

S.Z. Imamaliyeva

Tl₄GdTe₃ and Tl₄DyTe₃ – Novel Structural Tl₅Te₃ Analogues

*Institute of Catalysis and Inorganic Chemistry named after acad. M. Nagiyev, Azerbaijan National Academy of Sciences,
Baku, Azerbaijan, samira9597a@gmail.com*

The novel ternary compounds Tl₄GdTe₃ and Tl₄DyTe₃ - structural analogs of Tl₅Te₃ (Sp.gr.*I4/mcm*), were synthesized and identified by DTA and XRD methods. From powder XRD data, their crystal lattices parameters were calculated: $a = 8.8766(7)$, $c = 13.0846(13)$ Å, $Z = 4$ (Tl₄GdTe₃); $a = 8.8588(9)$, $c = 13.0524(16)$ Å, $Z = 4$ (Tl₄DyTe₃). It was found that the synthesized compounds melt with decomposition by peritectic reactions at 770 and 767 K, respectively.

Keywords: thallium-REE tellurides, differential-thermal analysis, powder X-ray diffraction, crystal lattice.

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Introduction

The process of discovering and developing new materials is currently being carried out in the direction of searching for complex structural analogs of already known compounds with the same properties and optimization of their characteristics by direction doping [1-3].

Among thallium chalcogenides, Tl₅Te₃ is one of the most suitable matrix compounds for the fabrication of new ternary compounds - structural analogs and multicomponent phases. According to the phase diagram of the Tl-Te system, Tl₅Te₃ compound melts congruently at 725 K and is a phase of variable composition with a wide range of homogeneity (34.5 - 38 at% Te) [4, 5]. This compound crystallizes in a tetragonal structure of the Cr₅B₃ type (Sp.gr.*I4/mcm*) [6, 7]. The structural features of this compound are discussed in detail in [3, 6]. It was shown that thallium atoms occupy two different positions in the Tl₅Te₃ crystal lattice and exhibit +1 and +3 oxidation states (Fig. 1). Some thallium atoms (Tl2) are located in octahedral voids, and the other part (Tl1) - in voids of the tellurium anionic framework. Substitution of half of the thallium atoms located in the centers of octahedra (Tl2) with B+3 cations leads to the formation of Tl₉BTe₆ -type compounds, while their complete replacement with A+2 cations leads to the formation of Tl₄ATE₃-type compounds [3, 8-10].

A new class of compounds - thallium-REE tellurides with common formula of Tl₉LnTe₆, which are ternary structural analogs of the Tl₅Te₃, was obtained in [11-13].

It should be noted that ternary compounds of the indicated types exhibit thermoelectric, optical, magnetic properties, as well as properties of topological insulators [14-26].

It is known that lanthanides show +2 and +3 oxidation states. In the Tl₉LnTe₆ compounds, lanthanides have an oxidation state +3. Taking into account the existence of Tl₄A^{IV}Te₃-type compounds, we assumed the possibility of the formation of Tl₄LnTe₃ compounds, in which the REE will exhibit +2 oxidation state.

This work describes the synthesis of the first representatives of Tl₄LnTe₃-type compounds, namely, Tl₄GdTe₃ and Tl₄DyTe₃, and presents their crystallographic and thermal characteristics.

I. Experimental part

1.1. Materials and synthesis

For research, we used elements purchased from Alfa Aesar (Table 1).

Thallium is stored in water to prevent oxidation in air, so it was dried immediately before use. Due to the toxicity of thallium and its compounds, protective gloves were worn when working with it.

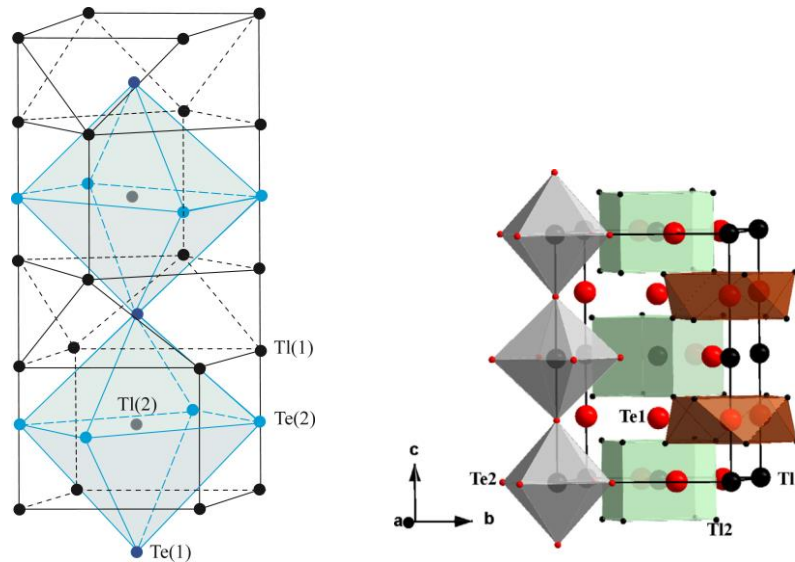


Fig. 1. Tl₅Te₃ crystal structure: the main structural element projected on the plane *b* (a) [3] and plane *c* (b) [25].

