Chemistry and Technology of Samarium Monosulfide

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Abstract

Samarium monosulfide SmS (Fm3m, a = 5.967 Å, ΔE = 0.23 V, n = 1020 cm–1, σ = 500 Ω–1 cm–1, α = 350 µВ/K) is a thermoelectric material (Z>1) and, at the same time, a pressure-sensitive material (K≥40–50). Samarium monosulfide is a daltonide phase with a solid solution whose extent is mostly in the range of cationic vacancies: Sm1+хS1-x↓2x (x = 0–0.035; 1750 K). The congruent melting temperature of SmS is 2475 K. In the Sm–S system, Sm3S4 crystallizes from melt without change in composition. Samarium monosulfide thermally dissociates to Sm3S4 and Sm. Large-scale SmS lots are produced from samarium and sulfur. Synthesis is carried out in sealed-off silica glass ampoules at 500–1350 K followed by heat treatment in tantalum crucibles at 1500–2400 K. The reaction of metal samarium with sulfur results in the formation of sulfide phases that coat the samarium surface in the following order: SmS, Sm3S4, Sm2O3S, and Sm. Subsequent annealing at 1500–1800 K provides SmS yields up to 96–97 mol %.

1. Introduction

Samarium monosulfide is an advanced material that has a unique set of physical and chemical properties [1–3]. In the compound Sm2+S2– (Sm 4f65d6s2), the 6s electrons of samarium atoms are involved in bonding with sulfur anions. The 4f level lies within the bandgap. Samarium monosulfide is an n-type conductor with charge carrier concentrations on the order of 1020 cm–3 [4, 5]. The electrical conductivity of SmS is 500 Ω–1 cm–1 and changes considerably over the extent of Sm1+хS1-x↓2x solid solution (↓ stands for an anionic vacancy; х = 0–0.035). SmS is distinguished from the other Ln2+S compounds by the least energy difference between the 4f level and the bottom of the bandgap, equal to 0.23 eV [4, 6]. When a SmS sample is exposed to linear or volumetric pressure, its electrical conductivity increases linearly as a function of the applied pressure. The linear trend is observed at temperatures of up to 345 K, in some cases up to 470 K. SmS samples are superior to metal pressure sensors in their pressure sensitivity coefficients K (for SmS, K ranges from 40–50 in polycrystalline films to ≤260 in single crystals, against K = 2–4 for metals) [2, 7, 8]. In some technological and performance aspects, SmS pressure sensors are also advantageous over sensors based on compound semiconductors (K = 50–100) and single-crystal silicon (K = 100–135) [9–11].

Samarium monosulfide is an efficient high-temperature thermoelectric material with the figure of merit Z>1 [12]. In thin films, SmS manifests a thermovoltaic effect; a voltage of about 1.1 V appears on a thin-film sandwich structure in a temperature range of 360–428 K [13, 14]. Heat absorption was observed in SmS single crystals in the temperature range 360–428 K [15].
range of the thermovoltaic effect. Heat absorption was shown to arise from the collective injection of electrons from donor levels into the conduction band [15, 16].

There are a lot of publications concerned with samarium monosulfide, but there have been no surveys on its chemistry and technology. This article summarizes the results of our studies and other published data on the chemistry and technology of samarium monosulfide.

2. Experimental

Samarium sulfides were prepared from distilled samarium metal (Sm⁺³ type) and sulfur (a special grade chemical). Weighted samples of the elements were placed in silica glass ampules, which were then degassed and sealed off. The ampoules with samples inside were treated in a muffle at 500–1500 K. As-prepared batches were stirred, compacted, and then heat-treated in tantalum crucibles under an argon atmosphere on a UIN-16-200 induction setup [3, 25, 30]. The compound Sm₂S₃ was prepared from Sm₂O₃ (D type) in an H₂S + CS₂ flow at 1200–1300 K [25].

Surface images of particles were obtained using a JSM-6510LV (JEOL) scanning electron microscope. The operation conditions were an accelerating voltage of 20–30 kV and SpotSize of 30–50 μm. Microstructural analysis was carried out with an AxioVert.A1MAT microscope using the AxioVision SE64 program package at a resolution of 0.5 μm [3].

