MEMORY EFFECT IN FERROELECTRIC - SEMICONDUCTOR WITH IN COMMENSURATE PHASE OF $TlGaSe_2$

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The paper is devoted to the research of the non-equilibrium properties of the incommensurate (INC) phase of the improper ferroelectric-semiconductor $TlGaSe_2$. The influence of the prehistory of the heat treating of the crystal, i. e. annealing at the fixed, stabilized temperature in the region of INC- phase on the dielectric constant (ε) behavior of the sample in the vicinity of the phase transition (PT) – INC phase – the commensurate (C) ferroelectric phase studied. The peculiar case of the memory effect realization leading to the temperature range change of the INC-phase existence is observed for the first time in $TlGaSe_2$.

INTRODUCTION

The layered crystal $TlGaSe_2$ belongs to the ferroelectrics-semiconductors group and attracts attention by its unusual dielectric [1], elastic [2, 3], thermodynamic [4-6], optical [7, 8] and other properties near the structural PT. In the paraelectric phase $TlGaSe_2$ is a monoclinic crystal with the space group (SG) of the symmetry C_{2h}^6 [9]. The X-ray investigations [10] have revealed the formation of the several polytypes of the monoclinic modification (C_2^2, C_s^4, C_{2h}^2) of $TlGaSe_2$. To the present time it has been experimentally shown, that the $TlGaSe_2$ polytype with SG in the paraphase C_{2h}^6 suffers the consequence of the structural PT with temperature decrease at the atmosphere pressure [11]. At T_i~116K the second order PT realizes from the high-temperature paraelectric phase into INC-phase, and the first order PT from the INC-phase into the improper ferroelectric C-phase, T_c≈106K, accompanied by the quadrupling of the crystallographic axis $\vec{c}$. In the polar phase the spontaneous polarization vector is placed on the layer plane. The modulated structure of the INC-phase is caused by the soft mode condensation near the Brillouin zone edge with the wave vector $\vec{k}_i = (\delta, \delta, 0.25)$, where δ is the incommensurable parameter. In spite of numerous attempts the symmetry of the low-temperature polar phase and the temperature dependence of δ in the INC-phase region have not been established up to the present time.

It was shown in [7, 8, 12-15], that the temperature behavior of some physical parameters of $TlGaSe_2$ demonstrates the strong sensitivity to the thermocyclization due to which the physical properties of $TlGaSe_2$ are ambiguous and depend on the sample prehistory. The impurity and defect states in $TlGaSe_2$ and their influence on PT and physical properties of this crystal have not yet been revealed.

In the present work we describe for the first time the anomalous memory effect in $TlGaSe_2$ demonstrated itself on the curve $\varepsilon(T)$ in the C-phase near T_c as a result of the annealing of the sample at the fixed temperature in the INC-phase region.

SAMPLES AND EXPERIMENT METHODS

The $TlGaSe_2$ sample in the form of the plane-parallel plate of the sizes *3,3x4x4 mm*^{3}, cut out from the monocrystal ingot grown by the modified Bridgeman-Stockberger method was used. Electrical contacts were provided by application of Ag-paste to the working surfaces of the crystal. Measurements of $\varepsilon(T)$ have been conducted in a quasi-static regime with the temperature change velocity 0,5 K/min far from and 0,1 K/min near T_c by the application of the alternating current bridge at the frequency 50 KHz. The sample has been in the thermostatic chamber of the cryostat during the measurement. The temperature has been measured by the platinum thermometer. The stabilization precision of the temperature has not been worse than $\pm 0{,}01K$.

The following measurement procedure has been applied. At first the sample has been cooled up to the liquid nitrogen temperature and kept at this temperature during 30 min. This condition provides the disappearance of the initial non-equilibrium states in the C-phase. Then in the smooth temperature change regime the sample has been heated up to the given temperature in the region of the INC-phase and kept (annealed) at this temperature during an hour and cooled again up to the liquid nitrogen temperature. The $\varepsilon(T)$ curve has been recorded during the subsequent sample heating up to the thermostabilization temperature. The subsequent $\varepsilon(T)$ measurement cycles have been conducted by the analogous temperature conditions of the experiment. Before the change of the annealing temperature of the sample, the latter has been heated up to the room temperature, then cooled and kept during an hour at the liquid nitrogen temperature.

