

## VOLATILE LIQUID PRECURSORS FOR THE CHEMICAL VAPOR DEPOSITION (CVD) OF THIN FILMS CONTAINING ALKALI METALS

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### ABSTRACT

The first volatile, liquid compounds of alkali metals were synthesized and used for the CVD of materials containing alkali metals. Amides of the type  $MNR^1(SiMe_2R^2)$  and  $MN(SiMe_2R^2)_2$  [ $M = Li, Na, K$ ;  $R^1 = t\text{-butyl, t-amyl}$ ;  $R^2 = \text{ethyl, n-propyl, i-propyl, n-butyl, i-butyl, n-hexyl, n-octyl}$ ] were made and characterized. The lithium amides were prepared via the deprotonation of the parent amine using butyl lithium. The sodium and potassium amides were formed by transamination of sodium amide and potassium bis(trimethylsilyl)amide with the parent amines. For example, lithium bis(ethyltrimethylsilyl)amide was prepared from butyl lithium and bis(ethyltrimethylsilyl)amine and was distilled as a clear, colorless liquid at 122 °C (0.2 Torr) having a viscosity of 37 cP at 40 °C. These alkali metal amides can be used as convenient liquid sources for CVD of mixed metal oxides containing alkali metals, such as the non-linear optical material lithium niobate, lithium-containing materials for battery electrodes, electrochromic tungsten bronzes, and the pyroelectric and ferroelectric material potassium tantalate.

### INTRODUCTION

Chemical vapor deposition (CVD) is a versatile method for preparing solid materials in the form of films, powders, and fibers. Successful use of CVD requires reliable sources of reactant vapors, which are most easily generated from liquids. Solids are less convenient as sources of vapors for a variety of reasons. Solids often have low vapor pressures, and the kinetics of vaporization of solids is usually slow. The surface area from which solids evaporate changes as a function of time, causing a non-reproducible vapor flux. Decomposition products and impurities can segregate on the surface of a solid, further degrading their reproducibility as vapor sources. In fact, most practical applications of CVD use liquid sources, rather than solids.

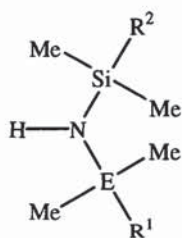
Solid sources can also be dissolved in a liquid solvent, and the liquid solution can subsequently be flash-vaporized. This approach, however, introduces large amounts of solvent vapors into the CVD reactor. The solvent vapors can be hazardous because of flammability or toxicity and may introduce impurities, such as carbon, into the deposited material. Solvents also increase the effort needed to dispose of wastes from the process.

Alkali metals are essential components of many important materials, such as those listed in the abstract. Unfortunately, volatile liquid compounds have not been available for the alkali metals, so CVD of these materials has had to rely on sublimation of inconvenient solid sources, like lithium bis(trimethylsilyl)amide.<sup>1</sup>

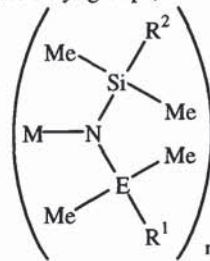
In the present paper, the first room-temperature liquid, volatile compounds are reported for lithium, sodium, and potassium, and methods for their synthesis are given. These liquid compounds can be distilled or flash-vaporized to form vapors suitable for CVD of materials containing alkali metals, particularly lithium, sodium, and potassium. Because they are miscible

with each other and with many organic solvents, they may also be useful for forming liquid mixtures or solutions for spray coating, spin coating or sol-gel deposition.

These amine and alkali amide compounds have a general formula as given below, where M is an alkali metal, E<sup>1</sup> and E<sup>2</sup> are silicon or carbon, R<sup>1</sup> and R<sup>2</sup> are alkyl groups, and n is 2 or 3.



