RADIOGRAPHIC INVESTIGATIONS OF MELTS OF $TlInC_2^{VI} - InGaC_2^{VI}$ SYSTEMS

E.A. ALLAHYAROV
Azerbaijan Technical University, Baku
Baku, 1025, H. Javid av., 25

In the paper the parameters of elementary cells of melts of $TlInC_2^{VI} - InGaC_2^{VI}$ (C-Se, Te) systems are defined by the radiographic investigations.

The carrying out of the corresponding analysis it is need for the obtaining of the necessary information about nature of chemical connections between atoms as the elementary compounds, so the complex phases. In the connection with this fact, the crystal-structure investigations are the one of the important question of crystal chemistry. These investigations create the experimental base of crystal chemistry.

As it is known, the complex of physical properties of solid bodies is defined by chemical composition and spatial location its constituent atoms. The character of electron interaction between them though is defined by the position of constituent atoms; however, the clear conception is created in the limits of the one and the same concrete crystal structure. Thus, the solution of the one of concrete problems of physics and chemistry of semiconductors mainly is defined by the accurate definition of concrete bonds of physical peculiarities of semiconductors with chemical composition, crystal structure and bond nature. However, nowadays, the investigations of new complex semiconductors are carried out one-sidedly, often limited by the revealing and studying of their physical properties. The necessary attention doesn't pay to the study of the construction of crystal lattice structure. In spite of the fundamental meaning of crystal structure, it has been deciphered widely enough only for few complex semiconductors.

The state diagrams of $TlInC_2^{VI} - InGaC_2^{VI}$ systems have been constructed in [1,2] by the methods of differentially-thermal and microstructural analysis and it is revealed, that new compositions $TlIn_2GaC_2^{VI}$ are created in these systems and wide solubility regions on the base of initial compounds are observed. However, the roentgen-phase analysis of these melts wasn't carried out.

In this connection in present paper the melts of the $TlInC_2^{VI} - InGaC_2^{VI}$ systems are treated by roentgen-graphic investigations.

The powder had been prepared previously for the obtaining of roentgenograms of each $InTl_{1-x}Ga_xC_2$ composition. The notations of electronic reflections were carried out on CuK_α, ($\lambda_{Cu_\alpha} = 1{,}54178E$), DRON-2 difractometer of radiation with nickel filter at the similar modes. In the measurements of reflection angles the mistake didn't exceed the value $\theta = \pm 0{,}02°$.

The bar-diagram of the melts of $TlInSe_2$-$InGaSe_2$ system is given on the fig.1. As it is seen from the figure the some tendency to the increase of the intensity of corresponding reflexes is observed in the solubility regions at the partial replacement of thallium atoms by Ga atoms in $TlInSe_2$ lattice.

The increase of the intensity of the lines in the given system probably is connected with the fact, that Ga atoms have the big tendency to hybrid bond sp^3 creation in contrast to thallium atoms that is caused to the decrease of metallic part of chemical connection between the composing atoms. In this case the shifting of maximum of electron density to the skeletons of Se atoms at the partial replacement of thallium atoms by Ga atoms in $TlInSe_2$, i.e. the possibility of fitting out of external electron membrane of Se atoms till the stable configuration s^2p^6 increases. In this connection the bond ionicity of chemical bond between the atoms of given melts increases.

The roentgenograms of $InTl_{0,5}Ga_{0,5}Se_2$ composition and solid solutions on its base significantly differ from the roentgenograms of initial compositions of $TlInSe_2$, $InGaSe_2$ and solid solutions on their base that proves the creation of the new quadrantal phase $TlIn_2GaSe_4$ in $TlInSe_2$-$InGaSe_2$ system.

