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MEMORY EFFECT IN FERROELECTRICS WITH LAYER STRUCTURE $TlInS_2$ and $TlGaSe_2$

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The temperature dependences of the dielectric constant of ferroelectrics-semiconductors with layered crystalline structure $TlInS_2$ and $TlGaSe_2$ have been studied after their annealing inside the incommensurate phase. The “classic” memory effect consisting in appearance of an inflexion point on dielectric constant temperature behavior have been revealed. The peculiarities of memory effect in the investigated crystals are considered in the frame of the model of defect density waves (DDW). It is shown that memory effect in layered crystals embraces the wide temperature interval due to the specific type of mobile defects in crystals with layered crystalline structure.

INTRODUCTION

The ternary compounds $TlInS_2$ and $TlGaSe_2$ belong to the group of semiconductors having layered crystalline structure. According to structural investigations [1], the crystals possess monoclinic structure with space symmetry group of C_{2h}^6. It has been established that both of investigated crystals exhibit a sequence of structural phase transitions to an incommensurate, IC, (at T_i =216K in $TlInS_2$ and 120K in $TlGaSe_2$) and commensurate, C, ferroelectric (at T_c =201K in $TlInS_2$ and 107K in $TlGaSe_2$) phases. Note, that in different works the phase transition points can differ from those shown above, depending on the samples under investigation. According to existing data the transition to IC phase is associated with condensation of a soft mode at point q(δ,δ,0.25) of the Brillouin zone, where δ is the incommensurate parameter. On subsequent cooling both crystals exhibit phase transitions into the commensurate phase with quadrupling of the unit cell parameter along the direction perpendicular to the layers. In polar phase the spontaneous polarization vector lies in the plane of the layers [2,3].

As it is known, the presence of incommensurately modulated structure in crystals leads to so-called memory effects [4-7], which were observed after annealing of the crystals at some fixed temperature within the IC phase. The fact is that when scanning the temperature after annealing, the crystals “remembered” the annealing temperature on subsequent heating or cooling cycle. According to widely accepted explanation existing in the literature, these effects are caused by mobile defects interacting with a modulated distortion. The mobile defects move to the new positions during the long time annealing of the crystal within the IC phase. These defects still remain at their new positions on subsequent heating or cooling and, as a result, some changes in measuring parameters are registered.

The influence of annealing as well as thermocycling between the ferroelectric and incommensurate phases in $TlInS_2$ and $TlGaSe_2$ crystals were investigated in [8-11] using dielectric constant measurements in the temperature interval of successive phase transitions. Low temperature shifts of the commensurate phase transition point in both of crystals after annealing the sample inside the IC phase (the type of memory effect) as well as changes in dielectric constant curves shapes were observed.

The present paper reports the results of detailed investigations of temperature behavior of dielectric constants in ferroelectrics-semiconductors $TlInS_2$ and $TlGaSe_2$ after the annealing the crystals at some fixed temperatures within the IC phase. The memory effect of classic type has been observed for the first time in the investigated crystals together with peculiarities, which are specific for the layer structure. These peculiarities are attributed to the specific type of mobile defects in these crystals, namely, interlayer defects that have very high concentration and mobility due to the weak bonding between the layers.

