

DIELECTRIC FUNCTION AT PHASE TRANSITION FOR DIFFERENT POLYTYPES OF MONOCLINIC MODIFICATION OF TlInS₂ CRYSTALS

O.Z.ALEKPEROV, A.I.NADJAFOV, V.R.ABDURRAHMANOV

*Institute of Physics, Azerbaijan National Academy of Sciences,
AZ 1143, Baku, Javid av.33*

For different polytypes of monoclinic modification of TlInS₂ crystals the dielectric function temperature dependencies $\varepsilon(T)$ at phase transition ($T=190\div 220\text{K}$) are compared with the room temperature X-diffractograms. From this comparison we established correlation between polytypes and $\varepsilon(T)$ - dependence of crystals. For samples containing the pure $c\approx 15\text{\AA}$ polytype the dielectric function $\varepsilon(T)$ has a single anomaly with one narrow peak at $T\approx 205\text{K}$. The peak positions in $\varepsilon(T)$ -dependence for $c\approx 30\text{\AA}$ and $c\approx 60\text{\AA}$ polytypes also are established. For the samples being the admixture of different polytypes the corresponding heights of peaks in $\varepsilon(T)$ -dependence are in accordance with the corresponding lines intensity of X-diffractograms.

INTRODUCTION

Depending on growth technology TlGaSe₂ and TlInS₂ compounds are crystallized in different structural modifications. TlInS₂ is known in tetragonal [1], hexagonal [2-3] monoclinic [4-5] and orthorhombic [4] modifications. The monoclinic modification of TlInS₂ being the layered crystal, has numerous polytypes with different lattice parameters $c = c', 2c', 4c', 8c'$ ($c' \approx 15\text{\AA}$, c - is lattice parameter in the direction normal to layers). For one pocket crystal with $c\approx 15\text{\AA}$ all covalent couplings between atoms is directed inside of pocket, as a result the coupling between pockets are weak van-der Waals forces. For this reason they easily can be shifted concerning to one another. The relative shifting of unit pockets in layer plane along the lattice parameters a or b causes forming of polytypes with different number of pockets $c=2c', 4c' \dots$ in unit cell. The obtaining of this or that polytype is uncontrolled and has random character. Moreover in a given sample many polytypes can exist simultaneously. These polytypes have the same lattice parameters ($a=10.90\text{\AA}$, $b=10.95\text{\AA}$, with angle between them $\alpha = 90^\circ$ and between layer plane and c $\beta = 100.21^\circ$ [5]) in the layer plane. They exhibit the second order structural phase transitions (PT) from high symmetric paraphase to lower symmetric ferroelectric phase [6-8] at temperature fall. Such a PT is accompanied by appearing of spontaneous polarization in low symmetric commensurate and incommensurate phase [7]. The crystal structure of incommensurate phase was established in [9] by detailed low temperature X-ray study of this crystal. Anomalies of physical parameters of a crystal take place near the critical temperatures T_c . For example, the order of value of the dielectric function ε_0 in TlInS₂ increases more than two times reaching the values 10^3 and more in IC phase. This anomaly is believed due to of optic phonon energy softening ($\omega_o \sim |T-T_c|$) as a result of which $\varepsilon(\omega, T) \sim f/(\omega^2 - \omega_o^2(T))$ have the anomaly at $T=T_c$. As a rule $\varepsilon(T)$ -dependence in dielectric measurements differs from sample to sample, having maximums at different temperatures with different heights in the temperature region 220-190K. The only peak at $T\approx 195\text{K}$, which appears in all samples, in many cases as a shoulder, is believed due to ferroelectric commensurate phase transition [8-9]. It is natural to suppose that the different polytypes have slightly different optic phonon energies, which are softening at slightly different temperatures at PT temperature region. In this report we made an

attempt to connect the pictures of $\varepsilon(T)$ -dependencies in variety of TlInS_2 with their X-diffractograms. The X-diffractograms were recorded in DRON-2 (filtered K_α -line of Cu) at room temperature with bias voltage $\sim 40\text{kV}$. The dielectric function measurements were made using the alternate current bridge E7-12 at frequency 1kHz . at temperatures $180\div 240\text{K}$.

