Solutions of Lithium Salts in Liquid Lithium: Interaction between Silicon and Nitrogen to form the Ternary Compound, Li_5SiN_3

Andrew T. Dadd and Peter Hubberstey *
Department of Inorganic Chemistry, University of Nottingham, Nottingham NG7 2RD

The interaction between silicon and nitrogen when dissolved in liquid lithium (mol fraction Li $\geqslant$ 0.97) at 750 K has been monitored using electrical resistivity methods. Resistivity–time data indicate that an insoluble product is formed and that the kinetics of the various dissolution and precipitation processes are such that addition of gaseous nitrogen to Li–$Li_{22}Si_5$ solutions leads to a homogeneous solution reaction, whereas addition of solid silicon to Li–Li_3N solutions leads to a heterogeneous reaction mechanism at the solid–liquid interface. Resistivity–concentration data show that the reaction product has a Si : N ratio of approximately 1 : 3. *X*-Ray powder diffraction studies of the product when embedded in the lithium matrix and when isolated from the lithium (by vacuum distillation of excess lithium) confirm its identity as Li_5SiN_3. This material was also obtained from the corresponding 875 K solid state reaction between 1 : 3 and 1 : 4 mol ratios of $Li_{22}Si_5$ and Li_3N. Both Li_2SiN_2 and Li_8SiN_4 were also prepared, characterised by *X*-ray powder diffraction methods, and their stabilities to vacuum distillation conditions ascertained.

In previous work on the chemistry of liquid lithium solutions containing two non-metallic solutes, we have shown that the Li–C–N ternary system is the only one in which an interaction occurs. Thus, whereas no interaction was observed in the Li–H–C [1] and Li–H–N [2] ternary systems, the dilithium salt of carbodi-imide (cyanamide), Li_2NCN, was crystallised from solutions containing both Li_2C_2 and Li_3N.[3,4] As a continuation of our studies of the reaction chemistry of solute species in liquid alkali metals, we now wish to report the results of similar experiments in which the interaction between silicon and nitrogen when dissolved in liquid lithium is monitored at 750 K using the resistivity technique. The results were corroborated with an *X*-ray powder diffraction study of the 875 K solid state reaction between $Li_{22}Si_5$ and Li_3N, the salts which precipitate from dilute solutions of silicon [5] and of nitrogen [6] respectively, in liquid lithium.

A study of this reaction is of particular significance to nuclear fusion technology, since liquid lithium has been proposed as a tritium breeder and/or primary coolant in several designs of the deuterium-tritium fuelled thermonuclear reactor.[7] Owing to its extreme reactivity, contamination of the liquid metal by non-metals, including silicon and nitrogen, is inevitable. The ingress of silicon may arise either by contact with stainless steels (both ferritic and austenitic) or by reaction with silicon-containing ceramics or oils; that of nitrogen will occur as a result of unavoidable atmospheric contamination. Obviously, an elucidation of the interactions between dissolved impurities is an essential and integral pre-requisite to technological applications of liquid lithium.

Previous studies of the Li–Si–N system have concentrated on either synthetic routes to ternary nitrides, starting from Li_3N and Si_3N_4,[8–12] or compatibility tests between Si_3N_4 and liquid lithium.[13–15] The isolation of four ternary compounds, $LiSi_2N_3$, Li_2SiN_2, Li_5SiN_3, and Li_8SiN_4, has been claimed; their identification and characterisation has been effected primarily by *X*-ray diffraction techniques. Although diffraction patterns have been reported for all four compounds,[8–12] only those for $LiSi_2N_3$ (orthorhombic, space group $Cmc2_1$, a = 918.6, b = 530.2, c = 477.6 pm) [9] and Li_5SiN_3 (cubic, space group $Ia3$, a = 944 pm) [8] have been indexed.

