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# SOLID-PHASE EQUILIBRIA IN THE $TlBiTe_2$-$TlTbTe_2$ SYSTEM

**G.I. Alakbarzade**

*National Aerospace Agency of the Azerbaijani Republic*
*e-mail: alakbarzadegi@gmail.com*

***Abstract:*** *The solid-phase equilibria in the $TlBiTe_2$-$TlTbTe_2$ system were studied by using the powder X-ray diffraction method. Despite isostructural character of the starting compounds (hexagonal structure, Sp. Gr. R-3m), it was shown that the system is characterized by a limited mutual solubility of the initial components. The solubility based on $TlBiTe_2$ reaches ~45 mol%, and base on $TlTbTe_2$ is about 22 mol%. The lattice parameters of the intermediate solid solutions were calculated using the powder roentgenograms. The solid solutions obtained are of great interest as potential magnetic topological insulators.*

***Keywords:*** *$TlBiTe_2$-$TlTbTe_2$ system, solid solutions, powder X-ray diffraction, topological insulator.*

## 1. Introduction

Multicomponent heavy metal chalcogenides, including thallium, are of great interest as prospective functional materials with different properties such as magnetic, optical, thermoelectric[1-14]. Moreover, new characteristics of topological effects have been realized experimentally in chalcogenides such as $PbBi_6Te_{10}$, $TlBiX_2$, $Pb_{1-x}Sn_xTe$ [14-17].

Purposeful changes in the composition of the above compounds can lead to optimization of functional properties of the above materials. For this, it is necessary to study systems consisting of structural analogs, since it can be expected that they form wide areas of solid solutions [18-20].

Earlier, we investigated some systems, characterized by formation of variable composition phases: $Tl_4PbTe_3$-$Tl_9GdTe_6$-$Tl_9BiTe_6$ [21], $Tl_9SbTe_6$-$Tl_9Gd(Tb)Te_6$ [22].

The aim of the present work is the investigation of the mutual solubility of components in the $TlBiTe_2$-$TlTbTe_2$.

$TlBiTe_2$ melts congruently at 820 K [23] and crystallizes in a hexagonal structure (Sp. Gr.R-$\bar{3}$m) with parameters: $a$=4.526; $c$=23.12 Å; z = 3 [24, 25].

$TlTbTe_2$ compound is structural analogue of $TlBiTe_2$ with lattice parameters: $a$ = 4.416; $c$ = 24.27 Å; z = 3 [26].

The isostructural character of initial compounds makes it possible to expect the formation of wide areas of substitutional solid solutions between them.

## 2. Experiments and results

### 2.1. Materials and synthesis

Initial compounds of $TlBiTe_2$ and $TlTbTe_2$ were synthesized by direct melting of high purity elements. The provenance and purity of the elements used in this investigation are shown in Table 1.

**Table 1.** Provenance and purity of the materials used in this investigation

| Chemical | Mass fraction of Purity | Source | CAS No | Form | Purification and purity analysis methods |
|---|---|---|---|---|---|
| Bismuth | 0.99999 | Alfa Aesar (Germany) | 7440-69-9 | broken ingots | as stated by the supplier |
| Thallium | 0.99999 | Alfa Aesar (Germany) | 7440-28-0 | rod | -"- |

| | | | | | |
|---|---|---|---|---|---|
| Tellurium | 0.9999 | Alfa Aesar (Germany) | 13494-80-9 | broken ingots | -"- |
| Terbium | 0.999 | Alfa Aesar (Germany) | 7440-27-9 | pieces | -"- |

The synthesis of initial components was carried out in an evacuated (~ $10^{-2}$Pa) quartz ampoule. To achieve an equilibrium state, after synthesis, the intermediate ingot of the $TlBiTe_2$ was subjected to heat treatment 700 K for 500 h and cooled in the furnace.

The synthesis of the $TlTbTe_2$ was carried out by means of the ceramic method. First, the quartz tube was heated slowly to 1000 K in a furnace, allowed to remain at 1000 K for 100 h, and then slowly cooled down to room temperature. An intermediate ingot of $TlTbTe_2$ was crushed in an agate mortar, pressed into pellets and then, the heating procedure was repeated at 900 K for 500 h.

Intermediate alloys of the $TlBiTe_2$-$TlTbTe_2$ system were also synthesized by the ceramic method by melting of the pre-synthesized ternary compounds at 1000 K in evacuated quartz tubes with subsequent thermal annealing at 750 K (1000h.). Then the samples were ground, thoroughly mixed, pressed into tablets and annealed under the same conditions.

