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Mössbauer Effect of ^{119}Sn in Tin Sulfides Produced through Thermal Decomposition of SnS_2

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The intermediate tin sulfides produced through thermal decomposition of SnS_2 were studied by quenching and Mössbauer spectroscopy. The thermal decomposition of SnS_2 in a nitrogen gas flow proceeded to SnS *via* Sn_2S_3. The existing phases of the decomposition products in the range of the S/Sn ratio less than 1.50 were Sn_2S_3 and $Sn_{1-x}S$. A new peak observed in the Mössbauer spectrum of tin sulfides with the S/Sn ratio less than 1.04 was assigned to Sn^{4+} in the nonstoichiometric compound $Sn_{1-x}S$.

The tin-sulfur system was studied by many workers.[1-8] Albers *et al.* gave a phase diagram (Fig. 1).[1] In the diagram, the existence of the compounds SnS_2 and SnS is clearly indicated. The intermediates Sn_2S_3, Sn_3S_4, Sn_4S_5, and $Sn_{1-x}S$ have been reported so far, but there are inconsistencies. G. H. Moh identified Sn_2S_3 and $Sn_{1-x}S$ as the intermediate compounds on the basis of his detailed studies by quenching, high-temperature X-ray powder diffraction, and differential thermal analysis; however he refuted the existence of Sn_3S_4 and Sn_4S_5.[7] Bartenov *et al.* studied the Sn–S system by Mössbauer spectroscopy and reported that the intermediate compound such as Sn_2S_3 and Sn_3S_4 did not exist.[8] On the other hand, P. I. Seregin *et al.* asserted the existence of Sn_2S_3 and Sn_3S_4 with intrinsic crystal lattice structures by Mössbauer spectroscopy.[9]

Previously the authors have examined the tin sulfides produced through thermal decomposition of SnS_2 and identified Sn_2S_3 as an intermediate by quenching, Mössbauer spectroscopy, thermogravimetry, differential thermal analysis, and X-ray powder diffraction.[10,11] In this study, the existing phases of tin sulfides in the range S/Sn=1.5 to 1.0 produced through thermal decomposition of SnS_2 in a nitrogen gas flow are examined by Mössbauer spectroscopy.

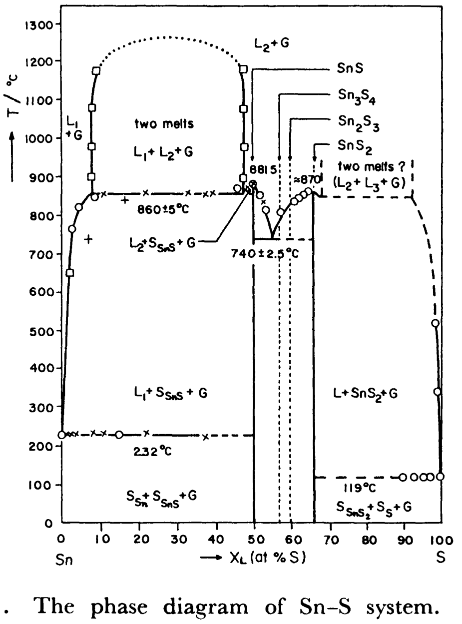

Fig. 1. The phase diagram of Sn–S system. (From Ref. 1)

Experimental

Preparation of the Tin Sulfide Sample. The tin sulfide samples were prepared by thermal decomposition of tin(IV) sulfide. The tin(IV) sulfide to be decomposed was prepared by the addition of 2 mol dm^{-3} -HCl to an aqueous solution of $Na_4SnS_4\cdot14H_2O$. To remove the reaction products NaCl and S throughly the crystals were washed with distilled water several times, then with methanol and carbon disulfide alternately. The thermal decomposition of SnS_2 was carried out by heating SnS_2 to 878 K at a rate of 3 K/min in a nitrogen gas flow and maintaining it at this temperature from 2 min to 60 min. After heating the decomposition products were quenched to room temperature without breaking the inert atmosphere. The S/Sn ratio of the sulfides was determined by analysing the tin in the sample gravimetrically in which the sample was calcined at 1173 K for 5 h in air.

Measurements. The Mössbauer spectra were measured using a constant acceleration type spectrometer with an accuracy within 0.05 mm s^{-1}. The γ-ray source of calcium stannate was used at room temperature and the absorber was cooled at 93 K in a liquid nitrogen cryostat. The velocity scale was calibrated against the spectra of $BaSnO_3$ and β-tin at room temperature. All isomer shifts are reported relative to $BaSnO_3$. Mössbauer parameters were deduced from Lorentzian curves computer-fitted to the spectra by a least-squares method.