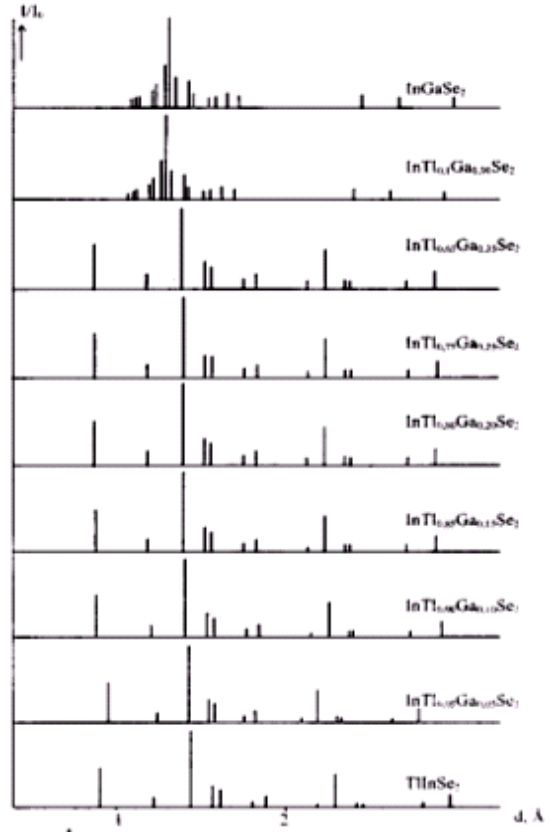

Fig.1. The bar-diagram of the melts of $TlInSe_2$-$InGaSe_2$ system.

The indicating results of obtained roentgenograms showed, that the investigated melts of $InTl_{1-x}Ga_xC_2$ systems are crystallized in tetragonal syngony.

Table 1.1

Interfacial distances (on Å), indexes on melt roentgen grams of $InTl_{1-x}Ga_xSe_2$ system

hkl	$TlInSe_2$			$InTl_{0,95}Ga_{0,05}Se_2$			$InTl_{0,9}Ga_{0,1}Se_2$			$InTl_{0,85}Ga_{0,15}Se_2$			$InTl_{0,3}Ga_{0,7}Se_2$			$InTl_{0,72}Ga_{0,28}Se_2$		
	$a=8.02$, $c=7.15$ Å			$a=8.00$, $c=7.13$ Å			$a=7,97$, $c=7.10$ Å			$a=7,94$, $c=7.07$ Å			$a=7,90$, $c=7.05$ Å			$a=7,88$, $c=7.02$ Å		
	d_x Å	d_m Å	θ	d_x Å	d_m Å	θ	d_x Å	d_m Å	θ	d_x Å	d_m Å	θ	d_x Å	d_m Å	θ	d_x Å	d_m Å	θ
1	2	3	4	2	3	4	2	3	4	2	3	4	2	3	4	2	3	4
211	3,206	3,211	13°51′	3,198	3,202	13°55′	3,185	3,185	14°00′	3,173	3,173	14°03′	3,159	3,160	14°06′	3,149	3,151	14°09′
112	3,024	3,040	14°41′	3,016	3,024	14°45′	3,004	3,004	14°51′	2,991	2,992	14°55′	2,981	2,985	14°57′	2,970	2,970	15°02′
202	2,668	2,674	16°45′	2,661	2,662	16°49′	2,651	2,651	16°49′	2,640	2,641	16°58′	2,630	2,633	17°01′	2,621	2,621	17°06′
221	2,636	2,635	17°00′	2,629	2,636	17°00′	2,619	2,619	17°06′	2,609	2,609	17°10′	2,597	2,597	17°16′	2,590	2,590	17°18′
301	2,504	2,504	17°55′	2,498	2,505	17°55′	2,488	2,488	18°02′	2,479	2,479	18°06′	2,467	2,467	18°12′	2,460	2,460	18°15′
311	2,390	2,390	18°48′	2,384	2,381	18°53′	2,375	2,375	18°56′	2,366	2,366	19°00′	2,355	2,355	19°06′	2,348	2,348	19°09′
312	2,069	2,068	21°52′	2,062	2,063	21°56′	2,055	2,055	22°01′	2,047	2,047	22°07′	2,038	2,039	22°12′	2,032	2,032	22°17′
123	1,985	1,984	22°51′	1,980	1,979	22°55′	1,972	1,972	23°00′	1,964	1,964	23°06′	1,957	1,959	23°10′	1,949	1,950	23°16′
303	1,779	1,784	25°36′	1,774	1,774	25°45′	1,767	1,767	25°51′	1,760	1,760	25°58′	1,753	1,755	26°03′	1,747	1,747	26°10′
313	1,737	1,736	26°21′	1,732	1,732	26°25′	1,725	1,725	26°32′	1,718	1,719	26°38′	1,712	1,713	26°44′	1,706	1,706	26°51′
214	1,600	1,599	28°49′	1,595	1,595	28°54′	1,589	1,589	29°01′	1,582	1,582	29°09′	1,577	1,579	29°13′	1,571	1,571	29°22′
530	1,375	1,376	34°04′	1,372	1,372	34°10′	1,367	1,367	34°19′	1,362	1,362	34°28′	1,355	1,355	34°40′	1,351	1,351	34°47′
371	1,042	1,040	47°49′	1,039	1,039	47°53′	1,035	1,035	48°08′	1,031	1,031	48°23′	1,026	1,026	48°42′	1,024	1,024	48°49′