Differential scanning calorimetry was performed on a Setsys Evolution 1750 (TGA–DSC 1600) setup using the SETSOFT 2000 program package, Pt/PtRh (10%) thermocouple in a temperature range of 300–1870 K. Overlapping peaks were resolved by the Thermogram Analyser program [3, 43]. The atmosphere was argon (99.9999 wt.% pure). Simultaneous thermal analysis was carried out on an ST449 F3 Jupiter analyzer in the temperature range 400–2000 K using a tungsten–rhenium thermocouple. A high-purity (99.9999999 wt.%) helium flow was created in the system during the experiment. Peak areas were determined by the Proteus 6 2012 program. Visual polythermal analysis was performed on a VPTA-1M setup with a precision of within 1% of the measured value [43].

X-ray powder diffraction patterns were recorded on a PANalytical X′Pert PRO diffractometer (CuKα radiation, Ni filter, PIXcel detector) over the 2θ range from 10° to 100° [43].

The phase composition of surface layers (to depths of 0.5–1.0 nm) was studied by Auger spectroscopy (VG ESCALAB 210) [31]. Films were prepared on a flash evaporation setup [43] or a Nanofab-100 magnetron sputtering experimental aggregate [17].

3 Results and Discussion

The Sm–S system forms samarium sulfides represented by rational formulas with integer indices, namely SmS, Sm₁₂S₅, α-Sm₂S₃, and γ-Sm₂S₅ [18], as well as compounds represented by irrational formulas, namely SmS₁.₈₆ SmS₁.₈₉, and SmS₁.₉₆ [19].

The samarium sulfides are mainly categorized into sulfides proper and polysulfides. In full-valence sulfides SmS, Sm₁₂S₅, Sm₂S₄ (Sm₂⁺⁺Sm₃⁺⁺S₄), α-Sm₂S₃, and γ-Sm₂S₅, there exist only sulfide sulfur anions S²⁻ in the structure. In polysulfide compounds, there are (S–S)₃ groups [18, 19].

Cubic polysulfide Sm₂S₄ₓ (x = 0–0.18; 64–66.6 at. % S) is formed by the direct reaction of samarium with sulfur inside a silica glass ampoule (Table 1). Thus-prepared samples are not equilibrated. Vasileva [19] measured vapor pressure above solid polysulfides and discovered that three compounds of constant composition, namely SmS₁.₈₆ (65.03 at. % S), SmS₁.₈₉ (65.4 at. % S), and SmS₁.₉₀ (65.52 at. % S), are formed in the range of 64.5–66.6 at. % S. We have not found structure data for these compounds.

The thermal stability of samarium sulfides and polysulfides is determined by the type of sulfur anion involved.

The cubic unit cell of SmS is a basic one and can be transformed to unit cells of other samarium sulfides (Fig. 1, Table 1) [20].

![Fig. 1. Scheme of transition from (a) the cubic unit cell to (b) Th₃P₄ type and (c) α-LnS₅ type unit cells of rare-earth sulfides. m, n, and p are integers [18, 20].](image-url)
Table 1
Crystal data for samarium sulfides [3, 4, 18]

| Sulphide | Color  | Crystal structure | Space group | Structural type | Period of cell, Å | Density, g/cm³ |
|----------|--------|-------------------|-------------|----------------|------------------|----------------|
| SmS      | Black  | Cubic             | Fm3m        | NaCl           | 5.967            | 5.64 5.67     |
| SmS₄     | Black  | Cubic             | I43d        | Th₃P₄          | 8.556            | 6.11 6.14     |
| α-SmS₂S₃| Cherry | Rhombic           | Pnma        | α-La₃S₃       | 7.382 3.974 15.372 | 5.59 6.09     |
| γ-SmS₂S₃| Yellow | Cubic             | I43d        | Th₃P₄          | 8.448            | 5.77 5.83     |
| SmS₂ₓₙ   | Black  | Cubic             | LaS₂        |                | 7.965            | 5.56 5.66     |

In the γ-Sm₂S₃ cubic structure, every ninth position in the cationic sublattice is vacant; the crystal formula is [Sm₈₋ₓ]S₁₂. When the vacancies are completely occupied, the composition is SmS₄ [3, 18].

