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

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The thermal decomposition products of $SnSe_2$ and SnSSe were investigated by Mössbauer effect. No intermediate decomposition product was found. Tin(IV) selenosulfide decomposes to tin(II) selenosulfide, which is an isomorphous compound of SnS and SnSe.

In the preceding paper,[1)] the existence of Sn_2S_3 as an intermediate product through thermal decomposition of SnS_2 was reported by the authors. In this connection, the thermal decomposition of tin(IV) selenide $SnSe_2$ and tin(IV) selenosulfide SnSSe were examined in the same way. A few workers[2,3)] have studied the Sn-Se system by Mössbauer effect and reported that no intermediate compound between $SnSe_2$ and SnSe existed.

Tin(IV) selenide and tin(IV) selenosulfide to be decomposed were prepared by heating the mixture of the constituent elements in the stoichiometric ratio in an evacuated quartz ampoule at 873 K for a week. The thermal decomposition experiments were carried out by heating the sample at a rate of 3 K/min in a flow of nitrogen gas and subsequently quenching it to room temperature in the inert atmosphere. The measurements of Mössbauer effect, differential thermal analysis (DTA), thermal gravimetry analysis (TGA), and chemical analysis of tin were made as previously described.[1)] The X-ray diffraction data were obtained by Ni filtered $CuK\alpha$ radiation.

The TGA curve of both samples is the sigmoid curve characteristic of thermal decomposition and a corresponding endothermic peak appeared in the DTA curve. The thermally decomposed and quenched products were obtained at the pertinent temperatures depending on the thermal analysis curves. The Mössbauer spectrum of the product samples was measured and the parameters such as the isomer shift (δ), the quadrupole splitting (Δ), and the line width (Γ_{ex}) were computed by the least squares method. The values of the parameters are shown in Table 1 and 2, along with the Se/Sn and SSe/Sn_2 ratio, respectively.

As can be seen in the tables, the values of the isomer shift of Sn(IV) and Sn(II) do not vary throughout the decomposition reaction in both cases. This means that $SnSe_2$ and SnSSe decomposed without producing any intermediate compounds. The values of the Mössbauer parameters of Sn(II) in the decomposition

Table 1. Mössbauer parameters for the thermal decomposition products of $SnSe_2$

Heating temp. (K)	Atomic ratio (Se/Sn)	Sn(IV)		Sn(II)			Existing phase
		δ (mm/s)	Γ_{ex} (mm/s)	δ (mm/s)	Δ (mm/s)	Γ_{ex} (mm/s)	
298	1.99 ± 0.01	1.32	1.02	—	—	—	$SnSe_2$
823	1.97 ± 0.02	1.38	0.98	—	—	—	$SnSe_2$
863	1.92 ± 0.02	1.38	1.01	3.37	0.81	0.84	$SnSe_2$ + SnSe
883	1.83 ± 0.03	1.38	0.98	3.36	0.81	1.13	$SnSe_2$ + SnSe
903	1.81 ± 0.03	1.38	1.09	3.37	0.81	0.80	$SnSe_2$ + SnSe
913	1.41 ± 0.02	1.38	0.97	3.37	0.81	1.01	$SnSe_2$ + SnSe
923	1.09 ± 0.01	1.38	0.93	3.34	0.82	1.13	$SnSe_2$ + SnSe
943	0.98 ± 0.01	—	—	3.37	0.83	1.11	SnSe

Table 2. Mössbauer parameters for the thermal decomposition products of SnSSe

Heating temp. (K)	Atomic ratio (SSe/Sn_2)	Sn(IV)		Sn(II)			Existing phase
		δ (mm/s)	Γ_{ex} (mm/s)	δ (mm/s)	Δ (mm/s)	Γ_{ex} (mm/s)	
298	1.99 ± 0.01	1.18	1.07	—	—	—	SnSSe
823	1.90 ± 0.02	1.19	1.02	—	—	—	SnSSe
863	1.89 ± 0.01	1.21	1.05	3.35	0.86	0.95	SnSSe + Sn_2SSe
883	1.88 ± 0.02	1.21	1.08	3.33	0.80	0.99	SnSSe + Sn_2SSe
903	1.81 ± 0.03	1.21	1.01	3.36	0.84	0.96	SnSSe + Sn_2SSe
923	1.52 ± 0.03	1.20	0.98	3.32	0.85	0.97	SnSSe + Sn_2SSe
943	1.06 ± 0.03	1.22	1.01	3.35	0.85	1.09	SnSSe + Sn_2SSe
963	1.02 ± 0.02	—	—	3.35	0.84	1.11	Sn_2SSe

product of $SnSe_2$ are in good agreements with the literature values of SnSe.[2-4) The values of the parameters of Sn(II) in the decomposition product of SnSSe is scarcely different from the values of SnSe. However, it is identified to be Sn_2SSe by the chemical analysis data and X-ray diffraction diagrams shown in Fig. 1. So we can conclude that the thermal decomposition of SnSSe proceeds as

$$2SnSSe \longrightarrow Sn_2SSe + SSe$$

and does not form SnS or SnSe. Tin(II) selenosulfide is new compound and isomorphous with SnS and SnSe as is seen in Fig. 1.