Table 1.2

	$InTl_{0.7}Ga_{0.3}Se_2$			$InTl_{0.65}Ga_{0.35}Se_2$			$InTl_{0.6}Ga_{0.4}Se_2$				$InTl_{0.55}Ga_{0.45}Se_2$			$InTl_{0.5}Ga_{0.5}Se_2$		
	$a = 7.85$, $c = 6.99$ Å			$a = 7.82$, $c = 6.97$ Å			$a = 7,78$, $c = 6.94$ Å				$a = 6,48$, $c = 6.87$ Å			$a = 6,46$, $c = 6.85$ Å		
hkl	$d_{эк}$ Å	$d_{теор}$ Å	θ	$d_{эк}$ Å	$d_{теор}$ Å	θ	$d_{эк}$ Å	$d_{теор}$ Å	θ	hkl	$d_{эк}$ Å	$d_{теор}$ Å	θ	$d_{эк}$ Å	$d_{теор}$ Å	θ
1	2	3	4	2	3	4	2	3	4	1	2	3	4	2	3	4
211	3,137	3,137	14°13′	3,125	3,126	14°16′	3,110	3,110	14°21′	200	3,240	3,240	13°45′	3,230	3,230	13°48′
112	2,958	2,958	15°06′	2,948	2,948	15°09′	2,935	2,935	15°13′	210	2,898	2,898	15°25′	2,889	2,889	15°28′
202	2,610	2,611	17°10′	2,602	2,601	17°14′	2,589	2,590	17°18′	211	2,670	2,670	16°46′	2,662	2,662	16°49′
221	2,580	2,580	17°22′	2,570	2,570	17°18′	2,557	2,557	17°32′	222	1,906	1,906	23°51′	1,900	1,900	23°55′
301	2,451	2,451	18°19′	2,442	2,441	18°24′	2,429	2,429	18°30′	302	1,828	1,828	24°56′	1,823	1,823	25°00′
311	2,339	2,339	19°14′	2,331	2,331	19°18′	2,319	2,319	19°24′	312	1,760	1,760	25°58′	1,755	1,755	26°03′
312	2,024	2,024	22°22′	2,017	2,017	22°26′	2,007	2,007	22°34′	004	1,718	1,717	26°40′	1,713	1,713	26°44′
123	1,941	1,942	23°22′	1,935	1,935	23°28′	1,926	1,926	23°35′	400	1,620	1,620	28°24′	1,615	1,615	28°30′
303	1,740	1,740	26°17′	1,734	1,734	26°23′	1,726	1,726	26°31′	322	1,592	1,592	28°57′	1,588	1,588	29°02′
313	1,699	1,699	26°58′	1,693	1,693	27°04′	1,685	1,685	27°13′	204	1,517	1,517	30°32′	1,513	1,513	30°39′
214	1,564	1,564	29°31′	1,560	1,560	29°36′	1,553	1,553	29°45′	214	1,478	1,477	31°19′	1,473	1,473	31°33′
530	1,346	1,346	34°55′	1,341	1,341	35°04′	1,334	1,334	35°18′	420	1,449	1,449	32°08′	1,444	1,444	32°15′
371	1,020	1,020	49°05′	1,016	1,016	49°21′	1,011	1,011	49°40′	332	1,396	1,396	33°30′	1,391	1,391	33°39′
-	-	-	-	-	-	-	-	-	-	005	1,374	1,374	34°07′	1,370	1,370	34°14′
-	-	-	-	-	-	-	-	-	-	500	1,296	1,296	36°30′	1,292	1,292	36°39′
-	-	-	-	-	-	-	-	-	-	510	1,271	1,271	37°19′	1,267	1,267	37°28′
-	-	-	-	-	-	-	-	-	-	215	1,242	1,241	38°24′	1,238	1,238	38°30′