Results and Discussion

The Mössbauer spectra of tin sulfides in the ranges S/Sn=1.50 to 1.07 and less than 1.04 are shown in Figs. 2 and 3, respectively. The spectra are apparently superposition of two spectra, *i.e.* the spectrum characteristic of SnS and the spectrum characteristic of SnS_2. Mössbauer parameters deduced from the spectra are shown in Table 1 along with the area ratio of Sn^{IV} to total. In Table 1, Sn_2S_3 with intrinsic lattice are distinguished from the other for the reason that the isomer shift and quadrupole splitting for Sn^{II} at S/Sn=1.50 are larger than those of SnS as reported previously.[10] Sn_2S_3 was decomposed further by heating the sulfide at 878 K for various times. The heating durations and the S/Sn ratios of the sulfides obtained are also shown in Table 1. The absorption peak for Sn^{IV} at about 1.1 mm s^{-1} decreased with the decreasing S/Sn ratio and disappeared at S/Sn=1.04. On the other hand, the peak for Sn^{II} increased with the decreasing S/Sn ratio. The value of the isomer shift for Sn^{IV} was almost the same in the range

TABLE 1. MÖSSBAUER PARAMETERS FOR TIN SULFIDES PRODUCED THROUGH THERMAL DECOMPOSITION OR SnS_2

Duration of heating at 878 K (min)	Atomic ratio (S/Sn)	Sn^{IV}		Sn^{II}			Sn^{IV}/Sn(total)
		δ / mm s^{-1}	Γ / mm s^{-1}	δ / mm s^{-1}	Δ / mm s^{-1}	Γ / mm s^{-1}	
0	1.50±0.02	1.12	1.20	3.55	1.01	1.12	0.50
2	1.38±0.02	1.17	1.23	3.45	0.95	1.15	0.37
4	1.33±0.03	1.18	1.21	3.47	0.96	1.15	0.32
7	1.24±0.02	1.10	1.23	3.41	0.92	1.14	0.28
12	1.23±0.02	1.16	1.54	3.38	0.96	1.13	0.27
17	1.20±0.01	1.01	1.43	3.42	0.91	1.14	0.20
22	1.07±0.03	1.12	1.56	3.38	0.88	1.11	0.15
23	1.04±0.02	−0.01	3.65	3.38	0.92	1.15	0.13
25	1.03±0.03	−0.51	2.88	3.39	0.93	1.18	0.09
27	1.02±0.03	−0.24	2.05	3.38	0.96	1.16	0.06
32	1.01±0.02	−0.44	1.54	3.36	0.90	1.15	0.05
57	1.01±0.02	—	—	3.38	0.93	1.17	—

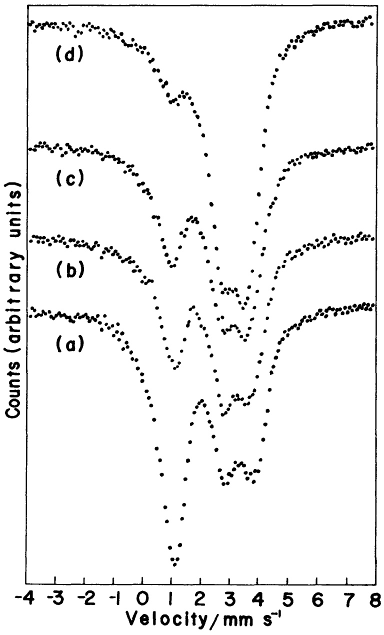

Fig. 2. Mössbauer spectra for tin sulfides produced through thermal decomposition of SnS_2. S/Sn ratio, (a) 1.50; (b) 1.33; (c) 1.24; (d) 1.07.

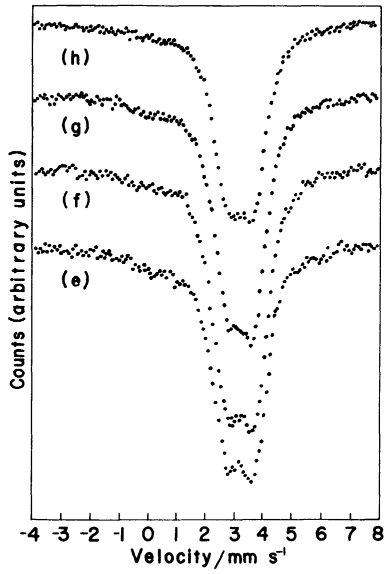

Fig. 3. Mössbauer spectra for tin sulfides produced through thermal decomposition of SnS_2. S/Sn ratio, (e) 1.04; (f) 1.03; (g) 1.02; (h) 1.0.