**Parent amine**



**Alkali amide**

**Table 1. Amine ligands**

Amine	E	R <sup>1</sup>	R <sup>2</sup>	<i>t</i>
bis(n-octyldimethylsilyl)amine	Si	n-Oct	n-Oct	14
bis(n-hexyldimethylsilyl)amine	Si	n-Hex	n-Hex	10
bis(n-butyldimethylsilyl)amine	Si	n-Bu	n-Bu	6
bis(i-butyldimethylsilyl)amine	Si	i-Bu	i-Bu	4
bis(n-propyldimethylsilyl)amine	Si	n-Pr	n-Pr	4
tert-amyl(n-butyldimethylsilyl)amine	C	Et	n-Bu	4
tert-amyl(i-butyldimethylsilyl)amine	C	Et	i-Bu	3
tert-amyl(n-propyldimethylsilyl)amine	C	Et	n-Pr	3
tert-butyl(n-butyldimethylsilyl)amine	C	Me	n-Bu	3
tert-amyl(i-propyldimethylsilyl)amine	C	Et	i-Pr	2
bis(ethyldimethylsilyl)amine	Si	Et	Et	2
tert-amyl(ethyldimethylsilyl)amine	C	Et	Et	2
tert-butyl(n-propyldimethylsilyl)amine	C	Me	n-Pr	2
tert-amyl(trimethylsilyl)amine	C	Et	Me	1
tert-butyl(ethyldimethylsilyl)amine	C	Me	Et	1

Table I identifies a list of some suitable amine ligands. The number *t* in this table is the number of angular variables (torsion angles corresponding to rotation around C-C single bonds) in excess of those present in the reference compound bis(trimethylsilyl)amine, whose alkali salts are solid at room temperature. Methyl rotations about their three-fold axes were not counted, since these motions do not change the intermolecular interactions as much as the other torsions do. As *t* increases, the number configurations available to the ligand increases, and thus its ability to impede crystallization increases. Hence, larger *t* is, the greater is the ability of the ligand to keep the corresponding metal-ligand compounds in liquid form at room temperature.



The large alkyl groups ( $R^1$  and  $R^2$  larger than methyl) adopt multiple molecular conformations that frustrate the crystallization of the compounds and keep them in liquid form.

## SYNTHESIS OF LIQUID ALKALI COMPOUNDS

Synthesis of Bis(Trialkylsilyl)Amide Ligands. The preferred bis(trialkylsilyl)amines may be prepared by known methods, such as the condensation of ammonia with a trialkylchlorosilane.<sup>2</sup>

As a specific example of this method, the synthesis of bis(*n*-propyldimethylsilyl)amine is given as follows: All experimental manipulations were carried out using standard Schlenk techniques under dry nitrogen either in a glove box or on a Schlenk line unless otherwise stated. Commercial (Gelest or United Chemical Technologies) *n*-propyldimethylchlorosilane (25.0 g, 0.183 mmol) was dissolved in 150 mL of dry ether. Ammonia gas was bubbled into the solution until it was no longer absorbed and continued for an additional hour in order to ensure the completion of the reaction. The solution was refluxed for one hour, and the solid byproduct  $NH_4Cl$  was removed by filtration. Distillation was used to remove the ether and excess ammonia, yielding a colorless liquid (17.2 g, 86 %) which was shown to be the desired product, bis(*n*-propyldimethylsilyl)amine, by NMR analysis, and was used without further purification.

Other bis(trialkylsilyl)amines were made in a similar manner, by substituting other trialkylchlorosilanes for *n*-propyldimethylchlorosilane.

Synthesis of Alkyl(Trialkylsilyl)Amide Ligands. Alkyl(trialkylsilyl)amines may be synthesized by condensation of primary amines with trialkylchlorosilanes. For example, *n*-butyldimethylchlorosilane reacts with tert-amylamine (Acros) to form tert-amyl(*n*-butyldimethylsilyl)amine.