In the solid solution [(Sm³⁺)ₙ₋ₓ(Sm²⁺)ₓ]ₙ₋ₓ[SmₓS₄₋ₓ] (x = 0–1), there exists a general sulfur anionic sublattice. The cationic sublattice contains randomly distributed divalent samarium ions and cationic vacancies. In the range of compositions from γ-SmS₁₄ to γ-SmS₁₅, vacancy ordering can occur [21, 22].

Fig. 2. Sm–S phase diagram. The state of samples as shown by VPTA: (1) incipient melting and (2) complete melting. The state of samples as shown by microstructure observation and X-ray powder diffraction measurements: (3) a single phase and (4) two phases [3, 4, 22].
A eutectic is formed between SmS and Sm$_{1-x}$S$_x$, which is distinctly identified by microstructure observation. The phase ratio in the eutectic is 0.3278 SmS + 0.6722 Sm$_{1-x}$S$_x$. The eutectic melting point in samples containing 52–56 at. % S is 2140 K as determined by VPTA (Fig. 2). Liquidus temperatures for compositions in the range 50–57.1 at. % S were determined by VPTA.

The solidus–liquidus region between Sm$_{1-x}$S$_x$ and Sm$_{3}$S$_1$ is cigars-shaped and classified with type 1 according to Roozeboom’s classification [3].

An experimental determination of Sm-SmS eutectic coordinates meets difficulties. During synthesis, metallic samarium is deposited on ampoule walls and does not form any compact sample. The eutectic temperature as determined by DSC is (1300±10) K. The eutectic composition (2 at. % S) was calculated by empirical relationships and averaged [24].

Attempts to construct a liquidus line in the range 0–45 at. % S using high-temperature differential thermal analysis failed. Metallic samarium was sublimed from the sample in the course of heating. We have not found any data on the liquidus position in the ranges 0–45 at. % S and 60–100 at. % S. The liquidus is outlined tentatively in view of the similarity of phase equilibrium in Ln-S (Ln = La-Lu; Se) systems [3, 23, 25].

Lanthanide monosulfides LnS (Ln = La-Lu) form solid solutions extending both toward an excess of rare-earth atoms and an excess of sulfur atoms [4, 18].

Solid solutions can be formed to the left and to the right of the SmS line by the following suggested scenarios.

In a samarium-rich region Sm$_{1+x}$S$_{1-x}$, solid solutions occur due to the generation of vacant sulfur anion sites with the formation of the cationic sublattice by samarium atoms.

In a sulfur-rich region Sm$_{1+y}$S$_{1-y}$, solid solution formation is due to the generation of samarium cation vacancies with the formation of the anionic sublattice by sulfur atoms [4, 24, 25].

The extent of samarium monosulfide solid solution is 46.5–(50.0)–50.2 at. % S [3, 4, 26-28].

Golubkov and Sergeeva [4] prepared samples of tailored compositions from the range 40–52 at. % S in sealed air-right (molybdenum or tantalum) crucibles, annealed them at 1770 K, and rapidly cooled (Table 2). Neither X-ray powder diffraction nor microstructure observation showed noticeable SmS-base solubility in the sulfur excess region.

The diagram in Fig. 2 yet shows solid solution in the range 50–50.2 at. % S. Samarium monosulfide samples that contain Sm$_{3}$S$_1$ traces have decreased electrical conductivities, most likely because of the appearance of cationic vacancies in the solid solution.

When samarium atoms are in excess, Sm$_{1+x}$S$_x$, solid solution exists in the range 46.5–50 at. % S (x = 0–0.035). Composition-dependent solid solution densities were calculated on the assumption that excessive samarium atoms reside either in interstices or in anionic vacancies of the SmS structure. A comparison of pycnometric densities with the calculated values implies that both types of structural alterations occur upon solid solution formation [4, 26, 27].

Electrical conductivity, thermo-EMF, and charge carrier density versus composition curves measured in the Sm$_{1+x}$S$_x$ solution region each feature a break point at 49.7 at. % S [4, 6], 49.2 at. % S [29].

While the composition only slightly deviates from the SmS stoichiometry (49.7–50.0 at. % S, x = 0–0.003), samarium atoms prefer to occupy cationic sites, so that the electrophysical properties of samples change only insignificantly. As samarium percentage in Sm$_{1+x}$S$_x$ solid solution increases further, the concentration of anionic vacancies increases progressively, and this inevitably results in their filling with samarium atoms [4, 29].