The compound $LiSi_2N_3$ is well established and has been prepared by four groups of workers by high-temperature reaction of 1 : 2 mol ratios of Li_3N and Si_3N_4 in an atmosphere of nitrogen; [9–12] it has also been detected as a product of the reaction of lithium vapour with Si_3N_4.[13] Some uncertainty surrounds the synthesis of Li_5SiN_3. It has been prepared by Juza *et al.*[8] by reaction of Li_3N and Si_3N_4 in a 10 : 1 mol ratio under nitrogen at 1 075 K. In an attempt to repeat this work, Lang and Charlot [10] obtained somewhat complex results. Although reaction at 1 075 K gave a product with an *X*-ray powder diffraction pattern with similar interplanar spacings to those quoted by Juza *et al.*[8] for Li_5SiN_3 but with markedly different intensities (unfortunately no quantitative data are reported), reaction at 1 200 K afforded Li_8SiN_4. Furthermore, reaction of Li_3N and Si_3N_4 in a 5 : 1 mol ratio at 1 275 K gave a mixture of Li_2SiN_2 and Li_8SiN_4 in an approximate 1 : 1 mol ratio. Evidence for these latter two ternary nitrides has only been provided by Lang and Charlot [10] who obtained them in a pure state by reaction of Li_3N and Si_3N_4 in 2 : 1 and 8 : 1 mol ratios at 1 275 and 1 200 K, respectively; their existence has yet to be confirmed by independent authors.

Three independent studies of the interaction of Si_3N_4 with liquid lithium have shown that the ceramic undergoes decomposition, even at relatively low temperatures (525 K); [13–15] in none of the studies was the reaction product identified.

Experimental

Resistivity Studies.—The efficacy of the resistivity technique for the study of interactions in liquid alkali metal solutions [16] is based on the observation that individual solutes exert characteristic resistivity (ρ) increases which are linearly dependent on concentration, c. The magnitude of the gradients of these linear relationships (the dρ/dc coefficients) fall in the range (0.2—11.8) $\times 10^{-8}\ \Omega$ m (mol %)$^{-1}$; [17,18] those for silicon [18] and nitrogen,[2] 10.5 $\times 10^{-8}$ and 7.2 $\times 10^{-8}\ \Omega$ m (mol%)$^{-1}$ respectively at 750 K, being sufficiently large to enable small changes ($\pm$0.01 mol %) in the concentrations of these solutes to be accurately monitored.

If the solutes do not interact, the resistivity changes are additive (*e.g.* the Li–H–N system [2]); but when an interaction occurs the variation in the equilibrium resistivity as a function of concentration can be used to ascertain reaction stoicheiometry and assist in the identification of solvated solute species (*e.g.* the Na–Ba–N system [19]).

The AISI type 321 stainless steel apparatus for the resistivity studies was essentially that described previously.[16] It consists of a cylindrical reservoir (length 300 mm, diameter 50 mm) which contains the bulk of the liquid metal (30 g). Two independent loops, through which the metal could be continuously circulated using small electromagnetic pumps, were attached to the bottom part of the vessel. The liquid metal was circulated through one loop (internal diameter 5 mm) to maintain homogeneity of the solution, and through the other (internal diameter 1.5 mm) so that changes in the resistivity of the metal could be continuously monitored. Resistivities were calculated from calibration and sample resistance data, and from the dimensions of the capillary. In this way, solution and precipitation processes were followed as a function of time and concentration.

Binary solutions were prepared *in situ* either by weighing in a series of small aliquots of silicon (Koch Light, 99.999%, 0.1 g) under argon, or by exposing a series of small known volumes of nitrogen gas (Air Products, 99.98%, 10^4 mm^3 at s.t.p.) to the liquid lithium (Koch Light, 99.98%, 30 g). Argon (Air Products, 99.99%) was used to protect the liquid metal at all times. Lithium, nitrogen, and argon were purified as described previously; [2] silicon was used as received.