Synthesis of Alkali Amides. Alkali metal compounds can be formed between these amide ligands and the alkali metals in various ways. For lithium, it is convenient to react a solution of butyl lithium with the amine. The sodium and potassium amides were most readily formed by the transamination of the parent amine with sodium amide or potassium bis(trimethylsilyl)amide, respectively.

*Lithium bis(n-propyldimethylsilyl)amide* was prepared by the slow addition via syringe of a hexane solution of butyl lithium (11.7 mL of 2.73 M solution, 31.9 mmol) to a stirred hexane solution (75 mL) of bis(*n*-propyldimethylsilyl)amine (6.93 g, 31.9 mmol) at room temperature. Stirring was continued for several hours, and the solution was then refluxed for one hour. The hexane was evaporated under vacuum, leaving 5.8 g of a pale yellow liquid. It was distilled at a temperature of 130 °C and a pressure of 0.15 torr to yield 5.25 g (74%) of clear liquid lithium bis(*n*-propyldimethylsilyl)amide. Its viscosity was measured to be 23.3 centipoise at 40 °C.

Similar methods were used to prepare other distillable liquid lithium compounds having the properties listed in Table 2. The molecular masses of these new compounds were determined by cryoscopy in *p*-xylene solution. Their “molecular complexities,” defined as the ratio of the cryoscopic molecular mass to the theoretical monomeric value, fall between 2 and 3. Thus the solutions are most likely to contain dimers and trimers.

**Table 2. Liquid lithium amides**

Lithium amide	E	R <sup>1</sup>	R <sup>2</sup>	Viscosity (centipoise @ 40°C)	Molecular Complexity	Vapor Pressure (°C/Torr)
bis(ethyltrimethylsilyl)amide	Si	Et	Et	37	2.45	122/0.2
tert-amyl(i-propyldimethylsilyl)amide	C	Et	i-Pr	409	2.41	137/0.2
bis(3,3-dimethylbutyldimethylsilyl)amide	Si	Z <sup>i</sup>	Z <sup>i</sup>	247	2.02	225/0.9
tert-amyl(i-butyldimethylsilyl)amide	C	Et	i-Bu	497	2.65	145/0.1
tert-amyl(n-propyldimethylsilyl)amide	C	Et	n-Pr	810	2.74	171/0.3
bis(n-propyldimethylsilyl)amide	Si	n-Pr	n-Pr	23.3	2.16	130/0.15
bis(i-butyldimethylsilyl)amide	Si	i-Bu	i-Bu	32.9	1.97	145/0.05
tert-amyl(triethylsilyl)amide	C	Et	Et <sup>ii</sup>	162	2.20	157/0.095
bis(n-butyldimethylsilyl)amide	Si	n-Bu	n-Bu	22.4	2.28	145/0.085

<sup>i</sup>Z = (CH<sub>2</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>; <sup>ii</sup> Me<sub>2</sub> replaced by Et<sub>2</sub>

*Sodium bis(n-propyldimethylsilyl)amide* was prepared as follows: Sodium amide (1.26 g, 0.0322 mol) was placed in dry benzene and bis(n-propyldimethylsilyl)amine (7.00 g, 0.0322 mol) was added. The mixture was stirred and refluxed for several hours. The benzene solution was filtered through celite, and then the benzene was evaporated under vacuum, leaving 6.31 g (82 %) of a yellow liquid product, sodium bis(n-propyldimethylsilyl)amide. Its viscosity was measured to be  $7.1 \times 10^4$  centipoise at 40 °C. It was distilled at a temperature of 213 °C and a pressure of 0.3 torr.

Similar methods were used to prepare other distillable liquid sodium compounds having the properties listed in Table 3.