The delocalization of two 6s electrons of samarium atoms (4f$^2$6s$^2$) in anionic positions, increases the electrical conductivity of solid solution samples and reduces their thermo-EMF values (Table 2).

Second phases that appear at the boundaries of SmS-base solid solution have been identified by physicochemical methods. Bluish-colored Sm$_{3}$S$_1$ crystals appear on polished sections as bands 1-3 μm wide embedded in between orange grains of the SmS phase. Isles of fine-grained SmS + Sm$_{3}$S$_1$ eutectic can also appear. In samples having compositions in the Sm + SmS solid solution region, metallic samarium appears as intergrain inclusions on the polished sections through inner portions of the sample (Table 2) [3].

The constituent elements of the Sm–S system have high partial vapor pressures. The sulfur vapor pressure versus temperature curve (590–1273 K) was fitted by a polynomial [3]:

\[
\log(P_s) = 60.9106 - 24971/T + 1.0817 \cdot 10^7/T^2 - 2.2060 \cdot 10^9/T^3 - 14.4102 \cdot \log(T),
\]

where $P_s$ is saturated vapor pressure, atm; and $T$ is temperature in degrees Kelvin.

The samarium vapor pressure is 1.28·10$^{-5}$ atm at 1000 K, 8.26·10$^{-4}$ atm at 1200 K, and 0.88 atm at 1800 K [3].
Heat treatment in vacuo or under argon changes the stoichiometry of a samarium sulfide phase, so that it is necessary to generate a samarium vapor or sulfur vapor atmosphere in the reactor [3, 30]. Stoichiometric \( \text{Sm}_S \) (57.14 at. % S) samples were prepared by crystallization from melt under an argon atmosphere (102 KPa) and by crystallization under a residual pressure of less than 0.1 Pa in the reactor. The \( \text{Sm}_S \) line conventionally divides the Sm–S diagram into two portions.

In order for phases containing more than 57.5 at. % S to retain their stoichiometries during heat treatment, an increased sulfur vapor pressure should be maintained in the reactor [30]. Samples of tailored compositions from the \( \text{Sm}_{1+x}S_{1-x} \) solid solution range \((x = 0–0.035)\) can be prepared provided that an increased samarium vapor pressure is created in the reactor (Fig. 3) [4].

The sulfur vapor pressure in the reactor with a graphite crucible inside (Fig. 3) is heated to 403–443 K to provide sulfur boiling during heat treatment. This is inappropriate for an excess samarium vapor pressure to be created (the samarium melting temperature is 1345 K). One should keep in mind that metallic samarium is sublimed when heated above 1100 K, adsorbed on the walls of silica glass reactors, and then desorbed only to an insignificant degree.

The easiest-to-control conditions for treatment in samarium vapor appear in a sealed tantalum crucible containing the sample to be treated and a weighed metallic samarium sample. When the crucible is equipped with a cover and is manufactured by spot welding, a system of three-dimensional screens is mounted in the reactor to provide a local increase in samarium vapor pressure [3].

