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**INTERMETALLIC PHASES OF THE  $A^I B^V X^{VI}_2$  TYPE  
IN THE  $Tl_2Se - Bi_2Se_3$  AND  $Tl_2Te - Bi_2Te_3$  SYSTEMS****FAZY MIĘDZYMETALICZNE TYPU  $A^I B^V X^{VI}_2$   
W UKŁADACH  $Tl_2Se - Bi_2Se_3$  I  $Tl_2Te - Bi_2Te_3$** 

Searching for new semiconductive materials focused interest of many scientists on ternary systems  $A^I - B^V - X^{VI}$  where  $A^I = Ag, Tl, Cu$ ;  $B^V = As, Sb, Bi$ ;  $X^{VI} = S, Se, Te$ . A special attention was paid to quasibinary systems of the type  $A^I_2 X^{VI} - B^V_2 X^{VI}_3$  in which many ternary compounds were formed. In the most of these systems two types of compounds occur of general formulae  $A^I B^V X^{VI}_2$  and  $A^I_9 B^V X^{VI}_6$ . From the review of the data on these compounds a question arises whether they are those of stoichiometric compositions or intermediate phases of variable composition.

The concentration cell EMF measurement method has been proposed as the best one to solve the problem. One of the most advantageous qualities of the method is a possibility to discriminate between solid phases of a berthollide and a daltonide type. Employing the method it has been shown that a compound formed in the middle concentration range of the systems  $Tl_2Se - Bi_2Se_3$  was a phase of variable composition of the daltonide type existing within a concentration range 2 mole % wide. This conclusion results from that the inflexion point on the concentration dependence of the EMF temperature coefficients occurred at 50.0 mole %  $Bi_2Se_3$ . Accordingly, to the compound a stoichiometric formula  $TlBiSe_2$  may be ascribed.

The  $Tl_2Te - Bi_2Te_3$  system was studied by several groups of investigators but their results differ considerably from one another. The divergences concern mainly nature of the compound  $TlBiTe_2$  formed in the system at 50.0 mole %  $Bi_2Te_3$ . From the considerations in the present work it follows that the only way of solution of the question is the concentration cell EMF measurement method.

W wyniku poszukiwań nowych materiałów półprzewodnikowych, wielu badaczy zainteresowało się układami trójskładnikowymi  $A^I - B^V - X^{VI}$  gdzie  $A^I = Ag, Tl, Cu$ ;  $B^V = As, Sb, Bi$ ;  $X^{VI} = S, Se, Te$ . Szczególną uwagę poświęcono układom kwazibinarom typu  $A^I_2 X^{VI} - B^V_2 X^{VI}_3$ , w których tworzą się liczne związki potrójne. W większości takich układów spotyka się dwa typy związków o ogólnych wzorach  $A^I B^V X^{VI}_2$  i  $A^I_9 B^V X^{VI}_6$ . Z przeglądu danych o tych związkach

powstaje pytanie czy są to związki o składach stechiometrycznych, czy też fazy pośrednie o zmiennym składzie?

Jako najlepszą metodę rozwiązania tego zagadnienia zaproponowaliśmy metodę pomiaru sił elektromotorycznych (SEM) ogniw stężeniowych. Jedną z najkorzystniejszych cech tej metody jest możliwość rozróżnienia między fazami typu bertolidów i daltonidów. Stosując tę metodę wykazano, że związek tworzący się w środkowej części zakresu stężeń układu  $Tl_2Se - Bi_2Se_3$ , jest fazą o zmiennym składzie typu daltonidu, istniejącą w zakresie stężeń o szerokości 2% molowych. Wniosek ten wypływa z faktu, że punkt przegięcia na krzywej zależności współczynników temperaturowych SEM od stężenia, przypada przy 50,0% mol.  $Bi_2Se_3$ . Wobec tego, temu związkowi można przypisać wzór stechiometryczny  $TlBiSe_2$ .

Układ  $Tl_2Te - Bi_2Te_3$  był badany przez kilka grup autorów ale ich wyniki różnią się znacznie między sobą. Rozbieżności dotyczą głównie natury związku  $TlBiTe_2$ , który tworzy się w tym układzie przy 50,0% mol.  $Bi_2Te_3$ . Z rozważań podanych w niniejszej pracy wynika, że jedyną metodą rozwiązania tego zagadnienia jest metoda pomiaru SEM ogniw stężeniowych.