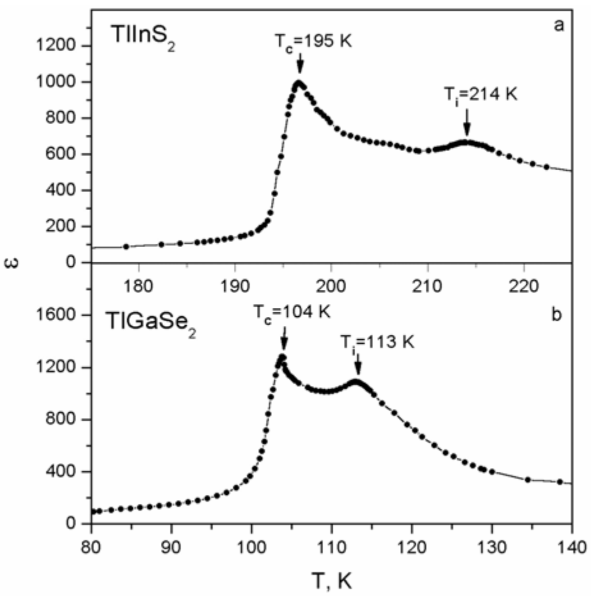
EXPERIMENTAL DETAILS

The crystals were grown by Bridgman method and oriented along the polar axis, which lies in the cleavage plane. The samples had rectangular form and the surfaces perpendicular to the layers plane were polished and covered with silver paste. The dimensions of the electrodes were $6\times2mm^2$ with an inter electrode distance of 2mm. Measurements of the real part of the dielectric susceptibility, ε(T), were performed using a capacitance bridge at the frequency of 1kHz in the temperature range of 77÷300K. A cryostat and automatic temperature controller allowed to scan the temperature with a rate 1K/min and to stabilize the temperature with accuracy better than 0.05K.

The measurements were performed according to following procedure. Firstly the samples were cooled down to 77K and kept at this temperature during 20min. Then the samples were heated and annealed at the some fixed temperature within the IC phase during some hours. Then the samples were cooled again and the temperature dependences of the dielectric constant were measured on a heating cycle. After each measurement the sample was heated up to the room temperature then cooled, and the next cycle of measurement was performed.

EXPERIMENTAL RESULTS

The temperature dependences of dielectric constants for $TlInS_2$ and $TlGaSe_2$ crystals obtained after cooling the samples from room temperature are shown in Fig.1.



Both ε(T) curves are characterized by peaks, which correspond to phase transition points T_i and T_c. Thermal annealing within the incommensurate phase leads to the shifting of phase transition points, as it was observed in [8,9]. The main problem discussed in the present paper is how the classic memory effect reveals itself in crystals under investigations.

Fig.1.
The temperature dependencies of the real part of dielectric constant in $TlInS_2$ –‘’a’’ and $TlGaSe_2$ – ‘’b’’, crystals measured on heating cycle without annealing.

The Figs.2 and Figs.3 demonstrate the memory effects in $TlInS_2$ and $TlGaSe_2$ crystals as they usually observed in other crystals with incommensurate phase, that is the changes of dielectric constant temperature behavior after and before annealing, $\nabla\varepsilon/\varepsilon$. In the case of experimental conditions realized during the registration of $\varepsilon(T)$ curve, after annealing of the crystals during the 2÷5 hours within the IC phase the classic memory effect is observed with inflexion point at annealing temperature in both crystals.

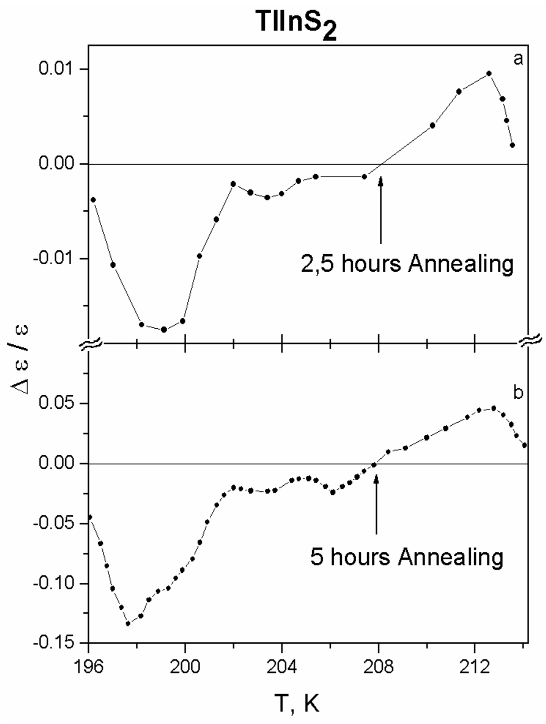


Fig.2.

The temperature dependencies of the deviations of the real part of dielectric constant, $\nabla\varepsilon/\varepsilon$, in $TlInS_2$ crystals measured on heating cycle after the annealing at 208K: for 2.5hours-a and 5hours –''b''.