Since both Li–$Li_{22}Si_5$ and Li–Li_3N solutions interact with major constituents of stainless steel (nickel and chromium, respectively), once sufficient solute was deemed to have been added, the binary solutions were allowed to equilibrate with the submerged surfaces of the resistivity vessel. The solute concentration was accurately monitored by continuously following the solution resistivity. Reaction was very slow and limited, equilibrium being attained after 200 h; the amount of solute absorbed from solution differed for each resistivity vessel, approximating 0.1 mol % Si or 0.3 mol % N. Ternary solutions were then prepared by adding the corresponding solute in a series of small aliquots to the binary solutions as described above.

Solid State Studies.—Pure $Li_{22}Si_5$ and Li_3N were obtained from the elements; $Li_{22}Si_5$ was prepared by heating silicon (3 g) with a stoicheiometric quantity of purified lithium (3.5 g) to 1 000 K under an atmosphere of argon for 24 h; Li_3N was synthesised by reaction of nitrogen (3.6×10^6 mm^3 at s.t.p.) with a solution of lithium (7 g) in sodium (23 g) at 675 K in a steel beaker contained in a distillation vessel, using the method described previously.[20]

Finely ground and intimately mixed samples of $Li_{22}Si_5$ and Li_3N were pelleted together in 1 : 15 and 1 : 20 mol ratios. All manipulations were carried out under argon. The pellets were heated to 875 K under argon for 24 h in a standard reaction vessel.

Following completion of the resistivity experiments, the reaction products were isolated from the ternary solutions by vacuum distillation of excess lithium (875 K, 10^{-3} Pa, 100 h).

The starting materials, $Li_{22}Si_5$ and Li_3N, and all the reaction products were characterised by *X*-ray powder diffraction techniques. The diffractometer (Philips Ltd.) comprised a PW 1050/25 goniometer and PW 1130/90 generator in conjunction with a PW 1390 electronic system; nickel-filtered Cu-K_α unresolved radiation (λ = 1.5418 Å) was used for all samples.

Results

Three totally independent series of experiments were performed. The results obtained for the addition of 19 aliquots of nitrogen gas to a dilute Li–$Li_{22}Si_5$ solution originally containing 0.50 mol % Si, of eight aliquots of nitrogen gas to a dilute Li–$Li_{22}Si_5$ solution originally containing 1.65 mol % Si, and of nine aliquots of silicon to a dilute Li–Li_3N solution originally containing 1.67 mol % N at 750 K are described. Unfortunately, one series of experiments (addition of nitrogen to the 1.65 mol % Si solution) could not be taken to completion, owing to premature failure of the resistivity vessel. The solution concentrations chosen for the study are considerably lower than the solubility limits for silicon (3.06 mol %) [5] and for nitrogen (2.84 mol %) [6] in liquid lithium at 750 K.

Non-equilibrium Resistivity Change–Time Data.—Typical resistivity change–time data for the addition of 0.2 mol % aliquots of silicon and of nitrogen to Li–Li_3N and Li–$Li_{22}Si_5$ solutions, respectively, are shown in Figure 1 (lines O–C–D–E and O–F–G–H). The data are quite different from those for the additions of similar sized aliquots to the pure liquid metal (lines OA and OB), which are consistent with rapid dissolution of both solutes to give homogeneous solutions.

