UDC 544.344.3:546.289'24

PHASE EQUILIBRIA IN THE TlTe-Tl₉ErTe₆ SYSTEM

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Received 01.07.2019

Accepted 02.10.2019

Phase equilibria in the TlTe-Tl₉ErTe₆ system were experimentally studied using differential thermal analysis, powder X-ray diffraction. The system was shown to be non-quasibinary due to the incongruent nature of the melting of both starting compounds, but stable under the solidus. Limited solid solutions (~5 mol%) based on Tl₉ErTe₆ are revealed in the system.

Keywords: thallium-erbium tellurides, phase equilibria, polythermal section.

doi.org/10.32737/0005-2531-2020-2-74-77

Introduction

Heavy *p*-elements chalcogenides attract a lot of attention of scientists due to their functional properties, such as thermoelectric, photoelectric, optical, magnetic et al. properties [1–7]. Furthermore, despite the toxicity of thallium, complex thallium chalcogenides are closely monitored as topological insulators [6, 8, 9], Weyl semimetals [10], photo-, X-ray and gamma radiation detectors [11–13], as well as thermoelectric materials [4, 14, 15]. Doping by rare-earth elements can improve their properties and give them additional functionality, such as the magnetic properties [16, 17].

This work is a continuation of the studies on the phase equilibria in the ternary systems based on thallium-rare earth elements tellurides.

Earlier authors of [18–20] showed the formation of compounds of the Tl₉LnTe₆ type (Ln-Ce, Nd, Sm, Gd, Tm, Tb), and determined the nature and temperature of their melting as well as the crystal lattice parameters. According to [21], unlike the indicated lanthanides, ytterbium does not form a compound of the Tl₉LnTe₆ type. The authors of [16, 17] confirmed the data of [18–20] and investigated the crystal structures and thermoelectric and magnetic properties of some compounds of the Tl₉LnTe₆ type.

The results of the phase equilibria investigations in the Tl₂Te-Tl₅Te₃-Tl₉LnTe₆ (Ln – Gd, Tb, Sm, Er, Tm) [22–26] systems showed

that the studied systems are characterized by the formation of a wide field of δ -solid solutions with the Tl₅Te₃ structure, occupying of the significant part of the concentration triangle.

The aim of the present work is the investigation of the phase relations in the TlTe-Tl₉ErTe₆ system.

TlTe and Tl₉ErTe₆ compounds melt incongruently at 573 [27] and 705 K [28] and have the tetragonal structure (Sp.Gr.*I4/mcm*) with the following parameters: $a = 12.953$, $c = 6.173$ Å, $z = 16$ [29]; to $a = 8.8501$; $c = 12.9524$ Å, $z = 2$ [28].

Experimental part

Starting compound TlTe was synthesized by melting of high purity elements in evacuated ($\sim 10^{-2}$ Pa) quartz ampoules at 750 K with following slow cooling. After fusion, given the incongruent nature of the melting of this compound, the intermediate ingot was annealed at 550 K for 500 h in order to achieve a homogeneous state.

Obtaining homogeneous Tl₉ErTe₆ requires the development of a special synthesis technique, which is described in detail in [28].

The purity of the synthesized compounds was checked by differential thermal analysis (DTA) and powder X-ray diffraction (XRD) techniques.

Alloys of the TlTe-Tl₉ErTe₆ system were prepared by melting the stoichiometric quantities of the TlTe and Tl₉ErTe₆ in evacuated silica

tubes at 1000 K in a tube furnace. After the synthesis, alloys were powdered in an agate mortar, pressed into pellets and annealed at 550 K within 500 h. In order to prevent a reaction between the ampoule walls and erbium, the silica tubes were coated with a carbon film via the decomposition of ethanol.

DTA and XRD analyses were employed to analyze the samples.

DTA was performed using a NETZSCH 404 F1 Pegasus differential scanning calorimeter. The crystal structure was analyzed by a powder X-ray diffraction technique at room temperature using a Bruker D8 diffractometer utilizing $\text{CuK}\alpha$ -radiation within $2\theta = 10$ to 70° .

Results and discussion

Based on DTA data the phase diagram of the TlTe–Tl₉ErTe₆ system was plotted (Table and Figure 1).

DTA results of the alloys of the TlTe–Tl₉ErTe₆ system

Composition, mol % Tl ₉ ErTe ₆	Thermal effects, K
0(TlTe)	573, 635
10	570–615, 650
20	570–640
40	570–665
60	570–680, 1050
80	570–690, 1090
90	570–700, 1110
100	705, 1120

Fig. 1. Phase diagram of the TlTe–Tl₉ErTe₆ system.

