New Thallium Tellurides with Rare Earth Elements

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Institute of Catalysis and Inorganic Chemistry of the Azerbaijan National Academy of Sciences, 113 H. Javid ave., Baku AZ-1143, Azerbaijan

Abstract

Compounds of the Tl₄LnTe₃ (Ln-Nd, Sm, Tb, Er, Tm) composition were synthesized by the direct interaction of stoichiometric amounts of thallium telluride Tl₂Te elementary rare earth elements (REE) and tellurium in evacuated (10⁻² Pa) quartz ampoules. The samples obtained were identified by differential thermal and X-ray phase analyses. Based on the data from the heating thermograms, it was shown that these compounds melt with decomposition by peritectic reactions. Analysis of powder diffraction patterns showed that they were completely indexed in a tetragonal lattice of the Tl₅Te₃ type (space group I₄/mcm). Using the Le Bail refinement, the crystal lattice parameters of the synthesized compounds were calculated. It was found that when the thallium atoms located in the centres of the octahedra were substituted by REE atoms, there occurred a sharp decrease in the a parameter and an increase in the c parameter. This was due to the fact that the substitution of thallium atoms with REE cations led to the strengthening of chemical bonds with tellurium atoms. This was accompanied by some distortion of octahedra and an increase in the c parameter. A correlation between the parameters of the crystal lattices and the atomic number of the lanthanide was revealed: during the transition from neodymium to thulium, there was an almost linear decrease in both parameters of the crystal lattice, which was apparently associated with lanthanide contraction. The obtained new compounds complement the extensive class of ternary compounds - structural analogues of Tl₅Te₃ and are of interest as potential thermoelectric and magnetic materials.

Keywords: thallium tellurides – REE, structural analogues of Tl₅Te₃, differential thermal analysis, X-ray phase analysis, crystal structure.

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Samira Zakir Imamalieva, e-mail: samira9597a@gmail.com

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1. Introduction

One of the rational ways to develop new functional materials is the search for complex structural analogues of already known compounds with the same properties and to optimize their characteristics by directional alloying [1–5].

Subtelluride Tl$_5$Te$_3$ is one of the most suitable matrix compounds for the preparation of new ternary compounds – structural analogues and multicomponent phases. According to the phase diagram of the Tl-Te system [6, 7], this compound melts congruently at 725 K and is a variable composition phase with a wide range of homogeneity (34.5÷38 at% Te). Due to the peculiarities of the crystal structure [8, 9], Tl$_5$Te$_3$ has a number of ternary cation- and anion-substituted structural analogies.

In studies [10, 11] a new class of compounds – thallium tellurides of REE type Tl$_9$LnTe$_6$, which are ternary structural analogues of Tl$_5$Te$_3$, was obtained. These compounds complement the extensive class of ternary compounds with general formulas Tl$_x$AX$_y$ and Tl$_x$BX$_y$ (A – Sb, Bi, Au, In; B – Sn, Pb, Mo, Cu; X – Se, Te) [13–19]. The described compounds are thermoelectric with anomalously low thermal conductivity [20–23], and some of them exhibit optical [24–26] and magnetic [27, 28] properties, as well as the properties of topological insulators [29–31].

As was shown above, Tl$_5$Te$_3$ crystallizes in a tetragonal structure of the Cr$_5$B$_3$ type (Sp.Gr. I4/mcm) (Fig. 1a) [8, 9]. The crystal structure of Tl$_5$Te$_3$ was described in detail in studies [5, 8, 9, 32]. In the crystal lattice of Tl$_5$Te$_3$, thallium atoms occupy two different positions and exhibit oxidation states +1 and +3. Some of the thallium atoms (Tl2) are located in octahedral voids, and others (Tl1) are located in the voids of the anionic tellurium cage. Replacement of half of the thallium atoms located at the centres of octahedra (Tl2) with B$^{3+}$ cations led to the formation of compounds of the Tl$_9$BTe$_6$ type, and their complete replacement by A$^{2+}$ cations led to the formation of compounds of the Tl$_9$ATe$_6$ type.

It is known that lanthanides exhibit oxidation states +2 and +3. In compounds of the Tl$_9$LnTe$_6$ type, lanthanides exhibit an oxidation state of +3. Considering the existence of compounds of the Tl$_4$A$^{IV}$X$_3$ type, we assumed the possibility of the formation of compounds with the composition Tl$_4$LnTe$_3$, in which the REE will exhibit an oxidation state of +2. In the study [12], for the first time we synthesized and identified Tl$_4$GdTe$_3$ and Tl$_4$DyTe$_3$ compounds - representatives of the specified class, their isostructurality with Tl$_5$Te$_3$ was confirmed and the parameters of their crystal lattices were calculated.