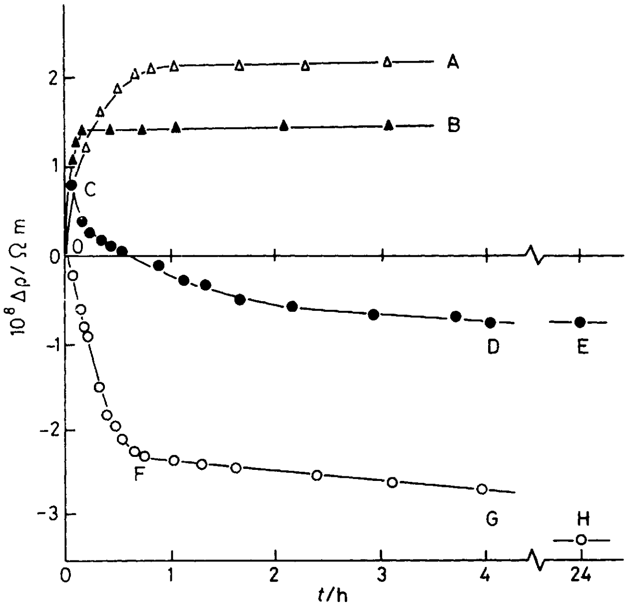

Figure 1. Resistivity changes observed as a function of time at 750 K on addition of (*i*) nitrogen to pure lithium (▲), (*ii*) silicon to pure lithium (△), (*iii*) nitrogen to lithium containing dissolved silicon (●), and (*iv*) silicon to lithium containing dissolved nitrogen (○)

The data for the ternary solutions are indicative of a chemical reaction between the dissolved species to form an insoluble product. The curve for the addition of gaseous nitrogen to the Li–$Li_{22}Si_5$ solution (line O–C–D–E) shows an increase in resistivity (OC), followed by a decrease (CD), eventually reaching an equilibrium value (E) having a resistivity below that of the original solution. This can be rationalised in terms of a homogeneous solution reaction. The initial increase is attributed to the formation of Li_3N, and its dissolution in the liquid metal. The subsequent decrease is due to reaction of dissolved silicon with dissolved nitrogen and the concomitant loss of both solutes from the solution as an insoluble product is produced. The form of the curve implies that the rate of dissolution of nitrogen is faster than the rate of formation of the reaction product. Equilibrium was achieved within 12 h, when all dissolved nitrogen had been consumed.

The curve for the addition of solid silicon to the Li–Li_3N solution (line O–F–G–H) is markedly different. Thus, instead of the curve described above, an initial rapid decrease in resistivity (OF) was observed, which was followed by a slower decrease (FG) to equilibrium (H). This can be understood in

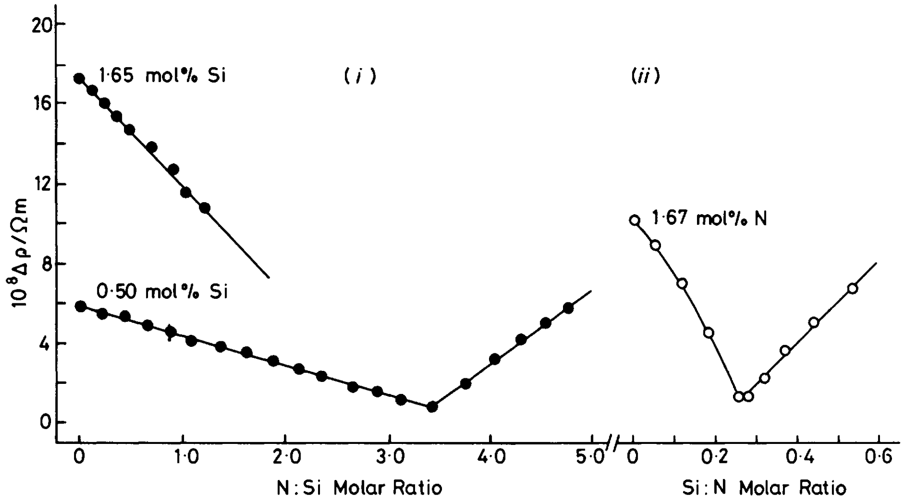

Figure 2. Resistivity changes observed as a function of concentration at 750 K on addition of (*i*) nitrogen to Li–Li$_{22}$Si$_5$ solutions containing 1.65 and 0.50 mol % Si (●), and (*ii*) silicon to Li–Li$_3$N solutions containing 1.67 mol % N (○). The Δρ values are based on the resistivity of pure lithium

terms of a heterogeneous reaction mechanism in which the product is formed at the solid silicon–solution interface by attack of dissolved nitrogen. Hence the only observed effect of silicon on the resistivity of the melt was that due to loss of dissolved nitrogen from solution. This obviously implies that the rate of reaction between silicon and dissolved nitrogen must be greater than that at which solid silicon dissolves in the liquid metal.

