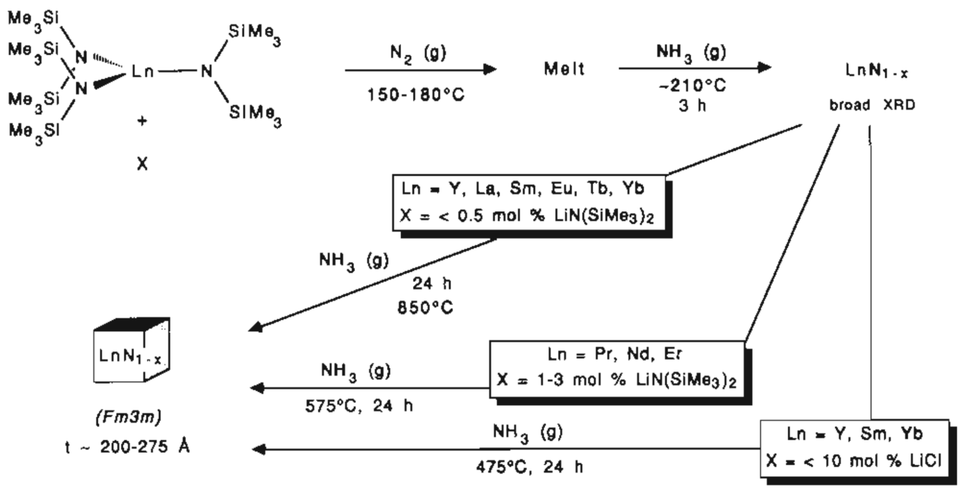

Table I. Physical Characteristics of LnN Produced from $\{(Me_3Si)_2N\}_3Ln$ According to Scheme I[a–c]

LnN	color at 210 °C	color after annealing[a–c]	% wt loss		a, Å		crystallite size, Å[e]
			calcd	obsd	lit.[d]	obsd	
YN[a,c]	brick-red	blue-violet	82	81	4.894	4.893 (1)	250
LaN[a]	orange	gray	75	76	5.30	5.296 (2)	>275
PrN[b]	purple	purple-black	75	72	5.165	5.163 (2)	275
NdN[b]	green	dark green	75	69	5.141	5.137 (2)	>275
SmN[a,c]	purple	dark purple	74	76	5.048	5.048 (1)	>275
EuN[a]	orange	brown	74	72	5.014	5.007 (2)	>275
TbN[a]	orange-red	black	73	73	4.933	4.945 (6)	200
ErN[b]	orange	purple-black	72	70	4.839	4.836 (6)	200
YbN[a,c]	orange	orange-brown	71	71	4.786	4.778 (4)	275

[a] Sample contained <0.5 mol % $LiN(SiMe_3)_2$; annealed at 850 °C for 24 h. [b] Sample contained 1–3 mol % $LiN(SiMe_3)_2$; annealed at 575 °C for 24 h. [c] Sample contained <10 mol % adventitious LiCl;[27] annealed at 475 °C for 24 h. [d] Reference 23. [e] References 3 and 22.

$\{(Me_3Si)_2N\}_3Ln$ precursor was melted in an alumina boat and then subjected to a flow (~0.8 mL/min) of dry ammonia at ~210 °C for 3 h. Ammonolysis was induced, and $(Me_3Si)_2NH$ was observed downstream from the boat. The boiling point of $(Me_3Si)_2NH$ (bp 125 °C) is below that of the melt, reducing the possibility of amine occlusion and degradation. For precursors containing adventitious LiCl[21] or 1–3 mol % $LiN(SiMe_3)_2$ impurities, some order was observed in the material obtained at ~210 °C, as evidenced by very broad peaks in the powder X-ray diffraction pattern (XRD). From the Scherrer equation,[3,22] the LnN_{1-x} (*Fm3m*) crystallite size at this stage is roughly 40–50 Å. In the second stage, the material was annealed under NH_3 for 24 h at higher temperatures to obtain crystalline LnN_{1-x}, whose sharp lines in the XRD roughly correspond to a crystallite diameter of ~200–275 Å. Although the lattice constants of these compounds are virtually identical to those obtained for conventionally prepared black LnN_{1-x} (Table I),[11–13,23,24] the majority displayed distinct, albeit dark, colors.

The initial ammonolysis is thought to be rapid, since the corresponding solution chemistry occurs almost instantly. When $\{(Me_3Si)_2N\}_3Y$ (<0.5 mol % $LiN(SiMe_3)_2$) was subjected to NH_3 in benzene-d_6, loss of 3.0 (3) equiv of $(Me_3Si)_2NH$ was noted by ^1H NMR spectroscopy (relative to Cp_2Fe internal standard), with concomitant precipitation of a pyrophoric white material. Thermolysis of the latter at 500 °C for 48 h also yields YN_{1-x} (*Fm3m*).