Table 2.1

Interfacial distances (on Å), indexes on melt roentgen grams of $InTl_{1-x}Ga_xTe_2$ system

$TlIn_2GaSe_4$				$TlIn_2GaTe_4$				$Tl_{0.8}InGa_{0.2}Te_2$				$Tl_{0.7}InGa_{0.3}Te_2$			
$a=6{,}46$, $c=6.85$ Å				$a=6.60$, $c=7.22$ Å				$a=8.38$, $c=7.14$ Å				$a=8{,}31$, $c=7.12$ Å			
hkl	$d_{эк}$ Å	$d_{изм}$ Å	θ	*hkl*	$d_{эк}$ Å	$d_{изм}$ Å	θ	*hkl*	$d_{эк}$ Å	$d_{изм}$ Å	θ	*hkl*	$d_{эк}$ Å	$d_{изм}$ Å	θ
1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
200	3,226	3,230	13°50′	200	3,228	3,300	13°49′	012	3,283	3,281	13°35′	210	3,823	3,816	11°38′
210	2,863	2,889	15°37′	210	2,948	2,952	15°09′	003	2,385	2,380	18°52′	302	2,148	2,146	21°02′
211	2,664	2,662	16°50′	211	2,738	2,732	16°21′	312	2,118	2,120	21°21′	401	1,978	1,974	22°56′
222	1,906	1,900	23°51′	300	2,225	2,200	20°16′	331	1,890	1,893	24°04′	420	1,871	1,878	24°20′
302	1,832	1,823	24°53′	310	2,135	2,139	21°10′	114	1,702	1,708	26°56′	402	1,788	1,794	25°32′
312	1,759	1,754	25°59′	113	2,081	2,087	21°45′	403	1,570	1,567	29°24′	114	1,696	1,704	27°02′
004	1,706	1,712	26°52′	203	1,941	1,944	23°24′	441	1,441	1,442	32°21′	520	1,549	1,543	29°51′
400	1,615	1,615	28°31′	213	1,866	1,865	24°24′	105	1,396	1,407	33°31′	441	1,414	1,439	33°02′
322	1,583	1,588	29°08′	321	1,767	1,774	25°24′	305	1,256	1,270	37°52′	600	1,390	1,385	33°41′
204	1,513	1,513	30°38′	104	1,738	1,741	26°37′	443	1,238	1,252	38°31′	630	1,242	1,239	38°22′
214	1,474	1,473	31°32′	400	1,647	1,650	27°55′	542	1,215	1,222	39°23′	533	1,216	1,222	39°21′
420	1,433	1,444	32°33′	331	1,523	1,521	30°25′	700	1,180	1,190	40°48′	720	1,134	1,144	42°50′
332	1,388	1,391	33°44′	402	1,488	1,501	31°12′	623	1,150	1,152	42°06′	425	1,129	1,130	43°04′
005	1,366	1,370	34°21′	421	1,442	1,446	32°19′	216	1,127	1,134	43°10′	731	1,079	1,079	45°36′
500	1,282	1,292	36°58′	105	1,400	1,411	33°25′	515	1,073	1,075	45°56′	515	1,070	1,072	46°06′
510	1,268	1,267	37°27′	422	1,368	1,366	34°18′	517	1,070	1,065	46°06′	800	1,036	1,039	48°05′
215	1,234	1,238	38°40′	502	1,230	1,240	35°25′	800	1,040	1,041	47°48′	426	1,000	1,000	50°26′
440	1,148	1,142	42°11′	600	1,084	1,100	48°12′	734	0,931	0,933	55°54′	661	0,969	0,970	52°42′
441	1,127	1,126	43°09′	-	-	-	-	931	0,871	0,871	62°16′	900	0,913	0,923	57°36′
116	1,106	1,108	44°11′	-	-	-	-	636	0,855	0,859	64°22′	911	0,893	0,910	59°41′
425	0,992	0,994	50°58′	-	-	-	-	313	0,840	0,845	66°36′	931	0,869	0,869	62°31′