## 1. Introduction

Considerable achievements of the contemporary computer techniques were possible due to the development of electronics which in turn depended on the progress in materials science. Much effort has gone into the searching for new semiconductive materials among compounds formed in the ternary systems  $A - B - X$  (where  $A$  and  $B$  were any metals and  $X$  was an element of VI main group of periodic system).

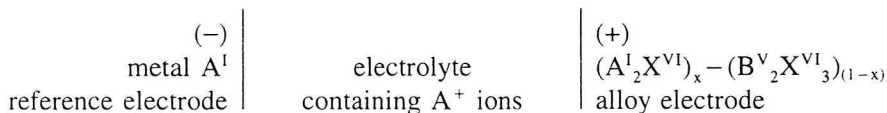
The greater is the difference in electronegativities of components of side binary systems (i.e.  $A - B$ ,  $B - X$  and  $A - X$ ) the higher the probability of a chemical compound formation. Accordingly, it is required that  $B$  and  $X$  should be elements of Vth (especially  $As$ ,  $Sb$ ,  $Bi$ ) and Vith ( $S$ ,  $Se$ ,  $Te$ ) group, respectively. This is the reason why during the last decades the interest of many researchers focused on the ternary systems of the type  $A^I - B^V - X^{VI}$ , where  $A^I$  was  $Ag$ ,  $Tl$  or  $Cu$ . The components of these systems form a lot of ternary compounds with various stoichiometric compositions. The compounds are formed in so called quasibinary systems of the type  $A^I_2X^{VI} - B^V_2X^{VI}_3$  which are polythermal cross-sections of the  $A^I - B^V - X^{VI}$  ternaries. The most important requirement is that the compounds  $A^I_2X^{VI}$  (e.g.  $Ag_2Te$ ,  $Tl_2Te$ ,  $Tl_2Se$ ) and  $B^V_2X^{VI}_3$  (e.g.  $As_2Te_3$ ,  $Sb_2Te_3$ ,  $Bi_2Se_3$ ) should melt congruently.

In the  $Tl_2(Se,Te) - (Sb,Bi)_2(Se,Te)_3$  quasibinary systems, among chemical combinations of different compositions, two main groups of ternary compounds with general formulae  $A^I B^V X^{VI}_2$  and  $A^I_9 B^V X^{VI}_6$  may be distinguished. Most of the compounds melt congruently with well-marked maximum on the liquidus line of respective system.

The aim of the present work is to elucidate whether the  $A^I B^V X^{VI}_2$  compounds may be considered as those of exactly stoichiometric compositions or as intermetallic phases of variable composition within a narrow stoichiometry range.

## 2. The EMF measurement method in studies on phases of variable composition

The nature of the compounds may be successfully studied employing an electrochemical method by electromotive force (EMF) measurements of appropriate concentration cells:



An essential problem lies in getting a sufficient number of experimental points within the probable existence range of the phase of variable composition. Available phase diagrams are often not precisely determined and, consequently, the phase of variable composition may be incorrectly taken for a chemical compound of stoichiometric composition. Besides, the EMF measurements are usually performed employing alloy

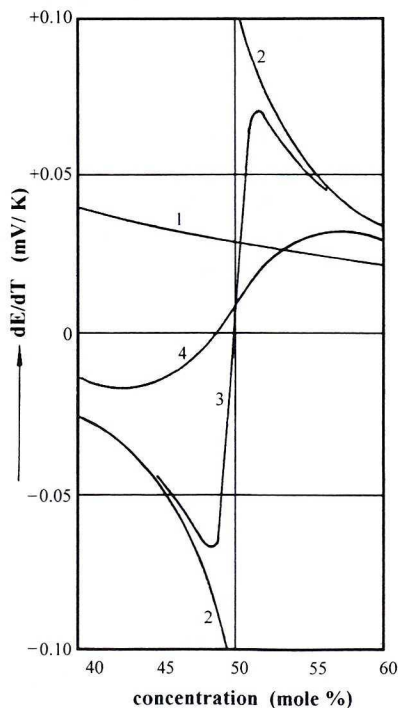


Fig. 1. Changes of  $dE/dT$  coefficients vs. concentration within the range of intermediate phase of variable composition (1 - berthollide, 2 - theoretical, 3 - daltonide, 4 - ordered phase) according to [1]

electrodes of successive compositions differing by a few mole percent from one another. Accordingly, the phase of variable composition may not be observed. An essential condition for the measurements to be successful is therefore the requirement that the