| \( \text{Sm}_X \) | Atomic \% Sm | Measured density, \( d_\text{as}, \) g/cm\(^3\) | Unit cell parameters, \( a, \) Å | Electrical conductivity \((300 \text{ K}) \), \( \sigma, \) \( \Omega^{-1} \text{cm}^{-1} \) | Thermo-EMF, \( \alpha, \) \( \mu\text{V/K} \) | Thermal conductivity, \( \chi, \) \( \text{cal/(cm} \times \text{s} \times \text{K}) \) | Activation energy, \( E, \) eV | Electron density \((\text{Sm}_S), \) \( \text{mol} \% \) | Second phase \( \text{Sm}_{1.9} \) \( \text{Sm}_{0.1} \) | SS \( \text{Sm}_S + \) Sm |
|-----------------|------------|---------------------|------------------|-----------------------------|-------------------------|---------------------------|-------------------|---------------------|-------------------|-------------------|
| 1.184 | 45.8 | 5.93 | 5.9702 ± 2 | 6 | 240 | - | 0.18 | 0.30 | 0.94 | 46 (SmS) |
| 1.128 | 47.0 | 5.87 | - | 17 | 270 | 5.7 | - | - | 1.0 | 30 |
| 1.065 | 48.4 | 5.66 | 5.9712 ± 1 | 18 | 325 | - | 0.22 | 0.22 | 1.1 | 10 |
| 1.028 | 49.3 | 5.71 | - | 57 | 200 | - | 0.10 | 0.17 | 2.0 | 3 |
| 1.024 | 49.4 | 5.65 | - | 24 | 282 | 6.96 | - | - | 1.2 | 1 |
| 1.014 | 49.7 | - | - | - | 300 | - | 0.10 | 0.20 | 1.9 | 0.5 |
| 1.013 | 49.7 | 5.69 | - | - | 260 | 13.79 | 0.00 | 0.14 | 4.6 | solid solution (SS) |
| 1.000 | 50 | 5.69 | - | 36 | 360 | 15.34 | 0.12 | 0.28 | 9.0 | SmS |
| 0.988 | 50.3 | 5.76 | - | 39 | 380 | 12.95 | 0.11 | 0.24 | 6.0 | |
| 0.986 | 50.3 | 5.73 | - | 513 | 115 | - | - | - | 9.5 | |
| 0.980 | 50.5 | 5.75 | 5.9694 ± 3 | 500 | 150 | 10.87 | - | - | 7.5 | |
| 0.964 | 50.9 | 5.74 | 5.9693 ± 5 | 550 | 124 | - | 0.00 | 0.00 | - | |
| 0.905 | 52.5 | - | - | 870 | 82 | - | - | - | 19 | |
| 0.903 | 52.5 | 5.83 | - | 690 | 91 | - | 0.00 | 0.00 | 25 | |
| 0.887 | 53 | - | - | 740 | 96 | 12.2 | 0.00 | 0.00 | - | |
| 0.869 | 53.5 | 5.89 | 5.9706 ± 3 | 980 | 92 | - | - | - | - | |
| 0.861 | 53.7 | 5.88 | 5.9714 ± 3 | 1020 | 65 | 10.86 | - | - | 30 | |
| 0.841 | 54.3 | 5.83 | 5.9718 ± 4 | 1000 | 64 | 13.24 | 0.00 | 0.00 | 39 | |
| 0.815 | 55.1 | - | - | 1005 | 65 | - | - | - | 20 | |

Table 2
Compositions and properties of \( \text{Sm}_S \) phases [4, 26, 29].

The easiest-to-control conditions for treatment in samarium vapor appear in a sealed tantalum crucible containing the sample to be treated and a weighed metallic samarium sample. When the crucible is equipped with a cover and is manufactured by spot welding, a system of three-dimensional screens is mounted in the reactor to provide a local increase in samarium vapor pressure [3].
Samarium monosulfide samples intended for use in flash evaporation and magnetron sputtering should have phase and chemical compositions meeting the requirements formulated as follows. Those samples should contain at least 95 mol % SmS. Desired samarium monosulfide compositions are those within a samarium-rich region. The batch should comprise only those impurity phases that are in equilibrium with samarium monosulfide, namely Sm₃S₄ and Sm₂O₂S [31, 32]. The impurity contents in SmS as low as 1–2 mol % enhance the performance of a pressure sensor [33, 34].

In regard of the precursors and synthesis parameters, the routes to prepare samarium monosulfide may be classified in two major groups:
- inorganic syntheses;
- syntheses using organometal samarium compounds.

Inorganic syntheses have the following distinguishing features, namely: high-purity precursors, staged character, high treatment temperatures (500–2000 K), special hardware, and high-cost auxiliary materials (silica glass ampoules and reactors, and tantalum or Alundum crucibles) [3, 35, 36].

Samarium monosulfide is produced in several chemical reactions:
- when samarium sulfides are reacted with metallic samarium:
  \[ \text{Sm} + \text{Sm}_3\text{S}_4 \rightarrow 4\text{SmS} \] (2)
  \[ \text{Sm} + \text{Sm}_2\text{S}_3 \rightarrow 3\text{SmS}; \] (3)
- or when samarium sesquisulfide and samarium oxysulfide are reacted with strong reducing agents.
  \[ 3\text{Sm}_2\text{O}_3 + 3\text{Sm}_2\text{S}_3 + 4\text{Al} \rightarrow 12\text{SmS} + 2\text{Al}_2\text{O}_3 \] (4)
  \[ \text{Sm}_2\text{O}_3 + 2\text{Sm}_2\text{S}_3 + 3\text{C} \rightarrow 6\text{SmS} + 3\text{CO} \] (5)

The last two reactions are unsuitable for the production of samarium monosulfide. Al₂O₃ is produced in reaction (4) as a polycrystalline phase. Reaction (5) actually combines the production of metallic samarium and the reaction of the nascent metal with Sm₂S₃. These reactions occur under appreciably differing conditions. Even if the synthesis succeeds, SmS yields do not reach 60–70 mol % SmS [35, 36].