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

The temperature dependence of ε in $TlGaSe_2$ in wide temperature range, including the structural PT points, has been measured at the sample heating after its cooling from the room temperature is shown in fig.1,a. As it is seen from fig. 1a, the curve $\varepsilon(T)$ is characterized by anomalies in the form of precise maxima at the PT point from the paraelectric phase to the INC- phase at T_i=114,9K and near PT point from INC-phase to the C - phase at T_c=106,5K. It follows from the measurements, that the *ε(T)* dependence in the high-temperature paraelectric phase follows the Curie-Weis law. The Curie constant value and PT temperature values are in good agreement with the existing data [16-18]. The distinct anomaly on the *ε(T)* curve from the C-phase side at *T*=102 K has been revealed in $TlGaSe_2$ sample of the given technological quality (see fig.1a). It has been shown on the example of the layered $TlInS_2$ crystal, isostructural to $TlGaSe_2$, that the similar anomaly is also observed on the *ε(T)* dependence below T_c and is connected with the coexistence in the registered temperature range of the polar regions of the C-phase and non-disintegrated parts of the INC-phase modulation wave [19]. It is possible to suppose, that the anomaly below T_c in the *ε(T)* curve in $TlGaSe_2$ has the same nature as in $TlInS_2$.

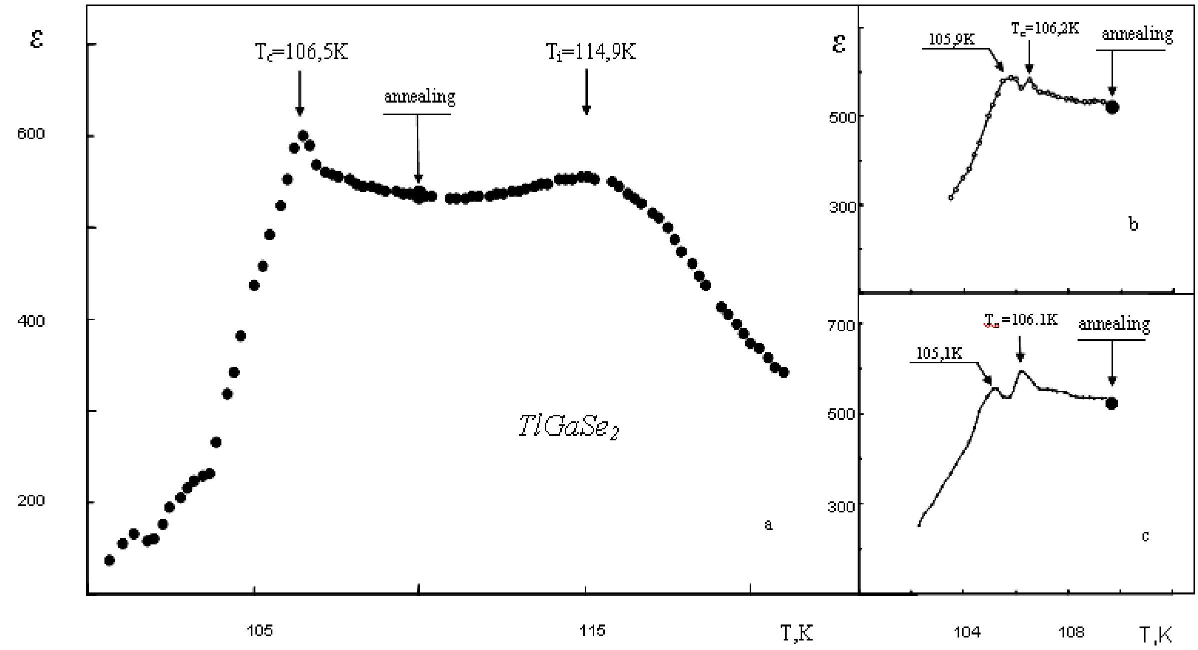

Fig.1. The temperature dependence ε of the layered crystal $TlGaSe_2$, measured at the heating mode after: a) previous cooling of the crystal from the room temperature, b) the four hours annealing of the crystal inside the INC-phase at T_{an} *=110K*, c) the five hours annealing of the sample inside the INC-phase at T_{an} *=110K*.