Table 1

Provenance and purity of the materials used in this investigation

Chemical	Mass fraction purity	CAS No	Form
Gadolinium	0.999	7440-54-2	foil, 0.25mm
Dysprosium	0.999	7429-91-6	foil, 0.25mm
Thallium	0.99999	7440-28-0	rod, 12.7mm
Tellurium	0.9999	13494-80-9	broken ingots

The congruently melting Tl₂Te compound was synthesized by the melting of stoichiometric amounts of the thallium and tellurium in evacuated (~ 10⁻²Pa) quartz ampoules at 750 K, followed by slow cooling.

Taking into account the previous experience on the synthesis of the Tl₉LnTe₆ compounds [3, 11-13, 27-29], namely, the REE refractory, and the incongruent character of their melting, the Tl₄GdTe₃ and Tl₄DyTe₃ compounds were synthesized by the ceramic method according to a special technique. In the synthesis, not elementary components were used, but stoichiometric amounts of thallium telluride Tl₂Te, lanthanide, and tellurium. This due to lanthanides with thallium form thermodynamically stable compounds that prevent the further synthesis of ternary compounds. After alloying at 1000 K, to achieve a state as close as possible to equilibrium, the cast non-homogenized samples were ground into powder, thoroughly mixed, pressed into a cylindrical tablet, and annealed at 700 K for 1000 h.

To prevent the interaction of lanthanides with the inner walls of the quartz ampoule, the synthesis of the Tl₄GdTe₃ and Tl₄DyTe₃ was carried out in graphitized ampoules. Graphitization was performed by thermal decomposition of toluene.

The single-phase nature of the synthesized compounds was controlled by DTA and XRD methods.

1.2. Methods

DTA and XRD analyses were used to analyze the

samples of the investigated system.

The phase transformation temperatures were determined using a NETZSCH 404 F1 Pegasus differential scanning calorimeter within room temperature and ~1200 K at a heating rate of 10 K·min⁻¹ and accuracy about ±2 K.

Phase identification was performed using a Bruker D8 diffractometer utilizing CuK_α radiation. The powder diagrams of the ground samples were collected at room temperature in the 2θ range of 6 - 65°. The unit cell parameters of intermediate alloys were calculated by indexing of powder patterns using Topas V3.0 software.

II. Results

The combined analysis of experimental data showed the existence of the Tl₄GdTe₃ and Tl₄DyTe₃ compounds, allowed to explain the possibility and character of their formation.

Analysis of powder X-ray diffraction patterns of the synthesized compounds showed that they have diffraction patterns identical to those of Tl₅Te₃ (Fig. 2). Their X-ray diffraction patterns were indicated in the Tl₅Te₃- type structure using the Topas V3.0 computer program, and the tetragonal lattice parameters were obtained:

$$\text{Tl}_4\text{GdTe}_3: a = 8.8766(7), c = 13.0846(13) \text{ \AA}, Z = 4$$

$$\text{Tl}_4\text{DyTe}_3: a = 8,8588(9); c = 13,0524(16) \text{ \AA}, Z = 4$$

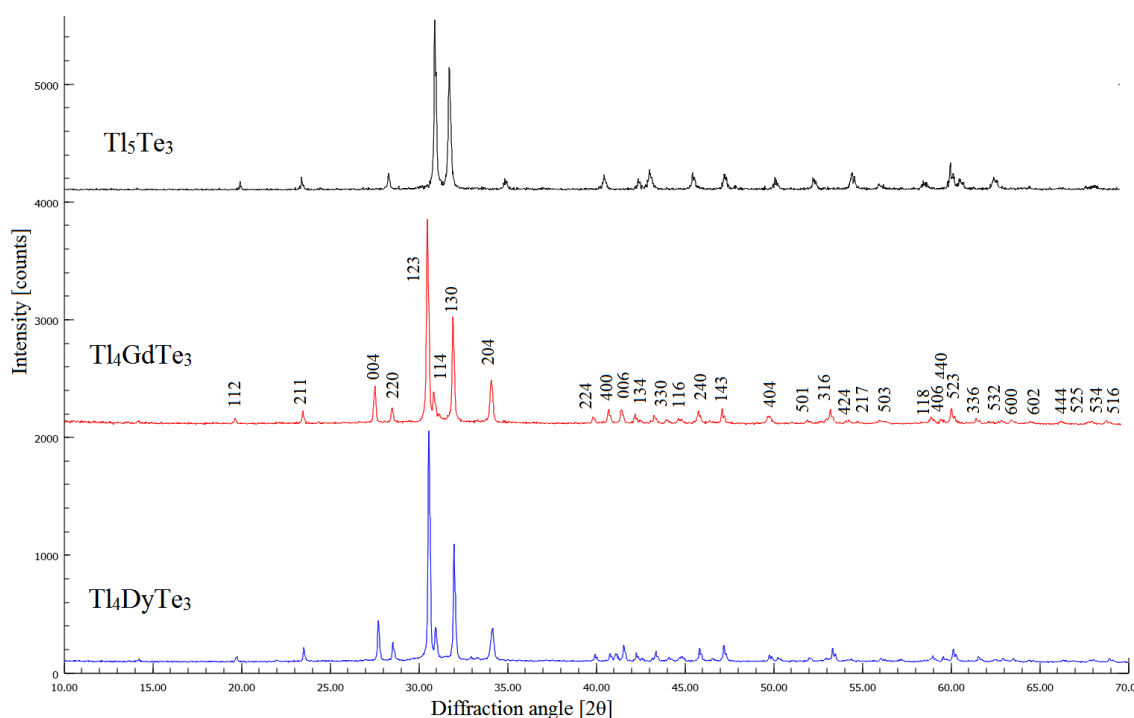


Fig 2. The powder XRD patterns of the Tl_5Te_3 , Tl_4GdTe_3 , and Tl_4DyTe_3 compounds.

On the heating thermograms in the temperature range from room temperature to 1200 K, we found peaks at 770 (Tl_4GdTe_3) and 767 K (Tl_4DyTe_3). Given the difficulty in homogenizing the samples obtained by melting, these effects cannot be attributed to the congruent melting. Apparently, both compounds melt with decomposition by peritectic reactions and their complete transition to a liquid state occurs at temperatures above 1200 K.

Conclusion

This work presents the new Tl_4GdTe_3 and Tl_4DyTe_3 ternary compounds -structural analogs of Tl_5Te_3 (sp. gr. $I4/mcm$). The powder diffraction patterns were completely indicated in the tetragonal structure, and their crystal lattices parameters were calculated: $a = 8.8766(7)$, $c = 13.0846$ (13) Å, $Z = 4$ (Tl_4GdTe_3); $a = 8.8588$ (9), $c = 13.0524(16)$ Å, $Z = 4$ (Tl_4DyTe_3). According to DTA data, it was found that the synthesized compounds melt with decomposition by peritectic reactions at 770 and 762 K, respectively. The obtained

new compounds complement a wide class of compounds - structural analogs of Tl_5Te_3 and exhibit interest as potential thermoelectric and magnetic materials.

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Imamaliyeva S.Z. – PhD on Chemistry, Associate Professor, Senior Researcher of 'Thermodynamics of functional inorganic compounds' laboratory.

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C. Імамалієва

Tl₄GdTe₃ та Tl₄DyTe₃ як нові структурні аналоги Tl₅Te₃

Інститут каталізу та неорганічної хімії імені акад. М. Нагієва, Національна академія наук Азербайджану, Баку, Азербайджан, samira9597a@gmail.com

Нові потрійні сполуки Tl₄GdTe₃ та Tl₄DyTe₃ - структурні аналоги Tl₅Te₃ (Sp.gr.I4/mcm) були синтезовані та ідентифіковані методами DTA та XRD. За даними XRD порошку розраховували параметри їх кристалічних решіток: $a = 8,8766(7)$, $c = 13,0846(13)$ Å, $Z = 4$ (Tl₄GdTe₃); $a = 8,8588(9)$, $c = 13,0524(16)$ Å, $Z = 4$ (Tl₄DyTe₃). Встановлено, що синтезовані сполуки плавляться при розкладанні перитектичними реакціями при 770 та 767 К відповідно.

Ключові слова: телуриди талій-РЗЕ, диференціально-термічний аналіз, X-променева дифракція порошку, кристалічна ґратка.