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SYNTHESIS AND RIETVELD CRYSTAL STRUCTURE REFINEMENT OF Tl_5Te_2Br

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Tl_5Te_2Br ternary compound have been prepared from proper amounts of preliminary synthesized Tl_2Te and TlBr. It was crystallized using specially designed method by authors - from two immiscible liquid phases L_1+L_2. The crystal structure refinement was done using powder X-ray diffraction data measured on conventional diffractometer "D8 ADVANCE" with CuK_α- radiation and in the 2θ range of 5-130°. The Rietveld refinement program used in this study was the TOPAS-4.2 version of Bruker Company. The structure has been refined in the tetragonal space group, I4/mcm, and its' cell parameters were determined: a = 8.974(1), c = 12.812(3)Å, V = 1031.8(4) $Å^3$. It was found to be isostructural with Tl_5Se_2Br.

Keywords: *crystal structure, Tl_5Te_2Br, structure parameter, tetragonal space group*

Thallium shows different oxidation state numbers (+1 and +3) due to its location in the Periodic Table. It has Tl_5Te_3 binary compound with two different oxidation state numbers (+1 and +3) of thallium. Tl_5Te_3 crystallizes in a tetragonal structure, space group *I4/mcm,* with unit cell parameters a=8,929; c=12,620Å; z=4 [1]. There are several anion replacement ternary analogues of this compound with Tl_5Te_2Hal (Hal –Cl, Br,I) general composition [2-5]. They form during displacement of tellurium atoms with halogen atoms along the *c* parameter of the crystal lattice.

In recent publications the phase diagram of the Tl_2Te-TlBr system was investigated [4]. It was established that, the quasi-binary system Tl_2Te-TlBr is characterized by formation of ternary compound Tl_5Te_2Br that melts by synthetic reaction at 730 K [2,4]. Tl_5Te_2Br crystallizes in a tetragonal structure, space group *I4/mcm,* with unit cell parameters a=8.926, c=12.801Å; z=4 [4]. However, the literary analysis shows that, its exact structure is still a matter of discussion.

In order to get some more information about this structural issue, our present contribution is devoted to the investigation of crystal structure of Tl_5Te_2Br.

Congruently melting thallous telluride Tl_2Te was prepared from the proper amounts of high purity elemental solids (Tl, 99.999%, Alfa Aesar; Te, 99.999%, Alfa Aesar) by encapsulating them under vacuum in quarts ampoules. It was synthesized by one-step melting at 800K, followed by cooling in the switched-off furnace and annealing.

TlBr was prepared by an indirect method reported in the literature [3,4]. At first, metallic thallium was dissolved in the dilute sulfuric acid (~10 mol. %) at 350K to get the Tl_2SO_4 solution. Then diluted HBr was added into a hot 2% Tl_2SO_4 solution until complete precipitation of TlBr. Yellowish green TlBr was separated from the mother liquor and washed with icy distilled water. The product was dried over KOH in a desiccator at 300-350 K and stored in the dark to prevent its decomposition.

X-ray powder diffraction (XRD) and differential scanning calorimetry (DSC) methods were used to characterize the samples.

Ternary compound Tl_5Te_2Br was synthesized by melting appropriate amounts of the synthesized TlBr and Tl_2Te in vacuum-sealed quartz ampoule. It was prepared by specially designed method in order to control the process of crystallization from two immiscible liquid phases L_1+L_2. In this proposed method, the liquid phase L_1 is in dynamic equilibrium with another liquid phase L_2 and the compositions of the coexisting liquid phases in $L_1+ L_2$ two-phase mixture are constant at the given temperature. During slow (close to equilibrium state) crystallization from the melt L_1, the phase

L_2, dissolves in L_1, and provides constancy of its composition, consequently the constancy of the crystallization temperature, which is equal to the temperature of syntectic equilibrium (750K) at the phase diagram [4]. Finally, well crystallized brittle product of silvery color was obtained. The use of the proposed method improves the quality of the obtained material due to the homogeneity of the crystals by composition and size and elevation of the reproducibility of physical quantities.