The *ε(T)* dependences for $TlGaSe_2$ crystals, obtained at heating process after the crystal annealing in the fourth and fifth times in the INC-phase at T_{an}=110K during an hour are presented in figs. 1b and 1c, respectively. The fact of the extra anomaly appearance on the *ε(T)*, beginning with the fourth measurement cycle, in the form of the low maximum at *T*=105,9 K is clearly seen. At the same time temperature stabilization of the sample at T_{an} leads to the shifting of the PT temperature from INC phase to the C phase to the lower temperature side. This shifting for the fourth cycle of annealing is about 0,3K. The fifth annealing cycle does not practically change the T_c, but leads to the shifting of the second maxima from 105,9K to 105,1K.

As it is known [20-23], the annealing of the crystal during the long time within the incommensurate phase leads to the formation of the long-live metastable states, connected with the defects density wave (DDW) which is formed in the crystal, as a resuet of the spatial redistribution of impurities and structural defects in the periodic field of the INC phase. Since the relaxation time of the mobile defects, determined by their diffusion mobility, considerably exceeds the time, required for the measurement of *ε(T)* from the ferroelectric phase to T_{an}, it is possible to assume the conservation of DDW (and consequently solitons in the potential relief, created by the impurities and mobile defects) out of the INC-phase region. As it is shown in [24, 25] this peculiarity of INC phase leads to the shifting of the T_c in $TlInS_2$ crystals to the low temperature region.

To explain the appearance of the second peak in *ε(T)* dependence of $TlGaSe_2$ after annealing at T_{an} within INC phase one can suppose, that the structure of the real $TlGaSe_2$ crystal is essentially heterogeneous. The fracture of the investigated sample by cleaving has revealed the presence of two qualitatively distinct by its dielectric properties macroscopic parts: $TlGaSe_2$ –I and $TlGaSe_2$ –II. The *ε(T)* curves for $TlGaSe_2$ –I (fig. 2a) and $TlGaSe_2$ –II (fig. 2b), obtained at sample heating after its cooling from the room temperature, are presented in fig. 2.

As it is seen from fig.2a, the dependence *ε(T)* of the smaller by the size sample $TlGaSe_2$ –I (3,3x1,6x4 mm^3) is qualitatively similar to the initial crystal *ε(T)* with T_i=112,8K and T_c=106K. The temperature dependence *ε(T)* for the larger by its size sample $TlGaSe_2$ –II (3,3x2,3x4 mm^3) distinguishes essentially from *ε(T)* for $TlGaSe_2$–I. As it is seen from fig. 2b, the anomaly, connected with PT to INC – phase occurs at T_i=111,8K and becomes strongly diffused. The temperature T_c, determined from the given experiment for the sample $TlGaSe_2$ –II makes 106,2 K. The fact of the sudden rise of the ε for the sample $TlGaSe_2$ –II beginning from *T*=107K is connected with the significant growth of the electroconductivity of the indicated part of the sample. It should be noticed, that the multiple annealing of the samples $TlGaSe_2$ –I and $TlGaSe_2$ –II during an hour inside the INC-phase has not been accompanied by the extra anomaly appearance on the curve $\varepsilon(T)$. At the same time the thermal annealing of the samples within the INC phase leads to low temperature shifting of T_c in $TlGaSe_2$ –II by 1,9K, and 0,4K in $TlGaSe_2$ –I.

Taking into consideration the possible formation of different polytypes of $TlGaSe_2$, it is possible to assume, that

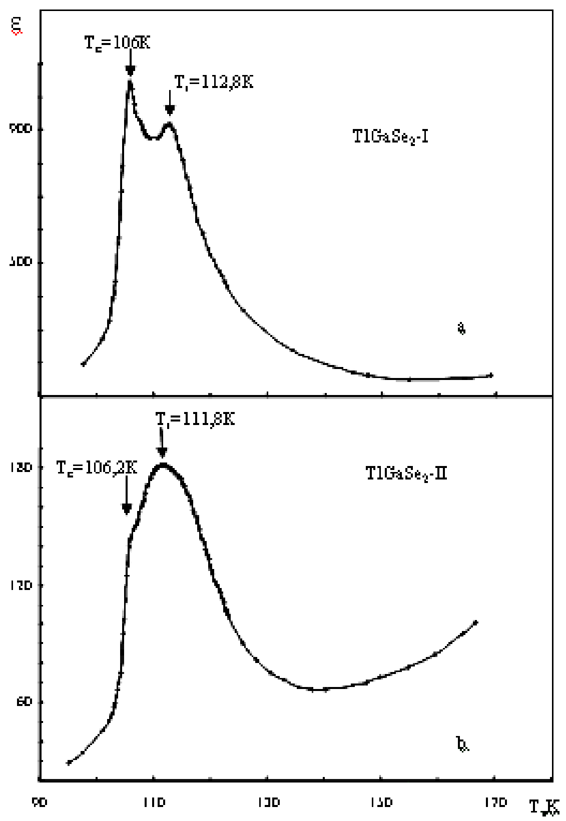

Fig. 2. The temperature dependence ε of the sample parts $TlGaSe_2$, obtained by the consequent spalling: a- $TlGaSe_2$-I; b- $TlGaSe_2$-II. The measurements have been conducted in the heating mode after the previous cooling of both samples from the room temperature.