Table 2.2

$Tl_{0,6}InGa_{0,4}Te_2$				$Tl_{0,2}InGa_{0,8}Te_2$				$Tl_{0,45}InGa_{0,55}Te_2$				$Tl_{0,55}InGa_{0,45}Te_2$			
$a=6,62$, $c=7.23$ Å				$a=8.20$, $c=7.10$ Å				$a=7.27$, $c=7.11$ Å				$a=6,61$, $c=7.22$ Å			
hkl	$d_\perp$ Å	$d_{\text{изм}}$ Å	θ	hkl	$d_\perp$ Å	$d_{\text{изм}}$ Å	θ	hkl	$d_\perp$ Å	$d_{\text{изм}}$ Å	θ	hkl	$d_\perp$ Å	$d_{\text{изм}}$ Å	θ
1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
212	2,287	2,290	19°42'	103	2,269	2,269	19°51'	311	2,179	2,187	20°36'	113	2,148	2,140	21°02'
222	1,961	1,965	23°09'	312	2,100	2,100	21°09'	302	2,006	2,002	22°39'	302	1,877	1,881	24°15'
321	1,783	1,780	25°37'	400	2,055	2,055	22°37'	401	1,770	1,761	25°49'	104	1,745	1,741	26°13'
204	1,588	1,586	29°03'	322	1,890	1,890	24°03'	114	1,709	1,680	26°49'	330	1,557	1,558	29°41'
421	1,441	1,450	32°21'	332	1,708	1,708	26°21'	331	1,664	1,666	27°36'	005	1,440	1,444	32°22'
324	1,289	1,288	36°44'	403	1,550	1,550	29°44'	403	1,450	1,442	32°07'	206	1,129	1,131	43°04'
225	1,233	1,230	38°42'	522	1,397	1,397	33°42'	215	1,306	1,303	36°11'	611	1,082	1,087	45°26'
305	1,213	1,209	39°28'	631	1,203	1,203	39°28'	531	1,229	1,228	38°51'	540	1,079	1,075	45°36'
513	1,144	1,143	42°22'	405	1,163	1,163	41°22'	325	1,159	1,162	41°42'	405	1,033	1,032	48°27'
523	1,096	1,095	44°42'	505	1,069	1,069	46°42'	405	1,123	1,120	43°21'	603	0,997	1,002	50°39'
443	1,051	1,053	47°13'	326	1,032	1,032	48°13'	720	1,004	0,999	50°10'	217	0,969	0,974	52°42'
117	1,013	1,009	49°33'	625	0,930	0,930	55°33'	217	0,978	0,970	52°01'	710	0,936	0,935	55°27'
316	0,991	1,004	51°04'	427	0,883	0,883	60°04'	426	0,956	0,958	53°45'	553	0,872	0,871	62°08'
701	0,944	0,938	54°45'	626	0,868	0,868	62°45'	731	0,952	0,946	54°04'	526	0,854	0,859	64°31'
621	0,922	0,917	56°44'	932	0,839	0,839	66°44'	650	0,935	0,931	55°32'	800	0,840	0,826	66°36'
407	0,878	0,876	61°24'	941	0,827	0,827	68°24'	800	0,911	0,909	57°48'	-	-	-	-
526	0,861	0,861	63°33'	-	-	-	-	108	0,885	0,882	60°35'	-	-	-	-
228	0,846	0,843	65°40'	-	-	-	-	832	0,825	0,828	69°08'	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

