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Thermodynamic Study of the SmS_2–$SmS_{1.5}$ System

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A detailed thermodynamic study of the SmS_2–$SmS_{1.5}$ system in the temperature range 350–1000°C was performed using high-quality crystals of the highest Sm-polysulfide and a sensitive static tensimetric method, a quartz Bourdon gauge with a membrane as a null-point instrument. The *P–T–x* diagram obtained has shown that the phase region covering the composition range $SmS_{2.00}$–$SmS_{1.82}$, which was previously described as a single grossly nonstoichiometric phase, consists of three discrete stoichiometric phases, $SmS_{1.900}$, $SmS_{1.893}$, and $SmS_{1.863}$. The polysulfide compositions were evaluated from the tensimetric data with an accuracy of ±0.001 f. u. The thermodynamic parameters of incongruent sublimation were calculated for each polysulfide, and then the standard heats of formation were estimated for these compounds. © 1999 Academic Press

INTRODUCTION

A single, grossly nonstoichiometric phase, LnS_{2-x} ($x \approx 0.15$–0.25), with sulfur vacancies distributed randomly for all compositions in the systems $LnS_{1.5}$–LnS_2 ($Ln =$ rare earth element), had been previously detected (1, 2). For the Sm system, the highest polysulfide was found to be $SmS_{2.00}$ (3) or $SmS_{1.94}$ (4). The phase homogeneity for SmS_2–$SmS_{1.82}$ compositions of powder materials was determined by pressure-temperature measurements using the intermittent weighing technique (3). For $SmS_{1.94}$–$SmS_{1.90}$ compositions, the tetragonal distortion of the cubic lattice was used. The $SmS_{1.94}$ powder diffraction pattern was found to be isostructural with cubic LnS_2, $Ln =$ La–Nd (4).

LnS_2 crystals of dimensions 4 × 3 mm (for all elements except Eu, Yb, Lu) were grown and characterized compositionally and by Raman spectroscopy (5). It was also shown that Sm disulfide with the composition $SmS_{1.90}$ was compositionally and structurally different from both stoichiometric disulfides, LnS_2, typical for light (La–Nd) elements, and nonstoichiometric disulfides, $LnS_{1.84}$, typical for heavy (Gd–Lu) ones. The position of Sm in the LnS_2 compound series may be a key for understanding the nonstoichiometry of the *Ln* disulfides, and thus the SmS_2–$SmS_{1.5}$ system invites more detailed study.

A new investigation of this system was performed using the highest Sm–polysulfide crystals of high quality and suitable for tensimetric studying, and a static tensimetric method, the Bourdon gauge (6), to examine the system in the equilibrium state. This method as has already been shown, is a most promising one for studying the LnS_2–$LnS_{1.5}$ systems ($Ln =$ Nd, Er), which are characterized by very slowly established solid–vapor equilibrium (7, 8). In this paper, precise experimental data were obtained to distinguish Sm–polysulfides with very close compositions, unrecognized by wet chemical analysis, to determine homogeneity ranges for these phases with an accuracy of about 0.02 at% and to calculate the thermodynamic properties of the compounds.

EXPERIMENTAL DETAILS

Equipment. The total vapor pressure was measured in the temperature range 350–1000°C by means of a quartz Bourdon gauge with a membrane as a null-point instrument. The main design of the equipment was close to that described in (6), except that our instrument could measure the pressure up to 2 atm (9). The Bourdon gauge was placed in a vertical furnace with uniform temperature field, which was controlled by Pt–Pt/Rh thermocouples with an accuracy of about 1 K. The equipment was calibrated by comparing the measured vapor pressure of metallic cadmium with tabulated pressure values.