There are three commercially available products that can be used to prepare samarium monosulfide, namely metallic samarium cooled from vapor phase, Sm₂S₃, and sulfur of high-purity grade.

Reaction (3) can serve to prepare samarium monosulfide, but actual SmS yields are as low as up to 85–90 mol % [3]. Sm₂S₃ can be prepared in a flow of sulfiding gases H₂S and CS₂ according to reactions [30].

  \[ 2\text{Sm}_2\text{O}_3 + 3\text{CS}_2 \rightarrow 2\text{Sm}_2\text{S}_3 + 3\text{CO}_2 \] (6)
  \[ \text{Sm}_2\text{O}_3 + 3\text{H}_2\text{S} \rightarrow \text{Sm}_2\text{S}_3 + 3\text{H}_2\text{O} \] (7)

Sm₂S₃ has a higher cost than SmS prepared from samarium and sulfur; it contains particulate carbon impurity. The grain-size composition of the powder is dominated by agglomerates having sizes of 20–50 μm, which makes difficult the occurrence of reaction (8) below to form Sm₃S₄ first and then SmS formation by reaction (2).
$4\text{Sm}_2\text{S}_3 + \text{Sm} \rightarrow 3\text{Sm}_3\text{S}_4 \quad (8)$

Samarium monosulfide formation from the constituent elements (metallic samarium and sulfur) involves two stages. A silica glass ampoule containing weighed samples of metallic samarium and sulfur is degassed, sealed off, and then heat-treated at 500–1200 K. The batch is sintered or alloyed inside a tantalum crucible placed in a high-frequency setup under an argon atmosphere. The reaction between metallic samarium and sulfur in a sealed ampoule involves the stage of forming layers of samarium sulfide phases in polycrystalline particles (Fig. 4) [3, 35, 36] (Fig. 4a).

In contact with metallic samarium, there is a SmS phase, next followed by Sm$_3$S$_4$, $\alpha$-Sm$_2$S$_3$, and SmS$_{2-x}$ phases. The samarium sulfide percentage in the heat-treated sample depends on the treatment temperature. At 550–700 K, a SmS$_{2-x}$ phase is the major product. The yields of Sm$_3$S$_4$ and SmS phases increase as treatment temperature rises. The SmS percentage in the sample after the ampoule synthesis stage is 70–90 mol%; the sample also contains Sm, Sm$_2$S$_4$, and Sm$_2$O$_2$S phases [32, 36] (Fig. 5).

The high-temperature treatment of the batch provides the occurrence of reaction (2) and the formation of tailored grain-size composition in the batch. Three temperature schedules were recognized to provide the formation of tailored phase and grain-size compositions in the batch (Fig. 5).

For reaction (2) to have the greatest completion at 1300–1600 K, an increased samarium vapor pressure should be created in the reactor. The highest SmS yields are provided by heat treatment of the batch at 1300–1800 K. At these temperatures dense grain structure starts forming [3].

In the batch annealed at 1800–2100 K, a Sm$_3$S$_4$ phase is also formed in an amount of up to 1 mol%, due to the thermal dissociation of SmS (2). Upon milling of dense-sintered samples the yield of the fraction sized 90–120 μm is up to 50%.

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Fig. 4. Phase and grain-size compositions of a sample obtained at the ampoule synthesis stage. (a) Phase composition: (1) metallic Sm, (2) SmS, (3) Sm$_3$S$_4$, (4) $\alpha$-Sm$_2$S$_3$, and (5) SmS$_{2-x}$. (b) Grain-size composition of the batch that contains 95 mol % SmS.