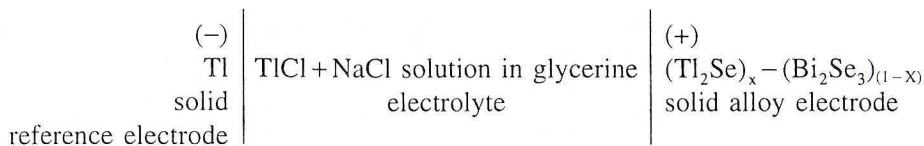
compositions of the alloy electrodes should vary by not more than 0.5 mole % of the least noble component.

The EMF values of the concentration cells containing electrodes prepared of alloys from the range of phase of variable composition enable the phase to be considered berthollide or daltonide. The properties of the berthollides resemble those of solid solutions while the daltonides are rather intermetallic phases corresponding to chemical compounds.

According to Terpiłowski [1] the berthollides are characterized by a continuous change of temperature coefficients  $dE/dT$  (where  $E = \text{EMF}$ ), and hence also the partial molar entropy of a least noble metal, with the change of the component content in the alloy. Instead, the daltonides are distinguished by a considerably abrupt change of the  $dE/dT$  coefficients from negative to positive values within the existence range of the intermediate phase. The longer the abruptness the higher ordering degree of atoms in a crystal structure of the phase. The inflexion point on the curve  $dE/dT$  vs. concentration (or on the entropy concentration dependence) determines a stoichiometric composition that may be ascribed to the phase of the daltonide type (Fig.1).

### 3. The $\text{Tl}_2\text{Se} - \text{Bi}_2\text{Se}_3$ quasibinary system

A good example of the investigations aimed at solving the problem whether the phase  $\text{TlBiSe}_2$  is a stoichiometric compound or an intermediate phase of variable composition, are the EMF measurements of cells of the type:



First information on the  $\text{Tl}_2\text{Se} - \text{Bi}_2\text{Se}_3$  system was obtained by Zbigli and Raevskii [2] who found the system to be a quasibinary one. The components of the system formed two compounds:  $\text{TlBiSe}_2$  and  $\text{Tl}_9\text{BiSe}_6$ , both of them congruently melting at temperatures 995 K and 795 K, respectively (Fig. 2). At the same time, from the phase diagram published by the authors for the system  $\text{Bi}_2\text{Se}_3 - 3\text{Tl}_2\text{Se}$  [2] it followed that both the compounds were rather phases of narrow but undetermined existence ranges.

Barchii et al. [3] reinvestigated the phase equilibria in the system  $\text{Bi}_2\text{Se}_3 - 3\text{Tl}_2\text{Se}$  and found the homogeneity region of  $\text{TlBiSe}_2$  to be not more than 4 mole % wide within the temperature range 867 – 946 K whereas at 523 K the region covered ca. 2 mole % only (Fig. 3).

Next studies on the same system by differential thermal analysis (DTA), EMF and microhardness, performed by Babanly et al. [4] were not aimed at refining data on the existence range of  $\text{TlBiSe}_2$ .

