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ON THE TERNARY SYSTEM Sn–Te–I: INVESTIGATION OF THE SnI_2–Te, TeI_4–SnI_2 AND SnTe–TeI_4 SUBSECTIONS

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ABSTRACT

The quasi-binary systems SnI_2–Te, TeI_4–SnI_2 and SnTe–TeI_4 have been studied by DTA and X-ray diffraction methods. The first system shows a monotectic shape while the others present a more complex form. On the TeI_4–SnI_2 section, the probable existence of a high-temperature solid solution of composition $SnTe_{0.5}I_4$, derived from the stoichiometry $SnTe_{0.6}I_{4.4}$, has been found of interest as it seems to correspond to the integration of tellurium atoms into the SnI_4 cubic network. The SnTe–TeI_4 section is interesting as it is representative of the complexity of the general system Sn–Te–I due to the redox reactions involved.

INTRODUCTION

Tellurium halides are currently of great interest due to their anticipated broad range of physical properties. Specifically, the optical, electrical and photoelectric characteristics of these compounds may prove useful in technological applications.

There is no doubt that well-defined crystalline tetrahalides exist. The formal oxidation state of tellurium in the tellurium halides is quite variable. The dihalides, on the other hand, are only observed in the gas phase [1,2]. During the last decade, subhalides of tellurium with the general formula Te_nX (X = Cl, Br, I; $n \geqslant 1$) have also been investigated. Lately, the extraordinary properties of these subhalides has led to a renewed interest in the field [3,4].

The structural chemistry of tellurium iodides is rather complex; the polymorphism of five allotropic forms of TeI_4 and the unusual intercalation compound $(Te_2)_2(I_2)$ have been recently reported [5–7]. To date, eleven species have been identified tentatively in the Te–I system: α, β, γ, δ, and ϵ-TeI_4, α and β-TeI, Te_2I, Te_3I, Te_nI_n and $(Te_2)_2(I_2)$ [3,5,8,9]. Of these, only δ-TeI_4 and α-TeI are stable compounds while the remainder exist either as metastable crystalline phases or as unstable gas phase moieties (diiodides

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and subiodides). The variety of TeI_4 phases reported might be an indication that this layer-type structure may exist in different order/disorder modifications of δ-TeI_4.

The tellurium iodides are expected to show different physical properties related to their crystallographic structures. The centrosymmetric α-TeI, for example, has been characterized as an isotropic insulator at room temperature with a high refractive index, an allowed band–band transition and a large region of transparency. Electrical conductivity experiments show that the α-TeI phase can be employed as a component of solid state galvanic cells. Moreover, α-TeI is likely to be a suitable material for use in optical devices [10,11]. Analogous properties might be inferred for the metal chalcogenide halides.

In this study of the ternary Sn–Te–I system, we have investigated the three pseudo-binary sections: SnI_2–Te, TeI_4–SnI_2 and SnTe–TeI_4. The SnI_2–Te system has been investigated previously and no intermediate ternary phases have been reported except the possible existence of $SnTeI_6$ [12]. However, there is no clear understanding of the structure of this compound. Some pseudo-binary cross-sections, i.e Sn–TeI_4, SnTe–SnI_2, SnTe–SnI_4, SnTe–TeI_4, SnI_2–SnTe, SnI_2–TeI_4, SnI_4–TeI_4, SnI_4–TeI and SnI_4–Te have already been studied [13], showing that the respective phase diagrams were either simple or more complex eutectics.

EXPERIMENTAL

Differential thermal analysis

Differential thermal analysis (DTA) experiments were performed using a Mettler TA 1 apparatus equipped with a Pt/Pt–10% Rh thermocouple. Aluminium oxide was chosen as an internal reference due to its high thermal stability over the temperature range 0–1100 °C.

Samples were prepared by melting and annealing, for a week, intimate mixtures of the appropriate compounds (tellurium metal, m5N; tin(II) iodide, 99%; tin telluride, 99.999%; tellurium(IV) iodide, 99%; Ventron) in pyrex ampoules, sealed under vacuum (10^{-2} hPa). After this treatment the mixtures were removed, ground and resealed under vacuum at liquid nitrogen temperature (to avoid thermal degradation of the sample). Platinum crucibles of adequate dimensions assured a good temperature homogeneity during the DTA analyses, which were performed at a heating rate of 4 °C min^{-1}.

