

PHASE EQUILIBRIA IN THE $Tl_2Te - Ag_2Te$ SYSTEM

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The phase diagram for the $Tl_2Te - Ag_2Te$ system has been established by thermal analysis and X-ray diffraction methods. The results obtained are compared with the data of other authors. Examples are given of using the disadvantages of thermal analysis for the correct interpretation of experimental data.

An increasing demand for new semiconductive materials with various physicochemical properties has provoked interest in ternary compounds, especially those formed in the $M - M' - X$ -type systems, where M and M' are different metals, and X is an element of the IV, V or VI B group of the periodic system. Such compounds are formed along the sections in the three-component systems: $M_nX_m - M'$ (compound-metal) and $M_nX_m - M'_uX_z$ (compound-compound), where m, n, u and z are stoichiometric coefficients. The ternary compound may be formed only when strong ionic interactions exist between the components in the binary side-systems: $M - M'$, $M - X$ and $M' - X$.

The pseudo-binary $Tl_2Te - Ag_2Te$ system constitutes one of the possible sections of the ternary $Ag - Tl - Te$ system [1]. The phase diagrams of the binary $Ag - Tl$ [2], $Ag - Te$ [3] and $Tl - Te$ [4, 5] side-systems are known. The phase equilibria in the $Tl_2Te - Ag_2Te$ system have been studied twice to date. According to the earlier data of Kovaleva et al. [6], two compounds are formed in this system: $AgTlTe$ (molar ratio of components $Tl_2Te : Ag_2Te = 1 : 1$) melting congruently, and Ag_9TlTe_5 (1 : 9), melting incongruently. The phase diagram given by Abishov et al. [7] indicates that two additional compounds are formed: 3 : 1 and 1 : 4, both melting incongruently. The investigation methods employed in [6] and [7] were essentially the same: differential thermal analysis, X-ray diffraction and microhardness.

However, the results of our electrochemical studies [8] on the $Tl_2Te - Ag_2Te$ system by EMF measurements on concentration cells appeared to be quite

inconsistent with either of the two phase diagrams [6, 7]. Accordingly, it has been necessary to verify the data existing hitherto on the phase equilibria in the above system, using thermal analysis and X-ray diffraction.

Experimental

Materials

Silver and thallium tellurides were prepared by fusing the components (Te spectrally pure, Johnson Matthey Chemicals; Ag and Tl 99.9% pure, POCh, electrolytically refined and then melted in vacuum) in a quartz vessel under a pure argon atmosphere.

Thermal analysis, apparatus

The phase equilibria in the Tl_2Te - Ag_2Te system were investigated by employing the cooling and heating curve technique in an apparatus [9] of classical construction for cryometric measurements.

The $Tl_2Te + Ag_2Te$ alloys in an alumina crucible (20 mm in diameter) were placed in the hermetic quartz apparatus filled with pure argon. Phase transition temperatures were measured by means of a thermopile (four Pt/Pt, PtRh thermocouples connected in series) calibrated at the freezing points of the standards tin, bismuth, lead, zinc, aluminium, potassium chloride and silver, and at the boiling point of water. The thermoelectric EMF of the thermopile was measured by the compensation method, and the temperature values were calculated from the resulting readings, using the thermometric characteristics equation $EMF = at + bt^2 + ct^3$, with an accuracy of $\pm 0.2^\circ$.

Throughout the measurements, liquid samples were vigorously stirred with a quartz stirrer (making vertical strokes) in the shape of a cylinder 5 mm in diameter. For some other shapes (e.g. a coil, crescent, ball or cone), the stirrer crumbled on solidification of the alloys. In spite of slow cooling (1–1.5 deg/min) and continuous stirring, supercooling frequently occurred, which made establishment of the true transition temperature difficult. In order to avoid this phenomenon, or at least to reduce its effect, small pieces of corundum were dropped into the cooling liquid to start the crystallization. The determination of the transition temperatures in the solid phase also demanded that the heating curves be delineated.

