



Beynəlxalq Konfrans "Fizika-2005" International Conference "Fizika-2005" Международная Конференция "Fizika-2005"

7 - 9

iyun
June 2005
Июнь

№44

səhifə
page 174-179
стр.

Bakı, Azərbaycan

Baku, Azerbaijan

Баку, Азербайджан

GROWTH OF ORTHORHOMBIC AND TETRAGONAL MODIFICATIONS OF $TlInS_2$ FROM MONOCLINIC CRYSTAL

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The growth technology, roentgenograms and some physical properties of single crystals of orthorhombic and tetragonal modification of $TlInS_2$ are investigated. The lattice parameters and the syngony of the grown crystals are defined from the X-ray investigations (Laue, Weissenberg, oscillating crystal and powder diffractions). The following values of the lattice parameters - $a = 6.88 \text{ \AA}$, $b = 14.04 \text{ \AA}$, $c = 4.02 \text{ \AA}$, $Z = 4$ and $a = b = 7.76 \text{ \AA}$, $c = 29.6 \text{ \AA}$, $Z = 20$ are established for orthorhombic and tetragonal modifications correspondingly. The space groups were defined for orthorhombic and tetragonal crystals as $P2_12_12_1$ and $P4_12_12$ correspondingly. It was shown that transition of different polytypes ($c \approx 15 \text{ \AA}$, $c \approx 30 \text{ \AA}$ and $c \approx 60 \text{ \AA}$) of monoclinic crystals to both modifications takes place through the intermediate state of monoclinic crystals. In this state the unit cell consists of unit packets with $c \approx 15 \text{ \AA}$ being situated randomly in the direction of the c-axis. The results of the dielectric constant in the temperature range 170-300K and the spectral dependence of photoconductivity at $T=300\text{K}$ are presented. It is established that the orthorhombic modification of $TlInS_2$ has a slightly higher band gap ($E_g = 2.52 \pm 0.01 \text{ eV}$) than the monoclinic one. But the band gap of the tetragonal modification ($E_g = 1.87 \pm 0.01 \text{ eV}$) is sufficiently lower than that of the monoclinic modification.

1. INTRODUCTION

It is known that the composition $TlInS_2$ has five stable structural modifications [1-6]. They are the following: monoclinic (MCM) [1,2], orthorhombic (ORM) [1], tetragonal (TM) [3], hexagonal (HM) [4,5] and triclinic [6] modifications. Not all the mentioned modifications are defined precisely in the state diagrams (pressure – temperature ($p-T$) and temperature-composition ($T-x$)). So, it is difficult to obtain any modification except the MCM. While investigating the state diagram of the $TlS-InS$ system the authors of [7] observed the only phase transition (PT) at a temperature 905K, interpreting it as a transition of HM to MCM. It is known that crystallization from the stoichiometric melt (Bridgman-Strocbarcer method) leads to forming of the MCM only (space group $C2/c$). The transition of MCM of $TlInS_2$ into other modifications takes place by varying temperature $T < T_{\text{melt}}$ and pressure- p . It was shown in [4] that MCM $TlInS_2$ at $p=30\text{kbar}$ and $T=573\text{K}$ transforms to metastable rhombohedral phase (space group (s. g.) $R\bar{3}m$, $a = 3.83 \text{ \AA}$, $c = 22.23 \text{ \AA}$ and $Z=3$). Both MCM and rhombohedral crystals transforms to stable HM (s.g.

$P6_3/mmc$, $a = 3.83 \text{ \AA}$, $c = 14.88 \text{ \AA}$ and $Z=2$) at $T=673\text{K}$ and $p=30\text{kbar}$, which at $T>693\text{K}$ transforms back to the MCM. According to [9] the transition from HM to the MCM is an endothermic process and takes place at normal pressure as a result of long-time annealing at $T=785\text{K}$.

