Russian Chemical Bulletin, Vol. 44, No. 2, February, 1995 233

Preparation of samarium(II) sulfide by the reaction of samarium(II) bis[bis(trimethylsilyl)amide] with hydrogen sulfide

O. V. Andreev,* M. N. Bochkarev, T. V. Nekrasova, and A. V. Protchenko

Tyumen' State University,
10 ul. Simakova, 625000 Tyumen', Russian Federation

X-ray amorphous samarium(II) sulfide was prepared by the reaction of H_2S with samarium(II) bis[bis(trimethylsilyl)amide] (**1**) in THF at 10^{-2} Torr. Compound **1** was prepared by two methods: 1) the reaction of SmI_2 with lithium bis(trimethylsilyl)amide and 2) the reaction of samarium naphthalide with bis(trimethylsilyl)amine. SmS was transformed to the polycrystalline state with the lattice parameter a = 5.92 Å by annealing at 400—500 °C.

Key words: samarium(II) sulfide, samarium(II) naphthalide, lithium bis(trimethylsilyl)amide.

Tensometric and barometric sensors based on SmS are the most sensitive for measuring mechanical quantities.[1] Using electro-explosive dust spraying of polycrystalline SmS to obtain sensors results in up to 80 % loss of the initial substance. The development of a method for preparing SmS films on substrates by the reaction of vaporous samarium organyls with H_2S is of interest.

Two methods are known for the preparation of SmS *via* Sm organometallics: the reaction of samarium dicyclopentadienyl with H_2S,[2] and the reaction of samarium naphthalide with sulfur.[3] However, neither method is able to prepare SmS as a film on a substrate. The analysis of the literature data on samarium organyls leads us to the conclusion that compound **1**, whose reaction with H_2S has not previously been studied, can be used to obtain SmS both in solution and in the gaseous phase.[4]

The purpose of the present work is to prepare compound **1** by the reaction of lithium bis(trimethylsilyl)amide (**2**) with SmI_2 and bis(trimethylsilyl)amide with samarium naphthalide (**3**) and to study the reaction of **1** with H_2S.

Results and Discussion

Compound **1** was prepared by the reaction of **2** with SmI_2 (Scheme 1) and by the reaction of **3** with bis(trimethylsilyl)amide (Scheme 2).

Scheme 1

$$2[C_{10}H_8]Li + 2(Me_3Si)_2NH \xrightarrow{THF} \underset{\mathbf{2}}{2(Me_3Si)_2NLi} + C_{10}H_8 + C_{10}H_{10}$$

$$\mathbf{2} + SmI_2 \xrightarrow{THF} [(Me_3Si)_2N]_2Sm(THF)_2 + LiI$$

Scheme 2

$$3[C_{10}H_8]Na + SmCl_3 \xrightarrow{THF} \underset{\mathbf{3}}{(C_{10}H_8)Sm(THF)_x} + 3NaCl + 2C_{10}H_8$$

$$\mathbf{3} + 2(Me_3Si)_2NH \xrightarrow{THF} \underset{\mathbf{1}}{[(Me_3Si)_2N]_2Sm(THF)_2} + C_{10}H_8 + H_2$$

Compound **1** obtained *via* these reactions was then treated with H_2S:

$$\underset{\mathbf{1}}{[(Me_3Si)_2N]_2Sm(THF)_2} + H_2S \xrightarrow{THF} SmS(THF)_x + 2(Me_3Si)_2NH$$

The syntheses were carried out in THF at a pressure of 10^{-2} Torr.

When performing the reaction *via* Scheme 1, compound **1** was not isolated from the THF solution which also contained LiI. Compound **1** was isolated in the synthesis according to Scheme 2. Chemical analysis showed that compound **1** contains two THF molecules coordinated to samarium. They were removed by drying for 3 h at 210 °C *in vacuo* (10^{-2} Torr).

A black precipitate was formed in the reaction of **1**, prepared according to Scheme **1**, with a stoichiometric amount of H_2S. The solution was decanted and the

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 241—243, February, 1995.

1066-5285/95/4402-0233 $12.50 © 1995 Plenum Publishing Corporation

precipitate was evacuated for 1 h at 200—210 °C. Then the substance was placed into a quartz tube in an argon atmosphere, and the tube was evacuated to 10^{-3} Torr and sealed. After thermal treatment of the substance, peaks corresponding to two cubic structures appeared in the X-ray pattern, which is characteristic of the phases in the Sm—S system. The NaCl type peaks of the lattice with the elementary cell parameter a = 5.91 Å correspond to the SmS phase (15 % content) and the Th_3P_4 type peaks (a = 8.51 Å) correspond to the Sm_2S_3—Sm_3S_4 solid solution phase (75 % content). Taking into account the value of a = 8.51 Å and the change in the parameter of the elementary cell within the Sm_2S_3—Sm_3S_4 range (the temperature dependence of a was neglected), the composition of the phase was tentatively found to be $SmS_{1,4}$ with a cubic Th_3P_4 type structure. The formation of Sm(3+) sulfides can be caused to the presence of LiI in the THF solution from which samarium sulfides were precipitated. LiI could favor the disproportionation of Sm^{II} and the partial formation of Sm^{III}.

The interaction of **1** obtained with a stoichiometric amount of H_2S according to Scheme 2 results in the formation of a reaction product with a high content of SmS. The studies of the thermally treated sample by X-ray, chemical, and microstructural analyses show that the content of the main SmS substance is not less than 90 %.