Experimental procedure. The total vapor pressure, $P = f(T)$, was measured in a closed system over the highest Sm–polysulfide with exact initial composition and for various weight-per-reaction-volume ratios (m/V). These ratios were taken so that the initial polysulfide could be completely transformed to sesquisulfide due to incongruent sublimation of the former. Previously, convincing evidence was obtained that the equilibrium vapor above the Sm–polysulfides consists largely of pure sulfur. The $P = f(T)$ dependencies reflected transitions from the three-phase equilibrium (solid–solid–vapor) to the two-phase one (solid–vapor) and

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vice versa as breaks in the lines. These breaks indicated boundaries of discrete phases and regions where one or two phases were in equilibrium with the sulfur vapor. Coordinates of the break (*P* and *T*) were found from the intersection of the two-phase equilibrium line with the three-phase one. Combining these values with data on the vessel volume and the quantitative composition of vapor, the amount of sulfur transferred into the gaseous phase may be determined using the equation $a = V \cdot \sum n \cdot P_{\mathrm{Sn}}/RT \cdot N^v$. The N^v value was calculated by solving the equations $P_{\mathrm{total}} = P_{\mathrm{Sn}}$ and $K_n = (P_{\mathrm{Sn}})^{n/2}$, $n = 1$–8, using the equilibrium constants of the reactions $S_n(g) = 1/2n\ S_2(g)$ from (10).

The measurements were carried out only on heating. Samples were heated in a step-by-step procedure (each step was 10–15 K, or sometimes 6 K) and kept at each temperature until the pressure attained a value constant within 1 Torr.

Samples. Special attention was given to grow Sm-polysulfide crystals suitable for the tensimetric experiment. The $Sm_2S_3 + S$ mixture of molar ratio from 1 to 4 and the eutectic KCl + KI flux were used as starting materials. The crystals grew at 973 K as thin plates (3×4 mm^2) with a mirror-smooth surface and zero sulfur surface absorption. Crystal composition was determined as $SmS_{1.900 \pm 0.005}$ by spectrophotometric analysis of the sulfur content. This composition was invariant to the change of sulfur pressure up to 25 atm, which allowed us to regard this phase as the highest polysulfide of the Sm system. Before each experiment, the crystals were crushed, placed in the vessel, and heated for 4 h at 350°C under vacuum; then the vessel was sealed.

RESULTS

Phase relationship in the $SmS_{1.50}$–$SmS_{1.90}$ system. In order to characterize the phase relationship within the system, the pressure values were plotted as a function of temperature for four sets with $m/V = 1{,}70$, 2,00, 2,19, and 3.5 mg/cm^3 (Fig. 1). The incongruent sublimation of the $SmS_{1.90}$ phase manifested itself in this plot by three steep lines (AB, CD, and FG) and three flat, almost horizontal lines. This means that the transition of the initial $SmS_{1.90}$ phase to the terminal $SmS_{1.50}$ one is realized through the formation of two intermediate phases. Each straight line, AB, CD, and FG, was invariant to the *m*/*V* ratio and corresponds to the three-phase equilibrium between two adjacent polysulfides and vapor (*s*–*s*–*v*). The break points (a_1–a_4, b_1–b_4, c_1–c_4, d_1–d_4) corresponding to the crossovers from steep to flat parts of the plot reflect transitions to the two-phase (*s*–*v*) equilibrium. At the same time they show the boundaries where a polysulfide more enriched with sulfur disappears and the adjacent polysulfide remains as a single phase. The boundary composition saturated by sulfur for intermediate phases was calculated for the a_1–a_4, b_1–b_4, c_1–c_4, and d_1–d_4 points from the equation

