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MÖSSBAUER EFFECT OF ^{119}Sn IN THE THERMAL DECOMPOSITION PRODUCTS OF TIN(IV) SULFIDE

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Tin sesquisulfide, Sn_2S_3, was obtained as a single phase through thermal decomposition of SnS_2. The Mössbauer parameters of the phase were not the same as those of the mixture of SnS and SnS_2 and were consistent with those of Sn_2S_3.

As the intermediate products obtained through thermal decomposition of tin(IV) sulfide, Sn_2S_3 and Sn_4S_5 have been known so far.[1,2] However, the well defined characterization of those intermediate products has not been successful because it was difficult to obtain a single phase of the products. The crystal structure of Sn_2S_3 has been determined by X-ray diffraction method on a synthesized sample.[3]

In this study, the thermal decomposition products of tin(IV) sulfide, which were obtained by heating SnS_2 at high temperature followed by rapid quenching to room temperature, were investigated by Mössbauer effect as well as the differential thermal analysis (DTA), thermal gravimetry analysis (TGA), and X-ray powder diffraction method. The Mössbauer effect of Sn_2S_3 which were obtained as a single phase through thermal decomposition of SnS_2 was measured.

Tin(IV) sulfide to be decomposed was prepared by the addition of 2M-HCl to an aqueous solution of $Na_4SnS_4 \cdot 14H_2O$ or by the solid reaction of an equimolar mixture of SnS and S sealed in an evacuated quartz tube at 773 K for two weeks. The former is referred to as SnS_2(wet) and the latter as SnS_2(dry). Thermal decomposition reaction was carried out by heating the SnS_2 sample up to a pertinent temperature at a rate of 3 K/min in a flow of nitrogen gas and subsequently quenching the product to room temperature without breaking the inert atmosphere. Tin sesquisulfide was also synthesized by heating a mixture of SnS and S in the stoichiometric ratio in an evacuated quartz tube at 873 K for two weeks. To determine the S/Sn ratio, tin in the samples was analyzed by the calcination method.

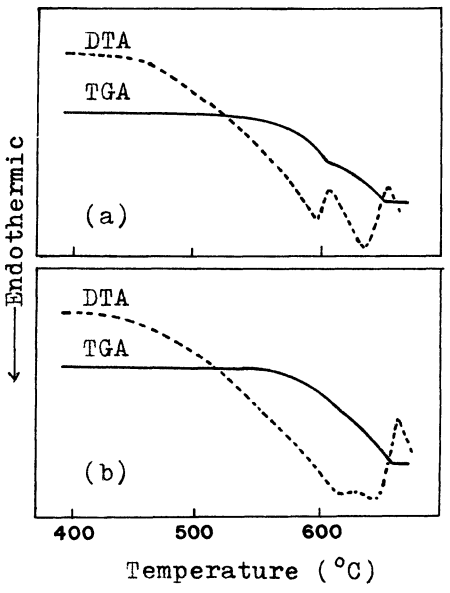

Fig. 1. TGA and DTA curves for (a) SnS_2(wet) and (b) SnS_2(dry).

The Mössbauer effect was measured by the use of a constant acceleration type spectrometer and the accuracy was within 0.05 mm/s. The γ-ray source was ^{119m}Sn in the barium stannate matrix and used at room temperature. The absorber was about 10 mg/cm^2 in thickness for tin and cooled with liquid nitrogen or other suitable cryogens. The velocity scale was calibrated by the use of ^{57}Co in Cu source and the absorber of metallic iron foil.

The TGA and DTA curves for the SnS_2(wet) and SnS_2(dry) samples are shown in Fig. 1 (a) and (b), respectively. Both the samples of SnS_2(wet) and SnS_2(dry) show two decomposition steps in TGA curves and two endothermic peaks in DTA curves which will correspond to the same chemical changes respectively. However, the curves for both the samples are somewhat unlike, probably because the preparation method was not the same. The samples in the course of thermal decomposition were quenched from different temperatures and the Mössbauer spectra of ^{119}Sn in the product samples were measured. From the spectra, the Mössbauer parameters, the isomer shift (δ), the quadrupole splitting (△), and the half width (Γ_{ex}) were

Table 1. Mössbauer parameters for SnS_2(wet)

