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Short communication

Low-temperature preparation of crystalline barium sulfide

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Barium sulfide (BaS) is a compound with many uses, both commercially and in the scientific research world. Normally, BaS is prepared from the high-temperature reduction of barite ($BaSO_4$) with carbon, a process that eliminates CO_2 as a by-product. Temperatures during the reduction step can be as high as 1200 °C. We now demonstrate that barium disilylamides can be used as precursors to the formation of crystalline BaS in their reactions with hydrogen sulfide gas. As a major advantage, the temperature of BaS production can be lowered to 25–200 °C. The by-products formed during the reaction are ammonium sulfides, resulting from the acid–base reaction of the liberated amines with excess H_2S. Fortunately, these salts decompose thermally in vacuum under mild conditions. As determined by X-ray powder diffraction, the BaS formed in this reaction is crystalline, in the face-centered cubic space group *Fm*3*m*. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: barium amides; barium sulfide; sulfidation; silylamides

INTRODUCTION

Much of the synthetic chemistry developed over the past 20 years has been geared towards the objective of preparing solid materials via unusual and/or more efficient procedures. More particularly, the area of chemical vapor deposition (CVD) has grown tremendously in use owing to the ability to form thin films or powders of desired solids supported on various substrates by using volatile precurors.[1] Generally in CVD processes, a reactive precursor species is added in the gas phase to a reacting gas to form at high temperature both the desired solid material and gaseous by-products. Compounds prepared via CVD range from synthetic diamonds, to nanoparticles, to GaAs, GaN, InP, and other materials useful in the electronics industry. Towards this end, many laboratory studies have been targeted to the synthesis of volatile organometallic compounds to serve as single-source volatile precursors, and the development of new ligands that provide volatility and chemical reactivity has been a key feature of these studies. Ligands have been based on almost every type of structure, including amines, thiols, alcohols, siloxides, perfluorinated organics, and the like, all designed to achieve the dual functions of volatility and chemical reactivity.[1] In this regard, the bis(trimethylsilyl)amido ($-N(TMS)_2$, where TMS = $-SiMe_3$) ligand and modifications thereof have been utilized for these purposes. Additionally, the $-N(TMS)_2$ ligand has been commonly used in organometallic chemistry to prepare amido derivatives of essentially every metal or metalloid in the periodic table.[2] In many cases, the bulky $-N(TMS)_2$ ligand or derivatives provide enough steric hindrance to form lower coordinate, monomeric metal amides, thus adding to the volatility and chemical reactivity of the metal amide.

Barium sulfide (BaS) is a compound produced commercially at very high temperatures (>1200 °C) from the reduction of barite ($BaSO_4$) using carbon as the reductant. BaS and derivatives are used industrially in the production of some paints.[3] More recently, pure BaS has been used in the preparation of electroluminescent phosphors, often doped with Eu^{2+} or Cu^{2+} ions.[4–7] Additionally, metal-doped BaS compounds have been shown to have significant interest as materials that undergo prominent conductor–insulator transitions,[8–12] or as new materials.[13]

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We now report a room-temperature synthetic route to crystalline BaS via the sulfidation of barium silylamides with hydrogen sulfide. Volatile ammonium sulfides, which can be easily removed via thermal decomposition to the gaseous free amine and H_2S under mild conditions, are the only by-products. This simple procedure using organometallic precursors avoids the high temperatures required for barite reduction, and is somewhat reminiscent of the procedures used in CVD.

EXPERIMENTAL

General comments

All manipulations were carried out in a glove box or by using standard Schlenk techniques.[14] Anhydrous solvents were purchased from Aldrich or Fisher Scientific Company, after which they were stored in a drybox over 4 Å molecular sieves. Anhydrous BaI_2, H_2S, (t-Bu)(TMS)NH and *n*-BuLi (2.5 M in hexanes) were purchased from Aldrich and used without further purification. $Ba[N(TMS)_2]_2(THF)_2$ (**1**) was synthesized according to the literature.[15] Powder X-ray diffraction analysis was performed with a Siemens D500 $\theta/2\theta$ diffractometer using Cu Kα radiation equipped with a graphite monochromator. The elemental analysis for barium was measured at Desert Analytics, Inc., Tucson, AZ, using inductively coupled plasma (ICP) spectrometry.

$Ba[N(t\text{-}Bu)(TMS)]_2(THF)_2$ (2)

(t-Bu)(TMS)NK (prepared from (t-Bu)(TMS)NH (4.83 g, 33.2 mmol)) and KH (1.33 g, 33.2 mmol in tetrahydrofuran (THF)) was treated with anhydrous BaI_2 (6.50 g, 16.6 mmol) in THF (50 ml). The mixture was stirred overnight and evaporated to dryness. The residue was held under vacuum for 6 h and was then extracted with 80 ml hexanes. The extracts were filtered through a glass frit using Celite® filter aid. Hexane was removed under vacuum, and the residue, a viscous light-yellow liquid, was recrystallized from a 6 : 1 toluene/hexane mixture to yield a white solid, $Ba[N(t\text{-}Bu)(TMS)]_2(THF)_2$, 3.00 g (32%.) ^1H NMR (C_6D_6): δ 0.37 (s, 18H, $Si(CH_3)_3$), 1.29 (m, 8H, $-CH_2-$), 1.48 (s, 18H, $(CH_3)_3C$), 3.64 (m, 8H, $-OCH_2-$). ^{13}C NMR (C_6D_6): δ 7.19 ($-Si(CH_3)_3$), 25.23($-CH_2-$), 36.23 ($(CH_3)_3C$), 52.87 ($(CH_3)_3C-$), 68.45 ($-OCH_2-$). Owing to the extreme air-sensitive nature of this compound we were unable to obtain an adequate elemental analysis; however, the ^1H NMR spectrum taken immediately after preparation was consistent with a high level of purity.

