STRUCTURAL ANALYSIS OF $TlInTe_2$ - $InGaTe_2$ SOLID SOLUTIONS BY X-RAY DIFFRACTION

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In this work, the structural properties of $TlIn_{1-x}Ga_xTe_2$ solid solutions were investigated by X-ray diffraction. Samples with different compositions (x=0-0.8) were synthesized and their crystal structure parameters were determined using a DRON-2 diffractometer with CuK_α radiation and a nickel filter. The results show that the solid solutions crystallize in a tetragonal lattice. With increasing Ga content, the unit cell parameters decrease systematically due to the higher ionicity and stronger hybridization of Ga atoms compared to Tl. At approximately $x \approx 0.5$, the X-ray diffraction pattern reveals the formation of a new quaternary phase, $TlIn_2GaTe_4$, with distinct structural characteristics compared to the initial compounds. The observed trends are explained by changes in the electronic configuration of the outer shells of Tl and Ga atoms, which modify the chemical bonding and the band gap of the material. These findings contribute to the understanding of phase formation and structure–property relations in Tl-based telluride solid solutions.

Keywords*:* solid solutions, tetragonal lattice, X-ray diffraction, unit-cell parameters, quaternary phase
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INTRODUCTION

Solid solutions of thallium-based chalcogenides have attracted considerable attention in recent years due to their unique structural, electronic, and optical properties, which make them promising materials for applications in infrared optoelectronics, thermoelectric devices, and radiation detectors [1, 2]. The ability to tailor the band gap, the degree of ionicity, and the crystal lattice parameters through compositional modifications renders these materials particularly valuable in modern semiconductor technology [3,4]. Therefore, understanding the relationship between the structural parameters and the composition of solid solutions is crucial for optimizing their functional characteristics [5].

The $TlInTe_2$ –$InGaTe_2$ system represents an interesting case of isovalent substitution, where thallium atoms can be partially replaced by gallium atoms [6]. This substitution significantly alters the electronic configuration of the constituent atoms, affects the degree of ionicity of chemical bonds, and modifies the band gap and other physical properties of the material [7]. Such materials, characterized by their high ionicity and tunable lattice parameters, are of significant interest in nanotechnology and energy conversion research [8]. However, most previous studies have focused mainly on the electrophysical features of these semiconductors, while their structural properties, particularly the influence of gallium content on the crystal lattice parameters and phase formation, have not been thoroughly investigated [9].

X-ray diffraction (XRD) remains one of the most effective and widely used methods for studying the crystal structure of solid solutions [10]. In particular, XRD allows determining the unit cell parameters, identifying possible phase transitions, and revealing the symmetry and space group of the lattice [11]. Therefore, investigating the structural evolution of

$TlIn_{1-x}Ga_xTe_2$ solid solutions as a function of gallium content by X-ray diffraction is not only of fundamental scientific interest but also essential for advancing their technological applications [12].

The aim of this study is to investigate the structural properties of $TlIn_{1-x}Ga_xTe_2$ solid solutions by determining the changes in the crystal lattice parameters and identifying the formation of possible new phases as a result of partial substitution of thallium with gallium. The work is intended to establish the correlation between the chemical composition and the structural parameters of the solid solutions, providing insight into the composition–structure–property relationships of Tl-based chalcogenides.

The results of this work contribute to the development of novel materials with tailored properties for optoelectronic and thermoelectric applications, and enhance the understanding of phase formation mechanisms in multicomponent semiconductor systems.

EXPERIMENTAL METHODS AND RESULTS

Solid solutions of the Tl-In-Ga-Te system were synthesized from high-purity elements by the method of direct melting in evacuated quartz ampoules. The weighed components were sealed under a vacuum of approximately 10^{-4} Torr, heated to 950–1000 °C to reach the melting point, and held for several hours to ensure complete reaction. The resulting ingots were then annealed at 400–450 °C for 48–72 hours to improve compositional homogeneity and relieve internal stresses [6,7].

X-ray diffraction patterns of the synthesized samples were recorded on a DRON-2 diffractometer using CuKα radiation ($\lambda = 1.5418A^0$) with a nickel filter. All samples were measured under identical conditions. The measurement error of the reflection angles did not exceed $\pm 0.02^{0.}$ The obtained diffraction patterns were indexed, and the unit-cell parameters of the solid solutions were calculated from the observed reflections using standard least-squares refinement methods [11].

