Phase relations in systems of tin chalcogenides

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Abstract

Phase relations in systems of tin chalcogenides were studied in the temperature range between 300 and 900 °C by using the sealed, evacuated glass capsule technique. Phase characterization was done by reflected light microscopy, X-ray powder diffraction and electron microprobe analysis. At 500 °C the system Sn–S–Se consists of two complete series of solid solutions along joins SnS–SnSe and SnS_2–$SnSe_2$, whereas in the systems Sn–Se–Te and Sn–S–Te liquid tellurium forms equilibrium assemblages with SnTe solid solution, SnSe solid solution and $SnSe_2$ in the former and with SnTe solid solution, SnS, Sn_2S_3 and SnS_2 in the latter.

Phase relations in the systems SnS–SnSe–SnTe are characterized by an equilibrium between two solid solution series. The orthorhombic series is stable in the region defined by SnS, SnSe and $Sn(Se_{0.74}Te_{0.26})$ and the cubic series extends from SnTe to $Sn(Se_{0.30}Te_{0.70})$ with a maximum of 3 mole% SnS.

1. Introduction

Tin chalcogenides are technically important because they are known to be semiconductors, and some have distinct thermoelectric properties. The variation in these properties with composition is of interest if appreciable solid solutions exist among them. Six chalcogenides (SnS, SnSe, SnTe, Sn_2S_3, SnS_2 and $SnSe_2$) have been characterized, although several others were also reported (Sn_4S_5 [1], Sn_3S_4 [2] and Sn_2Se_3 [3]). Both SnS and SnSe have the GeS-type structure and transform to the TlI type above 500 °C [4], while SnTe is cubic of the NaCl type [5]. Sn_2S_3 is orthorhombic and isostructural with NH_4CdCl_3 [6] and $RbCdCl_3$ [7]. Both tin disulfide and tin diselenide belong to the CdI_2 group [8].

Mineralogically, most selenides and tellurides have been found in deposits with sulfides, and many sulfides contain selenium. Among the six known tin chalcogenides, only the three sulfides occur in nature. They are herzenbergite (SnS), ottemannite (Sn_2S_3) and berndtite (SnS_2). The solubilities of selenium and tellurium in them have not been investigated.

The purpose of this study is to examine the formation of solid solutions in systems of tin chalcogenides.

2. Methods of investigation

Starting compositions were prepared from reagent grade tin, sulfur, selenium and tellurium, all of purity of 99.99% or better as specified by

suppliers' analysis. Samples were made by weighing these materials individually in the desired proportions to an accuracy of 0.1 mg, and heat treatment was performed in muffle furnaces using the conventional sealed, evacuated glass capsule technique [9]. Generally, the duration of treatment was 80 days at 500 °C, 2 days at 900 °C and 20–23 days between 600 and 900 °C. Half-way through the heat treatment time the samples were removed from the furnace for re-grinding to promote the desired reactions. Equilibrium was assumed to have been achieved when an increased run time produced the same assemblages, when compliance with the phase rule was noted and when similar phase assemblages were obtained in duplicate runs. A flux method using $LiCl + NH_4Cl$ eutectic mixture was employed at 300 °C for several runs in the systems Sn–Se–Te and Sn–S–Te.

X-ray powder diffraction and reflected light microscopy were used for phase identification, and compositions of selected samples were determined by electron microprobe analysis. Cell dimensions with an error of 0.005 Å were computed using a least-squares refinement program [10].

3. Results and discussion

3.1. Phase relations in the system Sn–S–Se

Phase relations in the system at 500 °C are shown in Fig. 1, based upon experimental data illustrated. A complete series of solid solutions exists along
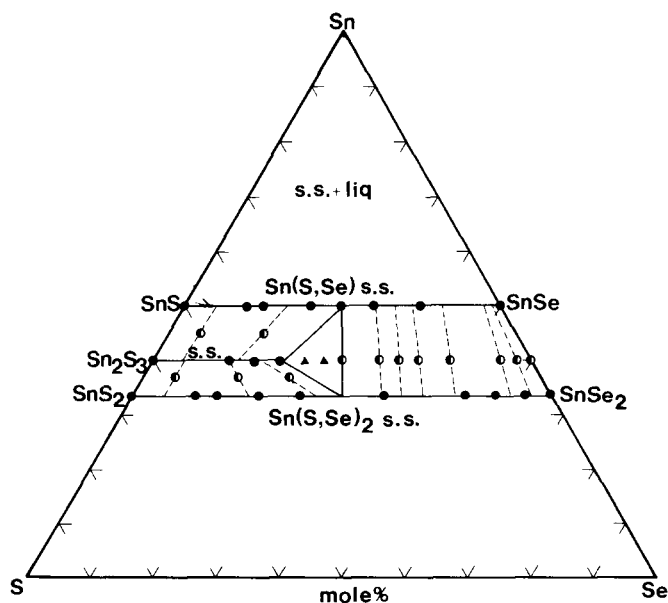