Fig. 5. Scheme of the ampoule stage and high-temperature treatment of the batch in the preparation of samarium monosulfide.
Dense-sintered samples subjected to short-term annealing at temperatures above 2100 K acquire the mechanical strength required for their use in thermoelectric generators. The routes to prepare samarium monosulfide from organometal compounds are distinguished by the following features: low reaction temperatures (298–398 K), suitability of various classes of organic samarium compounds, available hardware, use of either sulfur or hydrogen sulfide, and the feasibility to produce samarium monosulfide in an X-ray amorphous state [37–42].

Samarium monosulfide was prepared by reacting naphthalenide with sulfur in tetrahydrofuran (THF) [37]. The preparation scheme was as follows (9, 10):

\[
\text{SmI}_2 + 2C_{10}H_8Li → ^{\text{THF}}_\text{C}_{10}H_8\text{Sm} \cdot ^{\text{THF}}_x + 2\text{LiI} + C_{10}H_8 (9)
\]

\[
C_{10}H_8\text{Sm} \cdot ^{\text{THF}} + \text{S} → ^{\text{THF}}_\text{SmS} \cdot ^{\text{THF}}_x + ^{\text{C}_{10}H_8}_x (10)
\]

The final product contained SmS bonded to tetrahydrofuran. After tetrahydrofuran was removed, SmS was obtained as an X-ray amorphous black powder.

The reaction of volatile samarium compounds with gaseous \( \text{H}_2\text{S} \) is a way to prepare an X-ray-amorphous SmS film directly on a substrate [38]:

\[
[(\text{Me}_3\text{Si})_3\text{N}]_x\text{Sm(TTHF)}_y + \text{H}_2\text{S} → ^{\text{THF}}_\text{SmS}(\text{THF})_0 + ^{2(\text{Me}_3\text{Si})_3\text{NH}}_0 (11)
\]

The thus-prepared film is then thermally annealed in stages to be converted to a polycrystalline state [38].

In [40] the chemical synthesis of the Smx-SyOz compounds is performed by thermolysis of dithiocarbamate precursors, followed by the drop casting deposition of the synthesized material, and by the thermal treatment at different temperatures (250 °C, 500 °C and 900 °C) and atmospheric conditions (nitrogen and air). The temperature of 900 °C and the nitrogen atmosphere represent the optimal treatment conditions, among the process parameters, to obtain a single phase of SmO2.

At the work [41, 42] samarium dithiocarbamates were obtained in form dte,Smbipy, dte,Smphen, dte,Sm. Substances were distilled in pyridine and thermally decomposed on the pyroceramics support at 450–570 K. Polycrystalline films SmS \( a = 5.6–5.7 \) Å containing impurities were obtained.

The chemical properties of SmS are determined by the electronic structure of samarium and its oxidation state \( 2^+ \) in Sm\(^{2+}\)S\(^2\). In the settings of an air atmosphere where the oxygen partial vapor pressure \( p(\text{O}_2) \) = 0.21 atm, stable oxygenated and halide compounds are those where samarium has the oxidation state \( +3 \), for example Sm\(_2\)O\(_3\), SmF\(_3\), SmCl\(_3\), Sm\(_2\)(SO\(_4\))\(_3\), Sm\(_2\)O\(_3\)S, Sm\(_2\)S\(_3\) and others [3, 22, 32, 43].

Reactions of SmS with water or acids involve concurrent ion-exchange and redox reactions [31, 43]. Polycrystalline SmS powders are stable under air. The phase composition of a SmS powder (the fraction sized 60–100 μm) after 30 years of exposure to dry air changed only insignificantly, so that the percentage of the Sm\(_2\)O\(_3\)S increased by 3–5 mol % [31].

Samarium monosulfide should be regarded as a salt of a weak hydroxide Sm(OH)\(_3\) (an unstable compound) and a weak acid H\(_2\)S; such compounds are completely hydrolysable in aqueous media. A polycrystalline SmS powder (fraction sized 90–120 μm) experiences only surface hydrolysis when exposed to H\(_2\)O for 10 h. The degree of hydrolysis does not increase appreciably after the powder is exposed to boiling water for 1 h. In the bulk of polycrystalline grains, the phase composition remains unchanged.