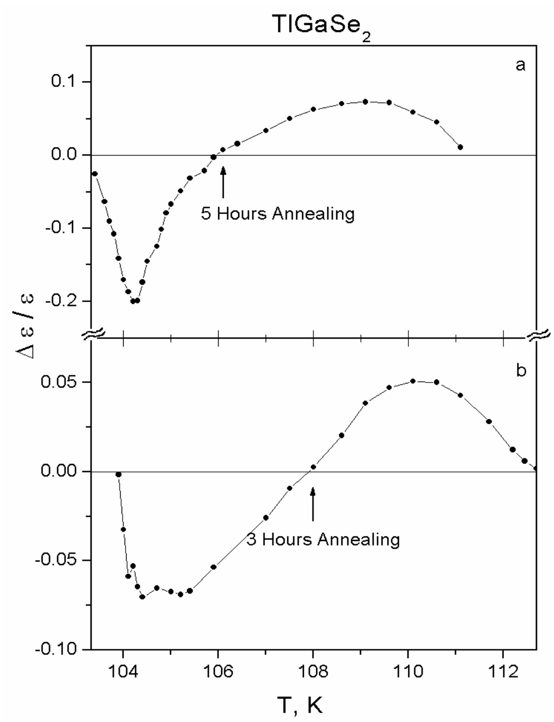


Fig.3.

The temperature dependencies of the deviations of the real part of dielectric constant, $\nabla\varepsilon/\varepsilon$, in $TlGaSe_2$ crystals measured on heating cycle after the annealing for 5hours at 106K – "a", and 3hours at 108K- "b".

As it is seen from Figs.2 and Fig.3 the amplitude of the $\nabla\varepsilon/\varepsilon$ increases with annealing time, but the shape of $\nabla\varepsilon/\varepsilon$ curve depends on the annealing temperature also. It is seen from Fig.3b that the negative peak near the 104÷105K becomes more pronounced when annealing temperature shifts to the lower temperatures. In both crystals the memory effect is not observed if the annealing temperature is choused within the commensurate phase. As in other crystals with memory effect, the amplitude of the $\nabla\varepsilon/\varepsilon$ function gradually decreases and memory effect is totally disappeared after the crystals heat to some temperature above the T_i. However, the clear peculiarities of memory effect manifestation in investigated crystals also exist. First of all, the temperature interval in which anomalous behavior of dielectric constant is observed is very large comprising almost all incommensurate phase intervals. Usually (see for ex. [4,5]), memory effect reveals itself in 1÷3K temperature interval after 15÷20hours annealing within the incommensurate phase. Besides, the amplitude of deviation of dielectric constant in our case is almost twice larger in spite of much shorter annealing time. At last, when annealing temperature shifts to the lower temperatures the $\nabla\varepsilon/\varepsilon$ curve becomes "asymmetric", Fig.3b, proving once again that the memory effect comprises the whole incommensurate phase.

DISCUSSION

According to [4-8] the memory effect in crystals with IC phase is due to formation of DDW. After the long time annealing at some fixed temperature within the IP mobile defects move to new positions and create periodic distribution of defects along the modulation direction.

If after the short (with respect to annealing time) period of time the crystal again is subjected to heating or cooling from some temperature far from annealing temperature some changes in physical parameters behavior are observed when temperature crosses the annealing temperature. The mechanism of such behavior of physical parameters (usually, dielectric constant and birefringence) is based on the interaction of modulated wave with periodic potential created by DDW [4,5]. The modulation wave becomes locked at temperature interval close to annealing temperature leading to anomalies like shown in Figs.2 and Fig.3. Usually this type of artificial lock-in manifests itself in temperature interval which depends on some parameters which describe the modulation wave, defect subsystem and their interaction which each other, namely: modulation wave-defect interaction potential, concentration of mobile defects, their diffusion constant, annealing time, temperature variation of modulation wavelength, etc. In theory [4,5], for example, the artificial lock-in temperature interval does not exceed 1÷2K after annealing 10÷15hours. The same order of lock-in temperature interval is characteristic for memory effects in other crystals. Substantially wider temperature interval, which is typical for $TlInS_2$ and $TlGaSe_2$ needs special explanation and we think that this peculiarity of memory effect is due to peculiar character of mobile defects in layered crystals. Really, it is well known [12,13], that the most typical defects in layered crystals are interlayer defects which are very mobile and have very high concentration due to the weak interlayer bonding. The modulation wave in $TlInS_2$ and $TlGaSe_2$ is created in the direction perpendicular to the layers, so that it can be well distorted by interplanar defects. Thus, all the important parameters which can lead to the widening of the artificial lock-in interval in layered crystals are extremely large comparing with that in other crystals in which the memory effect is observed.