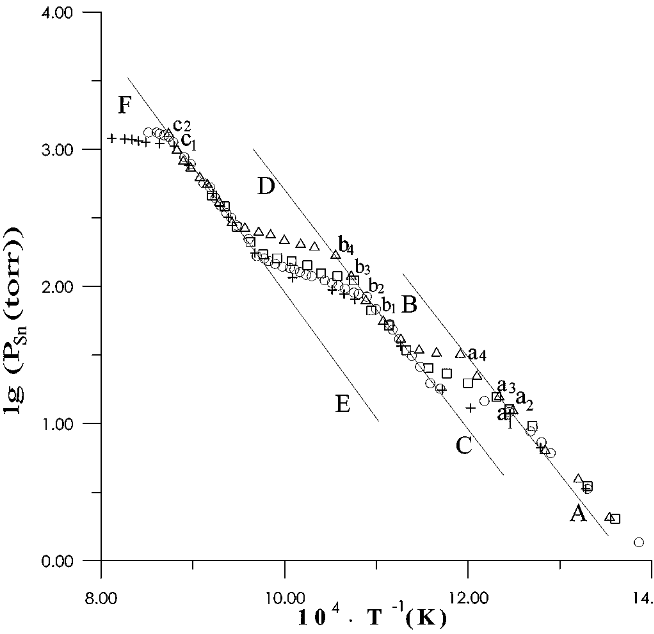

FIG. 1. *P*–*T* projection of the $SmS_{1.50}$–$SmS_{2.00}$ system. Evaporation of $SmS_{1.900}$ composition with *m*/*V* ratio: (+) – 1.70; (○) – 2.00; (□) – 2.19; (△) – 3.50 g/cm^3. 1 Pa = 7.5×10^{-4} Torr.

$$x,\ \mathrm{at\%} = 100 \cdot [(N_S - V\sum nP_{\mathrm{Sn}}/RT \cdot N^V)/N_{\mathrm{Sn}} + (N_S - V\sum nP_{\mathrm{Sn}}/RT)], \quad [1]$$

where *P* and *T* are the coordinates of these points, N_S and N_{Sn} are the gross composition of the initial polysulfide, *V* is the volume occupied by vapor, N^V is the quantitative vapor composition, and $V\sum nP_{\mathrm{Sn}}/RT$ is the quantity of sulfur transferred in vapor. The possibility of such calculation with an accuracy of ± 0.02 at% has already been shown in (6) for the following errors of measurements: ± 2 K for temperature, ± 0.00005 g for sample weights, $\pm 1 \times 10^{-4}$ cm^3 for the vessel volume, ± 1 Torr for the pressure, and ± 0.005 formula units for the initial composition. Results of the calculation are given in Table 1. Eventually, the compositionally close phases unrecognized by the common chemical analysis were unequivocally identified by this tensimetric static method.

In the two-phase (*s*–*v*) regions, the *P*/*T* ratio was not constant, in contrast to that expected for the ideal gas thermal expansion. In order to identify the line portions corresponding to temperature dependence of the saturated vapor pressure within the homogeneity range of the intermediate phases (the lower boundary), quantities of sulfur transfer into gas phase were calculated for each point of the lines using Eq. [1]. In most of the points, the sulfur quantity was constant, indicating expansion of an ideal gas

TABLE 1
Compositions of Intermediate Phases in the Break Points on the Three-Phase Lines

	AB line			CD line			EF line	
	at% S	T (K)		at %S	T (K)		at% S	T (K)
a_1	65.44	802	b_1	65.07	917	c_1	60.01	1157
a_2	65.42	803	b_2	65.06	929	c_2	60.03	1151
a_3	65.43	812	b_3	65.03	945	c_3	—	—
a_4	65.41	839	b_4	65.05	947	c_4	—	—
Compostion $SmS_{1.893}$			Compostion $SmS_{1.863}$			Compostion $SmS_{1.500}$		

accompanied by dissociation of gaseous sulfur polymers. The number of experimental points where the sulfur amount increased was not sufficient to find the exact homogeneity ranges of these phases; the homogeneity range was estimated at 65.43–65.41 at% for sulfur $SmS_{1.893}$ and 65.06–65.00 at% for $SmS_{1.863}$. No clear defined correlation between the temperature and the homogeneity range width was found.

This experiment has shown that in the range 66.7–60.0 at% S, besides the sesquisulfide, there are three discrete polysulfide phases, $SmS_{1.900}$, $SmS_{1.893}$, and $SmS_{1.863}$, with narrow homogeneity ranges. The phases can manifest themselves only under strictly controlled conditions including temperature, sulfur pressure, and particularly time. The time required to attain equilibrium at each temperature in the system was found to be five days along the AB line and 25–30 days along others. Therefore our presentation of the phase relationship in the Sm system differs from the previous one established for powder, poorly identified materials, which assumed a single grossly nonstoichiometric phase (Fig. 2). In our opinion there are many difficulties in obtaining equilibrium powder polysulfides. The nonequilibrium state is hard to check using only common techniques like wet chemical analysis, X-ray powder diffraction, and tensimetric weight methods, which are not sensitive to small variations of the polysulfides' state. These may be reasons for inadequate description of the phase relationship of the system.