The products of reaction (12) between SmS and H\(_2\)O in the course of thermohydrolysis are detected in the vapor phase when reaction zone temperatures are 600–650 K [3, 31, 44]. The presence of H\(_2\)O in the vapor phase was proven chromatographically. The hydrolysis yields a SmS\(_3\) phase, which subsequently also reacts with H\(_2\)O according to reaction (13) below.

\[
5\text{SmS} + 2\text{H}_2\text{O} = \text{Sm}_2\text{S}_3 + \text{Sm}_2\text{O}_3\text{S} + 2\text{H}_2 (12)
\]

\[
2(\text{SmS} \cdot \text{Sm}_2\text{S}_3) + 6\text{H}_2\text{O} = 3\text{Sm}_2\text{O}_3\text{S} + 5\text{H}_2\text{S} + \text{H}_2 (13)
\]

The chemism of SmS oxidation is in many traits similar to the hydrolysis chemism. A SmS powder after the ampoule synthesis stage having particle sizes of 3–15 μm, oxidizes in flowing air starting at 520–570 K. Sintered technical ceramics withstand oxidation when exposed to temperatures up to 650 K for 1 h. The oxidation of SmS powder is accompanied with an increase in Sm\(_2\)S\(_3\) percentage formed by reactions (13) and (14) (Fig. 6) [45].
Fig. 6. X-ray diffraction pattern for a SmS ceramic sample oxidized in the course of heat treatment. Phase contents in the sample: 53.34 mol % SmS, 9.84% Sm$_3$S$_4$, and 36.82% Sm$_2$O$_2$.

The reaction of SmS with an acid (HHal, HNO$_3$, or H$_2$SO$_4$) involves concurrent ion-exchange and redox reactions, described by reaction (16) below.

$$2\text{SmS} + 2\text{HCl} + 2\text{H}_2\text{O} = 2\text{Sm(OH)}_2\text{Cl} + \text{H}_2\text{S} + \text{H}_2\text{O}$$  (16)

Samarium monosulfide, a stable compound in polycrystalline state, has properties similar to isostructural compounds CaS, SrS, and BaS ($r$Ca$^{2+}$(CN=6) = 1.140 Å, $r$Sr$^{2+}$(CN=6) = 1.320 Å, $r$Ba$^{2+}$(CN=6) = 1.490 Å, and $r$Sm$^{2+}$(CN=6) = 1.360 Å) [30, 43].

Now there are two main routes to prepare samarium monosulfide films, namely flash evaporation and magnetron sputtering [3, 33, 46].

In flash evaporation, the precursor is a SmS fraction with grain sizes of 90–120 μm. Evaporation is performed in a high vacuum (0.001 Pa). A SmS powder is conveyed by the Archimedes screw from the hopper to a tungsten heater maintained at 2670 K. Optimal is the "blue torch" mode where a fallen SmS grain is sublimed immediately. Serial SmS sensors manufactured by flash evaporation have pressure sensitivity coefficients of 30–50 [33, 34].

A SmS disk to be used in magnetron sputtering should meet certain requirements as to mechanical strength. A ceramic disk 75 mm in diameter was manufactured by compacting SmS powder and then sintered at 1500–1600 K. Magnetron sputtering makes it possible to form films of tailored thickness with tailored sensor parameters. Thin SmS films in addition manifest the photoelectric effect, and thereby create additional opportunities for use of samarium monosulfide.

The materials that are in contact with SmS bulk samples or films, should not chemically react with those bulk samples or films. Chemical compounds or noticeable solid solutions formed in the contact layer change the resistance of the circuit and, with time, can interfere with the readings of sensor [33, 34].

Nickel is the major contact material used; metallic titanium, aluminum, and gold can also be used. No increase in ohmic resistance was detected during the performance of many hundreds of SmS sensors equipped with a nickel contact. Aluminum is of interest in this context for the fact that subsequent surface oxidation to Al$_2$O$_3$ provides chemical protection to the contact.

It is undesirable to use conventional electroengineering materials, such as copper and silver. There is a tie-line between Cu and SmS phases in Cu-Sm-S and Ag-Sm-S ternary systems. Cu$_{2-x}$S and Ag$_{2-x}$S phases are thermally stable, which makes their local formation possible. Copper and, especially, silver react with sulfur even at 300 K. When metallic silver or copper is in contact with a SmS phase for a long time Ag$_{2-x}$S or Cu$_{2-x}$S isles are formed; the film composition shifts to appear in the samarium-rich solid solution [49, 50].

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