Fig. 1. Phase relations in the system Sn–S–Se at 500 °C. In the diagram, solid circles, half-filled circles and solid triangles represent one-, two- and three-phase assemblages respectively; 's.s.' denotes solid solution.

the join SnS–SnSe. Experimental runs made at higher temperatures show a continuous melting of the solid solutions with a minimum at 853 °C and 50 mole% SnS. The separation of liquidus and solidus is very narrow, within a maximum of 5 °C. Samples of compositions $Sn(S_{0.75}Se_{0.25})$, $Sn(S_{0.50}Se_{0.50})$ and $Sn(S_{0.25}Se_{0.75})$ treated between 800 and 900 °C produced the following results. At 850 °C there was no melting. At 855 °C $Sn(S_{0.50}Se_{0.50})$ melts completely and no sign of melting was detected in $Sn(S_{0.75}Se_{0.25})$ and $Sn(S_{0.25}Se_{0.75})$, which melt at 860 °C with no trace of solid phases observed in polished sections using a reflected light microscope. This is not unexpected because of the small difference in the melting points between SnS (875 °C) and SnSe (865 °C).

Phase transitions were reported in both SnS and SnSe. The transition is of the second-order displacive type from the GeS structure to the TlI structure [11] and is completed at approximately 600 and 540 °C respectively [4]. The TlI-type phases cannot be quenched.
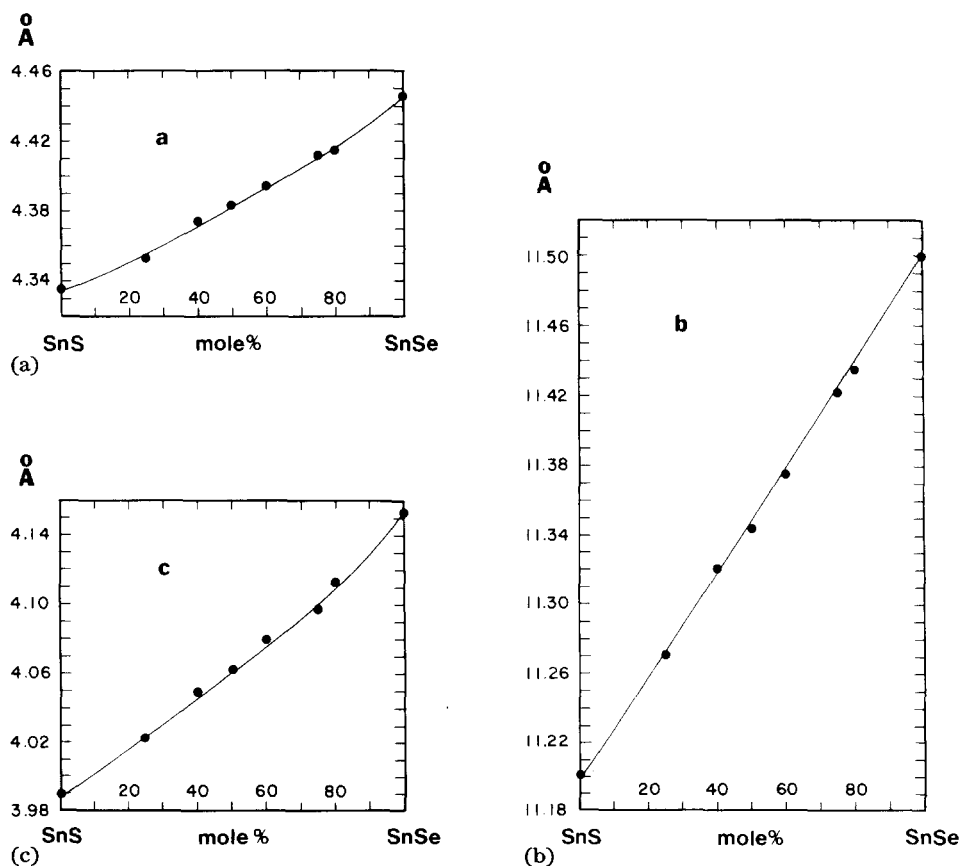

Fig. 2. Variations in cell parameters with composition along the join SnS–SnSe.