Phase diagrams were investigated by steps of $x = 0.1$ or sometimes by smaller increments, x being the molar value defined as $x = (\text{Te}/\text{Te} + SnI_2)$, $x = TeI_4/(TeI_4 + SnI_2)$ and $x = (TeI_4/TeI_4 + \text{SnTe})$, respectively, in the cross-section under consideration.

Eutectic and peritectic points as well as phase compositions have been located according to Tammann's representation [14].

X-ray diffraction

Room temperature X-ray powder diffractograms, taken before and after DTA experiments, were obtained with finely ground powders, using a Guinier camera. The films were scanned and evaluated using the program SCANPI [15].

A high-temperature X-ray powder investigation has been performed on a Guinier camera (Enraf-Nonius FR 553) with a shift of 1mm h^{-1} and a heating rate of 3° C h^{-1}, for the intermediate composition $x = 0.625$ in the quasi-binary system TeI_4–SnI_2.

RESULTS AND DISCUSSION

The SnI_2–Te system

As shown in Fig. 1, the phase diagram SnI_2–Te has a monotectic shape, without any ternary intermediate phases. The eutectic point is located at $x = 0.125$, corresponding to a temperature of 317° C. In spite of small differences on the liquidus curve at high tellurium content, these results are in agreement with preliminary data reported by Katryniok [16].

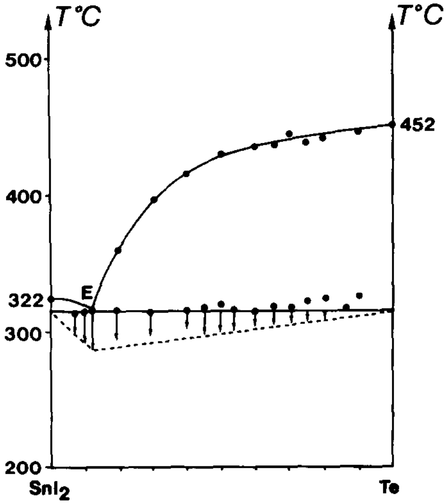

Fig. 1. Quasi-binary system SnI_2–Te.

The TeI_4–SnI_2 system

Figure 2 represents the cross-section TeI_4–SnI_2 which shows a different shape from all the quasi-binary sections previously studied in the ternary system Sn–Te–I. It seemed reasonable to keep the TeI_4–SnI_2 stoichiometry in Fig. 2, even though the redox phenomena lead to a much more complicated system, not easily represented in two dimensions.

Apart from two eutectic points, located at $x = 0.5$ and $x = 0.91$ respectively, the investigations show the presence, around the stoichiometry $SnTe_{0.6}I_{4.4}$ (molar ratio $x = 0.625$), of a new composition existing only at temperatures higher than 153° C and melting congruently at 438° C.

Room temperature X-rays studies of a sample of stoichiometry $SnTe_{0.6}I_{4.4}$, before and after the DTA experiments, did not show any crystalline phase corresponding to this composition. However, the existence of a solid solution of composition $SnTe_{0.5}I_4$ was confirmed above 153° C by means of high-temperature X-ray powder investigations. The sample used was of global composition $SnTe_{0.6}I_{4.4}$ and was previously melted and then annealed at low temperature.

In Fig. 3, the temperature scan between 50 and 250° C shows that above ~ 150° C, the majority of the Te lines disappear, while those of SnI_4 and TeI remain. No new lines were recorded, and thus the existence of a solid