Accuracy

Because of the dispersion of the experimental points, the temperatures of most of the phase transitions could be determined with an accuracy of $\pm 1^\circ$, while some of the freezing points (of pure Ag_2Te and eutectic on the Tl_2Te side) had an accuracy of only $\pm 2^\circ$. The freezing temperatures of pure Tl_2Te and the compound with a $\text{Tl}_2\text{Te}:\text{Ag}_2\text{Te}$ ratio of 1:1, as well as the temperature of the polymorphic transition $\alpha\text{-Ag}_2\text{Te} \rightleftharpoons \beta\text{-Ag}_2\text{Te}$, were determined with an accuracy of $\pm 0.2^\circ$.

The compositions of alloys were calculated from the masses of the components taken. Considering the possibility of tellurium evaporation, however, the composition was controlled analytically after each measurement series had been completed. The silver content was determined using ionoselective electrodes, and that of tellurium by polarography. In order to check the results of analysis, the compositions of some alloys were additionally determined by means of the atomic absorption method.

Taking into account both the results of analyses and the error in the graphical determination of co-ordinates for characteristic points of the phase diagram, the compositions are given with an accuracy of not less than ± 0.5 mole % Ag_2Te .

X-ray diffraction

Samples for the X-ray diffraction studies were prepared by fusing weighed (± 0.0001 g) amounts of components under an atmosphere of purified argon in a quartz tube at ca. 100 deg above the point of complete liquefaction. After solidifying, all the samples were powdered, then sealed in quartz tubes under pure argon and homogenized at various temperatures:

- pure components Tl_2Te and Ag_2Te , as well as alloys containing 4, 50, 66.7, 85 and 90 mole % Ag_2Te , at 350° (another sample of Ag_2Te for comparison was not homogenized),
- samples of alloys containing 35.7, 37, 40, 42.5, 45, 47 and 50 (high-temperature modification of the 1:1 compound) mole % Ag_2Te , at 420° ,
- an alloy from the area of the limited solid solution (4 mole % Ag_2Te), at 390° .

After homogenization for 4 weeks, the samples were quenched by dropping into liquid nitrogen.

X-ray phase examinations were accomplished by means of the TUR M 62 apparatus connected to the HZG-4 diffractometer.

Results

The phase diagram for the thallium telluride-silver telluride (Tl_2Te-Ag_2Te) system was established from the data obtained by thermal analysis and X-ray diffraction (Fig. 1).

In this system one congruently melting compound is formed at the component molar ratio $Tl_2Te:Ag_2Te = 1:1$ ($AgTlTe$), the melting point of which is $478.6 \pm 0.2^\circ$. The compound undergoes a polymorphic transition $\alpha-AgTlTe \rightleftharpoons \beta-AgTlTe$ at $386 \pm 1^\circ$. It has also been shown that three incongruently melting compounds are formed at $Tl_2Te:Ag_2Te$ ratios of 1:9, 1:2 and 9:5. Their decomposition temperatures are 499 ± 1 , 366 ± 1 and $443 \pm 1^\circ$, respectively. The last compound (9:5) also has a bottom temperature limit of existence ($381 \pm 1^\circ$), at which it decomposes when allowed to cool. In the system under consideration, two eutectics have been found with co-ordinates $371 \pm 2^\circ$, 15 mole % Ag_2Te and $442 \pm 1^\circ$, 69 mole % Ag_2Te , as well as a limited solid solution (α_s) of Ag_2Te in Tl_2Te , containing a maximum of 10 mole % Ag_2Te at 371° .

From a comparison of the data reported in [6] and [7] with those obtained in the present work (Table 1), it follows that our results confirm the general shape of the liquidus line, and the existence of the 1:1 and 1:9 compounds found in [6] and [7], but they contradict the formation of the 3:1 and 1:4 compounds suggested in [7].