### 2.2. Methods

We used the X-ray diffraction analysis (Bruker D8 diffractometer, $CuK_\alpha$ radiation) in order to control the purity of the synthesized compounds. The analysis was carried out between $10° \leq 2\theta \leq 70°$ at a room temperature. The lattice parameters of initial compounds and intermediate alloys were calculated by indexing powder patterns using Topas V3.0 software (Table 2). Calculated lattice parameters of $TlBiTe_2$ and $TlTbTe_2$ were close to the corresponding literature data [24, 26].

## 3. Results and discussion

Fig.1 presents powder X-ray diffraction patterns of some annealed intermediate alloys. The diffraction patterns of alloys containing 60, 80 and 90 mol% $TlBiTe_2$ are qualitatively similar to those for pure $TlBiTe_2$ while alloy 20 mol.% $TlBiTe_2$ has a diffraction pattern similar to $TlTbTe_2$. X-ray diffraction patterns of alloys with compositions of 30 mol% $TlBiTe_2$ consist of a set of diffraction lines of hexagonal phases with both initial compounds.

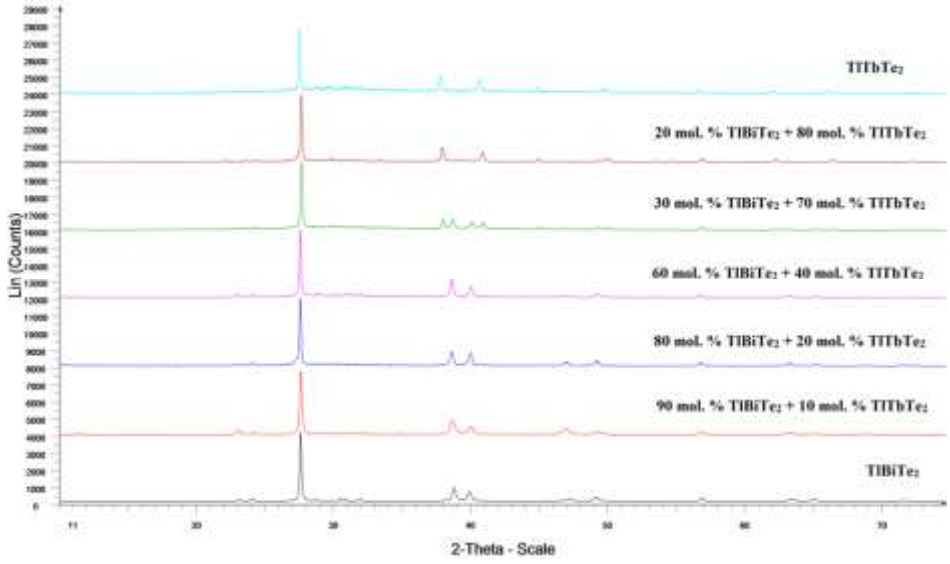


**Fig.1. P**owder X-ray diffraction patterns of some annealed intermediate alloys of the $TlBiTe_2$-$TlTbTe_2$ system

In order to determine the mutual solubility of initial compounds, we constructed concentration dependences of the hexagonal lattice parameters (Table 2, Fig. 2). These dependencies have fracture points at compositions of ~22 and ~45 mol% $TlBiTe_2$ which correspond to limiting compositions of α- and β-solid solutions based on $TlTbTe_2$ and $TlBiTe_2$, respectively. In the α + β two-phase region, the lattice periods of the two coexisting phases have constant values regardless of alloys' overall composition. Within the homogeneity region of the α- and β phases, the lattice constants is a linear function of the composition.

**Table 2. Phase compositions and crystallographic parameters of $TlBiTe_2$-$TlTbTe_2$ phases**

| Compositions, % $TlBiTe_2$ | Phase compositions | Hexagonal lattice parameters, Å |
|---|---|---|
| 0 ($TlTbTe_2$) | α | *a* =4.416; *c* = 24.27 Å; z = 3 |
| 10 | α | *a* =4.431; *c* = 24.140 |
| 20 | α | *a* =4.443; *c* = 24.043 |
| 30 | α+β | α – *phase: a* =4.446; *c* =24.001<br>β – *phase: a* =4.478; *c* =23.441 |
| 40 | α+β | α – *phase:a* = 4.448; *c* =23.999<br>β – *phase: a* = 4.483; *c* =23.501 |
| 50 | α+β | α – *phase:a* =4.447; *c* =24.025<br>β – *phase: a* =4.479; *c* =23.482 |
| 60 | β | *a* =4.488; *c* =23.581 |
| 70 | β | *a* =4.495; *c* =23.483 |
| 80 | β | *a* =4.506; *c* =23.374 |
| 90 | β | *a* =4.518; *c* =23.542 |
| 100 | β | *a* =4.526; *c* =23.12 Å; z = 3 |