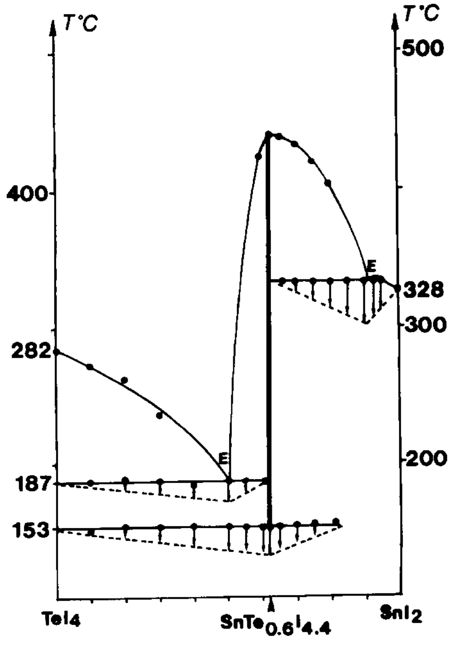

Fig. 2. Quasi-binary system TeI_4–SnI_2.

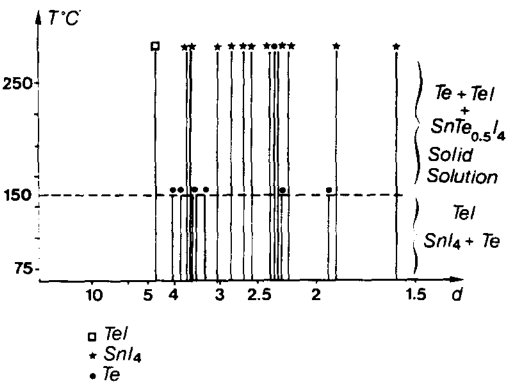

Fig. 3. X-ray powder pattern vs. temperature of the stoichiometry $SnTe_{0.6}I_{4.4}$ showing a phase transition at about 150 °C.

solution based on the SnI_4 arrangement around the stoichiometry $SnTe_{0.6}I_{4.4}$ is confirmed.

The formation of the solid solution around the stoichiometry $SnTe_{0.6}I_{4.4}$ is initiated by the following redox reaction

$$0.625\ SnI_2 + 0.375\ TeI_4 \rightarrow 0.625\ SnI_4 + x\ Te + (0.375 - x)\ TeI + (2.875 - x)/2\ I_2 \qquad (1)$$

The experiments showed formation of elementary iodine, and the reaction is in full agreement with the interpretation of Kniep and co-workers [1,13] concerning the redox phenomena occurring in the Sn–Te–I system. The reduction of tellurium from the formal oxidation state +IV(TeI_4) to +I(TeI) or 0(Te) seems to be common in this system.

From a structural point of view, the insertion of tellurium atoms into the SnI_4 network to form a solid solution can easily be modelled. SnI_4 has a cubic lattice [17], space group $Pa3$, with eight molecules in the unit cell. The structure can be visualized as deviating slightly from an idealized arrangement of iodine atoms on a face-centred cubic lattice with 1/8 of the interstices (tetrahedral sites) filled with tin atoms. Figure 4a is an idealized representation of SnI_4 where all atoms are situated at specific crystallographic positions. Considering the arrangement of the molecular crystal SnI_4, it is possible to imagine a structural model in which some tellurium atoms can adopt a D_{4h} symmetry between two tetrahedra, keeping their formal Te valence of 0 (Fig. 4b). The appearance of a $4mm$ tetragonal local symmetry due to the introduction of tellurium does not modify the global symmetry of the space group. Previous studies on SnI_4 [18] showed that two adjacent molecules have a structural tendency to form an associated dimer. The insertion of a tellurium atom between two tetrahedra (Fig. 4b) accentuates the dimeric nature of the structure, containing $Te(SnI_4)_2$ building blocks.

