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PHASE DIAGRAM FOR THE Tl_2Te–Bi_2Te_3 SYSTEM

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The phase equilibria in the Tl_2Te–Bi_2Te_3 system were studied by means of cooling curve determination, differential thermal analysis and X-ray diffraction methods; the results obtained with the former two methods were compared. The phase diagram established for the system differed considerably from three others published previously.

The Tl_2Te–Bi_2Te_3 system is one of the possible sections of the ternary Tl–Bi–Te system, the phase diagram of which is unknown, although different alloys containing thallium, bismuth and tellurium have already been studied many times. The considerable interest in these alloys is caused by the fact that their components form ternary compounds with semiconductive properties. From among them, the compound $TlBiTe_2$ is of some importance in studies on semiconductivity [1], yet it is still unknown whether the compound melts congruently or incongruently.

The following sections of the Tl–Bi–Te system have been investigated so far: Bi_2Te_3–Tl_2Te_3 [2–5], Bi_2Te_3–Tl [6, 7], (50% Tl + 50% Bi/Te [8], BiTe–TlTe [9], Bi_2Te_3–Tl_9BiTe_6 [10], Tl_2Te–Bi_2Te_3 [11, 12] and Tl_2Te–Bi_2Te_3–Te [13]. The phase equilibria in systems of the type Tl_2X^{VI}–$B^{V}_2X^{VI}_3$ have been discussed in [14]; it has been found that with increase in atomic weight of an element in Group V or VI of the periodic table, the number of compounds decreases in the succeeding system. For example, if four compounds are formed in the Tl_2S–As_2S_3 system, then only one congruently melting compound, of formula $TlBiTe_2$, should be expected in the Tl_2Te–Bi_2Te_3 system.

The investigation results published to date on the Tl_2Te–Bi_2Te_3 system [10–12] differ considerably from one another (the Bi_2Te_3–Tl_9BiTe_6 system [10] constitutes 90% of the Tl_2Te–Bi_2Te_3 system). In two of these papers [11, 12], it has been reported that the alloys rich in Bi_2Te_3 form a limited solid solution. According to [10] and [12] the compound $TlBiTe_2$ melts congruently, but according to [11] it undergoes decomposition. The compound does not contain exactly 50 mole%

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Bi_2Te_3 [10] (as results from its formula), but is a phase of variable composition [11, 12]. The co-ordinates of the characteristic points of the system under consideration, given in papers [10–12], differ by at most 5mole% and 27 deg. All three above papers are consistent in that the congruently melting compound Tl_9BiTe_6 is formed in the Tl_2Te–Bi_2Te_3 system, although it follows from the phase diagram published in [12] that it is a phase of variable composition. The authors of those papers used the same essential method of investigation: DTA, but also X-ray diffraction, microstructure, microhardness and concentration cell EMF measurements.

Experimental

Materials

Thallium and bismuth tellurides were prepared by fusing the components (thallium 99.9% pure, POCh; electrolytically refined, bismuth and tellurium specpure, Johnson Matthey Chemicals) in vacuum in a sealed quartz vessel, then mixed for ca. 15 min at temperatures ca. 200 deg above the respective melting temperatures of Tl_2Te and Bi_2Te_3.

Methods

Studies on the phase equilibria in the Tl_2Te–Bi_2Te_3 system were effected mainly by means of cooling curve determination and, in some doubtful cases, with the heating curve technique too, in the apparatus for cryometric measurements described in [15]. The phase transition temperatures were measured as in investigations of the Tl_2Te–Ag_2Te system [16].

DTA was applied as an auxiliary method. The measurements were made with a Q–1500 D derivatograph (MOM, Budapest). Alloy samples (2–3 g) were placed in evacuated and sealed quartz ampoules provided with a pocket for a thermocouple. The heating (and sometimes cooling) rate was 5 deg/min.

In order to confirm the results obtained with the methods mentioned above, X-ray diffraction studies were also executed. Alloy samples with compositions pure Tl_2Te, 5, 10, 15, 25, 40, 42, 50, 56, 60, 75, 87.5 and 92 mole% Bi_2Te_3 and pure Bi_2Te_3 were prepared by melting weighed amounts of components at 700° in quartz tubes under an argon atmosphere purified from oxygen and moisture. The solidified alloys were powdered and (except for pure Tl_2Te) homogenized for 4 weeks under vacuum in sealed quartz tubes at 450°. After homogenization, the samples were quenched in liquid nitrogen. The X-ray examinations were performed by means of the DRON–2.0 apparatus (USSR).