TlTe–Tl₉ErTe₆ system is non-quasibinary since both compounds melt with decomposition by the peritectic reactions (Figure 1). As can be seen, the section is not quasibinary, what is associated with the incongruent nature of the melting of both initial compounds. Liquidus consists of two curves of the primary crystallization of the δ-phase (0–20 mol% Tl₉ErTe₆) and TlErTe₂ (80–100 mol% Tl₉ErTe₆). Below the liquidus, in the composition interval of 25–100 mol % Tl₉ErTe₆ and temperatures of 650–705 K, a curve with a monovariant peritectic equilibrium $L + \text{TlErTe}_2 \leftrightarrow \delta$ is observed (Figure 1, p₁K curve). In the region of richer TlTe, this curve continues under the liquidus curve up to the composition of 3 mol% Tl₉ErTe₆. This indirectly indicates the transformation of the peritectic reaction $L + \text{TlErTe}_2 \leftrightarrow \delta$ into the eutectic $L \leftrightarrow \text{TlErTe}_2 + \delta$ (KU curve) at point K. Near TlTe in a narrow range of compositions (0–3 mol% Tl₉ErTe₆), the peritectic equilibrium $L + \delta \leftrightarrow \text{TlTe}$ (curve p₂U) is take place. The horizontal (U) at 570 K corresponds to the invariant transition reaction $L + \text{TlErTe}_2 \leftrightarrow \text{TlTe} + \delta$. As a result of this reaction, a two-phase region TlTe+δ is formed, which ensures the stability of this section below the solidus.

The results of X-ray phase analysis confirm the constructed phase diagram. The powder XRD results of annealed alloys along this section showed their two-phase state: TlTe + δ (solid solutions based on Tl₉ErTe₆). For example, Figure 2 shows a powder X-ray diffraction pattern of an alloy with a composition of 60 mol% Tl₉ErTe₆. As is seen, it consists of reflection lines of two initial compounds. Reflexes of other phases were not detected.

Conclusion

Phase relations in the TlTe–Tl₉ErTe₆ section of the Tl–Er–Te ternary system were experimentally studied based on differential thermal analysis and powder X-ray diffraction technique results. It was found that this section is generally non-quasibinary, but stably below solidus and forms limited (~5 mol%) solid solutions based on Tl₉ErTe₆.

Fig.2. Powder XRD pattern of the alloy with composition 60 mol% Tl_9ErTe_6 .

Acknowledgments

The work has been carried out within the framework of the international joint research laboratory “Advanced Materials for Spintronics and Quantum Computing” (AMSQC) established between Institute of Catalysis and Inorganic Chemistry of ANAS (Azerbaijan) and Donostia International Physics Center (Basque Country, Spain) and partially supported by the Science Development Foundation under the President of the Republic of Azerbaijan, a grant EİF/MQM/Elm-Tehsil-1-2016-1(26)-71/01/4-M-33.

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TlTe–Tl₉ErTe₆ SİSTEMİNDƏ FAZA TARAZLIĞI

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TlTe–Tl₉ErTe₆ sistemi differensial-terniki və rentgenfaza analizi üsulları ilə öyrənilmiş, onun faza diaqramı qurulmuşdur. Göstərilmişdir ki, sistem hər iki ilkin birləşmənin inkongruent əriməsi səbəbindən qeyri-kvazibinardır, lakin solidusdan aşağıda stabildir və Tl₉ErTe₆ əsasında 5 mol%-ə qədər bərk məhlul əmələ gətirir.

Açar sözlər: tallium-erbiyum telluridləri, faza tarazlığı, politermik kəsiklər.

ФАЗОВЫЕ РАВНОВЕСИЯ В СИСТЕМЕ TlTe–Tl₉ErTe₆

И.Ф.Мехдиева

Фазовые равновесия в системе TlTe–Tl₉ErTe₆ изучены методами дифференциально-термического и рентгенофазового анализов и построена диаграмма состояния. Показано, что система неквазибинарна в силу инконгруэнтного характера плавления обоих исходных соединений, но стабильна ниже солидуса и характеризуется образованием ~5мол% твердых растворов на основе Tl₉ErTe₆.

Ключевые слова: теллуриды таллия-эрбия, фазовые равновесия, политермическое сечение.