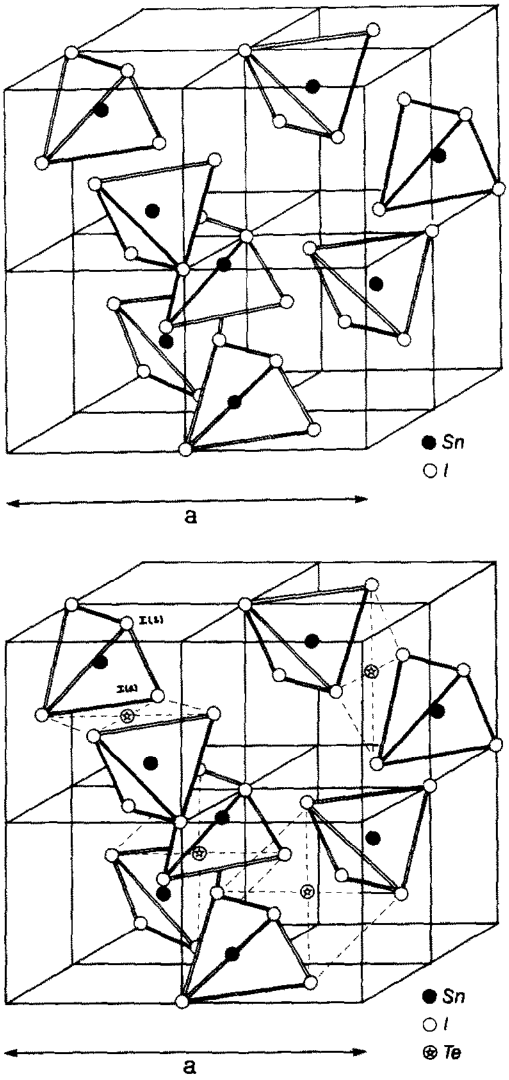

Fig. 4. Top, SnI_4 structural arrangement; bottom, simulated $SnTe_{0.5}I_4$, solid solution of insertion.

The stoichiometry of the proposed solid solution would then be $SnTe_{0.5}I_4$. This composition would change the coefficients of reaction (1) in the following way:

$$0.625\ SnI_4 + x\ Te + (0.375 - x)\ TeI + (2.875 - x)/2\ I_2$$
$$\rightarrow 0.625\ SnTe_{0.5}I_4 + (x - 0.3125)\ Te + (0.375 - x)\ TeI + (2.875 - x)/2\ I_2 \qquad (2)$$

Variable temperature X-ray powder data (Fig. 3) are compatible with this process, showing large amounts of Te below 150 ° C, but only small amounts

TABLE 1

Simulated $SnTe_{0.5}I_4$: atomic position

Atom	x	y	z
Sn	0.1250	0.1250	0.1250
I(1)	0.2500	0.2500	0.2500
I(2)	0.0000	0.0000	0.2500
Te(1)	0.2500	−0.2500	0.2500

above the phase transition. From a geometrical point of view, the solid solution model is also possible, since the space between two adjacent tetrahedra is large enough for the Te(0) atom to be inserted.

Structure factors and geometrical data of the proposed model $SnTe_{0.5}I_4$ were calculated on the basis of the SnI_4 structure [19] obtained from a single

TABLE 2

Crystallographic data of idealized SnI_4 and simulated corresponding $SnTe_{0.5}I_4$ solid solution of insertion

$h\ k\ l$	SnI_4		$SnTe_{0.5}I_4$	
	d	F_{hkl}	d	F_{hkl}
1 1 1	7.082	134	7.082	134
2 1 0	5.485	259	5.485	259
2 1 1	5.008	181	5.008	181
3 1 1	3.698	118	3.698	118
2 2 2	3.541	1360	3.541	1537
2 3 0	3.402	230	3.402	230
2 3 1	3.278	161	3.278	161
3 2 1	3.278	161	3.278	161
4 0 0	3.066	966	3.066	1136
3 3 1	2.814	107	2.814	107
4 2 1	2.677	209	2.677	209
3 3 2	2.615	146	2.615	146
5 1 1	2.361	97	2.361	97
3 4 2	2.277	191	2.277	191
2 5 0	2.277	191	2.277	191
5 2 1	2.239	133	2.239	133
2 5 1	2.239	133	2.239	133
4 4 0	2.168	1279	2.168	1444
6 2 2	1.849	890	1.849	1036
4 4 4	1.770	637	1.770	770
8 0 0	1.533	917	1.533	1039
6 6 2	1.407	642	1.407	751
8 4 0	1.371	451	1.371	563
4 8 0	1.371	451	1.371	563
8 4 4	1.252	674	1.252	777
10 2 2	1.180	472	1.180	569
6 6 6	1.180	472	1.180	569