Accuracy

Due to the relatively large mass (25–50 g) of the investigated alloys, insignificant supercooling and efficient stirring at the cooling rate of 0.8–1.5 deg/min, the values of the liquidus temperatures were determined with an accuracy of ±0.2 deg. The only exception was the region 3–5 mole% Bi_2Te_3, where the temperatures of the liquidus and those of the solidus were burdened with an error of ca. ± 5 deg. This was caused by the difficulty in the detection of a phase transition within this region of steep slope of both the liquidus and solidus lines.

The decomposition temperature of the compound $TlBiTe_2$ was determined with an accuracy of ±0.5 deg, and that of $TlBi_7Te_{11}$ (and its formation temperature), because of the greater scattering of the experimental points, with an accuracy of only ±1 deg.

The compositions of the examined alloys were calculated from the masses of the components taken. There was no need to analyse the samples after each measurement series had been completed, as the mass loss due to evaporation of more volatile components was negligible (it did not exceed 0.05 wt%). Taking into account the maximum error in the graphical determination of the co-ordinates of the characteristic points of the phase diagram, however, the compositions are given with an accuracy of not less than ±0.2 mole%.

Results

Phase diagram

The phase diagram for the thallium telluride–bismuth telluride (Tl_2Te–Bi_2Te_3) system was established from the data obtained with all three methods (Fig. 1).

In this system, four chemical compounds are formed. Two of them have compositions 10.0 (Tl_9BiTe_6) and 56.0 ($Tl_{0.83}Bi_{1.06}Te_2$) mole% Bi_2Te_3, melting congruently at 540.9° and 544.7°, respectively. The maximum on the liquidus line at 540.9° does not lie exactly at the composition of the compound Tl_9BiTe_6, at 11.2 mole% Bi_2Te_3. Between this compound and pure Tl_2Te, continuous solid solutions are formed. The two remaining compounds, with compositions 50.0 ($TlBiTe_2$) and 87.5 ($TlBi_7Te_{11}$) mole% Bi_2Te_3, undergo decomposition at 520.0° and 501.0°, respectively. The latter compound also has a lower temperature limit of existence (310.5°), at which it is formed from the compounds Bi_2Te_3 and $Tl_{0.83}Bi_{1.06}Te_2$. The eutectic on the Tl_2Te side, with composition 27.6 mole% Bi_2Te_3, melts at 495.8°; and that on the Bi_2Te_3 side, at 67.1 mole% Bi_2Te_3, melts at 537.5°.

From the X-ray diffraction studies (Fig. 2) it follows that on the Bi_2Te_3 side a limited solid solution (β) is formed. We have not succeeded in a precise

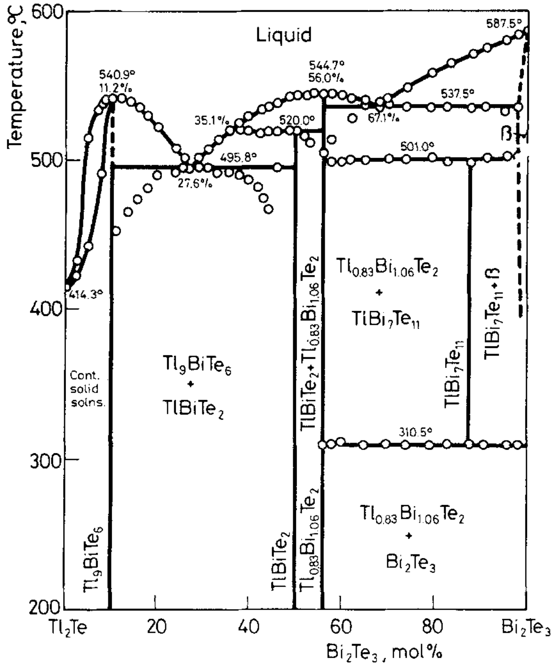

Fig. 1 Phase diagram for the Tl_2Te–Bi_2Te_3 system

determination of its existence range, but it certainly did not reach 2 mole% Tl_2Te in Bi_2Te_3. Figure 2 gives the X-ray diffraction patterns for samples with the compositions which are of the most importance for the identification of the phase occurring in the system under examination.