Equilibrium Resistivity Change–Concentration Data.—The resistivity change–concentration data are summarised in Figure 2; concentrations are expressed as atomic ratios to facilitate interpretation of the data. Comparable results were obtained for each of the three series of experiments, which are, in effect, titrations. Thus, the resistivity decreases linearly (indicating that only one product is formed during the course of the reaction) as the reaction proceeds, until the end-point is achieved when it is presumed that all of the dissolved silicon or nitrogen had been removed from solution, and resistivities close to those of the pure metal were observed (indicating that the reaction product was effectively insoluble in liquid lithium). Subsequent additions of nitrogen or silicon gave dρ/d*c* coefficients [7.3×10^{-8} Ω m (mol % N)$^{-1}$, 10.7×10^{-8} Ω m (mol % Si)$^{-1}$] characteristic of those expected for these solutes alone (see Experimental section), indicating that under these conditions, no further reaction was occurring, and that the product formed initially is the thermodynamically most stable in this system. The Si : N ratio in the precipitating phase can be derived from the gradients of the resistivity–concentration curves (by assuming the changes to be due solely to loss of solute from solution), and from the end-points of the titrations. These ratios are collated in Table 1; they all lie between 1 : 3.1 and 1 : 3.6 implying that the precipitating phase is either Li$_5$SiN$_3$ or Li$_8$SiN$_4$.

Table 1. Si : N ratios for the Li$_x$Si$_y$N$_z$ ternary product of the reaction as elucidated from resistivity experiments

Experiment	Si : N ratios end-point	Si : N ratios gradient
Addition of N to liquid Li containing Si (0.5 mol %)	1 : 3.3	1 : 3.5
Addition of N to liquid Li containing Si (1.65 mol %)		1 : 3.1
Addition of Si to liquid Li containing N (1.67 mol %)	1 : 3.6	1 : 3.2
	Average value 1 : 3.34 ± 0.11	

Solid State Studies.—*X*-Ray powder diffraction analysis of the products from the solid state reactions and from the resistivity experiments showed them to be almost identical. Peaks corresponding to elemental lithium were also present in the diffraction pattern of the solid state reaction products. Comparison of these data with those for the various ternary nitrides reported previously suggests that the product is Li$_5$SiN$_3$; interplanar spacings and relative intensities for our products and those reported by Juza *et al.*[8] for Li$_5$SiN$_3$ are compared in Table 2. Although the interplanar spacings are in very close agreement, the agreement between the relative intensities is poor. As pointed out earlier, a similar anomaly has been noted by Lang and Charlot.[10] In the absence of definitive single-crystal *X*-ray diffraction data, it is pertinent to note that Juza *et al.*[8] have shown that the calculated intensities (assuming space group *Ia*3; 8 N in 8*a* [0,0,0]; 24 N in 24*d* [0.215,0,0.25]; 48 Li in 48*c* [0.125,0.375,0.125]; 32/3 Si + 16/3 Li in 16*c* [*x*,*x*,*x*]) for the diffraction peaks were very sensitive to the precise location of the silicon atoms ($0.110 \leqslant x \leqslant 0.125$) in the antifluorite lattice.