**Table 3. Liquid sodium amides**

Sodium amide	E	R <sup>1</sup>	R <sup>2</sup>	Viscosity (centipoise @ 40°C)	Molecular Complexity	Vapor Pressure (°C/Torr)
bis(n-propyldimethylsilyl)amide	Si	n-Pr	n-Pr	$7.1 \times 10^4$	2.26	213/0.3
bis(i-butyldimethylsilyl)amide	Si	i-Bu	i-Bu	$2.8 \times 10^4$	2.08	189/0.08
bis(n-butyldimethylsilyl)amide	Si	n-Bu	n-Bu	$>10^7$	1.89	231/0.5
bis(n-hexyldimethylsilyl)amide	Si	n-Hex	n-Hex	$1.5 \times 10^4$	2.01	265/0.3

*Potassium bis(n-hexyldimethylsilyl)amide* was prepared as follows: Potassium bis(trimethylsilyl)amide (5.07 g, 25.6 mmol) and bis(n-hexyldimethylsilyl)amine (7.66 g, 25.6 mmol) were added to a flask and 50 mL toluene was added. The clear yellow solution was stirred at room temperature for 18 hours and then refluxed for two hours. The toluene and hexamethyldisilazane byproduct were removed from the brown toluene solution under vacuum with heating to 150°C to yield a brown oil (5.40 g, 63%). Its viscosity was measured to be 271 centipoise at 40 °C. It may be flash vaporized from a heated nozzle for CVD applications.



Alternatively, the potassium amide may be dissolved in small amounts of organic solvents to form concentrated solutions that may be flash vaporized.

Similar methods were used to prepare other vaporizable liquid potassium compounds having the properties listed in Table 4.

**Table 4. Potassium precursors**

Potassium amide	E	R <sup>1</sup>	R <sup>2</sup>	Viscosity (centipoise @ 40°C)	Molecular Complexity	Melting Point (°C)
bis(i-butyl dimethylsilyl)amide	Si	i-Bu	i-Bu	205	2.02	53
bis(n-butyl dimethylsilyl)amide	Si	n-Bu	n-Bu	230	1.90	45
bis(n-hexyl dimethylsilyl)amide	Si	n-Hex	n-Hex	271	1.80	<20
bis(n-octyl dimethylsilyl)amide	Si	n-Oct	n-Oct	183	1.63	<20

These liquid alkali metal amides are generally completely miscible with organic solvents, including hydrocarbons, such as dodecane, tetradecane, xylene and mesitylene, and with ethers, esters, ketones and chlorinated hydrocarbons. These solutions generally have lower viscosities than the pure liquids, so that in some cases it may be preferable to nebulize and evaporate the solutions rather than the pure liquids. In these instances, however, very concentrated solutions, e.g. greater than one molar, may be obtained. The liquids or solutions can also be evaporated with thin-film evaporators or by direct injection of the liquids into a heated zone.

The liquids and solutions all appeared to be non-pyrophoric. The precursors generally react with moisture in the ambient air, and should be stored under an inert, dry atmosphere such as pure nitrogen gas.

#### CVD EXPERIMENT

Liquid lithium bis(n-ethyl dimethylsilyl)amide was mixed with mesitylene to lower the viscosity below 5 centipoise so that the precursor could be nebulized into tiny droplets (about 20 microns in diameter) by a high-frequency (1.4 MHz) ultrasonic system.<sup>3</sup> The resulting fog was carried by nitrogen into the deposition zone where it mixed with O<sub>2</sub> at 200 °C. The precursor concentration in the deposition gas stream was 0.36 mol%, the oxygen concentration was 17 mol%, and the total flow rate was 0.60 L/min. A thin film was deposited on a silicon substrate placed on the bottom of the tube. The lithium-containing film was easily dissolved in water. The refractive index was determined to be 1.48-1.49, by using drops of Cargille certified index of refraction fluids, which more closely resembles lithium hydroxide (1.45-1.46) than lithium oxide (1.64).