Our attempt to find the tetragonal or orthorhombic modifications in the $p-T$ phase diagram of the stoichiometric $TlInS_2$ was failed. So in this paper we investigate the possibility of obtaining different modifications of $TlInS_2$ in non stoichiometric compositions. It is known that in $T-x$ phase diagram (x -is composition) of the $(TlS)_{1-x} - (InS)_{1+x}$ system there exists a sufficiently high region of solubility $x(\pm 0.05)$ and the crystallization of $Tl_{1+x}In_{1-x}S_2$ alloys takes place at lower temperatures ($\Delta T \approx 15\text{K}$ for $x = \pm 0.05$) with forming of MCM only. When cooling these crystals of MCM they transforms to HM at $T \approx 785\text{K}$ if $x > 0.001$. So growing from melt allows one to obtain $TlInS_2$ MCM crystals with excess or deficit of Tl or In. This method allows to grown the crystals

with deficit of S but gives no possibility to obtain crystals with excess of S from stoichiometry because at melting temperature sulphur being in vapor phase is separated from the composition. So if there is the possibility to transform the crystal of MCM to other modifications at cooling then this process would take a long time annealing. For this reason we used long-time annealing TlInS₂ of MCM crystals with an excess of an anion. In particular, it was established that both ORM and TM can be grown from the stoichiometric MCM of TlInS₂ with an excess of sulfur. This means that indicated modifications exist in phase diagram of p-T with $T < T_{melt}$ and p is pressure of sulfur vapor. The growth technology, the results of X-ray, photoelectric and dielectric investigation of samples of ORM and TM TlInS₂ crystals are given in this paper. It was shown in [5] that deviation from the stoichiometry due to excess of Tl and In atoms don't lead to forming of orthorhombic and tetragonal phases. However, the excess of Tl easily leads to forming of HM. It is known that excess of S does not lead to forming of other modifications, except of MCM, when growth while melting takes place. It is due to the fact that the existence region of orthorhombic phase corresponds to sufficiently lower temperatures than T_{melt} . It was established in [11-12] that the annealing of MCM of TlInS₂ at the temperatures $T < 750K$ in sulfur vapor at pressures up to 3-5at leads to filling of sulfur defects in the lattice and does not lead to forming of other modifications. So, in this paper the experiments with an excess of sulfur were made at temperatures $750 < T < T_{melt}$.

2. GROWTH TECHNOLOGY AND MEASUREMENTS

The crystals of ORM of TlInS₂ have been grown using the method of sublimation of MCM crystals in sulfur vapor at temperatures within 815-865K. TM of TlInS₂ was obtained by the same way at rather higher temperatures within 890-950K. The temperature gradient was within the interval of 5-6K/cm. The accuracy of the temperature established in the oven was $\pm 2K$. For stabilization of temperature the regulator BRT-2 was used. The crystals were grown in quartz ampoules evacuated up to $1.3 \cdot 10^{-2} Pa$. The amount of MCM crystals taken was 3-4g. To increase the efficiency of growth the crystals were crushed up to sizes of $1 \times 1 \times 1 mm^3$. The amount of sulfur was chosen according to the gas state equation $pV = RTm / \mu$ to obtain a pressure of sulfur vapor 3-5at. The calculations were done taking into account the volume of ampoule V and μ (the number of sulfur atoms in molecule S₄ at $800K < T < 900$ and S₂ at $T > 900K$). Because of a low rate of phase transition the growing process took a sufficiently long time (4-5 weeks). Laue, oscillating and rotating crystal X-ray of the grown crystals were done in a RCOP-A chamber using the URS-60 arrangement and RGNS goniometer. Powder X-ray patterns of the crystals were obtained by DRON-2 using a K α radiation line of Cu within the angles

$4^{\circ} < \vartheta < 35^{\circ}$. The calculation of inter-planar distances for the appropriate crystal structures were made according to the formulas given in [13]. Obtained ORM and TM crystals were investigated by differential thermal analysis (DTA) up to the melting point, using a low-frequency NTR-70 thermal detector. The dielectric measurements were made at temperatures of 120-650K with the use of the alternate current bridges E7-8 (1kHz) and E7-12(1MHz). The rapidity of temperature scanning was 0.1K/min. The spectral dependence of photoconductivity of samples were investigated using MDR-24 monochromator.

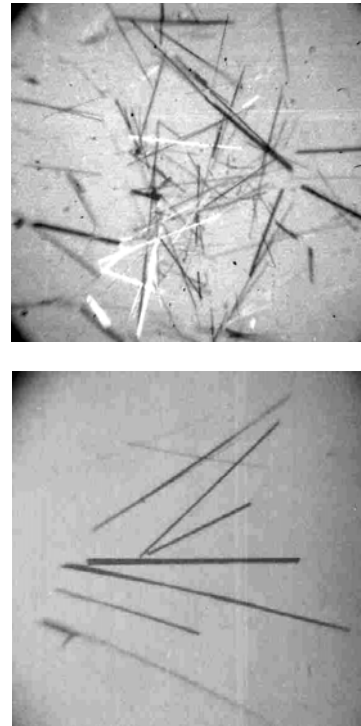


Fig.1. Appearance of ORM and TM of TlInS₂: a- TlInS₂ of ORM - scale 1x4; b- TlInS₂ of TM-scale 1x2.5.