Heating temp. (K)	Atomic ratio (S/Sn)	Sn(IV) δ (mm/s)	Sn(IV) Γ_{ex} (mm/s)	Sn(II) δ (mm/s)	Sn(II) △ (mm/s)	Sn(II) Γ_{ex} (mm/s)	Existing phase
298	2.56 ± 0.03	1.01	1.19	—	—	—	SnS_2
673	2.01 ± 0.04	1.04	1.08	—	—	—	SnS_2
753	1.98 ± 0.03	1.00	1.06	—	—	—	SnS_2
833	1.95 ± 0.03	1.11	1.06	—	—	—	SnS_2
863	1.86 ± 0.03	1.09	1.03	3.53	1.03	1.01	Sn_2S_3 + SnS_2
883	1.44 ± 0.02	1.08	1.04	3.45	1.03	0.98	Sn_2S_3 + SnS
903	1.40 ± 0.02	1.13	1.04	3.46	0.99	1.00	Sn_2S_3 + SnS
923	1.38 ± 0.02	1.11	1.10	3.41	1.01	1.09	Sn_2S_3 + SnS
943	1.34 ± 0.03	1.11	1.14	3.44	1.00	1.09	Sn_2S_3 + SnS
963	1.06 ± 0.03	—	—	3.26	0.96	1.12	SnS

Table 2. Mössbauer parameters for SnS_2(dry)

Heating temp. (K)	Atomic ratio (S/Sn)	Sn(IV) δ (mm/s)	Sn(IV) Γ_{ex} (mm/s)	Sn(II) δ (mm/s)	Sn(II) △ (mm/s)	Sn(II) Γ_{ex} (mm/s)	Existing phase
298	2.04 ± 0.02	1.06	0.96	—	—	—	SnS_2
823	1.89 ± 0.02	1.11	1.07	—	—	—	SnS_2
863	1.87 ± 0.02	1.07	1.20	3.54	1.08	1.03	Sn_2S_3 + SnS_2
883	1.81 ± 0.01	1.09	1.12	3.57	1.07	0.84	Sn_2S_3 + SnS_2
903	1.74 ± 0.03	1.08	1.17	3.58	1.07	0.91	Sn_2S_3 + SnS_2
923	1.43 ± 0.03	1.13	1.13	3.58	1.06	1.08	Sn_2S_3 + SnS
943	1.30 ± 0.03	1.19	1.01	3.42	0.91	0.99	Sn_2S_3 + SnS
963	1.04 ± 0.03	—	—	3.35	0.95	1.11	SnS

computed by the least squares method. The values of these parameters are summarized in Table 1 and 2 along with the S/Sn ratio. Then we have prepared the intermediate thermal decomposition products, the S/Sn ratio of which is just 1.50, from the two SnS_2 samples. The X-ray diffraction diagrams of these product samples are well consistent with that of Sn_2S_3 which has been reported by Mosburg et al.[4] This result shows that the thermal decomposition of SnS_2 proceeds via Sn_2S_3, that is, the decomposition is $SnS_2 \longrightarrow Sn_2S_3$ in the first step and $Sn_2S_3 \longrightarrow SnS$ in the second step at higher temperature range. Now, we can assign the existing phases of tin sulfide at various temperatures as shown in Table 1 and 2. Tin sesquisulfide does not appear until 863 K.

An example of the Mössbauer spectrum of Sn_2S_3(wet) (i.e., Sn_2S_3 obtained from SnS_2(wet)) is shown in Fig. 2. In the spectrum, the single peak for Sn(IV) and the doublet for Sn(II) are well distinguished. The Mössbauer parameters of both the decomposition products Sn_2S_3, synthesized Sn_2S_3(syn) and the equimolar mixture of SnS and SnS_2 at 296, 202, and 93 K are summarized in Table 3. From the table, it will be found that the Mössbauer parameters of Sn_2S_3 are different from the corresponding values of the mixture of SnS and SnS_2 in the following way: (1) the values of the isomer shift

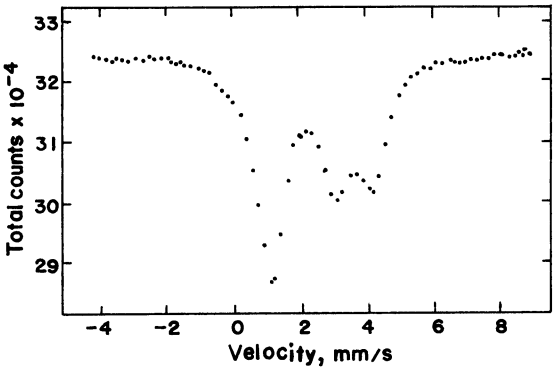

Fig. 2. Mössbauer spectrum of Sn_2S_3(wet).