Cell parameters of the GeS-type solid solutions along the join were measured and their variations with composition are shown in Fig. 2. Both a and c show a negative deviation from Vegard's law, while b has a linear relationship.

Along the join SnS_2–$SnSe_2$ another complete series of solid solutions exists, which confirms results of Rimmington and Balchin [12] and Harbec et al. [13]. Melting points of members of this series decrease with increasing amount of $SnSe_2$. They are 865, 795, 750, 730, 690 and 675 °C for compositions SnS_2, $Sn(S_{0.8}Se_{0.2})_2$, $Sn(S_{0.6}Se_{0.4})_2$, $Sn(S_{0.4}Se_{0.6})_2$, $Sn(S_{0.2}Se_{0.8})_2$ and $SnSe_2$, respectively. The melting curve is a continuous one and the separation of liquidus and solidus is similar to that along the join SnS–SnSe, too narrow to be characterized. Variations in cell parameters as a function of composition are shown in Fig. 3. A linear relation exists in a, whereas a positive deviation from Vegard's law is shown in c.

Sn_2S_3 has a range of solid solutions extending to a composition Sn_2S_2Se, which forms a three-phase assemblage with $Sn(S_{0.5}Se_{0.5})$ and $Sn(S_{0.5}Se_{0.5})_2$. Along this series, cell parameters increase with increasing amount of selenium. They are $a = 8.8641$, 8.9053, 8.9929, 9.0167 Å, $b = 14.0200$, 14.0602, 14.1335, 14.1675 Å and $c = 3.7472$, 3.7703, 3.7877, 3.7988 Å for Sn_2S_3, $Sn_2S_{2.4}Se_{0.6}$, $Sn_2S_{2.2}Se_{0.8}$ and $Sn_2S_{2.0}Se_{1.0}$ respectively. Sn_2Se_3 was reported by Palatkin and Levin [3] to be a tetragonal phase with $a = 6.77$ Å and $c = 5.86$ Å. Its existence in the system was not confirmed by Karathanova et al. [14]. In the present study, samples of Sn_2Se_3 composition prepared from starting raw materials and from melting at 800 °C were treated at 500
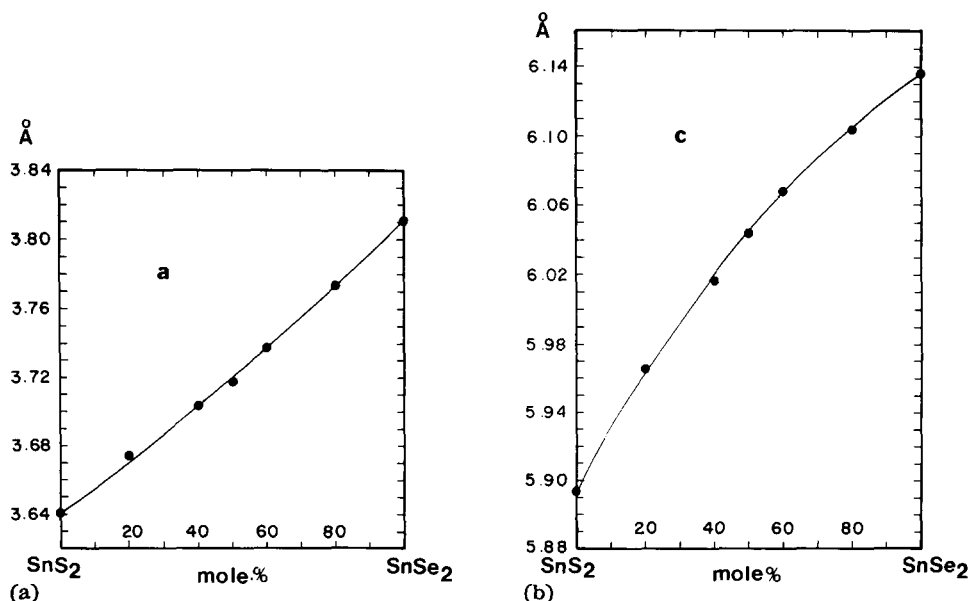

Fig. 3. Variations in cell parameters with composition along the join SnS_2–$SnSe_2$.

°C for a period of 3 months with two intermediate grindings. End products from both preparations are $SnSe + SnSe_2$. No Sn_2Se_3 was found.

3.2. Phase relations in the system Sn–Se–Te

Phase relations in the system at 500 °C are shown in Fig. 4. Tellurium liquid forms equilibrium assemblages with all tin chalcogenides stable in the system.