Comparison of the results obtained by cooling curve determination and DTA

Application of two techniques of thermal analysis to study one and the same system by one group of authors, as is the case with the present work, provides an opportunity for comparison and evaluation of the results obtained with the two methods. Each of them has its advantages and shortcomings, but fortunately these do not overlap one another and therefore the methods may complement each other.

The disadvantages of the cooling curve determination method consist in the need to use a comparatively large amount of an alloy and the difficulty in detecting a phase transformation connected with a small change of enthalpy of system. However, the method has the great advantage that it permits determination of the absolute values of the phase transition temperatures with considerable accuracy, in this instance ±0.2 deg and their differences with an accuracy ten times better

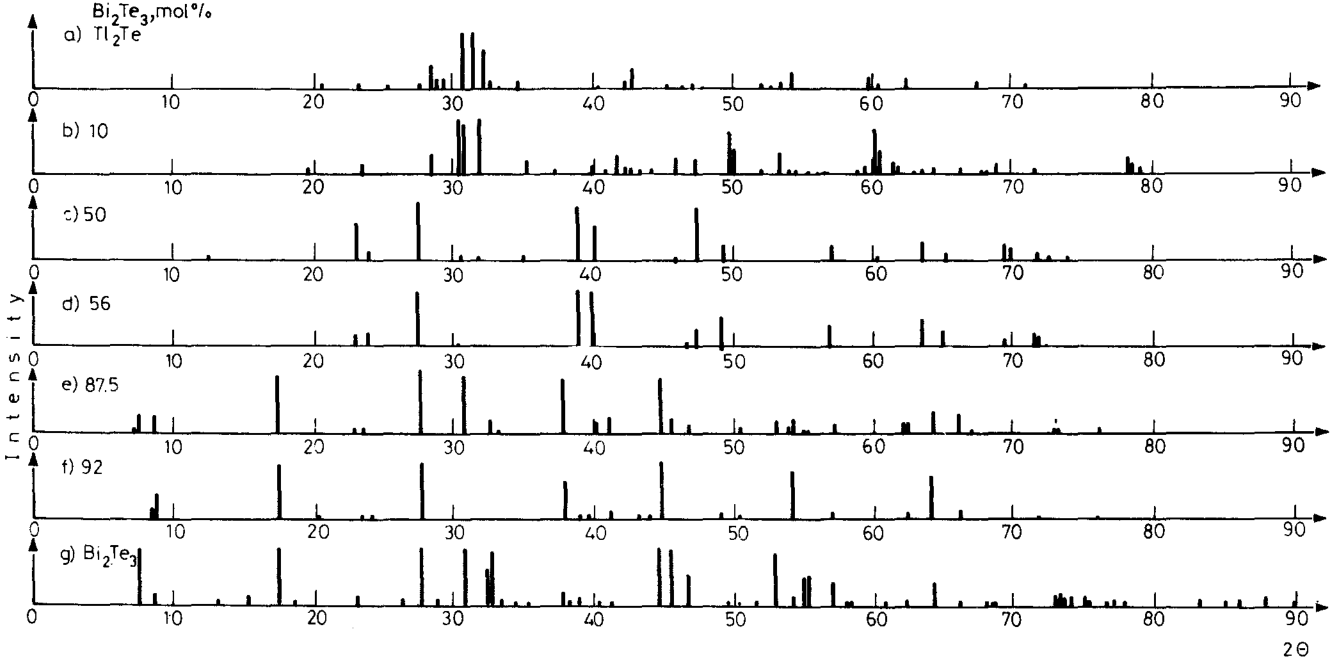

Fig. 2 Schematic diagrams of X-ray diffraction patterns for the Tl_2Te–Bi_2Te_3 samples with different compositions, homogenized (except for pure Tl_2Te) at 450°

(0.02 deg). The experimental points of the liquidus line of the Tl_2Te–Bi_2Te_3 system show an insignificant dispersion and are reproducible for different sets of measurements. Slightly greater dispersion is observed for transitions in the solid phase. The method gives the best results in the determination of cooling curves.