Table 3. Mössbauer parameters of the equimolar mixture of SnS and SnS_2 and the Sn_2S_3 samples

Samples	Temp. (K)	Sn(IV) δ (mm/s)	Sn(IV) Γ_{ex} (mm/s)	Sn(II) δ (mm/s)	Sn(II) Δ (mm/s)	Sn(II) Γ_{ex} (mm/s)
SnS + SnS_2	296	1.03	1.01	3.29	0.93	0.88
	202	1.05	0.92	3.26	0.91	0.94
	93	1.06	0.96	3.29	0.94	0.89
Sn_2S_3(wet)	296	1.16	1.01	3.44	0.93	0.89
	202	1.15	1.26	3.52	0.95	0.84
	93	1.08	1.18	3.51	1.04	0.93
Sn_2S_3(dry)	296	1.19	1.06	3.58	0.98	0.82
	202	1.16	1.29	3.55	0.95	0.96
	93	1.18	1.20	3.60	1.02	0.96
Sn_2S_3(syn)	296	1.09	1.13	3.48	0.99	0.82
	202	1.09	1.12	3.52	1.03	0.88
	93	1.10	1.16	3.51	1.04	1.00

of both the Sn(II) and Sn(IV) in Sn_2S_3 are higher, (2) the line width (Γ_{ex}) of Sn(IV) in Sn_2S_3 are broader, and (3) the quadrupole splitting of Sn(II) in Sn_2S_3 are larger.

The temperature dependences of the absorption intensity were also measured and the results are shown in Fig. 3. According to the X-ray diffraction study on a single crystal of Sn_2S_3 by Mootz and Puhl,[3] the crystal structure of Sn_2S_3 consists of infinite double rutile strings of $Sn(IV)S_6$ octahedra with the Sn(II) atoms attached laterally, as shown in Fig. 4. On the other hand, SnS has layer structure in which every Sn atom is surrounded by three S atoms as nearest neighbors. The environmental differences between the Sn(II) atoms in SnS and Sn_2S_3 are well reflected in the Mössbauer parameters. At the present stage, the existence of Sn_3S_4 and Sn_4S_5 was not ascertained because some oxidation occured at high temperature on account of the insufficient air tightness of the DTA-TGA apparatus.

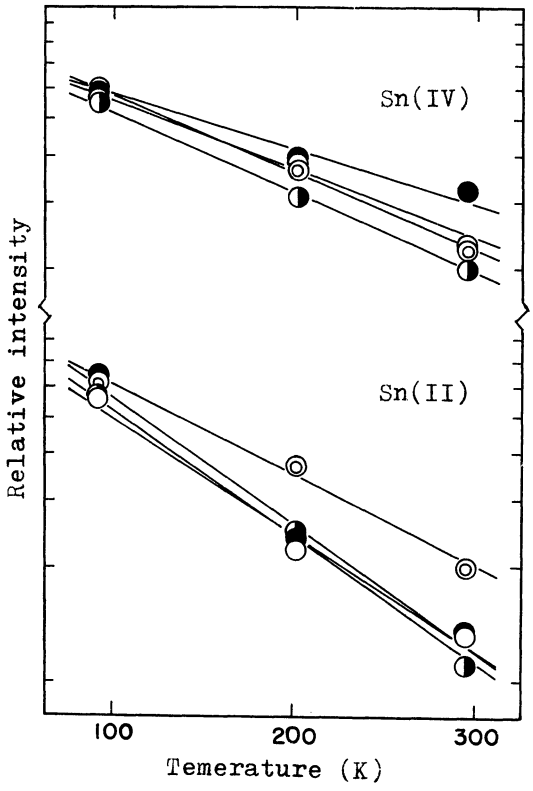

Fig. 3. Temperature dependence of the relative intensity of absorption.
◎: SnS + SnS_2, ○: Sn_2S_3(wet), ●: Sn_2S_3(dry) and ◑: Sn_2S_3(syn).

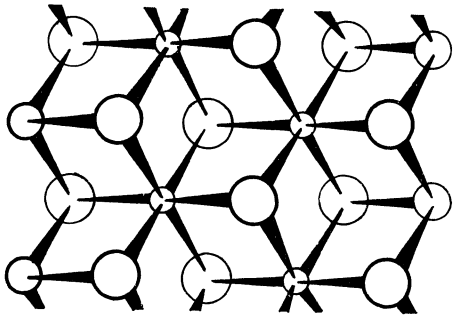

Fig. 4. Plan of the structure of Sn_2S_3. ◯: S, ◯: Sn(II), and ◯: Sn(IV). (From ref. [3]).

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