While the XRD studies of LnN_{1-x} indicate a lack of occluded metal, analytical measurements manifest typical nitrogen deficiencies. For example, spectrophotometric Kjeldahl nitrogen analyses of the neodymium and samarium nitrides revealed that $x \leq 0.1$ (Nd) and ≤ 0.2 (Sm).[25] Electron microprobe analysis[26]

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(20) Typical experimental procedure (e.g., YbN from $\{(Me_3Si)_2N\}_3Yb$): An alumina boat was charged with 273 mg (0.42 mmol) of $\{(Me_3Si)_2N\}_3Yb$ and placed into a 22-mm inner-diameter quartz tube. A Cajon fitting with a three-way valve was tightened onto one end, and an identical Cajon fitting with a toggle valve was placed on the other. The tube was set into a Lindbergh split furnace. A $^1/_8$-in. diameter stainless steel tube with Cajon fittings at each end was tightened onto the three-way valve inlet and connected to a glass adapter fitted to a 2-L round-bottomed flask containing liquid NH_3 dried over sodium. The NH_3 was purged through the three-way valve for 30 min. The sample was then heated under static N_2 atmosphere at 3.5 °C/min until the $\{(Me_3Si)_2N\}_3Yb$ was completely molten (mp 162–165 °C). Ammonia was then passed over the boat and out through a mineral oil bubbler. On the cool protruding part of the tube, $(Me_3Si)_2NH$ was observed to condense, and a yellow-green powder formed in the boat. The heating rate was slowed to 2 °C/min, and at 250 °C the powder appeared orange (~3 h). The sample was heated at 475 °C for 24 h and then cooled to room temperature at 5 °C/min. Both valves were closed, and the tube was taken into the drybox. XRD showed YbN_{1-x} and a small amount of LiCl. Total yield of orange-brown YbN was 79 mg (0.42 mmol, 71% weight loss, 71% calculated).

(21) Three origins of the LiCl impurity (estimated to be 5–15 mol %) are evident. Incomplete displacement of Cl^- from $LnCl_3$ may produce $\{(Me_3Si)_2N\}_2LnCl$ and unreacted $LiN(SiMe_3)_2$. See: (a) Aspinall, H. C.; Bradley, D. C.; Hursthouse, M. B.; Sales, K. D.; Walker, N. P. C.; Hussain, B. *J. Chem. Soc., Dalton Trans.* **1989**, 623–626. Formation of $[\{(Me_3Si)_2N\}_3LnCl]Li$ is also a possibility. See: (b) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131–177. (c) Tilley, T. D.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 3267–3270. (d) Watson, P. L.; Whitney, J. F.; Harlow, R. L. *Ibid.* **1981**, *20*, 3271–3278. (e) Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2015–2017. Third, an incomplete separation of LiCl from product tris(amide) is plausible. Removal of LiCl impurity may be undertaken by employing $MN(SiMe_3)_2$ (M = Na, K), followed by sublimation of the tris(amido)lanthanide: (f) Bradley, D. C. Personal Communication.

(22) From XRD, the crystallite diameter, $t = 0.9\lambda/B \cos \theta_B$, where $B^2 = B_M{}^2 - B_S{}^2$ (B_M = half-maximum line width (in radians) at $2\theta_B$, B_S = half-maximum line width (in radians) of a line near $2\theta_B$ corresponding to a standard).

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was used to test for possible silicon incorporation in ErN_{1-x} synthesized from $\{(Me_3Si)_2N\}_3Er$ contaminated with ~2 mol % $LiN(SiMe_3)_2$; an upper limit of Si as 1 wt % was found. The silicon content of Er_2O_3 (Aldrich 99.9%) used to prepare $ErCl_3$ is less than 15 ppm, and thus trace Si incorporation is possible. Mass balance supported the contention that the ammonolysis of $\{(Me_3Si)_2N\}_3Ln$ proceeded smoothly, as indicated by the calculated and observed weight losses in Table I.

A distinct advantage to the melt technique concerns the ready preparation of $Ln_{1-y}Ln'_yN_{1-x}$ solid solutions, provided the constituents possess compatible ionic radii. Following the standard procedure,[20] a melt containing a 1:1 ratio of $\{(Me_3Si)_2N\}_3Y$ and $\{(Me_3Si)_2N\}_3Sm$ in addition to traces of LiCl (vide infra)[21] led to $Y_{0.5}Sm_{0.5}N_{1-x}$ after annealing at 600 °C for 24 h. The diffraction lines (found: $a = 4.968$ (3) Å) of the mixed lanthanide compound are broad and between those of the binary compounds (average of literature[23] values: $a = 4.971$ Å), indicative of a solid solution (see supplemental Figure 1).[11,27]