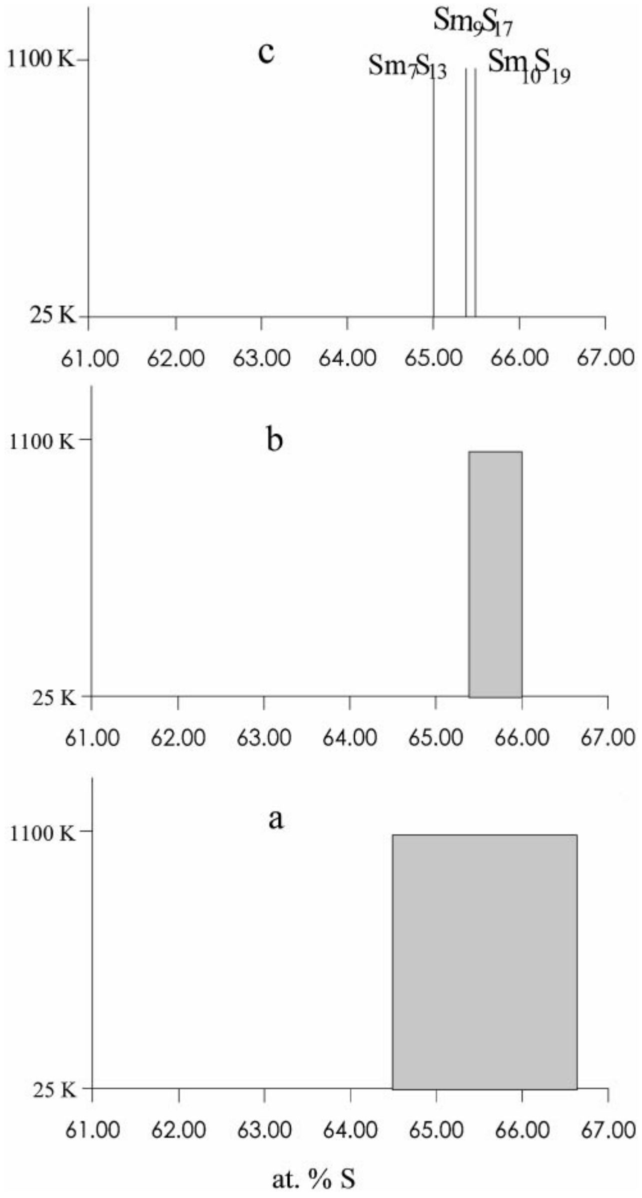

FIG. 2. The phase relationship within the $SmS_{1.50}$–$SmS_{2.00}$ system in the temperature range 500–1300 K: (a) from Ref. (2); (b) from Ref. (1); (c) this study.

Thermodynamics of the evaporation reactions of Sm-polysulfides. Each polysulfide evaporates incongruently and takes part in the appropriate *s–s–v* mono-variant reaction. These reactions are written below for the main gaseous species, S_2 (content in vapor about 80–95%):

$$285.7\ SmS_{1.900}(s) = 285.7\ SmS_{1.893}(s) + S_2(g) + \Delta_r H^\circ_T \quad (700\text{–}840\ K) \qquad [2]$$

$$66.7\ SmS_{1.893}(s) = 66.7\ SmS_{1.863}(s) + S_2(g) + \Delta_r H^\circ_T \quad (853\text{–}940\ K) \qquad [3]$$

$$35.0\ SmS_{1.863}(s) = 35.0\ SmS_{1.500}(s) + S_2(g) + \Delta_r H^\circ_T \quad (1030\text{–}1145\ K) \qquad [4]$$

$$\sum 285.7\ SmS_{1.900}(s) = 285.7\ SmS_{1.500}(s) + 57.14\ S_2(g) + \sum \Delta_{r[2\text{–}4]} H^\circ_T$$

$$\text{or} \quad SmS_{1.900}(s) = SmS_{1.500}(s) + 0.20\ S_2(g) + \Delta_r H^\circ_T \qquad [5]$$

The saturated vapor partial pressures, P_{S_2}, were extracted from the total pressure for 18, 20, and 30 points of the AB,

TABLE 2
Thermodynamic Parameters of the Evaporation Reactions [2]–[5]