$TlGaSe_2$ –I and $TlGaSe_2$ –II belong to the various polytypes. However, in this case, $TlGaSe_2$ polytype, whose symmetry of the high-temperature phase is distinguished from C_{2h}^6, should be supposed. The structural research data present in reference [9] testifies the presence of the INC-phase only in polytypes $TlGaSe_2$ with the symmetry of the high-temperature paraphase C_{2h}^6. In papers [18, 26-28] attempts, made to reveal the INC-phase in other modifications of $TlGaSe_2$ by the methods of the neuron diffraction and X-rays, have not been successful.

We suppose, that the concentration of impurities and mobile defects, essentially distinct in the various parts of the sample, has existed in the initial real crystal $TlGaSe_2$ and the part of the initial sample, i.e. $TlGaSe_2$ -II, is characterized by the higher concentration of impurities and structural defects in comparison with $TlGaSe_2$ -I. Therefore, in the initial sample $TlGaSe_2$ the phase transition from the INC-phase to the commensurate ferroelectric phase after a long stay of the sample inside the INC-phase will be realized in two neighboring temperature points, in accordance with the different values of shifting of T_c in different parts of the sample.

CONCLUSION

Thus, in the present paper the results of the qualitatively new case of the memory effect realization- influence of the sample prehistory on the temperature behavior of ε, presented by the extra anomaly appearance in $\varepsilon(T)$ in the neighborhood of INC-C PT point have been for the first time represented in the $TlGaSe_2$ crystal. It is suggested, that in the various parts of the crystal the "frozen" states of defects and impurities with the various concentration, occur after the annealing of the sample in the INC-phase due to the irregular distribution of the impurities and defects existed in the initial sample. Therefore, PT to the commensurate ferroelectric phase in the different parts of the initial sample $TlGaSe_2$, subjected to the thermal annealing in the INC-phase, occurs at various, but close temperatures.

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$TlGaSe_2$ KRİSTALININ NİSBƏTLİ SEQNETOELEKTRİK FAZASINDA TERMİK YADDAŞ EFFEKTİ

Məqalədə qeyri-məxsusi seqnetoelektrik $TlGaSe_2$ kristalının nisbətsiz fazasının (NF) qeyri-tarazlıq xassələri tədqiq olunur. Göstərilmişdir ki, kristalın nisbətsiz fazada stabilləşdirilmiş, müəyyən temperaturda saxlanması NF-dan nisbətli seqnetoelektrik fazaya keçidi ətrafında ilk dəfə olaraq NF-nın temperatur intervalının dəyişməsi və seqnetofazada T_c yaxınlığında $\varepsilon(T)$ asılılığında əlavə anomaliyanın əmələ gəlməsi kimi yaddaş effekti müşahidə olunur.

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ЭФФЕКТ ТЕРМИЧЕСКОЙ ПАМЯТИ В СОРАЗМЕРНОЙ СЕГНЕТОЭЛЕКТРИЧЕСКОЙ ФАЗЕ КРИСТАЛЛА $TlGaSe_2$.

Работа посвящена исследованию неравновесных свойств несоразмерной (НС) фазы несобственного сегнетоэлектрика полупроводника $TlGaSe_2$, а именно, изучению влияния предыстории – температурной выдержки кристалла во времени (отжиг) при определенной, стабилизированной температуре в области НС – фазы – на поведение диэлектрической проницаемости *(ε)* образца в окрестности фазового перехода (ФП) НС – соразмерная (С) сегнетоэлектрическая фаза. Впервые зарегистрирован своеобразный случай реализации эффекта памяти, сводящийся к изменению температурного интервала существования НС – фазы и к появлению дополнительной аномалии на кривой $\varepsilon(T)$ в сегнетофазе в окрестности T_c.

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