The crystal structure refinement was done using powder X-ray diffraction data measured on conventional diffractometer "D8 ADVANCE" with CuK_α- radiation and in the 2θ range of 5-120°. The Rietveld refinement program used in this study was the TOPAS-4.2 version of Bruker company. The structure has been refined in the tetragonal space group, *I4/mcm,* and has following cell parameters: *a = 8.974(1), c = 12.812(3)Å, V = 1031.8(4) Å*^{3}. The structure was found isostructural with Tl_5Se_2Br [6]. During the refinement the positions of all atoms and their isotropic temperature factors converged rapidly. The crystal structure of Tl_5Te_2Br contains two independent Tl sites, with different coordination polyhedrons. Around the Tl(1) atoms occurs slightly distorted octahedron of two Brome and four Tellurium atoms. These octahedrons are covered by cubes of thallium atoms, of second site. By interconnecting these octahedrons via common vertex and cubes via common edges occurs the three-dimensional structure. The coordination polyhedron forming around the other Thallium atoms quite complex and due to two Br, three Te, and three Tl atoms, the coordination number reches to 8.

The x-ray diffraction pattern of tetragonal Tl_5Te_2Br, the difference between observed and Rietveld calculated intensities are shown in fig.1. The refined unit cell parameters, atomic positions with isotropic temperature factor and interatomic distances shown in table 1&3. In fig.2 presented the three-dimensional frame of Tl(1) octahedrons, interconnecting via common vertex.

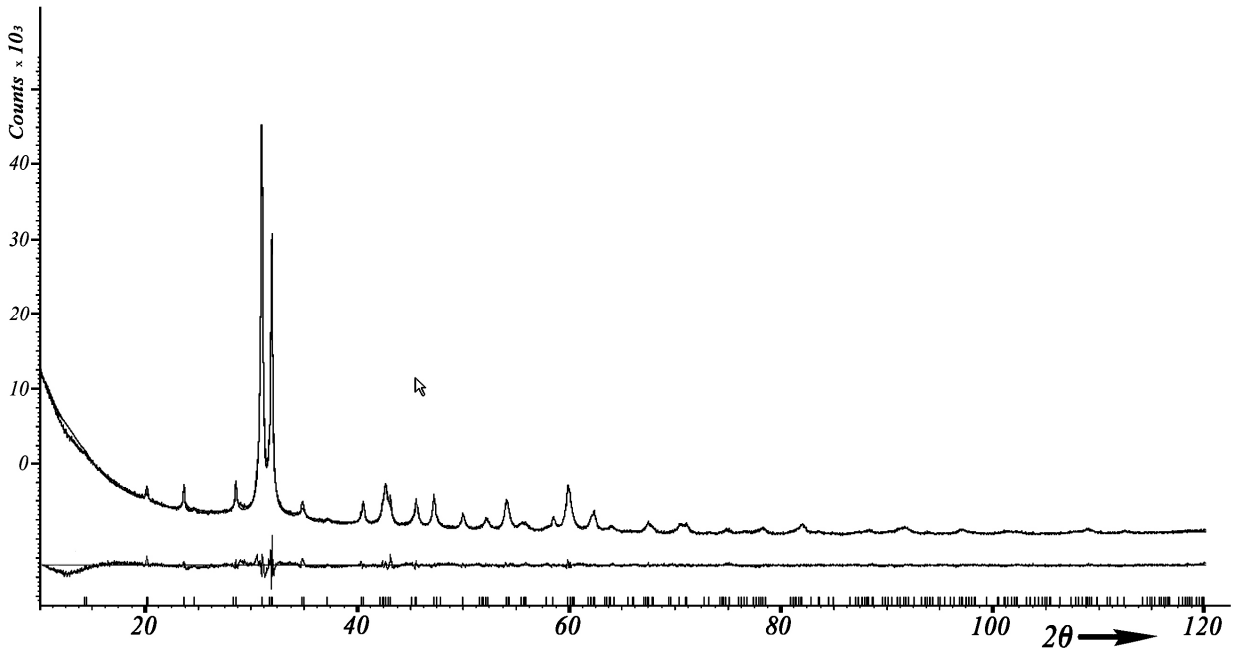

Fig. 1. X-ray diffraction (XRD) pattern of Tl_5Te_2Br, obtained using XRD "D8 ADVANCE". The difference between observed and Rietveld calculated intensities is shown under the XRD pattern

