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ROENTGENOGRAPHIC INVESTIGATION OF SOLID-PHASE EQUILIBRIA IN THE $TlSbTe_2$–$TlTbTe_2$ SYSTEM

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The solid-phase equilibria in the $TlSbTe_2$–$TlTbTe_2$ system been forts studied by using the powder X-ray diffraction method. It was established that despite the isostructural character of the starting compounds (hexagonal structure, *Sp. Gr. R-3m*), the system is characterized by a limited mutual solubility of the components. The solubility based on $TlSbTe_2$ reaches ~30 mol%, and base on $TlTbTe_2$ is about 10 mol%. The lattice parameters of solid solutions are calculated based on powder roentgenograms.

Keywords: *$TlSbTe_2$–$TlTbTe_2$ system, solid solutions, powder X-ray diffraction, crystal lattice.*

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Introduction

Complex chalcogenides of heavy metals, including thallium, have attracted great interest for decades as functional materials which possess thermoelectric, optical, photoelectric and other properties [1–9]. Recent studies have shown that they are of interest as topological insulators [9–13] and Weyl semimetals [14]. Some of them have photoconductivity and are promising for use as γ- and X-ray detectors [15, 16].

Optimization of the functional properties of the above-mentioned materials can be achieved by directed changing of their composition. This, in turn, requires the study of systems consisting of structural analogs, since they can be expected to form wide areas of solid solutions [17–19].

In this paper, we present the results of X-ray diffraction studies of solid-phase equilibria in the $TlSbTe_2$–$TlTbTe_2$ system.

Earlier, we investigated some similar systems, in which new phases of variable composition were revealed: Tl_9BiTe_6–Tl_9ErTe_6 [20], Tl_2Te–Sb_2Te_3–Bi_2Te_3 [21], $3Tl_2S+Sb_2Te_3 \leftrightarrow 3Tl_2Te+Sb_2S$ [22], $3Tl_2Se+Sb_2Te_3 \leftrightarrow 3Tl_2Te+Sb_2Se_3$ [23].

$TlSbTe_2$ compound melts with decomposition in a peritectic reaction at 753 K [24] and crystallizes in a hexagonal structure (*Sp. Gr.R-3m*) with parameters a = 4.425, c = 23.303Å, z = 3 [25].

$TlTbTe_2$ compound is structural analogue of $TlSbTe_2$ and has following lattice parameters: a = 4.416, c = 24.27 Å, z = 3 [26].

The thermodynamic properties of the $TlSbTe_2$ compound were studied in the [27].

Experiments and results

Initial compounds $TlSbTe_2$ and $TlTbTe_2$ were synthesized by direct melting of high purity elements (at least 99.999 at.%). All elements were purchased from Alpha Aesar. The synthesis of $TlSbTe_2$ was carried out in evacuated (~10^{-2}Pa) quartz ampoule at 1000 K, followed thermal annealing at 700 K for 200 h. To synthesize $TlTbTe_2$, the ampoule 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. In order to complete the reaction, the intermediate ingot of $TlTbTe_2$ was crushed in a dry box, pressed into pellets and then, the heating procedure was repeated at 900 K for 500 h.

The purity of the synthesized compounds was controlled by the X-ray diffraction analysis by using the Bruker D8 diffractometer (CuK_α radiation), between $10^0 \leq 2\theta \leq 70^0$ at room temperature. The unit cell constant of initial compounds and intermediate alloys were calculated by indexing of powder patterns using Topas V3.0 software (Table). Calculated lattice parameters of $TlSbTe_2$ and $TlTbTe_2$ were close to literature data [24, 25].

Alloys of the $TlSbTe_2$–$TlTbTe_2$ system were prepared by melting the initial compounds in evacuated (~10^{-2}Pa) quartz ampoules with subsequent thermal annealing at 700 K for 600 h.

The powder X-ray diffraction patterns of some annealed alloys are presented on Figure 1. As can be seen, the diffraction patterns of alloys

containing 70 and 90 mol% $TlSbTe_2$ are qualitatively similar to those for pure $TlSbTe_2$. X-ray diffraction patterns of alloys with compositions of 20, 50 and 70 mol% $TlSbTe_2$ consist of a set of diffraction lines of both phases.