X-RAY INVESTIGATIONS OF SAMPLES

For identification of polytypes of the same (monoclinic) modification of TlInS_2 it is enough to have x-diffractograms depending on an angle to the normal of layer surface ϑ . So all reflexes recorded would have $(00l)$ indexes, with l being the even numbers because of monoclinic structure of crystal. X-diffractograms of three samples are shown in Fig.1. The most intensive reflex in each diffractogram is taken as a unit. From the diffractogram of the first sample, consisting of 5 lines the parameter c is determined as $c=14,82\text{\AA}$. The identifications all reflexes $(00l)$ at the corresponding angles (according to formula $1/d_{00l}^2 = l^2 / (c^2 \sin^2 \beta)$) are indicated in Fig.1(a).

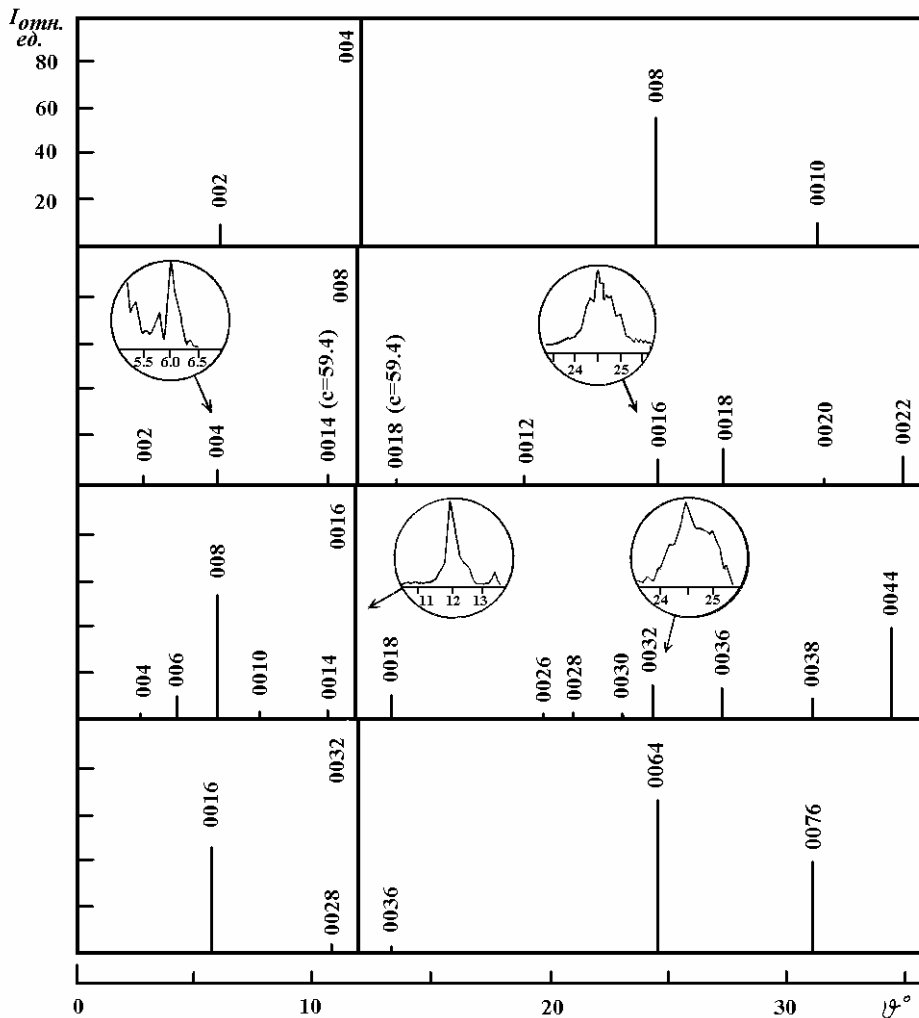


Fig.1.

X-Diffractograms obtained from layer surface of four samples of monoclinic TlInS_2 crystals at room temperature: a- sample1; b-sample2; c-sample3; d- sample4.