3. THE RESULTS OF EXPERIMENTS

3.1. ORM of TlInS₂.

Experiments show that ORM of TlInS₂ crystal growth takes place at temperatures of $815K < T < 865K$. At temperatures higher than 875K the growth ORM from MCM ceased. When MCM sample is placed at the indicated temperature range the growth of ORM takes place on a MCM crystal surface. If the MCM crystal is placed at $875 > T > 865K$ then the sublimation of the MCM occurs, and at some distance from it, where the temperature is about 850-860K, the growth of an ORM takes place. If an alloy of TlInS₂ is used instead of MCM crystal, the whole sample gradually transforms to randomly oriented columns of ORM chained crystals. Needle-shaped ORM crystals are yellow colored with truncated under 45° edges fig1(a).

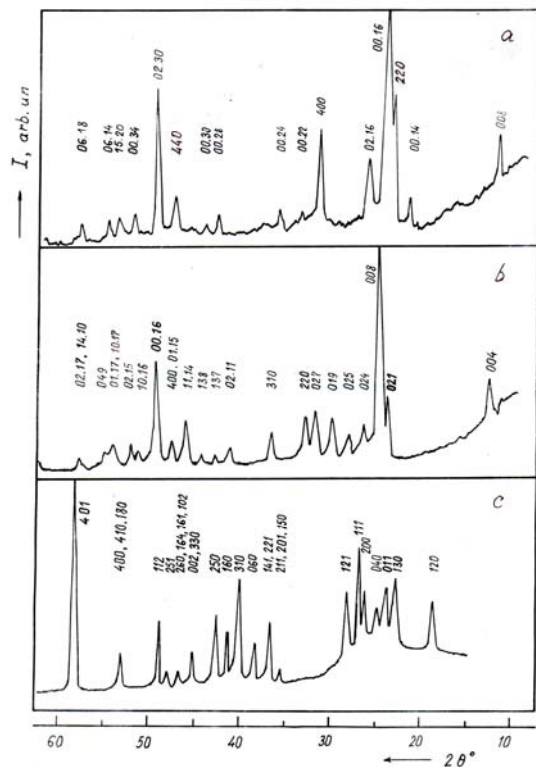


Fig.2 Powder X-ray patterns of: a-MCM (polytype $c=60$): b- TM; c-ORM

The process of transforming of MCM to ORM does not take place in the absence of sulfur vapor. The rate of process would be lowered considerably when the sulfur pressures is smaller than 3at. Note that this growth method resembles the gas transport one in which sulfur plays the role of the transport agent. Needle-shaped crystals are elastic on curving. When pressing they are easily split on needles of a smaller transverse size. The splitting takes place along the direction $\langle 010 \rangle$. ORM crystals have hole-type conductivity with the resistivity of the order 10^6 - $10^7 \Omega \cdot cm$, which is rather smaller than that of MCM 10^8 - $10^{10} \Omega \cdot cm$.

Sizes of ORM crystals are about $15 \times 0.03 \times 0.03 \text{ mm}^3$. The experimental data of diffraction line positions, their relative intensities, the calculated values of inter-planar distances and Miller indexes obtained from powder X-ray patterns of the TlInS_2 ORM are given in table 1. Note that as a base crystal of MCM

TlInS_2 we have taken the polytype with $c \approx 60 \text{ \AA}$. In fig.2 (a and b) for comparison are given powder X-ray patterns of base and ORM crystals. From the comparison of the experimental and calculated values of inter-planar distances and identification of reflexes according to [13,15] it was established that obtained crystals have an orthorhombic structure. From the analysis of X-ray data of powder and bulk crystals we could define the following parameters of the unit cell:

$a = 6.88 \text{ \AA}$, $b = 14.04 \text{ \AA}$, $c = 4.02 \text{ \AA}$, $Z=4$ and X-ray density $d=6.59 \text{ g/cm}^3$. From the identifications of powder X-ray pattern lines and conditions limiting possible reflections the only possible s.g.- $P2_12_12_1$ can be chosen for ORM of TlInS_2 . The direction of columns is along the b-axis i.e. $\langle 010 \rangle$ of the crystal. Our results slightly differ from that given in [1] for ORM of TlInS_2 : $a=6.56 \text{ \AA}$, $b=14.92$, $c=3.81 \text{ \AA}$, $Z=4$, with space group- $C222_1$ and $d=6.82 \text{ g/cm}^3$. It is known that for space group $C222_1$ for $(h k l)$ $h+k=2n$ and for $(00l)$ $l=2n$. As seen from table 1 these conditions are not satisfied for many reflexes given in it. To our mind these differences testifies on existing two different structures for orthorhombic crystals of TlInS_2 .