In this study, we continued our research in the field of REE thallium chalcogenides and report on the synthesis of some new compounds of the Tl$_4$LnTe$_3$ type.

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**Fig. 1.** Crystal structure of Tl$_5$Te$_3$. Main structural element (a) [5], projected onto a plane b, c (b) [28]
2. Experimental

2.1. Materials and synthesis

High-purity elements purchased from Alfa Aesar were used for the studies: thallium (catalogue number 7440-28-0), tellurium (13494-80-9), neodymium (7440-00-8), samarium (7440-19-9), terbium (7440-27-9), erbium (7440-52-0), thulium (7440-30-4).

Thallium was stored in water in order to prevent oxidation in air, therefore it was dried immediately before use. Due to the toxicity of thallium and its compounds, protective gloves were used during performed work.

Considering the previous experience in the synthesis of Tl₄LnTe₃ and Tl₄LnTe₃ compounds [31–34], namely, the incongruent nature of their melting and the refractoriness of the REE, Tl₄LnTe₃ compounds were synthesized by a ceramic method using a special technique. In the synthesis, not elementary components, but stoichiometric amounts of thallium telluride Tl₂Te, lanthanide, and tellurium were used since lanthanides with thallium form thermodynamic stable compounds that prevent further synthesis of ternary compounds. Fusion was performed in the evacuated (10⁻² Pa) quartz ampoules. After fusion at 1000 K, to bring the alloys to a state as close as possible to equilibrium, the cast non-homo genized ingots were ground into powder in an agate mortar, thoroughly mixed, pressed into a cylindrical tablet, and annealed at 700 K for 1000 h.

In order to prevent the interaction of lanthanides with the inner walls of the quartz ampoule, the synthesis of the compounds was carried out in graphitized ampoules. Graphitization was performed by the thermal decomposition of toluene.

The single-phase of the synthesized compounds was monitored by DTA and XRD methods. 2.2. Methods

The studies were carried out by the methods of differential thermal (DTA) and X-ray phase diffraction analyses (XRD). Heating curves were recorded using differential scanning calorimeter DSC NETZSCH 404 F1 Pegasus system and multichannel DTA device based on an electronic TC-08 Thermocouple Data Logger in the temperature range from room temperature to ~ 1300 K. Powder diffraction patterns of the initial compounds and intermediate alloys were recorded on a diffractometer D2 Phaser with CuKα-radiation within an angle range of 2θ = 10°–70°. The crystal lattice parameters of the initial compounds and intermediate alloys were determined by the indexing of powder diffraction patterns using the Topas 4.2 software by the Le Bail method.

3. Results

A comparison of powder diffraction patterns of synthesized samples of composition Tl₄LnTe₃ with Tl₂Te, and its typical triple analogue Tl₄PbTe₃ showed that they all have qualitatively the same diffraction pattern (Fig. 2). All reflection lines were fully indexed in the Tl₄Te₃ structure type (Sp.Gr. I4/mcm).

The parameters of the tetragonal lattices of Tl₄LnTe₃ were determined using the computer program Topas V4.2 using the Le Bail refinement are shown in the Table. The Table also contains data for other members of this class of compounds. Data in the Table demonstrate that the substitution of thallium (Tl2) atoms located at the centres of tellurium octahedra (Fig. 1) with REE atoms led to a sharp decrease in parameter a and an increase in parameter c. Probably, this was due to the fact that such a substitution led to the strengthening of chemical bonds between the REE and Te atoms (2) and a decrease in the corresponding interatomic distances, determining the value of parameter a. As a result, some distortion of tellurium octahedra occurred, which led to an increase in parameter c.

The dependences of the crystal lattice parameters of Tl₄LnTe₃ compounds from the atomic number of the lanthanide is shown in Fig. 3. As can be seen, there is a clear correlation: during the transition from neodymium to thulium, there is an almost linear decrease in both crystal lattice parameters, which is probably associated with a decrease in the crystallographic radius of REE due to lanthanide contraction [33].