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An analysis of the obtained X-ray diffraction patterns of $TlInTe_2$ - $InGaTe_2$ solid solutions showed that despite the difference between atoms of different types, there is a slight tendency to reduce the intensity of reflections with an increase in the average atomic weight of the solid solutions of the $InTl_{1-x}Ga_xTe_2$ system. The X-ray diffraction pattern corresponding to the composition x=0.5, respectively, differs from the X-ray diffraction patterns of the starting compounds and solid solutions based on them, which points to the formation of a new quaternary phase of $TlIn_2GaTe_4$.

As a consequence of indexing the obtained X-ray diffraction patterns, it was found that solid solutions of the $InTl_{1-x}Ga_xTe_2$ system crystallize in tetragonal system [3-5].

Table 1 presents the concentration dependence of the unit-cell parameters of $InTl_{1-x}Ga_xTe_2$ solid solutions.

Table 1.

Variation of unit-cell parameters in solid solutions of the $TlInTe_2$ –$InGaTe_2$ system as a function of composition

№	Compositions	Unit-cell parameters (A^0)	
		A	C
1	$InGaTe_2$	8.14	7.06
2	$InTl_{0.02}$ $Ga_{0.98}$ Te_2	8.145	7.082
3	$InTl_{0.04}$ $Ga_{0.96}$ Te_2	8.152	7.084
4	$InTl_{0.06}$ $Ga_{0.94}$ Te_2	8.158	7.084
5	$InTl_{0.08}$ $Ga_{0.92}$ Te_2	8.165	7.088
6	$InTl_{0.12}$ $Ga_{0.88}$ Te_2	8.176	7.096
7	$InTl_{0.16}$ $Ga_{0.84}$ Te_2	8.188	7.096
8	$InTl_{0.22}$ $Ga_{0.78}$ Te_2	8.205	7.12
9	$InTl_{0.26}$ $Ga_{0.72}$ Te_2	8.216	7.106
10	$InTl_{0.1}Ga_{0.9}$ Te_2	8.17	7.09
11	$InTl_{02}$ $Ga_{0.8}$ Te_2	8.20	7.10
12	$InTl_{0.3}$ $Ga_{0.7}$ Te_2	8.23	7.11
13	$InTl_{0.45}$ $Ga_{0.55}$ Te_2	6.48	6.87
14	$InTl_{0.5}$ $Ga_{0.5}$ Te_2	6.60	7.22
15	$InTl_{0.8}$ $Ga_{0.2}$ Te_2	8.43	7.14
16	$TlInTe_2$	8.38	7.17

The analysis of the X-ray diffraction patterns of the $InTl_{1-x}Ga_xTe_2$ system foundthat when the thallium atoms are partially replaced by gallium atoms, the unit cell parameters decrease. This apparently derives from the fact that gallium atoms, in contrast to thallium atoms, have a greater tendency to form an s^2 p^6 hybrid bond, which contributes to a decrease in the metal fraction of the bond. In this circumstance, with the partial replacement of thallium atoms by gallium atoms, the possibility of completing the outermost electron shell of atoms to a stable inert gas configuration increases. In this regard, the degree of ionicity of the chemical bond increases [8-10].

When thallium atoms are partially replaced by gallium atoms, the parameters of the elementary cells of solid solutions decrease. In this case, when the thallium atoms are partially replaced by gallium atoms in $TlInTe_2$, the shift of the maximum of the electron shell increases to a stable configuration of the inert gas (s^2 p^6). In this regard, the degree of ionicity of the chemical bond increases and, therefore, the band gap and the parameters of the tetragonal cell of solid solutions based on the starting compounds and the new phase, i.e. in $TlInTe_2$ the valence band is mainly formed by the splitting 5p levels of tellurium ions, partially 5p, 5s levels of indium ions and 6p levels of thallium ions. When thallium atoms are partially replaced by gallium atoms, the 4p states of gallium atoms, which are energetically located somewhat lower, also fall into the conduction band. In solid solutions of the $TlInTe_2$ – $InGaTe_2$ system, with an increase in the concentration of gallium atoms, the possibility of building up the outermost electron shell of atoms to a stable configuration increases and, therefore, the degree of ionization of the chemical bond increases and the band gap accordingly changes [12].