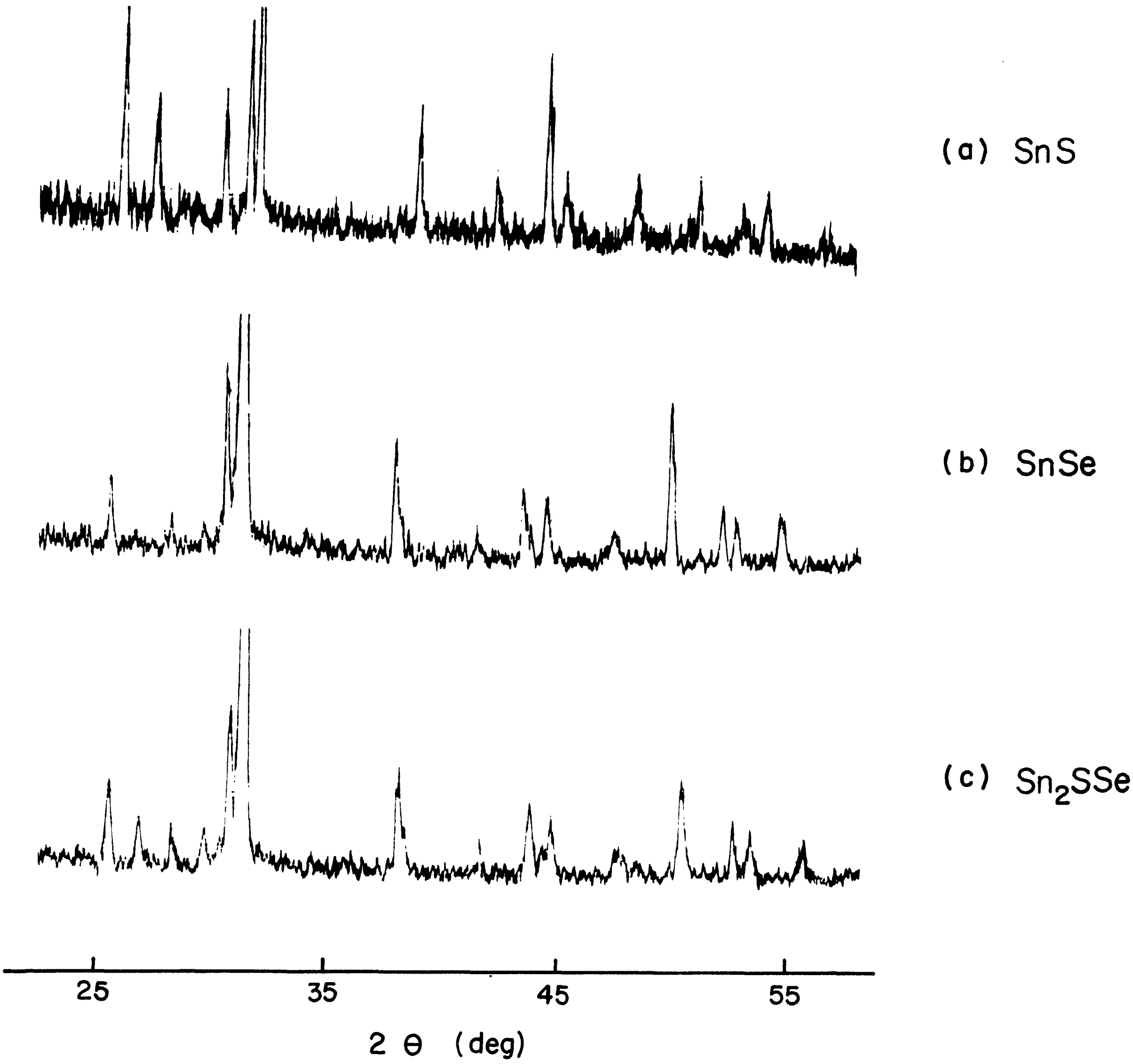

Fig. 1. The X-ray diffraction diagrams.

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