To discount the possibility that Li$_8$SiN$_4$ is produced in the liquid metal environment and is subsequently converted to Li$_5$SiN$_3$ in the distillation process, Li$_8$SiN$_4$ was prepared following Lang and Charlot [10] and subjected to distillation conditions. A mixture of Li$_8$SiN$_4$ and Li$_2$SiN$_2$ was obtained; there was no evidence for Li$_5$SiN$_3$. The compound Li$_2$SiN$_2$ was also prepared following Lang and Charlot [10] and an intimate 1 : 1 molar mixture of Li$_8$SiN$_4$ and Li$_2$SiN$_2$ was heated under distillation conditions; no interaction was observed although there was some evidence for an increase in Li$_2$SiN$_2$ content. These results show that Li$_8$SiN$_4$ partially decomposes to Li$_2$SiN$_2$ (not Li$_5$SiN$_3$) when heated to 875 K under vacuum for prolonged periods, and that the product of the liquid solution reaction must be Li$_5$SiN$_3$. All starting

Table 2. Interplanar spacings (d/Å) and relative intensities (I/I_0) for the products of solid state studies

Ternary product from reaction of $Li_{22}Si_5$–15 Li_3N		Distillation products		Li_5SiN_3 [a]		Product in the lithium matrix [b]		Assignment [c]
d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	
6.75	20	6.78	24					Li_5SiN_3 (110)
4.75	16	4.78	70	4.73	50			Li_5SiN_3 (200)
3.87	42	3.89	80	3.86	80	3.85	vs	Li_5SiN_3 (211); Li_3N
3.36	3	3.39	9	3.34	40			Li_5SiN_3 (220)
						3.14	m	Li_3N
2.72	100	2.75	100	2.73	100	2.72	s	Li_5SiN_3 (222)
2.53	9	2.54	16	2.53	40			Li_5SiN_3 (321)
2.49	45					2.48	vs	Li
2.36	4			2.36	10			Li_5SiN_3 (400)
2.23	1			2.23	5			Li_5SiN_3 (411)
2.11	2	2.13	6	2.11	40			Li_5SiN_3 (420)
2.02	9	2.02	13	2.02	50			Li_5SiN_3 (332)
						1.932	m	Li_3N
				1.929	10			Li_5SiN_3 (442)
1.857	7	1.865	10	1.850	30			Li_5SiN_3 (431)
1.759	10					1.754	m	Li
				1.726	10			Li_5SiN_3 (521)
1.668	60	1.682	60	1.671	100	1.676	s	Li_5SiN_3 (440)
				1.621	10			Li_5SiN_3 (433)
1.574	2	1.584	5	1.575	20			Li_5SiN_3 (600)
1.537	2	1.543	5	1.533	30			Li_5SiN_3 (611)
1.434	3	1.434	5	1.425	30	1.434	m	Li_5SiN_3 (622); Li
1.397	3	1.400	5	1.394	30			Li_5SiN_3 (631)

[a] Data taken from ref. 8. [b] Qualitative relative intensities are quoted for the lithium matrix studies because of the vast excess of lithium. [c] Values in parentheses are (hkl).

Table 3. X-Ray powder diffraction data for Li_2SiN_2 and Li_8SiN_4; comparison with previous data [10]

Li_2SiN_2				Li_8SiN_4			
This work		Ref. 10 *		This work		Ref. 10 *	
d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0
5.21	100	5.14	100	7.25	22	7.13	31
5.01	24	4.97	25	4.79	64	4.73	13
4.29	29	4.27	34	4.15	100	4.11	57
4.17	14	4.15	17	3.96	16	3.94	15
3.34	52	3.32	90	3.57	16	3.53	11
2.91	20	2.90	42	2.76	100	2.74	100
2.58	25	2.57	50	2.60	17	2.59	11
2.49	4	2.49	10	2.37	18	2.36	18
2.42	14	2.42	37	1.936	16	1.926	16
2.37	7	2.36	17	1.847	3	1.839	6
2.32	2	2.32	7	1.833	2	1.819	6
2.24	4	2.24	10	1.686	52	1.682	70
2.18	5	2.17	17	1.671	46	1.671	48
2.14	9	2.13	20	1.589	10	1.565	8
		2.05	34	1.424	12	1.418	12
2.04	33	2.03	95	1.390	10		
1.975	3	1.971	17				
1.920	3	1.914	14				
1.854	4	1.849	17				
		1.760	7				
1.607	4	1.601	13				
1.541	9	1.537	32				
1.500	4	1.498	17				