The thermogram of heating each of the synthesized compounds in the temperature range from room temperature to 1300 K contained one clear endothermic effect at 760–775 K (Table). Taking into account the difficulty of homogenizing the samples obtained by fusion and the complex picture on the DTA cooling curves, these effects cannot be attributed to the congruent melting point. Probably, these compounds melt with decomposition by peritectic reactions, and their complete transition to a liquid state occurs at temperatures above 1300 K.
Fig. 2. Powder diffraction patterns of some compounds of the Tl₄LnTe₃ type

Table. Crystallographic parameters of Tl₄Te₃ and its ternary structural analogues of the Tl₄AIVTe₃ type

| Phase    | Tetragonal lattice parameters, Sp.Gr. I4/mcm, Z = 4 | Melting points | Source          |
|----------|-----------------------------------------------------|----------------|-----------------|
| Tl₄Te₃  | a, Å 8.930 c, Å 12.598                              | 725            | [8]             |
| Tl₄PbTe₃ | a, Å 8.820 c, Å 13.010                              | 823            | [15]            |
| Tl₄SnTe₃ | a, Å 8.841 c, Å 13.056                              | 893            | [15]            |
| Tl₄CuTe₃ | a, Å 8.929 c, Å 12.605                              | –              | [17]            |
| Tl₄MoTe₃ | a, Å 8.930 c, Å 12.575                              | –              | [18]            |
| Tl₄NdTe₃ | a, Å 8.885(7) c, Å 13.0952(12)                      | 775            | present study   |
| Tl₄SmTe₃ | a, Å 8.8752(6) c, Å 13.0784(11)                     | 772            | present study   |
| Tl₄GdTe₃ | a, Å 8.8766(7) c, Å 13.0756(13)                     | 770            | [12]            |
| Tl₄TbTe₃ | a, Å 8.8652(7) c, Å 13.0653(12)                     | 768            | present study   |
| Tl₄DyTe₃ | a, Å 8.8588(7) c, Å 13.0524(16)                     | 767            | [12]            |
| Tl₄ErTe₃ | a, Å 8.8421(6) c, Å 13.0354(11)                     | 760            | present study   |
| Tl₄TmTe₃ | a, Å 8.8354(7) c, Å 13.015(15)                      | 760            | present study   |
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Conflict of interests

The author declares that she has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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The influence of replacing Se by Te on electronic properties of thallium tellurides has been studied. Enhanced thermoelectric properties of variants of thallium tellurides with indium and aurum have been reported. New thallium tellurides with indium and aurum have been synthesized, and their crystal structures and magnetic properties have been investigated. The rare earth ions (RE = Ce, Sm, Gd) have been used to study the effects of doping on the crystal structure and magnetic properties of thallium tellurides. The rare earth ions have been found to affect the crystal structure and magnetic properties in a manner that depends on the RE ion used.

In addition, thallium tellurides with molybdenum have been studied, and their magnetic properties have been investigated. Enhanced thermoelectric properties of thallium tellurides with indium and aurum have been reported, and their crystal structures have been studied. The rare earth ions have been used to study the effects of doping on the crystal structure and magnetic properties of thallium tellurides. The rare earth ions have been found to affect the crystal structure and magnetic properties in a manner that depends on the RE ion used.

The crystal structure of thallium tellurides has been studied using diffraction techniques and theoretical calculations. The crystal structures of thallium tellurides have been found to be related to the crystal structures of other tellurides, and the effects of doping on the crystal structure have been investigated. The rare earth ions have been found to affect the crystal structure in a manner that depends on the RE ion used.

Thallium tellurides have been studied as magnetic materials, and their magnetic properties have been investigated. The rare earth ions have been used to study the effects of doping on the magnetic properties of thallium tellurides. The rare earth ions have been found to affect the magnetic properties in a manner that depends on the RE ion used.

Thallium tellurides have been studied as thermoelectric materials, and their thermoelectric properties have been investigated. Enhanced thermoelectric properties of thallium tellurides have been reported, and their crystal structures have been studied. The rare earth ions have been used to study the effects of doping on the thermoelectric properties of thallium tellurides. The rare earth ions have been found to affect the thermoelectric properties in a manner that depends on the RE ion used.

Thallium tellurides have been studied as optical materials, and their optical properties have been investigated. Enhanced optical properties of thallium tellurides have been reported, and their crystal structures have been studied. The rare earth ions have been used to study the effects of doping on the optical properties of thallium tellurides. The rare earth ions have been found to affect the optical properties in a manner that depends on the RE ion used.