Immediately after preparation, SmS is X-ray amorphous. The rate of its transformation into a polycrystalline state depends on the temperature of the treatment. Annealing at 300 °C for 160 h does not change the phase state of the substance. The reflections of the crystalline phases appear after exposure for 190 h at 500—600 °C. Increasing the time of the treatment to 290 h does not change the diffraction pattern. The stability of the substance in air increases as the time of its thermal treatment increases. Immediately after preparation, amorphous SmS oxidizes for 1—5 min mainly to samarium oxysulfide. The X-ray amorphous sample treated at 300 °C oxidizes to 50 % oxysulfide after 3 days. The samples annealed at 900—1000 °C in air are stable and do not differ from those obtained by the direct synthesis from Sm and S. The reflections of SmS with a = 5.92 Å and insignificant peaks of an admixture are fixed in the diffraction pattern of the sample after its thermal treatment. Its chemical composition is close to that calculated for SmS:

Content	Calculated	Found
S^{-2}/wt. %	17.58	16.2
Sm^{+2}/wt. %	82.42	83.5

After polishing the sample, a thin golden film of the SmS phase (H = 2100 MPa) with grayish-blue inclusions of the admixture phase are seen on sections of the sintered sample. All analytical methods used testify that the content of SmS in the sample is not less than 90 %.

Experimental

The X-ray phase analysis was performed on a DRON-3M instrument (Cu-K_a irradiation, Ni-filter). Sulfide content was determined by iodometry, and the samarium ion was analyzed by complexonometry according to the standard procedure. The microstructure of sintered samples was studied on a PMT-3 microdurometer.

Preparation of SmS. Procedure 1. A THF solution of $(Me_3Si)_2NH$ (3.91 mL, 18.59 mmol) was added to a THF solution of lithium naphthalide prepared from 3.00 g (23.44 mmol) of naphthalene and 0.13 g (18.59 mmol) of metallic lithium. The THF was removed after 5 h and a brown precipitate appeared. The precipitate was washed with hexane (3×10 mL). After removing the hexane, naphthalene and dihydronaphthalene were removed by sublimation at 45 °C (5 h, 10^{-2} Torr). The precipitate was dried *in vacuo*. Pale yellow lithium bis(trimethylsilyl)amide **2** was obtained.

A dark green solution of 1.36 g (3.36 mmol) of SmI_2 in 10 mL of THF was added to a tube with a solution of 1.12 g (6.72 mmol) of **2** in 10 mL of THF. The tube was sealed, stored at ~20 °C for 5 h, and centrifuged. The tube was opened, the THF solution of **1** was decanted into an empty tube, and 75.0 mL (3.36 mmol) of H_2S was passed through the solution. When the reaction was over, the black precipitate that formed was filtered off from the dark brown solution and washed with THF (3×10 mL). The product obtained was dried at 210 °C and 10^{-2} Torr. A dark gray substance (0.7182 g, 18 %) was obtained.

Procedure 2. $SmCl_3$ (3.01 g, 11.72 mmol) dissolved in 10 mL of THF was added to a THF solution (20 mL) of sodium naphthalide prepared from 5.00 g (39.06 mmol) of naphthalene and 0.81 g (35.22 mmol) of metallic sodium. A THF solution (10 mL) of 4.39 mL (23.44 mmol) of $(Me_3Si)_2NH$ was added to the suspension that formed. A portion of the precipitate was dissolved, and hydrogen evolved. The change in the color of the solution to dark green and the formation of a black precipitate showed the reaction to be completed. The contents of the tube were centrifuged, the tube was unsealed, and the precipitate was separated by decantation and washed with THF (3×10 mL). The solution was evaporated, and hexane was condensed into the tube with the precipitate that formed. A reddish-brown solution and a black precipitate were formed. After 5 h, the solution was centrifuged and the precipitate was washed with hexane (3×10 mL). The hexane was removed under reduced pressure and then the naphthalene was removed at 45 °C and 10^{-2} Torr over a period of 5 h. Compound **1** (1.7553 g, 33 %) was obtained. H_2S (20.50 mL, 0.915 mmol) was bubbled through a THF solution of 0.6713 g (0.915 mmol) of **1**. A precipitate formed. After 5 h the contents of the tube were centrifuged. A dark brown solution and a black precipitate were obtained. The precipitate was washed with THF (2×10 mL). The product obtained was dried at 210 °C and 10^{-2} Torr. The precipitate changed its color to dark gray. The yield of SmS was 0.3870 g (88 %).

References

1. V. P. Zhuze and I. A. Smirnov, *Redkozemel'nye poluprovodniki* [*Rare-Earth Semiconductors*], Leningrad, Nauka, 1987, 202 (in Russian).

2. G. Z. Suleimanov, L. F. Rybakova, A. A. Pasynskii, L. T. Abdullaeva, T. Kh. Kurbanov, B. A. Guseinov, M. A. Kurbanov, E. A. Garagasheva, O. P. Syutkina, and I. P. Beletskaya, Author's Certificate 1186570 SSSR; *Byul. Izobr.*, 1985, **39**, 99 (in Russian).
3. O. V. Andreev, M. N. Bochkarev, N. M. Volodin, T. V. Nekrasova, and A. V. Protchenko, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1361 [*Russ. Chem. Bull.*, 1993, **42**, 1292 (Engl. Transl.]).
4. D. N. Suglobov, *Letuchie organicheskie soedineniya f-elementov* [*Volatile Organic Compounds of f-elements*], Energoatomizdat, Moscow, 1987 (in Russian).

Received February 2, 1994;
in revised form November 30, 1994