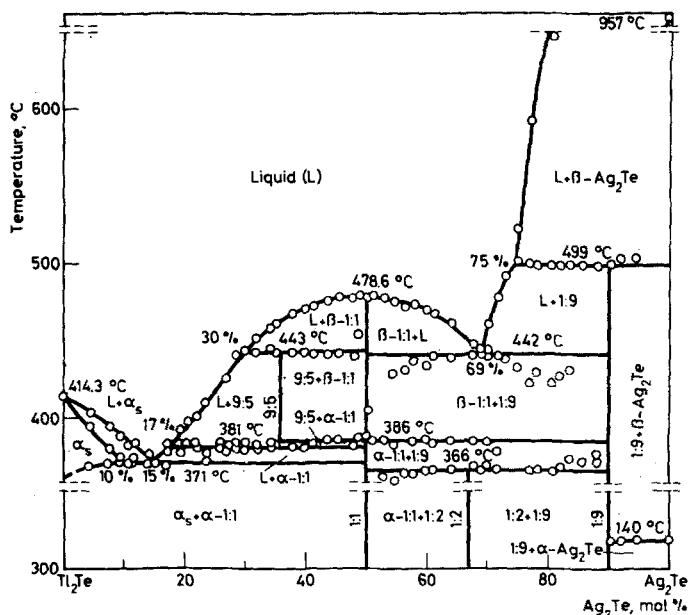


Fig. 1 Phase diagram for the Tl_2Te-Ag_2Te system

Table 1 Comparison of the most essential data on the phase equilibria in the Tl_2Te-Ag_2Te system

Specification	Ref. [6]	Ref. [7]	Present data
1 Tl_2Te melting point, °C	457	420	414.3 ± 0.2
2 Existence range of limited solid solution, mole % Ag_2Te	—	—	< 10
3 Eutectic on Tl_2Te side			
a) melting point, °C	365	365	371 ± 2
b) composition, mole % Ag_2Te	12	~ 10	15
4 Incongruently melting compound I	—	1 : 3	9 : 5
a) existence temp. range, °C		< 380	$381-443 (\pm 1)$
b) peritectic point position, mole % Ag_2Te		~ 19	17 and 30
5 Congruently melting compound	1 : 1	1 : 1	1 : 1
a) melting point, °C	485	480	478.6 ± 0.2
b) polymorphic trans. $\alpha \rightleftharpoons \beta$, at °C	390-400	—	386 ± 1
c) polymorphic trans. $\beta \rightleftharpoons \gamma$, at °C	440	435	—
6 Incongruently melting compound II	—	1 : 4	1 : 2
a) decomposition temp., °C		448	366 ± 1
b) peritectic point position, mole % Ag_2Te		69	
7 Eutectic on Ag_2Te side			
a) melting point, °C	450	442	442 ± 1
b) composition, mole % Ag_2Te	73	~ 70	69
8 Incongruently melting compound III	1 : 9	1 : 9	1 : 9
a) decomposition temp., °C	500	500	499 ± 1
b) peritectic point position, mole % Ag_2Te	80	~ 78	75
9 Ag_2Te melting point, °C	950	960	957 ± 2
a) polymorphic trans. $\alpha \rightleftharpoons \beta$, at °C	145	150	140 ± 0.2

Discussion

The most important results in the present study concern the finding of evidence of the formation of the 1 : 2 and 9 : 5 compounds, as well as the limited solid solution α_s in the Tl_2Te-Ag_2Te system.

The composition of the 1 : 2 compound was found by the Tammann triangle method: in the cooling curves for melts from 50 to 90 mole % Ag_2Te , the longest thermal arrests (at 366°) were observed near 66.7 mole % Ag_2Te . X-ray examination confirmed this compound formation (the X-ray diffraction patterns for specimens containing 50, 66.7 and 90 mole % Ag_2Te were different—Fig. 2 a, b, c).

The existence of the limited solid solution α_s is evidenced both by the arrangement of the experimental points in Fig. 1 and by the shifts in the peaks of the X-ray