Preparation of BaS using 1 as barium source

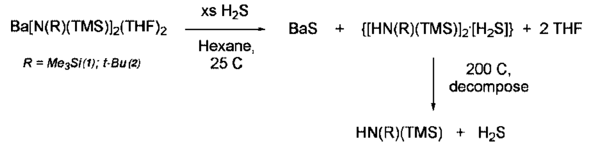
Anhydrous hydrogen sulfide (H_2S) gas was bubbled for 1 h through a solution of $Ba[N(SiMe_3)_2]_2(THF)_2$ (**1**) (2.00 g, 3.3 mmol) in 80 ml hexane. White solids immediately precipitate from the solution. The white precipitate was removed via filtration, washed three times with 50 ml portions of dry Et_2O, and then dried under vacuum. Approximately 1.10 g of crude white solid product (BaS mixed with the ammonium sulfide salt) remained at this step. This mixture was heated to 200 °C for 6 h under vacuum to yield crystalline BaS as a gray solid, 0.40 g (72%). Anal. Found: Ba, 79.12. Calc. for BaS: Ba, 81.07%. The identical procedure could also be utilized with **2** as the starting material in place of **1**.

RESULTS AND DISCUSSION

When either $Ba[N(TMS)_2]_2(THF)_2$ (**1**)[15] or $Ba[N(t\text{-}Bu)(TMS)]_2(THF)_2$ (**2**) is dissolved in hexane at room temperature and allowed to react with excess hydrogen sulfide gas, a reaction is visually seen to occur (see Scheme 1). A white precipitate forms immediately upon bubbling the H_2S gas into the barium solution. The addition of H_2S is continued for 1 h to ensure complete reaction. The protons of H_2S are of sufficient acidity to react with the basic amide groups on barium to liberate the free amine, with the concomitant formation of solid BaS. The free amine liberated does not stay as such; rather, it reacts with excess H_2S to form the ammonium sulfide, which is easily viewed as an acid–base adduct of the amine and H_2S. The ammonium sulfide helps give the initially formed precipitate the white color observed. Fortunately, these complexes are relatively thermally unstable and can be decomposed with gentle heating (<200 °C) under vacuum to liberate the free amine and hydrogen sulfide gases, which are easily removed from the remaining BaS solid. To ensure complete removal of the by-products the BaS is held at ~200 °C for several hours. It is important not to do the thermal treatment under air because of the possibility of oxidizing the BaS formed.

The BaS formed via sulfidation in 72% isolated yield has been characterized by elemental analysis and powder X-ray diffraction (XRD). The BaS formed in our low-temperature route has been shown by XRD to be crystalline BaS. Although there are several crystalline structures of BaS that have been previously identified, the crystalline form prepared in this new route is face-centered cubic (NaCl structure), space group *Fm*3*m* (225). The powder diffraction pattern of the BaS formed after sulfidation of the barium amides is shown in Fig. 1. The dotted lines correspond to the previously known cubic structure of BaS (International Centre for Diffraction Database PDF Card #08-0454).

Although comparable yields are obtained in the sulfidation reactions when either barium precursor is used, overall it is



Scheme 1. Synthetic route to crystalline BaS via elimination of amine.

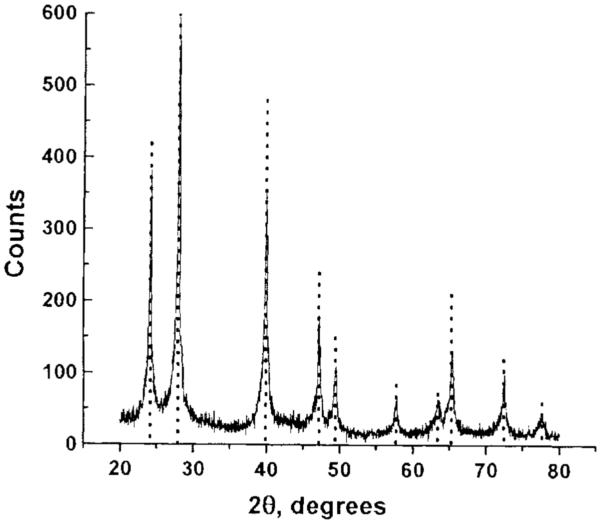


Figure 1. Powder XRD pattern for BaS prepared via sulfidation of barium amides. The dotted lines correspond to the structure for cubic BaS, *Fm*3*m* (225) (International Centre for Diffraction Database PDF Card#08-0454).

preferable to use the Ba[N(TMS)$_2$]$_2$(TMS)$_2$ compound as the starting source of Ba^{2+} ions. This is because of the higher yields obtained in preparing the barium amides when −N(TMS)$_2$ is used as a ligand versus −N(t-Bu)(TMS). We also note that **2** appears to be significantly more sensitive to trace levels of moisture and air than does **1**.

Summarizing, we have now shown that crystalline BaS can be produced in high isolated yields from the reactions of silylated barium amides with H_2S at room temperature. The BaS product, precipitated initially along with an ammonium sulfide by-product, can be isolated from the mixture by gentle heating and decomposition of the ammonium sulfide under vacuum. The grayish-colored product has been shown to be crystalline BaS by XRD. We believe that this reaction is general in scope, and a wide variety of barium silylamides should function well as barium precursors.

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