They were made in the first order of the interference $2d \sin \theta = n\lambda$ at $n=1$. All reflexes have the same line width but those of (008) and (0010) have noticeable value of the background signal without any satellite structure at the bottoms of reflexes. The diffractogram of the second sample in Fig.1(b) differs significantly from that of the first one. All reflexes, (except for small intensity ones, posed at angles $\vartheta = 10.72^\circ$ and $\vartheta = 13.33^\circ$ allow to identify this sample as a polytype with $c \approx 29.82\text{\AA}$. Note, that despite to apparent coincidence of some reflexes of sample 1 and 2 they slightly differs in angles position, and these differences allow one to make correct identifications of this sample as a polytype with $c=29.82\text{\AA}$. Angles of high intensity reflexes (004) and (008) of sample2 don't coincide with reflexes (0,0,2) and (0,0,4) of sample 1. But reflexes (004) and (008) of sample2 have considerable shoulder with satellite structure at higher angles with positions coinciding with reflexes (002) and (004) of sample1. The same takes place for reflexes (0,0,16) and (0,0,20) of sample2 which have satellites of small intensities at slightly higher angles coinciding with reflexes (0,0,8) and (0,0,10) of sample 1. So, comparative analysis of diffractograms of samples 1 and 2 shows that sample 2 mainly consists of polytype $c=29.82\text{\AA}$ and considerably smaller amount of polytype $c=14.82\text{\AA}$. It is worthwhile to note that the reflex (0,0,2) of sample 2 is placed at very small angle ($\theta = 2.95^\circ$) and for this reason can't be detected because of high background signal. The diffractogram of sample 3 in Fig.1(c) have more reflexes than that of sample 2. All reflexes in this diffractogram can be identified as shown in fig1(c) with $c=59.54\text{\AA}$. Now it is clear that the not identified reflexes of sample 2 at angles $\vartheta = 10.72^\circ$ and $\vartheta = 13.33^\circ$ belong to reflexes (0,0,14) and (0,0,18) of polytype $c=59.54\text{\AA}$. But the relative intensity of these reflexes 2.5 times lower in sample 2. The reflexes (0,0,2) and (0,0,4) must be at angles $\vartheta = 1.48^\circ$ and $\vartheta = 2.96^\circ$ correspondingly where background signal is high. More detailed analysis of reflexes structure of sample 3 shows that it contains some amounts of polytypes $c \approx 29.82\text{\AA}$ and $c \approx 14.82\text{\AA}$ also. For example the most intensive reflexe (0,0,16) of sample 3 contains reflexes (0,0,8) and (0,0,4) of polytypes $c=29.82\text{\AA}$ and $c=14.82\text{\AA}$ correspondingly as a satellites (see inset in fig 1(c)). So from our comparative analysis of diffractograms of three samples it was established that the sample 1 is pure $c=14.82$ polytype. Sample 2 consist of mainly from polytype $c=29.82\text{\AA}$ and some amount of polytype $c=14.82\text{\AA}$ and more less of $c=59.54\text{\AA}$. The main polytype in sample 3 is $c=59.54\text{\AA}$ and about 2.5-2 times smaller amount of $c=29.82\text{\AA}$ and $c= 14.82\text{\AA}$ polytypes correspondingly. Note that the repeated intensive reflexes for all polytypes are plaiced at slightly different angles.

DIELECTRIC FUNCTION AT PHASE TRANSITION TEMPERATURES FOR DIFFERENT POLYTYPES

The temperature dependence of dielectric function $\varepsilon(T)$ for above mentioned three samples at phase transition temperatures are shown in Fig.2 (curve1). All measurements are made in cooling regime. The polytype with one pocket crystal ($c=14.82\text{\AA}$) has a high intensity pick at $T \approx 205\text{K}$ and merely seen small intensity shoulders at $T \approx 201.5\text{K}$ and $T \approx 195\text{K}$. The last is seen for majority samples and is believed due to the transition to low symmetric commensurate phase [8-9]. So we can conclude that for pure one pocket polytype $T_c \approx 205\text{K}$. For the second sample Fig.2 (curve2) which is two pocket polytype the high intensity pick is placed at $T \approx 210.8\text{K}$. There are seen also a pick at $T \approx 206,3\text{K}$ and shoulders at $T \approx 214.5\text{K}$ and $T \approx 202\text{K}$. So it is clear that the intensive pick at $T \approx 210.8\text{K}$ corresponds to T_c for $c=29.82\text{\AA}$ polytype and pick at $T \approx 206,3\text{K}$ belongs to polytype $c=14,82\text{\AA}$. Because of high intensity pick at the right side it seems as if slightly