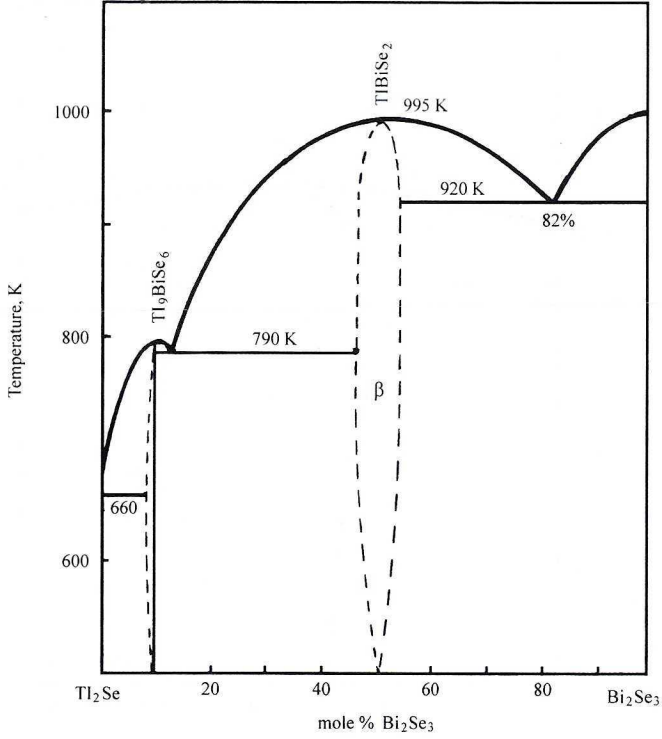


Fig. 2. Phase diagram for the Tl<sub>2</sub>Se - Bi<sub>2</sub>Se<sub>3</sub> system, according to [2]

We carried out the EMF measurements of the concentration cells given above, within the existence region of the TlBiSe<sub>2</sub> phase in the temperature range 353–493 K. All the EMF values showed a linear dependence on temperature:  $E = a + bT$  (where  $b = dE/dT$ ). The results are listed in Table. There are three only data reported in the table but it is

TABLE

Results of EMF measurements of the concentration cells containing Tl<sub>2</sub>Se - Bi<sub>2</sub>Se<sub>3</sub> alloy electrodes of the composition covering the existence region of the TlBiSe<sub>2</sub> phase within the temperature range 353–493 K

Composition (mole % Bi <sub>2</sub> Se <sub>3</sub> )	Equation $E = a + bT$ (mV)	E at 423 K (mV)
49.0	$520.0 - 0.3561 T$	369.4
50.0	$129.6 + 0.4397 T$	315.3
51.0	$161.4 + 0.2140 T$	251.9

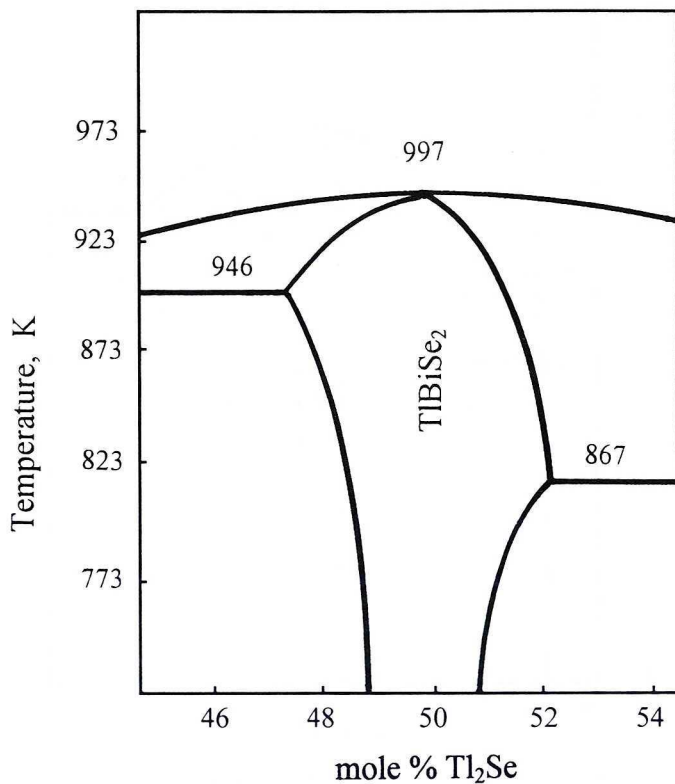


Fig. 3. Phase diagram (fragment) for the  $\text{Tl}_2\text{Se} - \text{Bi}_2\text{Se}_3$  system, according to [3]

enough to derive a conclusion on the examined phase. As it follows from the table the EMF values at 423 K ( $E_{423}$ ) decrease with increasing  $\text{Tl}_2\text{Se}$  content while the temperature coefficients  $b$  vary from negative to high positive value whereupon they decrease. Such behaviour is characteristic of daltonide type phases [1]. The concentration dependence of the  $b$  value shows an inflexion point at the composition to which a stoichiometric formula may be ascribed. In this case the inflexion occurs at 50.0 mole %  $\text{Bi}_2\text{Se}_3$ , accordingly, the formula is  $\text{TlBiSe}_2$ .