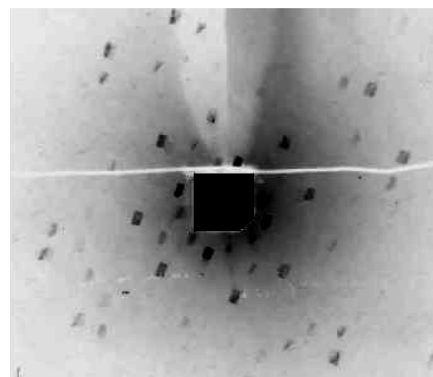
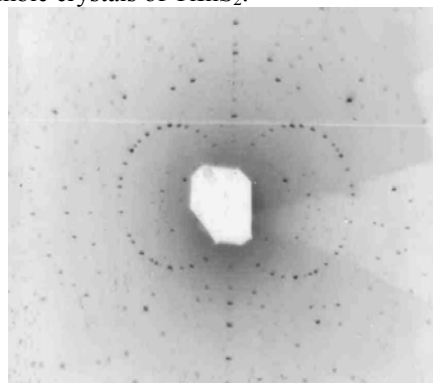


Fig.3 .Laue patterns of TlInS_2 crystals: a- ORM; b- TM.

The Laue pattern of ORM sample is shown in figure 3(a). The direction $\langle 010 \rangle$ of crystal was posed normally to the direction of radiation. Clearness of layout of points and the absences of haloes in them testifies to the high quality of the grown crystals. Three symmetry axis of the second order (one of which is normal to the plane of figure) is clearly seen in Laue.

We think that ORM of TlInS_2 is isomorphic to AgErSe_2 [14] which has the following crystallographic parameters: $a=6.87 \text{ \AA}$, $b=13.79 \text{ \AA}$, $c=4.17 \text{ \AA}$, $Z=4$, with the same s.g.- $P2_12_12_1$. AgErSe_2 also has column (chained) structure with the direction of columns along the b axis. It consists of tetrahedrons AgSe_4 and octahedrons ErSe_6 (correspondingly with Ag and Er inside) in the order indicated in fig.4.

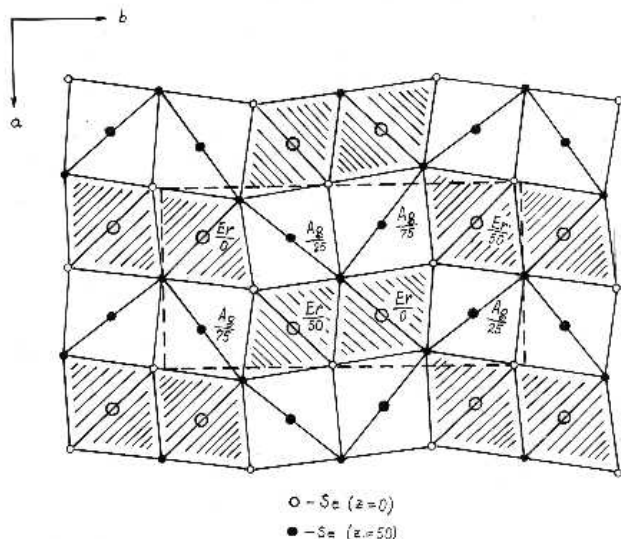


Fig.4. Projection of the unit cell of AgErSe_2 (ORM) crystal structure in plane (001) [14]. ORM of TlInS_2 has the same structure in which Ag and Er atoms are replaced with In and Tl ones correspondingly.