Reaction	$\ln P_{S_2}$ (atm)[a] $\pm 2\sigma$	σ^2	$-\Delta_r H^\circ_T$ (KJ/mole)	$\Delta_r S^\circ_T$ (J/mole·K)
[2]	$14.75–1516/T$	$31517600/T^2–7878/T+4.9$	126 ± 15	123 ± 18
[3]	$19.05–19598/T$	$203249/T^2–452/T+0.3$	163 ± 3.7	158 ± 4.2
[4]	$17.86–19983/T$	$58321/T^2–107.2/T+0.05$	166 ± 2.0	148 ± 1.8
[5]			33.0 ± 2.3	—

[a] 1 atm = 101.3 kPa.

CD, and EF lines, respectively, using the sulfur constants of molecular gas reactions, and treated by the least-squares method (95% confidence limit, Student distribution). The temperature dependencies of the equilibrium pressure with standard dispersion and the enthalpies and entropies were calculated from the second law (Table 2). These data were then used as the basis for estimating the standard heats of formation for the Sm–polysulfides, since such information is still lacking.

Thermodynamic properties of the Sm–polysulfides. The thermodynamic functions, $C^\circ_p(T)$, $(H^\circ_T - H^\circ_{298})$, and S°_T, are known for samarium, sulfur, Sm_2S_3, and SmS_2, though the highest polysulfide for Sm shown here has to have the composition $SmS_{1.90}$ (Table 3) (11, 12).

The heat of formation of the $SmS_{1.90}$ phase at 800 K, $\Delta_f H^\circ_{800} = -554.5$ kJ/mole (accuracy of about $\pm 7\%$), was calculated from the following cycle and the known thermodynamic data for samarium and sulfur:

$$\begin{array}{rr} SmS_{1.900}(s) = SmS_{1.500}(s) + 0.20\, S_2(g) + \Delta_r H^\circ_{800} & [6] \\ SmS_{1.500}(s) = Sm(s) + 0.75\, S_2(g) + \Delta_r H^\circ_{800} & [7] \\ 0.95\, S_2(g) = 1.90\, S(s) + \Delta_r H^\circ_{800} & [8] \\ \hdashline \sum 0.95\, SmS_{1.900}(s) = Sm(s) + 1.90\, S(s) + \sum \Delta_{r[6-8]} H^\circ_{800} & \end{array}$$

From the $\Delta_f H^\circ_{800}$ value together with the data of Table 3, the standard heat of formation, $\Delta_f H^\circ_{298}$ ($SmS_{1.900}$, s) was computed as -539.4 kJ/mole. This value is comparable to those for the strictly stoichiometric disulfides given in (12): 623.6, 612.3, 590.1, 577.5, and 539.4 kJ/mole for LaS_2, CeS_2, PrS_2, NdS_2, and $SmS_{1.90}$, respectively. Apart from this, the standard heat of formation was estimated for the intermediate Sm polysulfides assuming that the atomic C_p values of crystalline solids are not different from each other. The calculation was made from equation

$$\begin{aligned} &\Delta\{\Delta_f H^\circ_{298}(SmS_x, s) - \Delta_f H^\circ_{298}(SmS_y, s)\} \\ &= \Delta_{r[2,\,or\,3,\,or\,4]} H^\circ_{800} - (x-y)/2 \cdot \Delta_f H^\circ_{298}(S_2, g) \\ &\quad - (x-y)/2 \cdot \Delta(H^\circ_{800} - H^\circ_{298})(S_2, g). \end{aligned}$$

TABLE 3
Thermodynamic Properties of Substances Taking Part in the Reactions [2]–[8] (kJ/mole)

Substance	$\Delta_f H^\circ_{298}$	$\Delta(H^\circ_{800} - H^\circ_{298})$
Sm (s)	0	19.15
S (s)	0	18.56
S_2 (g)	127.56	17.71
Sm_2S_3 (s)	-1192.7	68.38
SmS_2 (s)	–	39.46

In this case x and y are formula coefficients of adjacent sulfides, $SmS_{1.900}$, $SmS_{1.893}$, $SmS_{1.863}$, and $SmS_{1.500}$. These results, in the form of $\Delta_f H^\circ_{298}$ in kJ/mole (error of about 7%), are given below:

Sulfide	$-\Delta_f H^\circ_{298}$
$SmS_{1.900}$	539.4
$SmS_{1.893}$	540.3
$SmS_{1.863}$	545.3
$SmS_{1.500}$	601.6

(The value $\Delta_f H^\circ_{298}(Sm_2S_3) = -1203.2$ kJ/mole is in good agreement with $\Delta_f H^\circ_{298}(Sm_2S_3) = -1192.7$ kJ/mole recommended in the reference book (12). So convincing evidence that no substantial errors existed in our tensimetric experiment was obtained. Therefore, the thermodynamic properties of the Sm–polysulfides obtained here may for the first time be regarded as reliable. See Fig. 3.

DISCUSSION

As has been shown, one of the main problems—namely, the precise compositional characterization of sulfur-deficient Sm–polysulfides—was unequivocally solved. We have succeeded in identifying the discrete phases of close compositions. However, the mechanism changing the composition is still not clear due to poor structural data on the compounds. Our study of the compounds by the single crystal method is now in progress, and the structure of the $SmS_{1.90}$ crystal isostructural with $LnSe_{1.90}$ (13) has already been determined. $SmS_{1.90}$ crystallizes in the tetragonal space group $P4_2/n$, $a = 8.796(1)$, $c = 15.889$ Å, and $Z = 20$. The stoichiometric composition, $Sm_{10}S_{19}$ derived by structural analysis, indicates no sulfur vacancies in the anion layer. The structure of the sulfur-deficient phase may also be interpreted in terms of an ordered arrangement of sulfur vacancies within a superlattice cell of the PbFCl-type ($P4/nmm$) structure. Such a model was already used for description of ordered intermediate polysulfides in the Dy-system (Ln_nS_{2n-1} with $n = 4$, 6) (14). The detailed results

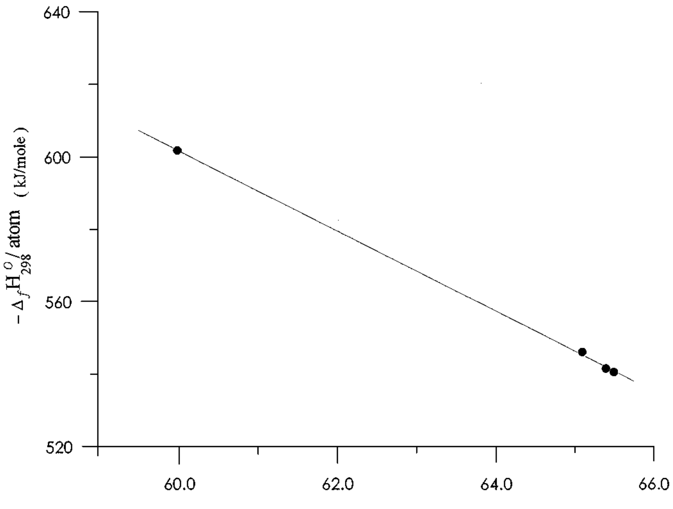

FIG. 3. The standard heats of formation related to the number of atoms of the appropriate Sm polysulfide against its composition, $-\Delta_f H^\circ_{298}$/atom.

and the ordering model for the Sm system will be published elsewhere.

Together with $Sm_{10}S_{19}$, the intermediate Sm–polysulfides converted to the rational chemical (and maybe even crystallographic) formulas, Sm_9S_{17}, Sm_7S_{13} constitute the homologous series with the same generic formula as in the Dy system, Ln_nS_{2n-1} and $n = 7, 9, 10$. For the Sm polysulfides the $\Delta_f H^\circ_{298}$ values related to the number of atoms, plotted as a function of composition, show a straight line without visible change in slope. The observed linearity may characterize related structures of the Sm–polysulfides with the same subcell, though the approximate character of the estimated thermodynamic values may also contribute. The existence of intermediate ordered phases following appropriate homologous series but relating to different structural families is typical for many systems, such as TiO_{2-x}, VO_{2-x}, $Ce(Tb,Pr)O_{2-x}$, and TiS_{2-x}, but the mechanisms generating these compositions vary greatly (15). More detailed compositional and structural studies are necessary before this mechanism can finally be established for *Ln* polysulfides.

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