is shifted to higher temperatures. The $\varepsilon(T)$ -dependence of the third sample in Fig.2 (curve3) as well it's diffractogram has more rich pick structure. Because of the four pocket polytype in this sample is in majority, it is natural to attribute the highest intensity pick at $T \approx 216.5\text{K}$ to this polytype. It is clear that the shoulder at $T \approx 214.5\text{K}$ of sample 2 belongs to this four pockets polytype.

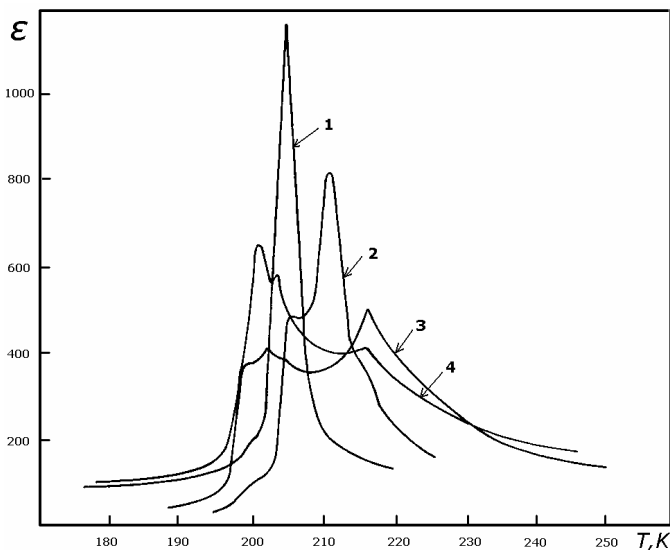


Fig.2.
Dielectric function temperature dependencies of samples 1-4: 1-sample1; 2- sample2; 3- sample3; 4- sample4.

In Fig.2 (2) this shoulder slightly is shifted to lower temperature by the influence of higher intensity pick at $T \approx 210.8\text{K}$. This supposition confirms with the diffractograms of sample 2 in which the reflexes belonging to sample 3 (0,0,14) and (0,0,18) are seen. The small intensity pick corresponding to one pocket polytype at $T \approx 205\text{K}$ is also seen in $\varepsilon(T)$ -dependence of sample 3. The another small intensity pick at $T \approx 202\text{K}$ sometimes dominates in $\varepsilon(T)$ dependency of TlInS_2 samples as it is seen from Fig.2(curve 4). The corresponding diffractogram is shown in Fig.1(d). It is obvious that if to change polytype contents in samples in arbitrary way it is possible to obtain the picks positions in $\varepsilon(T)$ -dependence at slightly different temperatures and with different relative intensities. The diffractograms of TlInS_2 samples with highest $\varepsilon(T)$ pick at $T \approx 202\text{K}$ shows that they consist mainly from eight pocket crystals with $c \approx 120\text{\AA}$ with some additional amounts of four ($c \approx 60\text{\AA}$), two ($c \approx 30\text{\AA}$) and one ($c \approx 15\text{\AA}$) pocket crystals.

CONCLUSIONS

From comparison of x-diffractograms and dielectric function temperature dependencies it was established that different polytypes of TlInS_2 monoclinic modification has different T_c - $T_c \approx 205\text{K}$ ($c=15\text{\AA}$), $T_c \approx 210\text{K}$ ($c \approx 30\text{\AA}$), $T_c \approx 215\text{K}$ ($c \approx 60\text{\AA}$). If several polytypes exist in sample these temperatures slightly can be shifted in accordance of their amounts.