Ag (Er) atoms in this structure form a frame consisting from doubled filaments of tetrahedrons (octahedrons) with common Se tops directed normal to the c-axis. We offer a similar structure for ORM of TlInS_2 with In (Tl) atoms inside the tetrahedrons (octahedrons). Note that TlInSe_2 is another representative of $A^3B^3C_2^6$ which differs from TlInS_2 by replacing the anion S with Se, when grown from melt has also column (tetragonal) structure. So, it is natural to expect that TlInS_2 would have a column structure too. ORM of TlInS_2 is stable up to melting temperature which is the same as for MCM ($T_{\text{melt}}=1033\text{K}$). DTA shows a single peculiarity corresponding to melting point. After melting it crystallizes in MCM again. It is natural that physical properties of ORM would differ from those of other modifications. The results of some measurements of ORM are given below. The temperature dependence of the dielectric function's real part $\epsilon(T)$ is the most characteristic for MCM of TlInS_2 because of known ferroelectric phase transition in the temperature range of 190-240K being accompanied by dielectric anomaly. $\epsilon(T)$ -dependence for ORM of TlInS_2 is shown in fig5 (curve1). For comparison, the same dependence for the initial MCM is given also (curve3). As it is seen from fig 5 the dielectric function of the ORM is almost constant in the temperature range 120-270K, testifying to the absence of PT. Rising of $\epsilon(T)$ at $T>280\text{K}$ is rather strange and unclear. The similar increase of $\epsilon(T)$ takes place in TlInS_2 of HM (curve2). The spectral dependence of photoconductivity (PC) $I(\hbar\omega)$ for different modifications of TlInS_2 at $T \approx 300\text{K}$ is shown in fig. 6. As against MCM

TlInS_2 having the maximum of PC at $2.35 \pm 3 \text{ eV}$ ($\lambda = 522 \pm 3 \text{ nm}$) for ORM the PC maximum takes place at $2.55 \pm 0.02 \text{ eV}$ ($\lambda = 487 \pm 3 \text{ nm}$). The PC spectrum of ORM differs from that of MCM by more sharp decrease at higher energies of quantum. From PC and absorption spectra the forbidden gap value for ORM was determined as $E_g = 2.55 \pm 0.02 \text{ eV}$, which is $\sim 0.2\text{eV}$ higher than that for MCM. The measurement of lux-ampere characteristics shows that photosensitivity of ORM is much less than that of hexagonal and MCM. For example, the ratio of dark to light resistance $\rho_d / \rho_l \approx 2$ for ORM, while that of MCM crystals is an order higher.

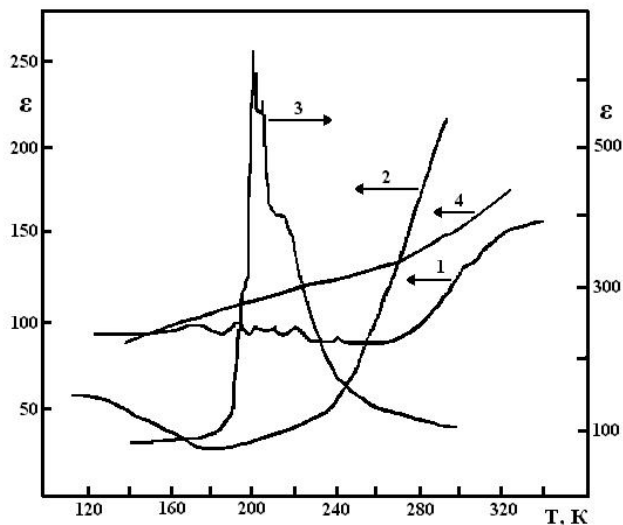


Fig.5. Dependence of real part of the dielectric function $\epsilon(T)$ on temperature -T for samples of different modifications of TlInS_2 : 1- ORM; 2- HM; 3-MCM; 4-TM.

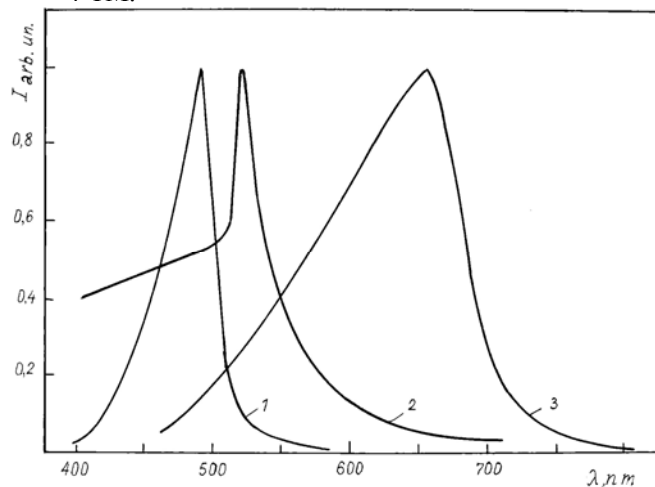


Fig.6. Spectral dependence of PC of different crystals of TlInS_2 : 1-OPM; 2-MCM; 3-TM.