The concentration dependences of the lattices parameters (Table, Figure 2) were constructed in order to determine the mutual solubility of the initial compounds. These dependencies have fracture points at compositions of ~10 and ~70 mol% $TlSbTe_2$, which correspond to the limiting compositions of α- and β-solid solutions based on $TlTbTe_2$ and $TlSbTe_2$, respectively. It should be noted that in the α +85 β two-phase region, the lattice periods of the two coexisting phases have constant values regardless of the overall composition of the alloys, while within the homogeneity region of the β-phase the lattice parameters are a linear function of the composition, i.e. obey the Vegard's law.

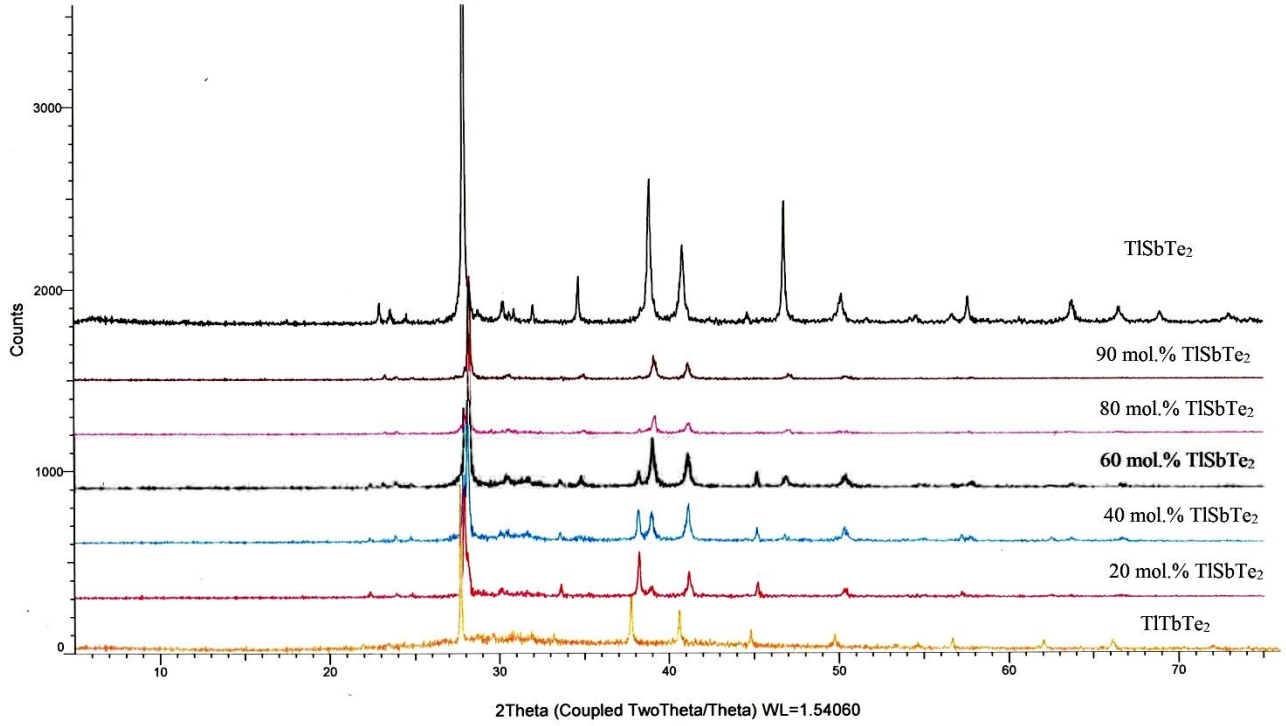

Fig. 1. The powder X-ray diffraction patterns of some annealed alloys of the $TlSbTe_2$–$TlTbTe_2$ system.

Phase compositions and crystallographic parameters of phases of the $TlSbTe_2$–$TlTbTe_2$

Compositions % $TlSbTe_2$	Phase compositions	Rhombic lattice parameters, Å
0 ($TlTbTe_2$)	α	*a* = 4.4245(4); *c* = 23.3025(20)
10	α	*a* = 4.42375 (4); *c* = 23.3751(21)
20	α+β	α-*phase: a* = 4.42374 (4), *c* = 23.3759(21) β-*phase: a* = 4.4180(5), *c* = 24.0061(20)
40	α+β	α-*phase: a* = 4.42376 (5), *c* = 23.3747(21) β-*phase: a* = 4.4183(4), *c* = 24.0024(20)
60	α+β	α-*phase: a* = 4.42375 (5), *c* = 23.3753(21) β-*phase: a* = 4.4184(5), *c* = 24.0052(20)
70	β	*a* = 4.4180(5), *c* = 23.9991(20)
80	β	*a* = 4.4173(4), *c* = 24.1754(20)
90	β	*a* = 4.4165(5), *c* = 24.2516(21)
100	β	*a* = 4.4155(5), *c* = 24.2682(21)