1. H.Han, and B.Wellman, *Die Naturwissenschaften*, **B54** N2 (1967) 42.
2. K-J.Range, G.Engert, and W.Muller, A.Weiss, *Zeitschrift fur Naturforschung*, **29b** (1974) 181.
3. S.N.Aliev, A.I.Najafov and O.Z.Alekperov, *Izv. AN SSR, Neorg. Mater.*, **27**,621.
4. D.Muller, F. E.Paltmann, and H.Han, *Zeitschrift fur Naturforschung*, **29b** (1974) 117.
5. W.Henkel, H.D.C.Carlone, A.Werner, S.Ves and H.G.Shering, **B26** (1969) 3211.
6. A.A.Volkov, Y.G.Goncharov, G.V.Kozlov, K.R.Allachverdiev, and R.M.Sardarly. 1983, *Sov. Phiz. Tver. Tel.*, **25** (год) 3583.

7. S.B.Vakhrushev, V.V.Zhdanova, B.E.Kvyatkovskii, N.M.Okuneva, K.R.Allakhverdiev, R.A.Aliev and R.M.Sardarly, JETP Lett., **39** (1984) 291.
8. K.R.Allakhverdiev, N.Turetken, F.M.Salaev. and F.A.Mikhailov, *Solid State Commun.*, **92** (1995) 827.
9. S. Kashida and Y. Kabayashi, *J. Phys. Condens. Matter.*, **11** (1999) 1027.

MONOCLİN MODİFİKASİYALİ $TlInS_2$ KRİSTALLARININ MÜXTƏLİF POLİTİPLƏRİNİN FAZA KEÇİDİNDƏ DİELEKTRİK FUNKSİYASI

O.Z.ƏLƏKBƏROV, A.İ.NƏCƏFOV, A.R.ƏBDÜRRƏHMANOV

Monoklin modifikasiyalı $TlInS_2$ kristallarının faza keçidində ($T=190-220K$) müxtəlif politiplərinin dielektrik funksiyası otaq temperaturu rentgenoqramları ilə müqayisə olunur. Bu müqayisə müxtəlif $TlInS_2$ nümunələrində $\varepsilon(T)$ asılılığı ilə politiplər arasında korrelyasiya olduğunu göstərir. $c \approx 15 \overset{\circ}{A}$ politipli kristallarının $\varepsilon(T)$ asılılığında yeganə anomaliya nöqtəsi $T=205K$ yerləşən dar xətdən ibarətdir. $c \approx 30 \overset{\circ}{A}$ və $c \approx 60 \overset{\circ}{A}$ politipli kristallar üçün də anomaliya temperaturu dəqiqləşdirilmişdir. Göstərilmişdir ki, politiplərin qarışığından ibarət olan kristalların $\varepsilon(T)$ asılılığındakı anomaliya xətlərinin intensivliyi müvafiq politiplərin rentgenoqram xətləri ilə uzlaşır.

ДИЭЛЕКТРИЧЕСКАЯ ФУНКЦИЯ РАЗЛИЧНЫХ ПОЛИТИПОВ МОНОКЛИННОЙ МОДИФИКАЦИИ КРИСТАЛЛОВ $TlInS_2$ ПРИ ФАЗОВОМ ПЕРЕХОДЕ

O.З.АЛЕКПЕРОВ, А.И.НАДЖАФОВ, В.Р.АБДУРРАХМАНОВ

Сравниваются рентгенограммы при комнатной температуре с температурной зависимостью диэлектрической функции $\varepsilon(T)$ различных политипов кристаллов моноклинной модификации $TlInS_2$ при фазовом переходе ($T=190-220K$). Из этого сравнения установлена корреляция между различными политипами кристалла и зависимостью $\varepsilon(T)$. Для кристаллов состоящих из чистого политипа с $c \approx 15 \overset{\circ}{A}$ зависимость $\varepsilon(T)$ - имеет аномалию с единственным узким пиком при $T \approx 205K$. Установлено положение пиков в зависимости $\varepsilon(T)$ так же для политипов с $c \approx 30 \overset{\circ}{A}$ и $c \approx 60 \overset{\circ}{A}$. Показано, что для кристаллов состоящих из смеси политипов интенсивности соответствующих пиков в $\varepsilon(T)$ -зависимости находятся в согласии с интенсивностями соответствующих линий в рентгенограммах образцов.

Редактор: Г.Аждаров