#### 4. The $\text{Tl}_2\text{Te} - \text{Bi}_2\text{Te}_3$ quasibinary system

The system was studied many times by different authors (Fig. 4). According to Berg and Abdulmanov [5] in the system two ternary compounds are formed:  $\text{TlBiTe}_2$  and  $\text{Tl}_9\text{BiTe}_6$ , both of them congruently melting. Popovich et al. [6] and Babanly et al. [7, 8] performed next studies on the system. In [5] and [7] it was stated that the compound  $\text{TlBiTe}_2$  melts congruently whereas according to [6] it undergoes a decomposition. In [6] and [7] it is considered a phase of variable composition. In paper [3] a fragment of the phase diagram for the system  $\text{Bi}_2\text{Te}_3 - 3\text{Tl}_2\text{Te}$  was reported from which it appears that  $\text{TlBiTe}_2$  is a phase of variable

composition 2.5 mole % wide at 812 K while at lower temperature (ca. 523 K) the width decreases to 1.3 mole %, the melting point being 851 K at the stoichiometric composition. Pradel et al. [9] studied another system BiTe – TlTe and found two intermetallic phases:  $Tl_{1-x}Bi_{1+x}Te_2$  ( $x = 0.06$ ) and  $Tl_{1-y}Bi_{1+y}Te_2$  ( $y = 0.2$ ). The former is a non-stoichiometric phase to which many authors ascribe formula  $TlBiTe_2$ , the latter is a high-temperature phase one, which melts incongruently at 688 K. The most recent studies on the system under consideration were performed employing DTA, common thermal analysis (TA) and X-ray diffraction [10] and EMF [11]. Maximum on the liquidus line was an indicative of the phase of composition  $Tl_{0.83}Bi_{1.06}Te_2$  while the compound  $TlBiTe_2$  appeared to be incongruently melting at 793.2 K.

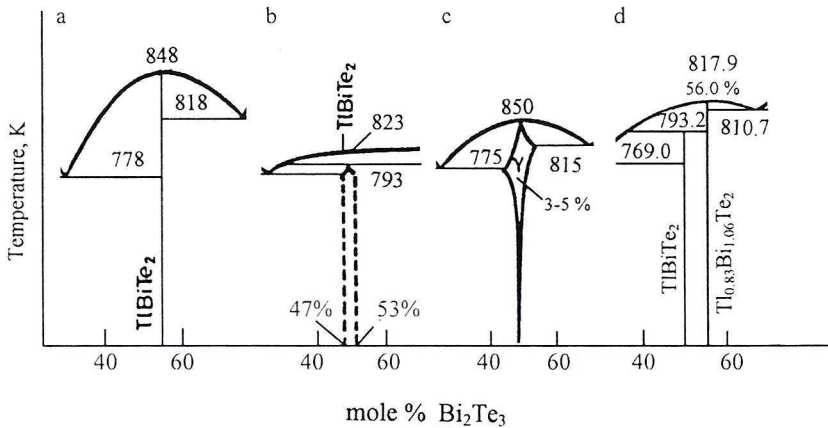


Fig. 4. Phase equilibria within the middle concentration range of the  $Tl_2Te - Bi_2Te_3$  system, according to different authors: a – [5], b – [6], c – [7], d – [10] (no temperature proportions are kept between a–d figures)

From the review of the data on the system  $Tl_2Te - Bi_2Te_3$  in the vicinity of the  $TlBiTe_2$  phase it follows that they considerably differ from one another. The discrepancies concern three essential problems:

- 1) what is the melting point of the phase  $TlBiTe_2$ ?
- 2) what is the nature of the melting process: is it congruent or incongruent?
- 3) is  $TlBiTe_2$  phase of variable composition or a stoichiometric compound?

Taking former discussion into account, it seems that the answer to the last of the three questions may be found by employing the concentration cell EMF measurement method.

The last part of the present work is aimed at encouraging further experimental and theoretical research on phase relations within the middle region of the  $Tl_2Te - Bi_2Te_3$  system.

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