The results of roentgenographical investigation of the melts of $InTl_{1-x}Ga_xSe_2$ systems are given in table 1.

In fig.2 the dependence of lattice parameters of the melts $InTl_{1-x}Ga_xSe_2$ on composition is presented.

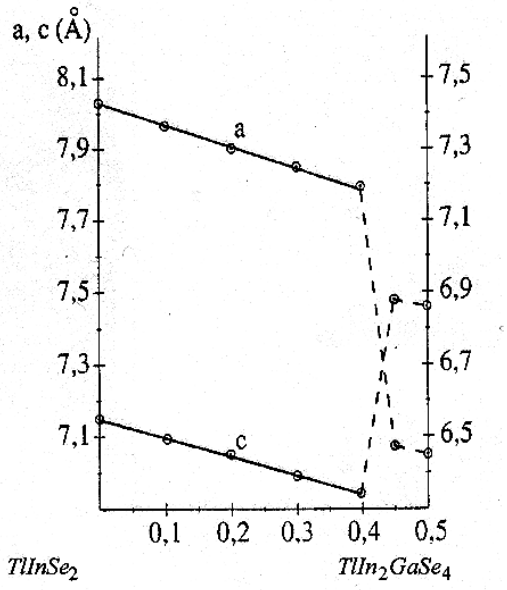

Fig.2. The dependence of parameters of elementary cells of the melts of $InTl_{1-x}Ga_xSe_2$ system on composition.

As it is followed from the fig.2 the parameters of elementary cells "*a*" and "*c*" orderly decrease at the partial replacement of thallium atoms by Ga atoms. The change of cell parameters is explained by the difference of interacting atom radiuses. The parameters of elementary cells of new phase $TlIn_2GaSe_4$ and solid solutions on its base significantly differ from lattice parameters of initial compounds and solid solutions on their base. This proves about the creation of new quadrantal phase in the given system. The change of lattice parameters in solubility regions takes place on the additivity law and essential inclinations from Vegard law doesn't observed in the investigated concentration interval.

As it was shown in [2] in $TlInTe_2$-$InGaTe_2$ system the big region of solubility is observed. That's why the lattice parameters of obtained solid solutions had been defined by us with the aim of the provement state diagram of this system. The experimental data, necessary for the definition of lattice parameters were based on difractograms. It is revealed the lattice parameters decrease to the side of $InGaTe_2$ compound in region 55-100 mol.% $InGaTe_2$. Such order change of lattice parameters is typically through the solubility region. Exactly, lattice parameters are increased from $InGaTe_2$ and $TlInTe_2$ compounds (fig.3).

The lattice parameters in region 52-70 mol.% $InGaTe_2$ strongly differ from the regions 0-20 mol.% $InGaTe_2$ and 55-100 mol.% $InGaTe_2$. Probably, in this region the solid solutions are created on the base of new phase. The decrease of parameter lattice on additivity law is the reason of the replacement of thallium atoms by small Ga atoms in the plane of structure base.