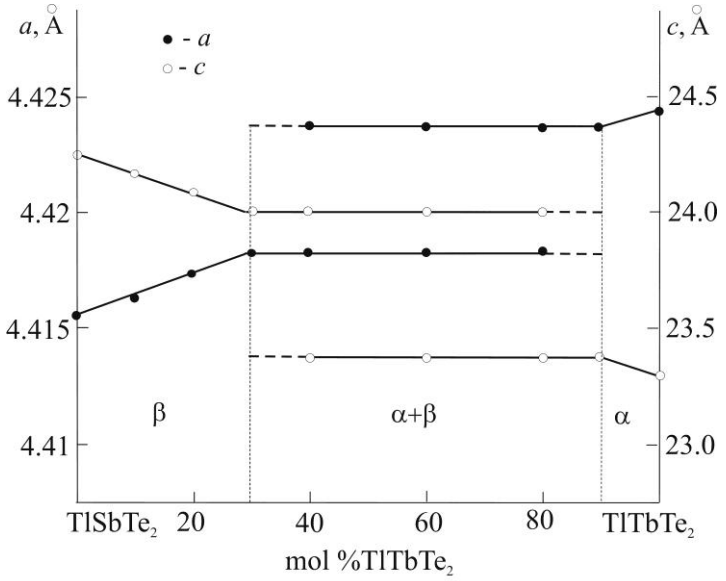

Fig. 2. The concentration dependences of the lattices parameters of some annealed alloys of the $TlSbTe_2$–$TlTbTe_2$ system.

Conclusion

Based on the XRD results, the formation of a wide area of solid solutions is the of on $TlSbTe_2$ (70 mol%) is established in the $TlSbTe_2$–$TlTbTe_2$ system. The solubility based on $TlTbTe_2$ is much lower and does not exceed 10 mol%. The crystal lattices parameters of the obtained solid solutions are determined. The solid solutions obtained are of practical interest as potential topological insulators.

Acknowledgments

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$TlSbTe_2$–$TlTbTe_2$ SİSTEMİNDƏ BƏRKFAZA TARAZLIQLARIN RENTGENOQRAFIJK TƏDQİQİ

G.İ.Ələkbərzadə

İlk dəfə olaraq $TlSbTe_2$–$TlTbTe_2$ sistemində bərkfaza tarazlıqları rentgenfaza analizi üsulu ilə tədqiq olunmuşdur. Müəyyən edilmişdir ki, ilkin birləşmələr eyni kristallik quruluşa (heksaqonal *F.q. R-3m*) malik olsa da, sistemdə ilkin komponentlərin məhdud qarşılıqlı həll olurlar. $TlSbTe_2$ əsasında həllolma ~70 mol.%, $TlTbTe_2$ əsasında isə 10 mol% təşkil edir. Ovuntu rentgenoqramları əsasında bərk məhlulların qəfəs parametrləri hesablanmışdır.

***Açar sözlər**: $TlSbTe_2$–$TlTbTe_2$ sistemi, bərk məhlullar, rentgenfaza analizi, kristal qəfəs.*

РЕНТГЕНОГРАФИЧЕСКОЕ ИССЛЕДОВАНИЕ ТВЕРДОФАЗНЫХ РАВНОВЕСИЙ В СИСТЕМЕ $TlSbTe_2$–$TlTbTe_2$

Г.И.Алекберзаде

Впервые методом рентгенфазового анализа изучены твердофазные равновесия в системе $TlSbTe_2$–$TlTbTe_2$. Установлено, что несмотря на изоструктурность исходных соединений (гексагональная структура, *пр.гр R-3m*), данная система характеризуется ограниченной взаимной растворимостью компонентов. Растворимость на основе $TlSbTe_2$ составляет ~70 мол%, а на основе $TlTbTe_2$ – 10 мол.%. На основании порошковых дифрактограмм рассчитаны параметры кристаллической решетки твердых растворов.

***Ключевые слова:** система $TlSbTe_2$–$TlTbTe_2$, твердые растворы, порошковая рентгенография, кристаллическая решетка.*