Table1. The experimental data of diffraction line positions, their relative intensities, the calculated values of inter-planar distances and Miller indexes obtained from powder X-ray patterns of TlInS₂ crystal of ORM.

N _{hkl}	θ°	d _{exp.} , Å	d _{calc.} , Å	Δd, Å	I _{rel}	hkl
1	9,00	4,9139	4,9136	0,0003	23	120
2	11,16	3,9716	3,8696	0,102	31	130
3	11,61	3,8164	3,8647	0,0483	35	011
4	12,15	3,6552	3,67	0,0148	23	040
5	12,90	3,4432	3,4400	0,0032	26	200
6	13,20	3,3663	3,3694	0,0031	70	111
7	13,90	3,1999	3,1113	0,0886	35	121
8	17,68	2,5311	2,5695	0,0384	6	211 201 150
9	18,20	2,4611	2,4680	0,0069	28	141 221
10	19,00	2,3611	2,3400	0,0211	23	060
11	19,90	2,2584	2,2633	0,0049	50	310
12	20,50	2,1950	2,2153	0,0203	28	160
13	21,15	2,1314	2,1752	0,0438	43	250
14	22,50	2,0087	2,0057	0,003	19	002 330
15	23,45	1,9324	1,9347	0,0023	13	260 164 161 102
16	23,90	1,8974	1,9131	0,0157	13	251
17	24,40	1,8608	1,9113	0,0505	38	112
18	26,75	1,7084	1,7005	0,0079	19	180 400 410
19	29,10	1,5806	1,5813	0,0007	100	401
20	31,75	1,4618	1,4667	0,0055	28	281 450
21	33,30	1,4001	1,4040	0,0039	14	0.10.0
22	34,80	1,3469	1,3400	0,0069	9	520
23	36,20	1,3015	1,3012	0,0003	38	412 470 1.10.1

3.2. TM of TlInS₂

TM of TlInS₂ was obtained by the same method but only in a temperature range of 930-950K. They were grown at some distance from the initial MCM crystals. They have the form of prismatic columns with sizes 0.5x0.5x10 mm³ and dark-brown color. At temperatures T>975K the sublimated crystals on an ampoule surface have a monoclinic structure again. TM as well as ORM would not be grown in the absence of sulfur vapor, the amount of which was not changed during the annealing process. Columns of TM crystals are also easily chopped to ones with smaller transversal sizes at pressing, which testifies to a layered-chain structure of TM. Resistivity along the direction <001> of TM samples is about 10⁶-10⁷ Ω · cm .

Table2. The experimental data of diffraction lines positions, their relative intensities, the calculated values of inter-planar distances and Miller indexes obtained from powder X-ray patterns of TlInS₂ crystal of TM

N _{hkl}	θ°	d _{exp.} , Å	d _{calc.} , Å	Δd, Å	I _{rel}	hkl
1	5,97	7,385	7,400	0,015	15	004
2	11,66	3,804	3,847	0,043	15	021
3	11,99	3,700	3,700	-	100	008
4	12,97	3,424	3,436	0,012	9	024
5	13,76	3,230	3,245	0,015	9	025
6	14,75	3,020	3,028	0,008	16,5	019
7	15,66	2,840	2,858	0,018	21	027
8	16,25	2,743	2,743	-	15,5	220
9	18,15	2,467	2,453	0,014	11,7	310
10	20,33	2,212	2,211	0,001	6,5	02.11
11	21,22	2,123	2,122	0,001	2,7	137
12	22,00	2,052	2,045	0,007	2,0	138
13	22,80	1,9837	1,973	0,010	16,5	11.14
14	23,65	1,9150	1,9124	0,002	9	400 01.15
15	24,45	1,856	1,856	-	42	00.16
16	25,55	1,7820	1,7995	0,017	4,5	10.16
17	25,97	1,7586	1,7580	-	6,4	02.15
18	26,97	1,6950	1,6980	0,003	6,3	01.17 10.17
19	27,33	1,6737	1,670	0,003	3,3	049
20	28,85	1,5926	1,588	0,004	2,7	02.17 14.10
21	31,33	1,4780	1,476	0,002	6,0	04.13