S/Sn=1.50 to 1.07, but the values of the shift and quadrupole splitting for Sn^{II} decreased with decreasing S/Sn ratio and approached the values for SnS. The area ratio coincided with the corresponding S/Sn ratio in the range S/Sn=1.50 to 1.33, however, in the range less than 1.24 the area ratio exceeded the corresponding S/Sn ratio.

Gerasimov *et al.* reported the existence of Sn_2S_3 and Sn_4S_5 as the intermediate products through thermal decomposition of higher sulfides, *viz.* $SnS_2 \rightarrow Sn_2S_3 \rightarrow Sn_4S_5 \rightarrow SnS$.[2] G. H. Moh synthesized the sulfides in evacuated, sealed silica tubes in which weighed amounts of tin and sulfur were heated at a predetermined temperature and the reaction products examined by X-ray powder diffraction and optical reflectivity. All the reaction products in the range of S/Sn ratio smaller than 1.50 were Sn_2S_3 and $Sn_{1-x}S$; but Sn_3S_4 and Sn_4S_5 did not exist.[7] P. I. Seregin *et al.* synthesized tin sulfides by melting initial components of tin and sulfur in evacuated quartz capsules and investigated the reaction products by Mössbauer spectroscopy. They assert the existence of Sn_3S_4 and Sn_2S_3, because the spectra of Sn_3S_4 and Sn_2S_3, obtained by different methods, have the same isomer shifts and quadrupole splittings, but the ratio of the area below the spectra of Sn^{II} and Sn^{IV} depends on the method of synthesis.[9]

In the present work, it seems likely that the existing phases of the decomposition products in the range of S/Sn less than 1.50 are Sn_2S_3 and $Sn_{1-x}S$, because the parameters were not anomalous at S/Sn=1.33 and 1.24, and the peak for nonstoichiometric $Sn_{1-x}S$ manifested itself in the range of S/Sn less than 1.04. The peak for Sn^{IV} characteristic of $Sn_{1-x}S$ becomes distinct at about 0 mm s^{-1} as the peak for Sn^{IV} characteristic of Sn_2S_3 disappeared and it diminished as the S/Sn ratio approached to the stoichiometric value, as shown in Fig. 3. The excess value of the area ratio to the corresponding S/Sn ratio in the range of S/Sn less than 1.24 may be caused by superposition of the peak in the spectrum characteristic of $Sn_{1-x}S$ to the spectrum of Sn_2S_3 if the recoilless fraction of Sn^{II} is equal in both $Sn_{1-x}S$ and Sn_2S_3.

Albers *et al.* showed that the existence region of solid SnS probably lies entirely on the excess sulfur side on the basis of their Hall effect measurements.[1] Rau also reported the sulfur rich boundary of the homogeneity region of SnS as the result of their measurement of the variation of sulfur pressure by a chemical method and that the doubly negatively charged tin vacancy is probably the prevailing imperfection at equilibrium.[12]

The lower thermal decomposition product of Sn_2S_3 can justifiably be refered to the formula $Sn_{1-x}S$. In $Sn_{1-x}S$ metal vacancies exist. The single metal vacancies act as acceptors with a level near the valence band and leave positive holes in the valence band. Trapping holes give rise to Sn^{4+} in $Sn_{1-x}S$. Besides this, association of the neutral vacancies will take place.

The pertinent quasi-chemical equations by the use of the Kröger's notation[13] are

$$V_{Sn}^{x} \rightleftarrows V_{Sn}'' + 2h^{\cdot}, \tag{1}$$

$$2V_{Sn}^{x} \rightleftarrows (V_{Sn})_2^{x}, \tag{2}$$

with neutrality condition $[h^{\cdot}]=2[V_{Sn}'']$.

The deviation from stoichiometry, x, is

$$x = [V_{Sn}^{x}] + [V_{Sn}''] + 2[(V_{Sn})_2^{x}]. \tag{3}$$

At high temperature, 878 K, where $Sn_{1-x}S$ was formed the association will be relatively unimportant and Eq. 3 may be approximated by $x \approx [V_{Sn}'']=[Sn^{4+}]$. Thus, the concentration of Sn^{4+} will be defined by the deviation from stoichiometry. In Table 1, the excess area ratio to the corresponding S/Sn ratio in the lower range may also be caused by still existing Sn_2S_3 as shown in the large line width of the peak.

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