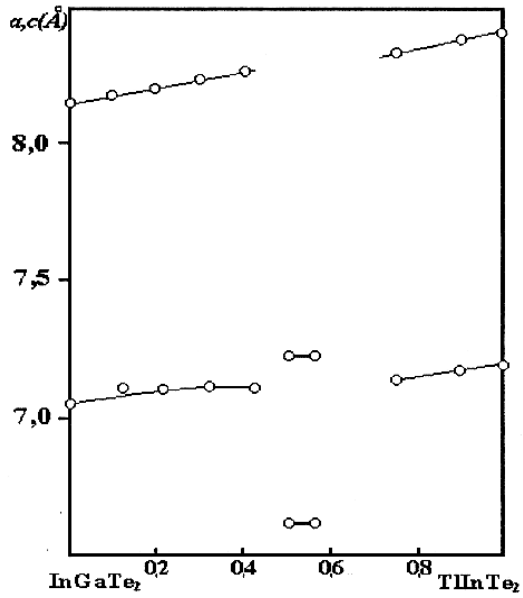

Fig.3. The dependence of lattice parameters on the composition of melts of $InTl_{1-x}Ga_xTe_2$ system.

The results of roentgenogaphic investigations of the melts $TlInTe_2$-$InGaTe_2$ are given in the table 2.

As we already mentioned, the melts $InGaTe_2$ with $TlInTe_2$ also as compounds $InGaTe_2$ and $TlInTe_2$ are crystallized in tetragonal lattice. That's why the superstructure lines don't appear on difractograms in solubility region. The absence of superstructure lines proves that all investigated melts of solid solutions in order and disorder states also as compounds $InGaTe_2$ and $TlInTe_2$ crystallize in the same syngony.

The lines, character for the $TlGaTe_2$ compound appear in solubility region on the base of $TlInTe_2$ (0-20 mol.%) $TlGaTe_2$ and continue to appear till the melt $Tl_{0,7}InGa_{0,3}Te_2$. The additional lines for the melts, consisting 60,55,50 mol/% $TlInTe_2$ appear in solubility region on the base of new phase. These results give us the foundation to prove in the rightness of state diagram of $TlInTe_2$-$InGaTe_2$ system.

The new compounds $TlIn_2GaSe_4$ (Te_4) revealed in $TlInTe_2$-$InGaTe_2$ systems are carried out by roentgen phase investigations.

The experimental necessary material for the calculation of $TlIn_2GaSe_4$ and $TlIn_2GaTe_4$ lattice parameters was consist from crystallograms also. On the base of the carried out investigation it is revealed that these phases crystallize in tetragonal syngony and have the following periods of elementary cells a=6,46Å; c=6,85Å correspondingly.

Thus, compounds $TlIn_2GaSe_4$ and $TlIn_2GaTe_4$ crystallize in tetragonal syngony as well as initial ones. But lattice parameters significantly differ from the parameters of double and triple analogues of TlSe. Probably, this is connected with the new reconstruction of component atoms.

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E.Ə. Allahyarov

$TlInC_2^{VI} - InGaC_2^{VI}$ ƏRİNTİLƏR SİSTEMİNİN RENTGENOQRAFİK TƏDQİQİ

Rentgenoqrafik tədqiqatlar yolu ilə $TlInC_2^{VI} - InGaC_2^{VI}$ ərintilər sisteminin elementar özəklərinin parametrləri təyin olunmuşdur.

Э.А. Аллахяров

РЕНТГЕНОГРАФИЧЕСКИЕ ИССЛЕДОВАНИЯ СПЛАВОВ СИСТЕМ $TlInC_2^{VI} - InGaC_2^{VI}$

Рентгенографическими исследованиями определены параметры элементарных ячеек сплавов систем $TlInC_2^{VI} - InGaC_2^{VI}$.

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