DTA (carried out with a derivatograph) appeared to be less useful for the determination of phase transition temperatures in the Tl_2Te–Bi_2Te_3 system, since the experimental points were highly scattered (within limits of 25 deg). Although both the starting materials and the compositions of the investigated alloys were the same, the location of the experimental points differed from one series of measurements to another. The DTA method is quite sensitive to non-equilibrium conditions of a phase transition with the result that supercooling and overheating may easily occur, since the liquid alloys are not stirred throughout the measurements. This fact has a negative effect on the results, especially when a system undergoes phase transformations in succession at temperatures not too distant from one another (up to about 25 deg) as in the Tl_2Te–Bi_2Te_3 system. In DTA studies on other systems where this is not the case, e.g. Tl_2Te–Sb_2Te_3 [18], the dispersion of the experimental points is considerably smaller: at most 10 deg. The accuracy of the indications of the derivatograph also depends on the temperature range of measurements. Thus, within the range up to 1000°, the deviation of the measured value from the real one may reach even 30 deg, whereas up to 250° it is only 1–2 deg. Advantages of DTA are the small mass of the sample, and especially the sensitivity of the method to the changes in enthalpy of a system. The sensitivity allows the detection of a transition connected with a small heat effect, whereas the same transition might not be recorded in the cooling curves. Formation of the compound $TlBi_7Te_{11}$ in the Tl_2Te–Bi_2Te_3 system was found with DTA, while its lowest temperature of formation (310.5°) was established by means of cooling curve determination.

From the above comparison it may be concluded that DTA should be applied in the preliminary determination of a phase diagram as an auxiliary method to cooling curve determination. This conclusion concerns especially the phase diagrams of greater complexity. The phase diagram for the Tl_2Te–Bi_2Te_3 system given in the present work was constructed by using experimental points obtained with the cooling curve method only.

Discussion

The most essential data reported on the investigated system by other authors, and those obtained in the present work, are listed in Table 1. It may be seen that all the authors agree that a congruently melting compound Tl_9BiTe_6 is formed in the

Table 1 Comparison of the most essential data on the phase equilibria in the Tl_2Te–Bi_2Te_3 system

Specification	Ref. [10]	Ref. [11]	Ref. [12]	Present data
1 Tl_2Te melting point, °C		420±3	421*	414.3±0.2
2 Tl_9BiTe_6 melting point, °C	560	550	557	540.9±0.2
3 Eutectic on the Tl_2Te side				
a) composition, mole% Bi_2Te_3	37**	28*	26	27.6±0.2
b) melting point, °C	505	490	502	495.8±0.2
4 $TlBiTe_2$				
a) composition, mole% Bi_2Te_3	59.5**	50	50	50.0±0.2
b) range of existence, mole% Bi_2Te_3	—	47–53	48–53*	—
c) melting point, °C	575		577	
or decomposition temp., °C		520		520.0±0.5
d) peritectic point position, mole% Bi_2Te_3		31*		35.1±0.2
5 $Tl_{0.83}Bi_{1.06}Te_2$				
a) composition, mole% Bi_2Te_3	—	—	—	56.0±0.2
b) melting point, °C	—	—	—	544.7±0.2
6 Eutectic on the Bi_2Te_3 side				
a) composition, mole% Bi_2Te_3	77.5**	—	72	67.1±0.2
b) melting point, °C	545	—	542	537.5±0.2
7 $TlBi_7Te_{11}$				
a) composition, mole% Bi_2Te_3	—	—	—	87.5±0.5
b) range of existence, °C	—	—	—	310.5–501.0 (±1)
8 Limited solid solution β				
a) range of existence, max. mole% Tl_2Te	—	$\leqslant 5$	3–5	<2
9 Bi_2Te_3 melting point, °C	585*	590*	588*	587.5±0.2

* approximate value (taken from respective phase diagram),

** composition calculated from that given in mole% Tl_9BiTe_6.

system under consideration (not taking into account paper [10]); this compound exhibits unlimited miscibility with thallium telluride in both liquid and solid phases. The fact observed in this work that the maximum on the liquidus line did not appear at the compound composition (10 mole% Bi_2Te_3), but at 11.2 mole% Bi_2Te_3, permitted the supposition that the compound Tl_9BiTe_6 should be regarded as a phase of variable composition at temperatures higher than the eutectic one (the authors of [12] were of a similar opinion, as follows from their phase diagram). It was not possible to determine the range of existence of the phase, but it certainly did not exceed the limit of 12 mole% Bi_2Te_3, since we obtained only two points for the alloy with this composition and the next ones: on the liquidus line and the extreme one corresponding to freezing of the eutectic. The maximum temperature, 540.9°, is only 0.6 deg higher than the temperature for 10 mole% Bi_2Te_3, but the difference should not be regarded as a result of any deficiency of the method employed; it has been verified by repeating the measurement series several times.