Along the join SnSe–SnTe a simple eutectic relation with two terminal solid solutions exists as shown in Fig. 5. Results obtained correlate well with the reported phase diagram of Totani *et al.* [15]. In the SnSe solid solution the orthorhombic cell parameters increase with SnTe content. They are $a = 4.4473$, 4.4690, 4.4872 Å, $b = 11.5312$, 11.6002, 11.6404 Å and $c = 4.1758$, 4.1991, 4.2157 Å for $Sn(Se_{0.9}Te_{0.1})$, $Sn(Se_{0.8}Te_{0.2})$ and
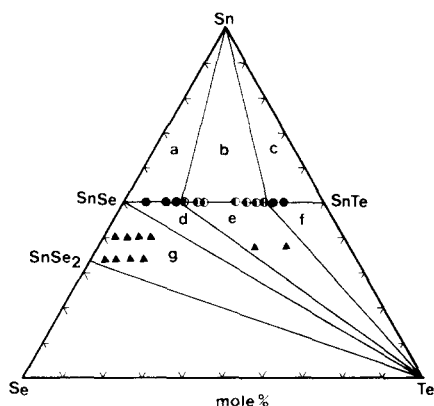

Fig. 4. Phase relations in the system Sn–Se–Te at 500 °C. Equilibrium phase assemblages are (a) liquid tin + SnSe solid solution, (b) liquid tin + SnSe solid solution + SnTe solid solution, (c) liquid tin + SnTe solid solution, (d) liquid tellurium + SnSe solid solution, (e) liquid tellurium + SnSe solid solution + SnTe solid solution, (f) liquid tellurium + SnTe solid solution and (g) $SnSe + SnSe_2 +$ liquid tellurium.

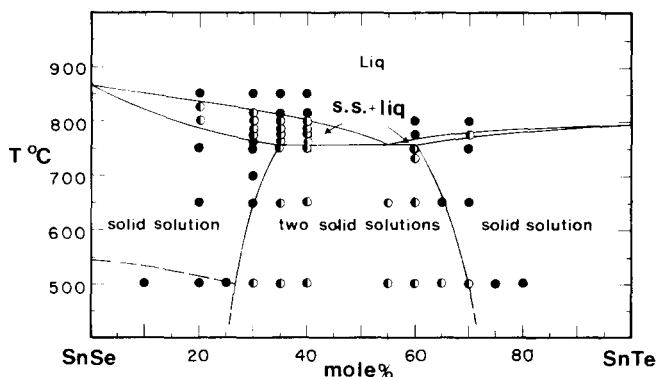Fig. 5. Phase relations along the join SnSe–SnTe. The dashed line represents the GeS-to-TlI phase transition in SnSe.

$Sn(Se_{0.75}Te_{0.25})$ respectively. In the cubic solid solution series a varies from 6.3029 Å° for SnTe, to 6.2433 Å° for $Sn(Se_{0.9}Te_{0.1})$ and to 6.2188 Å for $Sn(Se_{0.25}Te_{0.75})$.

At 300 °C the phase relations differ from those shown in Fig. 4 in two aspects: (1) tellurium is a solid phase at 300 °C and there is no liquid phase in the region of Te–SnTe–SnSe–SnSe$_2$; (2) the region occupied by the two-phase assemblages of SnSe solid solution + tellurium and SnTe solid solution + tellurium becomes smaller because of reduction in mutual solid solution between SnSe and SnTe at 300 °C.

3.3. Phase relations in the system Sn–S–Te

Phase relations in the system at 500 °C are shown in Fig. 6. As in the previous system, tellurium liquid forms equilibrium assemblages with all tin chalcogenides stable in the system. At 300 °C the region Te–SnTe–SnS–SnS$_2$ consists of no liquid phase.

Along the join SnS–SnTe a eutectic point exists at 729 °C and approximately 40 mole% SnS. At 500 °C SnTe can take a maximum of 2.5 mole% SnS and no solid solution of SnTe was detected in SnS. The ranges of solid solutions are 5.0 mole% SnTe in SnS and 8.5 mole% SnS in SnTe at 700 °C.