Onset of Crystallization. When higher purity $\{(Me_3Si)_2N\}_3Ln$ (Ln = Y, La, Sm, Eu, Tb, Yb; <0.5% $LiN(SiMe_3)_2$) was utilized in Scheme I, an annealing temperature of 850 °C (24 h) was required to provide LnN_{1-x}. However, if 1–3 mol % $LiN(SiMe_3)_2$ was present in $\{(Me_3Si)_2N\}_3Ln$ (Ln = Pr, Nd, Er) or when 10–15 mol % was ground and melted together with higher purity $\{(Me_3Si)_2N\}_3Yb$, crystalline LnN_{1-x} formed upon annealing for 24 h at 575 °C. Rapid ammonolysis of $LiN(SiMe_3)_2$ must occur, and the resulting $LiNH_2$ (tetragonal, *I*4, $a = 5.016$ Å, $c = 10.22$ Å)[28] catalyzes the crystallization of LnN_{1-x}. Transport processes mediated by protons or lithium from trace $LiNH_2$ (i.e., mineralization)[29] may increase nitrogen diffusion.

Lower annealing temperatures (Scheme I, 475 °C, 24 h) were also evident for LnN_{1-x} (Ln = Y, Sm, Yb) when adventitious LiCl was present.[21] In a control experiment, LiCl (10–15 mol %, *Fm*3*m*, $a = 5.1396$ Å)[23] was ground together with the higher purity $\{(Me_3Si)_2N\}_3Yb$. Evidence for crystalline YbN_{1-x} ($t \sim$ 40–50 Å) was obtained at 200 °C, and the material crystallized ($t \sim 100$ Å) upon annealing at 475 °C for 24 h. A mineralization process is again viewed as responsible for the lower onset of crystallization, although LiCl (mp 614 °C) may be capable of serving as a flux.

Since both LiCl and $LiNH_2$ possess lattice parameters near those of the lanthanide nitrides, a mechanism whereby the impurities seed the crystallization of LnN_{1-x} was considered. However, when YN_{1-x} ($a = 4.895$ (1) Å), prepared using the high temperature method of Klemm (i.e., Y + NH_3 at 950 °C),[12] was added (15 mol %) to the high-purity $\{(Me_3Si)_2N\}_3Ln$ (Ln = Y, Sm; <0.5% $LiN(SiMe_3)_2$) precursors, crystallization occurred near 850 °C (24 h). Since YN_{1-x} did not seed the formation of YN_{1-x} or SmN_{1-x}, mineralization mechanisms are considered the most likely explanation for the aforementioned catalyses.

LnN_{1-x} Properties. The colors of the lanthanide nitrides prepared via the melt technique (Table I) may indicate that their physical properties deviate from those of conventionally synthesized black powders. Unfortunately, attempts to measure accurate conductivities have been hampered by difficulties in producing clean pellets, presumably due to surface oxide impurities. Variable-temperature magnetic susceptibility measurements of PrN_{1-x} revealed paramagnetic behavior to 4.2 K, with an ambient temperature magnetic moment of 3.5 μ_B, a value similar to that previously reported for PrN_{1-x} prepared via high-temperature methods.[30] No magnetic ordering was observed, although such phenomena have been postulated for truly stoichiometic LnN_{1-x}.[31] It is proposed that fewer nitrogen deficiencies are present in the melt-prepared LnN_{1-x} due to lower annealing temperatures, yet the presence of interstitial hydrides,[32] amides, or imides may be the origin of some differences in physical properties, since NH_3 is used in the synthesis. Lanthanide vacancies may also play a role. Methods to detect hydrogen, such as elastic recoil spectrometry,[33] have not yet been attempted.

The molten molecular precursor technique is currently being extended to ternary systems, and mechanistic studies pertaining to the catalysis of the onset of crystallization are continuing.

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Supplementary Material Available: XRD patterns for $Y_{0.5}Sm_{0.5}N_{1-x}$, YN_{1-x}, and SmN_{1-x} prepared from a melt containing a 1:1 ratio of $\{(Me_3Si)_2N\}_3Y$ and $\{(Me_3Si)_2N\}_3Sm$ in addition to traces of LiCl (Figure 1) (1 page). Ordering information is given on any current masthead page.

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Isolation and Characterization of a (Diphenylamido)ruthenium(IV) Porphyrin

Transition-metal dialkylamides are of considerable importance possibly due to their stabilization of unusual coordination numbers and valence states of metal ions, their interesting reactivity, and their possible connection to catalytic amination procedures.[1] Our interest in the (dialkylamido)ruthenium complexes was inspired by the following considerations. Several types of ruthenium(IV) porphyrins have been reported, including dinuclear (μ-oxo);[2] dihalogeno-,[3] dialkyl-,[3-5] monooxo-,[6] and monomeric dialkoxyruthenium(IV)[7] porphyrin complexes. Since the dialkylamido

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