In the samples of the composition, the maximum value of the band gap is observed.

The results of the indexing of X-ray photographs of the solid solutions in the system are shown in Table 2.

Table 2.

Interplanar distances, Miller indices, and relative intensities of solid solutions of the $TlInTe_2$ –$InGaTe_2$ system.

$InGaTe_2$				
hkl	d_{exp}	d_{theor}	I/I_0	θ
200	4.072	4.069	34	10^0 55′
211	3.232	3.229	50	13^0 48′
112	3.022	3.020	100	14^0 48′
221	2.670	2.672	63	16^0 46′
310	2.577	2.579	43	17^0 24′
320	2.256	2.258	16	19^0 58′
400	2.036	2.038	11	22^0 14′
401	1.957	1.959	26	23^0 11′
330	1.920	1.922	46	23^0 39′
331	1.850	1.852	18	24^0 36′
421	1.767	1.764	10	25^0 55′
104	1.704	1.706	12	26^0 52′
430	1.632	1.630	18	28^0 13′
520	1.510	1.613	9	30^0 39′
440	1.434	1.431	10	32^0 36′

$InTl_{0.45}Ga_{0.55}Te_2$				
hkl	d_{exp}	d_{theor}	I/I_0	θ
200	4.120	4.060	29	10^0 47′
211	3.275	3.274	45	13^0 37′
112	3.045	3.044	93	14^0 04′
221	2.698	2.691	54	16^0 37′
310	2.606	2.605	32	17^0 12′
320	2.285	2.271	10	19^0 43′
400	2.061	2.050	7	21^0 59′
401	1.981	1.983	18	22^0 55′
330	1.943	1.940	38	23^0 23′
331	1.872	1.870	10	24^0 17′
421	1.784	1.782	6	25^0 36′
104	1.727	1.725	8	26^0 12′
430	1.648	1.644	12	27^0 54′
520	1.532	1.531	5	$30^0$15′
440	1.448	1.447	4	$31^0$57′

$InTl_{0.9}Ga_{0.1}Te_2$				
hkl	d_{exp}	d_{theor}	I/I_0	θ
200	4.180	4.186	32	10^0 39′
211	3.316	3.318	47	13^0 26′
112	3.062	3.064	100	14^0 34′
221	2.732	2.734	60	16^0 23′
310	2.646	2.640	37	16^0 57′
320	2.310	2.312	11	$19^0$29′
400	2.090	2.094	19	21^0 41′
401	2.012	2.013	11	22^0 30′
330	1.972	1.974	22	23^0 00′
331	1.900	1.904	44	23^0 54′
421	1.810	1.812	15	25^0 12′
104	1.753	1.755	7	26^0 04′
430	1.672	1.675	12	27^0 24′
520	1.552	1.555	9	29^0 43′
440	1.480	1.482	16	$31^0$14′

$TlInTe_2$				
hkl	d_{exp}	d_{theor}	I/I_0	θ
200	4.195	4.192	28	10^0 36′
211	3.343	3.321	48.4	18^0 21′
112	3.073	3.067	100	$14^0$21′
221	2.752	2.739	56	$16^0$17′
310	2.625	2.650	32	$16^0$42′
320	2.355	2.324	9	$13^0$18′
400	2.125	2.170	16	$21^0$19′
401	2.034	2.011	8	$23^0$34′
330	1.994	1.975	17	$22^0$43′
331	1.935	1.904	39	$23^0$31′
421	1.815	1.813	12	$25^0$10′
104	1.754	1.753	6	$26^0$01′
430	1.694	1.676	10	$29^0$42′
520	1.552	1.556	6	$29^0$42′
440	1.503	1.481	13	$30^0$56′

CONCLUSION

The solid solutions of the $TlInTe_2$–$InGaTe_2$ system crystallize in a tetragonal structure across the studied composition range. Gallium substitution systematically reduces the unit-cell parameters due to its smaller atomic radius and higher ionicity. At $x \approx 0.5$ a new quaternary phase, $TlIn_2GaTe_4$, forms, as evidenced by distinct diffraction patterns and compositional changes in lattice parameters. These results highlight the potential to tailor structure and stabilize new phases in Tl-based chalcogenides for optoelectronic and thermoelectric applications.

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