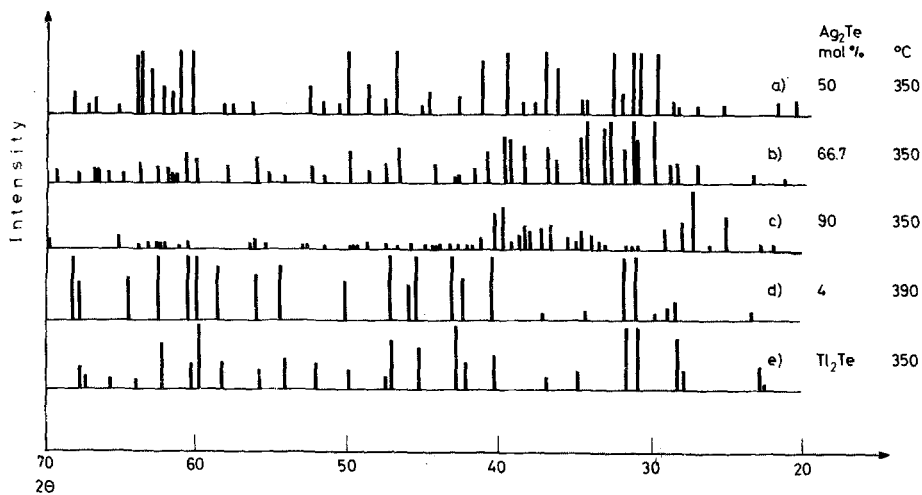


Fig. 2 Schematic diagrams of X-ray diffraction patterns for the Tl_2Te-Ag_2Te samples (compounds with component molar ratios 1:1 (a), 1:2 (b), 1:9 (c); an alloy from the limited solid solution α_2 area (d), pure Tl_2Te (e)), homogenized at appropriate temperatures

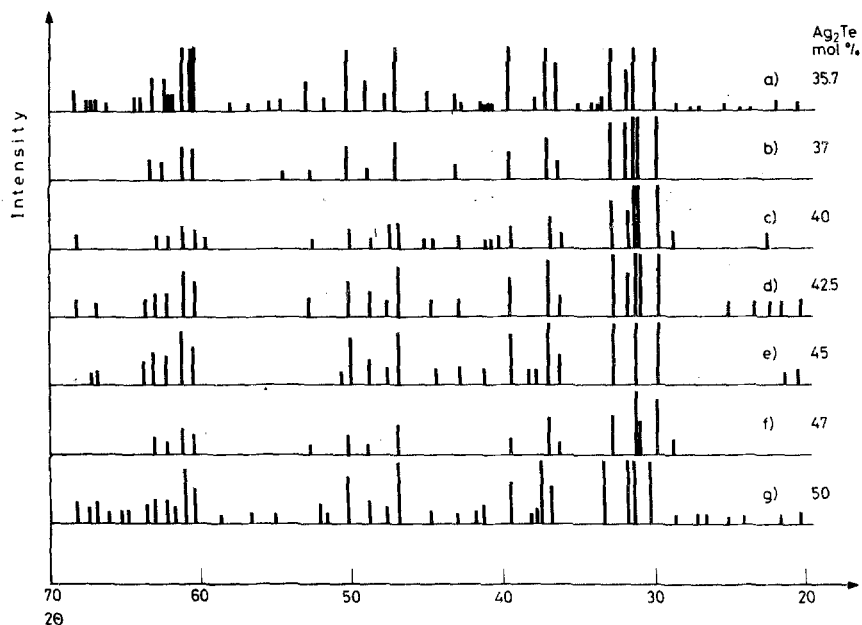


Fig. 3 Schematic diagrams of X-ray diffraction patterns for the Tl_2Te-Ag_2Te samples (9:5 compound (a), 1:1 compound (g) and alloys with intermediate compositions (b-h)), homogenized at 420°

diffraction pattern for the 4 mole % Ag_2Te alloy as compared to the corresponding pattern for pure Tl_2Te (Fig. 2 *d, e*).

The investigation of phase equilibria within the region 15–50 mole % Ag_2Te and the temperature range 371–443° presented the greatest difficulty, mainly due to the overlapping (during the determination of cooling curves) of the heat effects of the following neighbouring phase transitions: polymorphic transformation of the 1 : 1 compound at 386°, decomposition of the 9 : 5 compound at 381°, and eutectic solidification at 371°. The X-ray examination of samples from the concentration range 35.7–50 mole % Ag_2Te (Fig. 3) does not provide an explicit solution of the problem of whether the alloy with composition 35.7 mole % Ag_2Te is a distinct 9 : 5 chemical compound existing independently of the 1 : 1 compound, or it constitutes a boundary of a phase of variable composition covering the concentration and temperature ranges 35.7–50 mole % Ag_2Te and 381–443°, respectively. The X-ray patterns for the 35.7 and 50 mole % Ag_2Te alloys (i.e. the 9 : 5 and 1 : 1 compounds, respectively) show similarities as well as differences in the positions and heights of the corresponding peaks and the distances between them (Fig. 3 *a, g*). Similar conclusions can be drawn from a review of the patterns for samples with intermediate compositions (37, 40, 42.5, 45 and 47 mole % Ag_2Te —Fig. 3 *b–f*), but on passing from 35.7 to 50 mole % Ag_2Te , a gradual displacement of some peaks may be observed: initially towards smaller angles, and then (from 42.5 mole %) in the reverse direction.