As it was already mentioned, the annealing within the incommensurate phase in $TlInS_2$ and $TlGaSe_2$ crystals leads to the shifting of the phase transition temperatures also. Although, these effects need special explanation [8-11], it seems natural to suppose that the model of extremely mobile defects with high concentration can help in understanding of these phenomena also, thus proving the mechanism proposed in [8-11].

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1. D.Muller, H.Hahn, *Z. Anorg.allg.Chem.*, **38** (1978) 258.
2. S.B.Vakhrushev, V.V.Zhdanova, B.E.Kvyatkovsky, V.N.Okuneva, K.R.Allakhverdiev, R.A.Aliev and R.M.Sardarly, *JETP Lett.*, **39** (1984) 292.
3. D.F.McMorrow, R.A.Cowley, P.D.Hatton, and J.Banys, *J.Phys.: Cond.Matt.*, **2** (1990) 3699.
4. P.Lederer, J.P.Jamet and G.Montambaux, *Ferroelectrics*, **66** (1986) 25.
5. P.Lederer, G.Montambaux, J.P.Jamet and M. Chauvin, *J.Physigue Lett.*, **45** (1984) L627.
6. C.L.Folcia, M.J.Tello and J.M. Perez-Mato, *Phys.Rev. B*, **36** (1987) 7181.
7. X.Pan and H.G.Unruh, *J. Phys.- Cond. Matt.*, **4** (1992) 6899.
8. K.R.Allakhverdiev, F.A.Mikailov, A.M.Kulibekov, N.Turetken, *Phase Transitions*, **67** (1998) 457.
9. V.P.Aliyev, S.S.Babayev, T.G.Mammadov, Mir-Hasan Yu Seyidov, R.A.Suleymanov, *Solid State Communications*, **128** (2003) 25.

10. S.Ozdemir, R.A.Suleymanov, K.R.Allakhverdiev, F.A.Mikailov, *Sol.St.Comm.*, 96 (1995) 821.
11. S.Ozdemir, R.A.Suleymanov, E.Civan, T.Firat, *Solid State Communications*, **98** (1996) 385.
12. C.Manfredotti, R.Murri and A.Rizzo, *Phys.Rev.* **B10** (1974) 3387.
13. S.Amelinckx, *The direct observation of dislocations, N.Y. Academic Press,* (1964).

$TlInS_2$ VƏ $TlGaSe_2$ LAYLI STRUKTURALI SEQNETOELEKTRİKLƏRDƏ YADDAŞ EFFEKTİ

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$TlInS_2$ və TlGaSe laylı kristallik sturukturalı seqnetoelektrik-yarımkeçirici kristalların nisbətsiz fazada otciqindən sonra kristalların dielektrik nüfuzluğunun temperatur asılılığı tədqiq edilmişdir. Dielektrik sabitinin temperatur asılılığında əyilmə nöqtəsi ilə üzə çıxan “klassik” yaddaş effekti müşahidə edilmişdir. Tədqiq edilmiş kristallarda yaddaş effektinin xüsusiyyətləri defektlər sıxlığının dalğa modeli əsasında baxılmışdır. Göstərilmişdir ki, laylı kristallarda yaddaş effektinin geniş temperatur intervalını əhatə etməsi laylı strukturalı kristallarda müəyyən tipli mobil defektlərin olması ilə əlaqədardır.

ЭФФЕКТ ПАМЯТИ В СЕГНЕТОЭЛЕКРИКАХ $TlInS_2$ И $TlGaSe_2$ СО СЛОИСТОЙ СТРУКТУРОЙ

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Температурные зависимости диэлектрической проницаемости сегнетоэлектриков-полупроводников $TlInS_2$ и $TlGaSe_2$, обладающих слоистой кристаллической структурой, были изучены после отжига кристаллов в несоизмеримой фазе. "Классический" эффект памяти, состоящий в появлении точки перегиба на температурной зависимости диэлектрической постоянной, был продемонстрирован. Особенности эффекта памяти в исследованных кристаллах рассматриваются в рамках модели волны плотности дефектов. Показано, что эффект памяти в слоистых кристаллах охватывает широкий температурный интервал из-за определенного типа мобильных дефектов в кристаллах со слоистой структурой·

Редактор: Э.Гусейнов