The experimental data of angular positions of diffraction lines, their relative intensities, the calculated values of inter-planar distances and Miller indexes obtained from powder diffraction patterns of TlInS₂ TM are given in table 2. Comparison of the powder X-ray patterns of TM with MCM is given in fig.2(c). Identification of reflexes according to known method [13, 15] determines the structure of the crystal as a tetragonal. Using the sequences of X-ray investigations (powder, Laue, oscillating crystal and Weissenberg) the parameters of the unit cell were determined as a=b ≈ 7.76Å, c=29.60Å, Z=20. Miller indexes of all reflexes are satisfied to the conditions [17]: for (00l) l = 4n, for (h00) h = 2n and for (0kl)

2k + l = 2n + 1 or 4n. So the s. g. of TM was determined as P4₁2₁2. The Laue pattern of crystal when X-ray is directed along the “needle” (b-axes) is given in figure 3(b). The symmetry axes of the fourth order normal to fig. plane is clearly seen despite the not very good adjustment of sample. It is worth to note that for TlS layer-chained crystals the same space group with almost the same parameters “a” and “c” was established in [16]. The dielectric function temperature dependence of the TM crystal is shown in fig5 (curve 4). As it is seen from it there are no traces of MCM. But for some samples made from the pressed powder of TM a weak anomaly is seen at T=210K in ε(T), which is due presumably to the traces of MCM.

The spectral dependence of photoconductivity of TM is given in fig6 (curve3). The maximum of the photo signal is

at 1.87eV which corresponds to the inter-band absorption of light. The absorption and reflection experiments also give the same value of forbidden gap $E_g = 1.87 \pm 0.02$ eV for TM.

3.3. ONE DIMENCIONAL STACKING DISORDER STATE OF MONOCLINIC TlInS₂

When annealing in sulfur vapor at a temperature range of 815-830K (near to the low boundary of ORM obtaining temperature region), after 3-5 hours monoclinic TlInS₂ transforms to a state in which all X-ray reflexes received from the layer surface disappear gradually, except that of (002) located at angle $\vartheta \approx 6.25^\circ$. Note that for different polytypes of MCM these angle positions (6.25° - 5.85°) and identification of corresponding reflexes are different ((002)- for polytype $c \approx 15\text{\AA}$, (008) – for polytype $c \approx 60\text{\AA}$, (004)- for polytype $c \approx 30\text{\AA}$). Inter-planar distances for this reflex in different polytypes are 7.31-7.5 \AA , respectively. After the annealing of samples of different polytypes all of the mentioned reflexes moved to the same angle position at $\theta = 6.25^\circ$. At the same time all reflexes received in layer directions along the a- and b-axes do not change their angles. These facts allow one to conclude that in the outcome MCM crystals pass trough a one-dimensional stacking disorder state- a state in which layered packets lose translation symmetry in the direction of the c-axis, allocated

chaotically to each other, and save symmetry along the directions of the a- and b-axes.

4. CONCLUSIONS

1. It is established that there exist orthorhombic and tetragonal modifications in a state diagram p-T (p is pressure of sulfur gas) of TlInS₂, which can be obtained from monoclinic crystals by long time annealing in sulfur vapor at pressures of 3-5at. at temperatures of 815-865K and 930-950K, correspondingly.
2. The crystallographic parameters and space groups of ORM and TM are determined as $a=6.88\text{\AA}$, $b=14.04\text{\AA}$, $c=4.02\text{\AA}$, $Z=4$, s. g. P2₁2₁2₁, and $a=b=7.76\text{\AA}$, $c=29.60\text{\AA}$, $Z=20$, s.g. P4₁2₁2 correspondingly.
3. ORM and TM are stable phases of TlInS₂ are not subjected to any phase transitions up to melting points 1033K (for ORM) and 983K (for TM) respectively.
4. Both ORM and TM crystals of TlInS₂ are high band gap layer-chained semiconductors with $E_g=2.55$ eV and $E_g=1.87$ eV correspondingly.
5. At the first stage (3-5hours) of the annealing process of monoclinic crystals TlInS₂, in sulfur atmosphere at a pressure 3-5at. they pass through a quasi-one-dimensional glass state- the state for which layered packets lose translation symmetry in the direction of the c-axis, allocated chaotically to each other, and save symmetry along the directions of the a- and b-axes.

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