To complete the above considerations, it should be added that, despite the long homogenization of the samples at 420°, with quenching in liquid nitrogen and X-ray examination in a max. of 24 hours, the disturbance of the “frozen” equilibrium state cannot be excluded with certainty on heating again to room temperature.

The composition of the 9 : 5 compound was determined by observation of the stirrer motion. Throughout the cooling of the melts, the stirring speed was controlled within 10 strokes per second, the stroke length being 10 mm, but as the amount of the solid phase coming out of solution increased, the stroke length gradually decreased until the stirrer stopped at the solidus temperature. For melts with compositions of from 17 to 35 mole % Ag_2Te , the stirrer stopped at the temperature of eutectic solidification (371°), and for 38–49 mole % Ag_2Te melts at 443°. In the latter concentration range, therefore, the liquid phase disappeared as soon as the temperature reached 443°. The use of the Tammann triangle method for determination of the formula of the compound formed at 443° was pointless, due to the different phase compositions and therefore the different cooling conditions of the melts with < 35.7 and those > 35.7 mole % Ag_2Te in the temperature range 381–443°.

On the basis of the above considerations, it is concluded that the compound with Tl_2Te : Ag_2Te molar ratio 9 : 5 does exist and that its crystal structure resembles that of the 1 : 1 compound.

An essential condition that must be satisfied for the precise determination of a phase transition temperature is that the equilibrium state for which phases co-exist should be maintained at this temperature. The stopping of a stirrer during solidification results in non-equilibrium crystallization and is therefore a considerable disadvantage of the thermal analysis technique described above. Thus, the procedure of determining the composition of the 9:5 compound on the basis of observation of the stirrer motion is an example of the adoption of a shortcoming of the method for the correct interpretation of the experimental data.

The disadvantages of thermal analysis were also exploited in the interpretation of the experimental results relating to another part of the Tl_2Te-Ag_2Te system. The formation (on cooling) of the 9:5 compound and the freezing of the 69 mole % Ag_2Te eutectic arc, of course, two different phase transitions occurring at nearly the same temperature (443 ± 1 and $442 \pm 1^\circ$, respectively), so that they may easily be considered incorrectly to be one and the same transition, as was the case in [6] and [7]. The authors of [6] and [7] explained the observed transition as the second polymorphic transformation of the 1:1 compound ($\beta-1:1 \rightleftharpoons \gamma-1:1$ [6]). As concerns the results obtained by these authors, it must be admitted that they also found the phase transitions at 443 and 381° , though their temperature values and the interpretation were different from ours.

In the determination of phase diagrams by thermal analysis, it very commonly occurs that the experimental points corresponding to eutectic crystallization lie on a curve convex upwards, the maximum of which indicates the eutectic composition and temperature. The reason for such an arrangement of the points is the supercooling, resulting in non-equilibrium crystallization and consequently in lowering of the freezing temperature. The lowering is the greater, the more distant the examined sample composition is from that of the eutectic. This is the case with the determination of the eutectic temperature 442° in the thallium telluride-silver telluride system. The corresponding experimental points from such a curve, to which the extreme point of the co-ordinates 50.4 mole % Ag_2Te , 404° also belongs. Although resulting from a disadvantage of the method employed, the arrangement of these points provides strong evidence that the thermal arrests at 442° and 443° in the cooling curves relate to two different phase transitions which have no connection with the 1:1 compound.

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Zusammenfassung — Das Phasendiagramm von Tl_2Te-Ag_2Te wurde durch thermische Analyse und röntgendiffraktometrie ermittelt. Die erhaltenen Ergebnisse werden mit denen anderer Autoren verglichen. Beispiele werden angeführt, wie die Nachteile der thermischen Analyse zur korrekten Interpretation der experimentellen Daten benutzt werden können.

Резюме — Методом термического и рентгеноструктурного анализа установлена фазовая диаграмма системы Tl_2Te-Ag_2Te . Полученные результаты сопоставлены с данными других авторов. Приведены примеры применения недостатков термического анализа при корректной интерпретации экспериментальных данных.