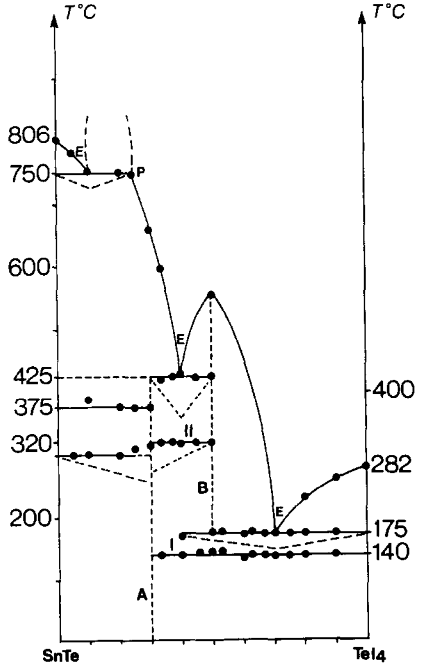

Fig. 5. Quasi-binary system SnTe–TeI$_4$.

crystal, using the programs LAZY PULVERIX [20] and PARST [21]. Atomic coordinates, considering the "ideal" host structure, are indicated in Table 1. Table 2 shows that the theoretical structure factors of $SnTe_{0.5}I_4$ are of similar magnitude to those of SnI_4, keeping the cell dimension constant at $a = 122.6$ nm. The theoretical distances are consistent with those of SnI_4, Sn–I = 26.5 nm, and Sn–Te, Te–I(1) and Te–I(2) being 26.5, 30.6 and 43.2 nm respectively in $SnTe_{0.5}I_4$.

The SnTe–TeI$_4$ system

Katryniok [16] has previously studied the phase diagram SnTe–TeI$_4$ but the representation given is unclear since he included the redox species (i.e. SnI_2, SnI_4, Te and TeI) as if they belonged to the binary SnTe–TeI$_4$ system. Such quasi-binary systems are very complex and were reinvestigated to give a complementary representation. The results of our experiments are presented in Fig. 5. This differs in shape from Katryniok's diagram, but its interpretation remains complicated. However, one peritectic point has been located at $x = 0.25$, while three eutectic points appeared at $x = 0.10$, 0.40 and 0.70, respectively.

This diagram also shows several invariant lines, pointing to the occurrence of various redox reactions in the system. Table 3 shows the correspondence between the melting point of the main compounds involved in the

TABLE 3

Melting point of the main redox species of the system SnTe–TeI_4

Species	T_f (°C)
SnI_2	320
SnI_4	144
TeI	185
Te	450

system and some of these lines. The invariant lines I and II in Fig. 3 correspond to the formation of SnI_4 and SnI_2, respectively. This confirms that the reduction of tellurium from the oxidation state +IV(TeI_4) to +I(TeI) or 0(Te) is common in the ternary system Sn–Te–I. For the diagram considered the global redox process may be expressed as:

$$x\mathrm{SnTe} + (1-x)\mathrm{TeI}_4 \rightarrow y\mathrm{SnI}_2 + z\mathrm{SnI}_4 + t\mathrm{TeI} + u\mathrm{Te}$$

with $x = TeI_4/(TeI_4 + SnTe)$ and $0 \leqslant y \leqslant 1$; $0 \leqslant z \leqslant 1$; $0 \leqslant t \leqslant 1$; $0 \leqslant u \leqslant 1$. This approach is in full agreement with room temperature X-ray studies, before and after DTA experiments, on each molar composition considered.

DTA indicates the existence of two ternary compounds, A and B, at the respective molar ratios $x = 0.30$ and $x = 0.50$ (Fig. 5). However, no new phases could be detected by X-ray diffraction at room temperature. Compound A decomposes before melting and is affected by the action of several redox species between 300 and 425 °C. This phase is metastable and therefore its existence depends on the decomposition kinetics. Compound B, corresponding to the special composition $SnTe_2I_4$, probably exists at temperatures higher than 175 °C, melting congruently at 556 °C. This phase would certainly not be a solid solution based on SnI_4, and is thus interesting as it might lead to a new approach to the chemistry of the Sn–Te–I ternary system.

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