The next two compounds in the examined system are formed at compositions lying close to one another: 50 and 56 mole% Bi_2Te_3. The first of them with a component molar ratio $Tl_2Te:Bi_2Te_3 = 1:1$, is $TlBiTe_2$, of course, while the formula $Tl_{0.83}Bi_{1.06}Te_2$ should be ascribed to the second (11 : 14). The formation of such a compound as the latter may be explained in that the thallium and bismuth atoms, which differ slightly in size, can replace each other in the crystal lattice. Both the proximity of the compounds and the facts that $Tl_{0.83}Bi_{1.06}Te$ melts congruently and $TlBiTe_2$ undergoes decomposition have given rise to considerable disaccord and even contradictions in the data [10–12]. To be truthful, the authors of [10] reported that the maximum on the liquidus line they gave did not lie at 50 mole% Bi_2Te_3, but surely they did not believe that such an unexpected composition, i.e. a formula other than $TlBiTe_2$, may be ascribed to the compound. On the other hand, they did not note that the compound $TlBiTe_2$ was really formed at its correct composition, nor that it was an incongruently melting one. From the phase diagram published in [12], it follows that the maximum on the liquidus line appears at exactly 50 mole% Bi_2Te_3, but the compound corresponding to it is a homogeneous γ phase 5 mole% wide at ca. 540°. The 5% range of existence of the phase approximates to the 6% difference between the compositions of the compounds $tlBiTe_2$ and $Tl_{0.83}Bi_{1.06}Te_2$ found in this work. In the absence of precise experimental data, the compositions of these compounds may easily be regarded as two boundaries of one-phase area (a phase of variable composition in the range 50–56 mole% Bi_2Te_3). In [11], the width of this phase was found to be 6 mole%; its range of existence was expressed in terms of the bismuth telluride molar fraction: $0.47 < x \leqslant 0.53$, and its formula was given as $TlBiTe_2$. At the same time, in [11] it was stated that the compound $TlBiTe_2$ melted incongruently at 520°, which was in quite good agreement with our results. Next, the same authors found no maximum on the liquidus line, either at 50 mole% Bi_2Te_3 or in the vicinity of that value. This was no surprise to us, since, in the early stages of our investigations of the Tl_2Te–Bi_2Te_3 system, an attempt was made to establish the phase diagram by means of DTA and the results obtained resembled those reported in [11], i.e. with no maximum at 40–50 mole% Bi_2Te_3 on the liquidus line. The negative result was undoubtedly caused by the slight difference (ca. 7 deg) between the melting temperatures of the compound at 56 mole% Bi_2Te_3 and the nearest eutectic (at 67.1 mole% Bi_2Te_3). A precise determination of the phase transition temperatures for consecutive alloys, whose compositions differed sightly from one another, was possible after heating curve determination had been employed, using a thermopile consisting of four Pt/Pt, Rh thermocouples connected in series. An arrangement of the experimental points (from 35.1 to 56 mole% Bi_2Te_3) corresponding to the decomposition temperature (520°) of the compound $TlBiTe_2$ provides strong evidence for its existence independently of the compound $Tl_{0.83}Bi_{1.06}Te_2$. The similarity of the X-ray diffraction patterns (Fig. 2c, d) of the two compounds, resulting from the closeness of the compositions, is not inconsistent with the above statement, although in another case it might suggest that the compounds either constitute boundaries of variable composition or form continuous solid solutions with one another. It should be noted that, as a consequence of supercooling, the convergence of the experimental points corresponding to the transitions at 520°, 537° and 501° at about 56 mole% Bi_2Te_3 and 504° is an unquestionable source of errors and uncertainties in the DTA measurements. Information on the compound $TlBiTe_2$ has also been given in [9]. The authors of [9] studied by DTA the TlTe–BiTe system, another section of the ternary Tl–Bi–Te system. This section has one common (crossing) point with the Tl_2Te–Bi_2Te_3 section, at 50 mole% BiTe. This is the composition of the same compound $TlBiTe_2$. According to [9], $TlBiTe_2$ melts with decomposition at 524° and the liquidus temperature corresponding to the compound composition is 536 (in this work: 520 and 542.4°, respectively).

To complete the discussion on the central part of the phase diagram, it is worthwhile to add that by superposition of the phase diagrams proposed in [10], [11] and [12] one would obtain approximately the phase diagram determined in the present work.