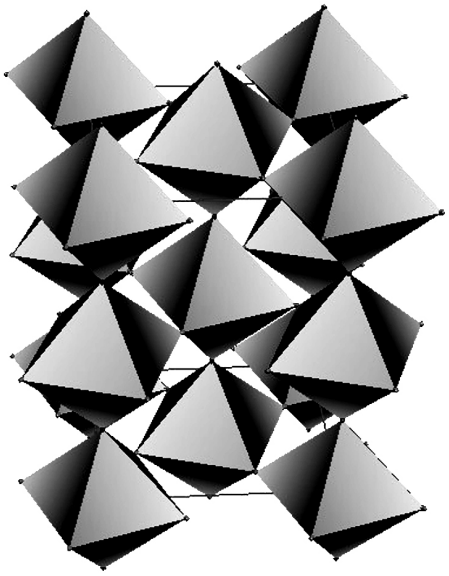

Fig.2. The three-dimensional arrangement of interconnecting Tl(1) octahedrons via common vertex

Table 1

Refined structure parameters for Tl_5Te_2Br

Space Group	I4/mcm
Unit cell dimensions at 298 K: a (Å) c (Å)	 8.974 (1) 12.812(3)
Cell Volume ($Å^3$)	1031.8(4)
Crystal Density (g/cm^3)	8.736(3)
R-Bragg (%)	0.665

Table 2

Atomic positional parameters in Tl_5Te_2Br

Site	Np	x	y	z	Atom Occ	Beq
Tl1	4	0.0	0.0	0.0	1	1.6(2)
Tl2	16	0.1530(5)	0.6530(5)	0.1556(4)	1	1.4(1)
Br	4	0.0	0.0	0.25	1	3.0(6)
Te	8	0.341(1)	0.841(1)	0.0	1	2.2(3)

Table 3

Interatomic distances in Tl_5Te_2Br

Tl(1)	2Br 4Te	3.2030 Å 3.3767 Å
Tl(2)	2Br Te 2Te Tl(2) 2Tl(2)	3.6119 Å 3.1098 Å 3.4372 Å 3.4516 Å 3.6594 Å

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Tl_5Te_2Br BİRLƏŞMƏSİNİN SİNTEZİ VƏ KRİSTAL QURULUŞUNUN RİTVELD METODU İLƏ DƏQİQLƏŞDİRİLMƏSİ

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Tl_5Te_2Br üçlü birləşməsi əvvəlcədən sintez edilmiş Tl_2Te və TlBr birləşmələrinin stexiometrik miqdarlarından hazırlanmışdır. O, müəlliflərin işləyib hazırladığı metodika ilə – təbəqələşən iki L_1+L_2 maye fazadan istiqamətləndirilmiş kristallaşma yolu ilə alınmışdır. Kristal quruluş tədqiqi CuK_α radiasiyalı "D8 ADVANCE" difraktometri vasitəsilə 2θ intervalı 5-130^o olmaqla ovuntu rentgenoqramı əsasında yerinə yetirilmişdir. Quruluş dəqiqləşdirilməsi üçün istifadə olunan proqram Bruker firmasının TOPAS-4.2 versiyası olmuşdur. Birləşmənin kristal quruluşu tetraqonal fəza qrupunda I4/mcm dəqiqləşdirilmiş və qəfəs parametrləri təyin edilmişdir: *a = 8.974(1), c = 12.812(3)Å, V = 1031.8(4) Å^3*. Və müəyyən olunmuşdur ki, Tl_5Te_2Br birləşməsi Tl_5Se_2Br ilə izostrukturdur.

Açar sözlər: *kristal quruluş, Tl_5Te_2Br, quruluş parametrləri, tetraqonal fəza qrupu*

СИНТЕЗ СОЕДИНЕНИЯ Tl_5Te_2Br И УТОЧНЕНИЕ ЕГО КРИСТАЛЛИЧЕСКОЙ СТРУКТУРЫ МЕТОДОМ РИТВЕЛДА

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Тройное соединение Tl_5Te_2Br приготовлено из стехиометрических количеств предварительно сиитезированных TlBr и Tl_2Te. Кристаллы получены по методике, разработанной авторами – направленной кристаллизацией из двух расслаивающихся жидких фаз. Исследование кристаллической структуры проведено на основе порошковой рентгенограммы, полученной на дифрактометре "D8 ADVANCE" с CuK_α излучением в интервале 5-130^0. Уточнение структуры выполнено с помощью программы фирмы Bruker TOPAS-4.2. Установлено, что соединение Tl_5Te_2Br кристаллизуется в тетрагональной пространственной группе I4/mcm с параметрами решетки: *a = 8.974(1), c = 12.812(3)Å, V = 1031.8(4) Å^3*. Также установлено, что соединение Tl_5Te_2Br изоструктурно с Tl_5Se_2Br.

Ключевые слова: *кристаллическая структура, Tl_5Te_2Br, параметры структуры, тетрагональная пространственная группа*