* Diffraction lines quoted by Lang and Charlot [10] with $I/I_0 \leqslant 5$ were not observed on our diffraction traces and have been omitted from the comparison.

materials and reaction products of this solid state study were characterised by *X*-ray diffraction techniques. Our powder diffraction data for Li_2SiN_2 and for Li_8SiN_4 are compared with those reported by Lang and Charlot[10] in Table 3. Although the correspondence between the two sets of data is immediately apparent, thereby corroborating the earlier work, there are minor differences in the interplanar spacings, our values being consistently larger than those quoted by Lang and Charlot. These discrepancies, although within the experimental error in the measurement of 2θ values ($\pm 0.1°$), may result from the fairly wide homogeneity ranges attributed to these materials by Lang and Charlot.[10]

Several attempts were also made to undertake *X*-ray diffraction analysis of the products of the resistivity experiments prior to distillation, *i.e.* when still embedded in the lithium matrix. A typical set of diffraction data are included in Table 2. After accounting for elemental lithium and Li_3N peaks (no peaks were observed for $Li_{22}Si_5$) only two peaks remained (d = 2.72 and 1.676 Å). These correspond to the two most intense peaks in the Li_5SiN_3 diffraction pattern; the third most intense Li_5SiN_3 peak occurs at d = 3.85 Å and hence coincides with an intense Li_3N peak. Although there was no evidence for any of the other less intense ($I/I_0 < 20\%$) Li_5SiN_3 peaks, this result is considered to be confirmatory evidence for the formation of Li_5SiN_3 in liquid lithium.

Discussion

Combined resistivity and solid state results indicate that silicon and nitrogen, when dissolved in liquid lithium, interact at 750 K to form the insoluble ternary product, Li_5SiN_3; no evidence for the formation of any other ternary products was obtained indicating that Li_5SiN_3 is the thermodynamically most stable ternary nitride in this system. Thermochemical arguments, based on the solid state reaction shown in equation (1), and using the standard enthalpy of formation data for

$$Li_{22}Si_5(s) + 15\,Li_3N(s) \longrightarrow 5\,Li_5SiN_3(s) + 42\,Li(s) \quad (1)$$

$Li_{22}Si_5$ (-735 kJ mol^{-1})[21] and Li_3N (-165 kJ mol^{-1}),[22] predict that the standard enthalpy of formation of Li_5SiN_3 is at least as negative as -642 kJ mol^{-1}.

The compound Li_5SiN_3 is the second member of the $Li_{2n-3}M^{n+}N_{n-1}$ ($2 \leqslant n \leqslant 6$) series of compounds to be formed in liquid lithium; Li_9CrN_5[23] has recently been characterised as the product of the reaction of particulate chromium with Li–Li_3N solutions.* The stabilities of these compounds towards liquid lithium is thought to be associated with their cubic antifluorite $(Li,M)_2N$ type lattice structure in which the metal atoms occupy all the tetrahedral sites in a face-centred-cubic array of nitrogen atoms.

The reactivity of three Group 4 elements (C, Si, and Ge) towards Li–Li_3N solutions has now been ascertained; whereas carbon[3,4] and silicon react to form Li_2NCN and Li_5SiN_3, respectively, germanium[18] is inert. Preliminary results for ternary Li–Pb–N solutions indicate that lead is also inert. A pattern of decreasing reactivity with increasing atomic number of the Group 4 element is apparent. It can be correlated to the decreasing M–N covalent bond energy and the concomitant decreasing stability of the ternary nitrides.

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* The apparently anomalous formation of high oxidation state compounds (Li_5SiN_3, Li_9CrN_5, Na_3NbO_4, and Na_2MoO_4) in liquid alkali metal solvents can readily be rationalised in terms of the immense oxidising potential of the non-metal impurities dissolved therein (Li_3N in liquid lithium, Na_2O in liquid sodium).