Unlike the other authors, we have found two additional phase transitions in the Tl_2Te–Bi_2Te_3 system, at 310.5° and 501.0°. The most rational explanation for the occurrence of the transitions is the formation of a compound existing only within the above temperature limits, but determination of the compound composition was difficult. The Tammann triangle method gave no explicit result, because of the small heat effects of the transitions. From the arrangement of the experimental points, forming lines exactly parallel to the concentration axis, again nothing can be concluded on the compound composition. Only the X-ray phase studies permitted the composition to be determined. The X-ray diffraction pattern for the alloy with composition 87.5 mole% Bi_2Te_3 (Fig. 2e) differs distinctly from those obtained for neighbouring compositions, although it resembles to a certain extent that for pure bismuth telluride (Fig. 2g). Accordingly, the formula $TlBi_7Te_{11}$ is to be ascribed to this compound. The composition (87.5 mole% Bi_2Te_3) of this compound (as well as those of $TlBiTe_2$, $Tl_{0.83}Bi_{1.06}Te_2$ and Tl_9BiTe_6) have been confirmed with an accuracy of ±0.5 mole% by means of electrochemical studies on the system, employing the EMF measurements of concentration cells [17]. The same method has also been used in [12]; however, they could not find the compound $TlBi_7Te_{11}$ as the EMF measurements were made at temperatures of about 400 K (127°), i.e. considerably lower than 310.5°, at which the compound is formed.

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References

1 M. L. Cohen, Phys. Rev., 134 (1964) A511.
2 L. A. Borisova, M. V. Efremova and V. V. Vlasov, Dokl. Akad. Nauk SSSR, 149 (1963) 117.
3 D. P. Spitzer and J. A. Sykes, J. Appl. Phys., 37 (1966) 1563.
4 P. W. Chiang and I. V. Gluck, J. Appl. Phys., 38 (1967) 4671.
5 S. A. Dembovskii, L. G. Lisovskii, V. M. Bunun and A. S. Kanishcheva, Izv. Akad. Nauk SSSR Neorg. Mater., 5 (1969) 2023.
6 L. A. Borisova, M. V. Efremova and F. I. Akhmedova, Zh. Neorg. Khim., 8 (1963) 2700.
7 E. Zaleska, Roczniki Chem., 46 (1972) 1229.
8 A. G. Abdulmanov and L. G. Berg, Sb. aspirantskikh rabot Kazansk. Un-ta Estestv. Nauk, khimia, geogr., geol., Kazan (1968) 47.
9 A. Pradel, J. C. Tedenac, G. Brun and M. Maurin, J. Solid State Chemistry, 45 (1982) 99.
10 L. G. Berg and A. G. Abdulmanov, Izv. Akad. Nauk SSSR Neorg. Mater., 6 (1970) 2192.
11 N. S. Popovich, V. K. Shura and D. V. Gitsu, J. Crystal Growth, 61 (1983) 406.
12 M. B. Babanly, A. Akhmadyar and A. A. Kuliyev, Zh. Neorg. Khim., 30 (1985) 2356.
13 M. B. Babanly, A.Akhmadyar and A. A. Kuliyev, Zh. Fiz. Khim., 59 (1985) 576.
14 V. B. Lazarev, S. I. Berul and A. V. Salov, Troinye poluprovodnikovye soyedineniya v sistemakh A^I-B^V- C^{VI}, Nauka, Moskva 1982, p. 114.
15 J. Terpilowski, W. Gawel and A. Bogacz, Roczniki Chem., 46 (1972) 3.
16 W. Gawel, E. Zaleska and J. Terpilowski, J. Thermal Anal., 32 (1987) 227.
17 E. Zaleska and W. Gawel, Pol. J. Chem., to be published.
18 W. Gawel, B. Fuglewicz and E. Zaleska, Pol. J. Chem., in press.

Zusammenfassung — Mittels Differentialthermoanalyse, der Bestimmung der Abkühlungskurven und röntgendiffraktionsaufnahmen wurde das Phasengleichgewicht des Systemes Tl_2Te–Bi_2Te_3 untersucht. Die Ergebnisse ersterer beider Methoden wurden miteinander verglichen. Das für das System entwickelte Phasendiagramm weicht erheblich von drei vorangehend veröffentlichten Phasendiagrammen ab.

Резюме — С помощью определения кривой охлаждения, дифференциального термического анализа и рентгеноструктурных методов изучено фазовое равновесие в системе Tl_2Te–Bi_2Te_3. Полученные первыми двумя методами результаты сопоставлены. Установленная фазовая диаграмма значительно отличается от трех ранее опубликованных.