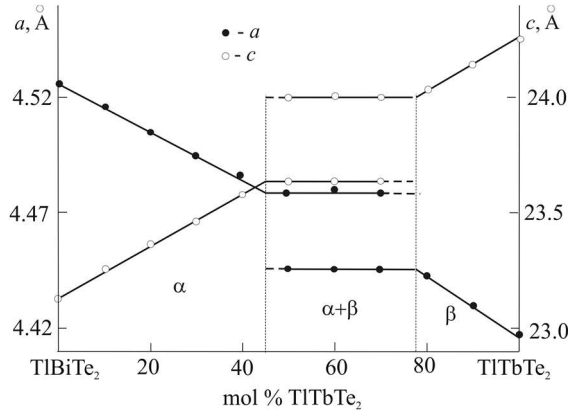


**Fig.2.** Concentration dependences of hexagonal lattice parameters of some annealed alloys of the $TlBiTe_2$-$TlTbTe_2$ system

It should be noted that, according to the data of [27], in the $TlSbTe_2$-$TlTbTe_2$ system, the solubility based on initial compounds reached 30 and 10 mol%, respectively. Somewhat higher mutual solubility in the $TlBiTe_2$-$TlTbTe_2$ system seems to be related to closer crystallographic radii of the Tb (1.063Å) and Bi (1.17Å) than that between Tb (1.063Å) and Sb (0.9Å) [28].

## 4. Conclusion

The formation of a wide area of solid solutions based on $TlBiTe_2$ (45 mol%) is established in the $TlBiTe_2$-$TlTbTe_2$ system based on the results of the powder X-ray diffraction analysis. The solubility based on $TlTbTe_2$ does not exceed 22 mol%. The crystal lattices parameters of the

obtained solid solutions are calculated. The solid solutions obtained are of great interest as potential magnetic topological insulators.

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## *$TlBiTe_2$-$TlTbTe_2$ SİSTEMİNDƏ BƏRKFAZA TARAZLIQLARI*

***Q.İ. Ələkbərzadə***

*Azərbaycan milli aerokosmik agentliyi*
*e-mail: alakbarzadegi@gmail.com*

*İlk dəfə olaraq $TlBiTe_2$-$TlTbTe_2$ sistemində bərkfaza tarazlıqları rentgenfaza analizi üsulu ilə tədqiq olunmuşdur. Ovuntu rentgenoqramları əsasında təyin olunmuş qəfəs parametrlərinin tərkibdən asılılıq qrafikləri əsasında müəyyən edilmişdir ki, $TlBiTe_2$ əsasında həllolma ~45 mol.%, $TlTbTe_2$ əsasında isə 22 mol% təşkil edir. Alınmış bərk məhlullar potensial maqnit xassəli topoloji izolyator materialları kimi maraq doğurur.*

***Açar sözlər**: $TlBiTe_2$-$TlTbTe_2$ sistemi, bərk məhlullar, rentgenfaza analizi, topoloji izolyator.*

# *ТВЕРДОФАЗНЫЕ РАВНОВЕСИЯ В СИСТЕМЕ $TlBiTe_2$-$TlTbTe_2$*

***Г.И. Алекберзаде***

*Национальное аэрокосмическое агентство Азербайджана*
e-mail: alakbarzadegi@gmail.com

*Впервые методом рентгенфазового анализа изучены твердофазные равновесия в системе $TlBiTe_2$-$TlTbTe_2$. Установлено, что несмотря на изоструктурность исходных соединений (гексагональная структура, пр.гр R-3m), данная система характеризуется ограниченной взаимной растворимостью компонентов. Растворимость на основе $TlBiTe_2$ составляет ~45 мол%, а на основе $TlTbTe_2$ - 22 мол%. На основании порошковых дифрактограмм рассчитаны параметры кристаллической решетки твердых растворов.*

***Ключевые слова:*** *система $TlBiTe_2$-$TlTbTe_2$, твердые растворы, порошковая рентгенография, топологический изолятор.*