Films were also produced containing both lithium and niobium by mixing liquid lithium bis(n-ethyl dimethylsilyl)amide and liquid niobium (V) diethylamide with mesitylene in a 1:1:5 mole ratio. The mixed precursor films were deposited by the same method used for the single precursor lithium films at 250°C. The concentration of the lithium precursor in the deposition gas stream was 0.27 mol%, the niobium precursor concentration was 0.27 mol%, the oxygen concentration was 16 mol%, and the total flow rate was 0.60 L/min. The silicon substrates were

coated with an iridescent film. The lithium to niobium ratio in the resulting film was determined by ablating the film with a 193 nm argon fluoride excimer laser and analyzing the ablated atoms by quadrupole mass spectrometry, Figure 1. The mole ratio of lithium to niobium was found to vary along the length of the silicon substrate. An approximate ratio of 0.3:1 Li:Nb was observed after several centimeters in the reaction zone, indicating that the niobium amide was more reactive than the lithium amide under these conditions. Interestingly, these silicon containing precursors do not deposit a silicon impurity in the film.

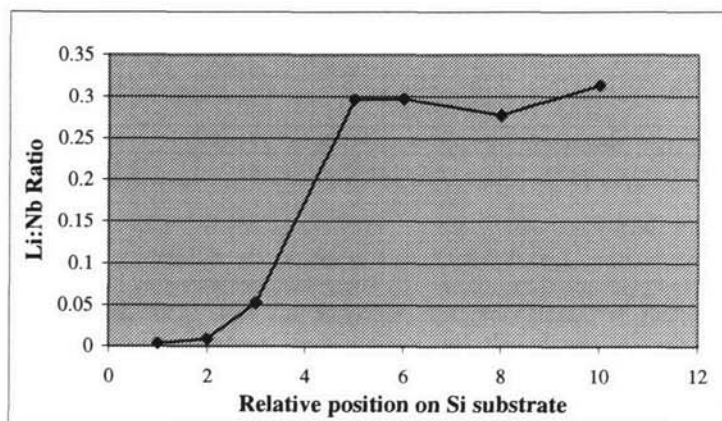


Figure 1. Mole Ratio of Li to Nb as Determined by Laser Ablation-Mass Spectrometry

## CONCLUSIONS

The first volatile liquid compounds of lithium, sodium and potassium have been synthesized using easily prepared amines from commercially available reagents. Films containing alkali metals can be deposited from vapors of the precursor compounds and oxygen or other sources of oxygen. As an example, lithium niobate films were prepared by CVD using one of the new liquid lithium compounds as a precursor. Similarly, a liquid precursor for potassium may be combined with a tantalum precursor to provide a process for depositing potassium tantalate films having nonlinear optical properties.

Many other alkali-containing compounds might be deposited using these volatile liquid precursors. For example, one might deposit lithium phosphorus oxide nitride materials for use as solid electrolytes in batteries.<sup>4</sup> Similarly, sodium-potassium niobate (NKN) films may be formed with low loss tangent and a strong electric field dependence of rather low dielectric permittivity and used in tunable microwave devices.<sup>5</sup>  $\text{Na}_{0.1}\text{K}_{0.9}\text{Ta}_{0.55}\text{Nb}_{0.45}\text{O}_3$  films with high pyroelectric sensitivity may be made and fabricated into night-vision devices.<sup>6</sup> By using a tungsten-containing precursor along with these precursors, tungsten bronzes having useful optical, electrical and electrochromic properties may be made and formed into electrochromic windows, mirrors and displays.<sup>7</sup> Similarly, by combining liquid lithium precursors with precursors for cobalt, nickel, vanadium, and/or other transition metals, electrochromic materials<sup>8</sup> or electrodes

for lithium batteries<sup>9</sup> may be deposited. LiAlO<sub>2</sub> buffer layers could be deposited as substrates for growth of GaN.<sup>10</sup> Vapors of a sodium-containing precursor can be used to supply a sodium dopant for copper indium diselenide solar cells.<sup>11</sup>

The liquid compounds may also be used for spray coating, spin coating and sol-gel deposition of materials containing alkali metals. The high solubility and miscibility of these precursors is an advantage in forming the required solutions needed for such applications.

#### ACKNOWLEDGMENTS

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