3.4. Phase relations in the system SnS–SnSe–SnTe

Figure 7 shows the phase relations among the tin monochalcogenides at 500 °C. The orthorhombic solid solution extends from the join SnS–SnSe into the system and occupies a region defined by SnS, SnSe and $Sn(Se_{0.74}Te_{0.26})$. Cell parameters of selected solid solutions were measured and are marked on the diagram. A trend of increase in all parameters with increasing amount of SnTe is seen. The cubic solid solution occupies a narrow, elongated region from SnTe to $Sn(Se_{0.70}Te_{0.30})$ and with less than 3 mole% SnS.
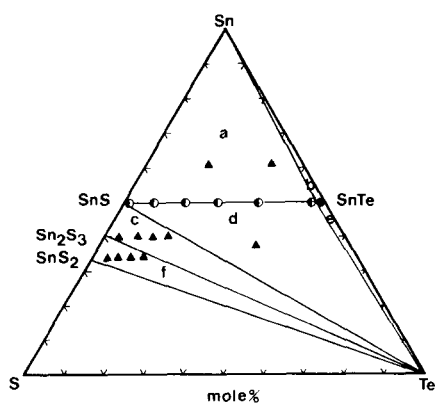

Fig. 6. Phase relations in the system Sn–S–Te at 500 °C. Equilibrium assemblages are (a) liquid tin + SnS + SnTe solid solution, (b) liquid tin + SnTe solid solution, (c) SnS + liquid tellurium + Sn$_2$S$_3$, (d) SnS + liquid tellurium + SnTe solid solution, (e) SnTe solid solution + liquid tellurium and (f) Sn$_2$S$_3$ + SnS$_2$ + liquid tellurium.
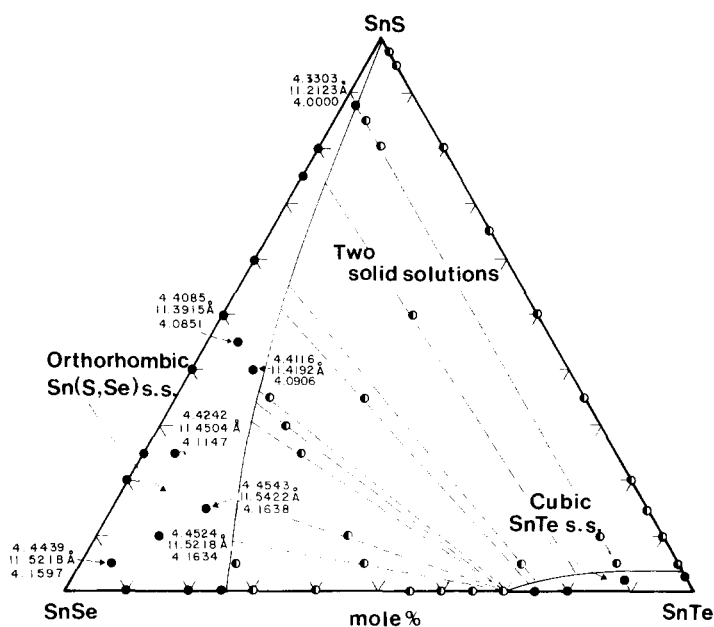
Fig. 7. Phase relations in the system SnS–SnSe–SnTe at 500 °C. Tie-lines are represented by the dashed lines in the two-solid-solution region.
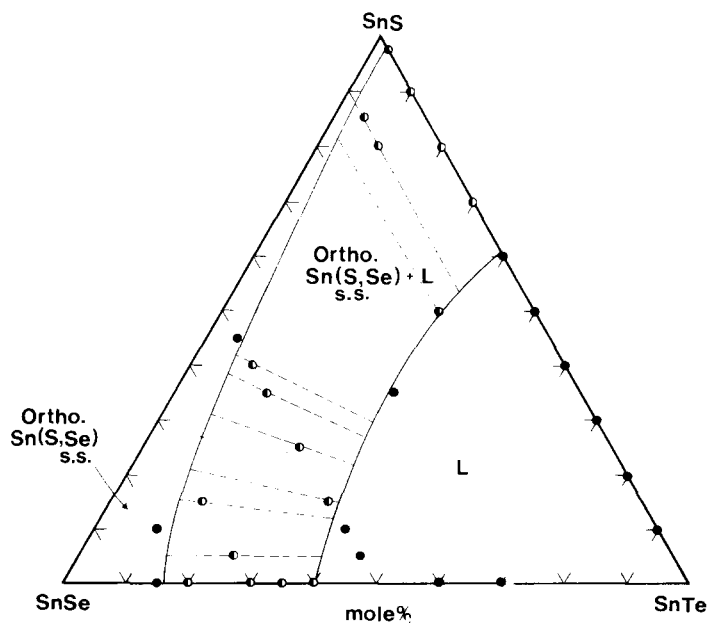

Fig. 8. Phase relations in the system SnS–SnSe–SnTe at 850 °C.

At 850 °C the system consists of the orthorhombic solid solution in equilibrium with liquid which occupies the region of more than 50 mole% SnTe (Fig. 8).

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