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Defects forming the optical absorption edge in $TlGaSe_2$ layered crystal

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ABSTRACT

In this work, we present the results of optical experiments designed to investigate the changes in optical absorption spectra of $TlGaSe_2$ ferroelectric-semiconductor with incommensurate (INC) phase in experimental conditions where crystal is kept several hours within the INC-phase (the regime of so called “memory” effect). The fundamental absorption of $TlGaSe_2$, experimentally investigated by optical transmission measurements performed in the temperature range 15–300 K. An extraordinary modification of the optical absorption edge in the range of Urbach's tail is discovered as a result of the annealing within the INC-phase. The role of native defects forming the band edge in the observed phenomena in $TlGaSe_2$ is discussed.

1. Introduction

A large number of ferroelectric crystals have been found to exhibit intermediate phases characterized by INC-modulations [1,2]. In INC-systems the periodicity of the modulation wave cannot be expressed as a rational fraction of the periodicity of the underlying lattice. INC-phase is stable in a limited range of external parameters such as temperature, pressure, electric field, etc. INC-phases usually transform to a periodic high symmetry paraelectric phase by increasing temperature and to a low symmetry ferroelectric commensurate lock-in phase by lowering the temperature.

One of the most remarkable characteristic features inherent to INC-phase in ferroelectrics is a so called “memory effect” [3–6]. The memory effect is observed after a long time annealing of the crystals within the INC-phase and explained on the basis of defect density wave (DDW) formation due to the diffusion of mobile defects in the modulated potential of the INC-wave. The native defects and impurities adapted to the INC-structure can lead to the realization of the memory effect. A DDW reflects the INC-modulation at the annealing temperature (T_{ann}) and has a tendency to pin INC-structure as the external conditions are valid. Even small concentrations of native impurities are expected to affect strongly static as well as dynamic properties of the INC-modulation wave at T_{ann}. If T_{ann} is again approached in a time shorter than the relaxation time of the DDW, the same interacts with the modulation wave, captures it, thus realizes the memory effect. Only small anomaly in dielectric constant and birefringence behaviour around the annealing temperature was reported in INC-insulators [3–6].

Thallium–gallium diselenide ($TlGaSe_2$) is one of the few ferroelectrics with INC-phase which is a semiconductor simultaneously [7]. Despite several decades passed since INC-phase was discovered in $TlGaSe_2$, it still remains as a unique candidate for the fundamental physical and practical applications.

At room temperature $TlGaSe_2$ has centrosymmetric monoclinic space group. On cooling from ambient temperature $TlGaSe_2$ undergoes successive phase transitions: from paraelectric phase to INC-phase at $T_i \sim 120$ K and from the INC-phase to polar ferroelectric C-phase at $T_c \sim 110$ K. The INC-modulation wave in $TlGaSe_2$ is formed due to atoms displacement in the (110) symmetry plane and is directed along [001] axis. A displaced atom does not exactly repeat itself in neighboring elementary cells, so the three dimensional translational invariance of $TlGaSe_2$ crystal is broken. The INC-modulation period is near 4 unit cells of the initial crystal structure of $TlGaSe_2$. This is characterized by satellite reflections with a modulation wave vector $\boldsymbol{k}=(\delta;\delta;0.25)$ where δ is misfit parameter. With the decrease of temperature the INC-modulation wave vector varies continuously and locks into the commensurate value $\boldsymbol{k}=(0;0;0.25)$ through a discontinuous vanishing of the misfit parameterat T_c or Curie point. This corresponds to quadrupling of the unit cell volume along the direction perpendicular to the layers. The phase transition from INC-phase to the ferroelectric C-phase is of the first order. Thus, $TlGaSe_2$ is an improper ferroelectric with a spontaneous polarization along the ***b***-direction.

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Many observations of the effect of thermal annealing within the INC-phase in single crystals $TlGaSe_2$ were presented in the series of publications [8–20]. In particular, a large anomaly in the temperature dependence of the linear thermal expansion coefficients, appearance of new satellite reflection peaks in XRD patterns, changes in the crystal transparency for light passing through crystal located between crossed polarizers, anomalies in electric properties and dramatic modification of TSC-spectra as well as unusual behavior of the Urbach tail after a prolonged annealing of crystal in the INC-phase are clear evidences of the great influence of incommensurate structure on various physical properties of $TlGaSe_2$ crystals.

From the theoretical point of view, anomalies (a small kink centered at the annealing point) on physical properties of the insulating materials, which are characterized as the memory effect should be only expected in the temperature behavior of dielectric susceptibility and optical birefringence characteristics. It has been shown [3–6], that deviations of dielectric susceptibility and optical birefringence between native and annealed sample constitute only few tenths of percent. In this context, the effects of annealing in $TlGaSe_2$ mentioned above are rather exotic [8–20]. The nature of such transformation was in the center of the present investigations. In our opinion, the presence of charged and mobile defects is the outstanding feature of $TlGaSe_2$ crystals. These specific defects form the unusual physical properties of the crystal and their transformation under annealing, illumination, electric field, etc. The absorption edge behavior under annealing within the INC-phase was of our main interest.

2. Experimental procedure and samples

$TlGaSe_2$ single crystal was grown from the melt by the standard Bridgman–Stockbarger technique. Samples were grown from high purity elements (at least 99.999%). Stoichiometric portions of the materials were sealed into an evacuated ($\sim 10^{-5}$ Torr) silica glass tube with a tip at the bottom which previously was cleaned and degassed by the standard procedure. The inner wall of the ampoule was coated with a thin layer of carbon to rule out any reaction with the container. To prevent the ampoule from exploding, it was heated in a temperature gradient furnace.

The crystals obtained by this treatment have a layered structure and was of a good optical quality and could easily be cleaved into plate parallel to (001) axis with a smooth mirror surface, thus no further polishing and cleaning treatments were required. The samples are a thickness of ~ 165–$180\ \mu m$.

The sample was mounted on a cold finger placed inside a Janis closed-cycle helium cryostat equipped with glass windows for optical measurements. A control sensor (diode DT-470) and a resistive control heater were mounted under the base and used to control the temperature with an accuracy of less than ~0.1 K by using a Lake Shore-340 auto tuning temperature controller. All of the measurements were made in a running vacuum of the order of 10^{-3} mbar. Temperature of the sample was controlled by a PID digital temperature controller within ± 0.1 K.

The stoichiometric composition of the samples was determined at several points by energy dispersive X-ray (EDX) spectroscopy using a system connected to a scanning electron microscope. It was found that the samples had a negligible amount of native impurities, such as carbon, oxygen and silicon, which are usually contained in undoped $TlGaSe_2$ crystals.

The optical transmission characteristics were studied with a fully automated Triax 550-type UV–visible spectrophotometer in the wavelength range of 200–900 nm with spectral resolution 0.2 Å. A 300W Xenon lamp (by Thermo Oriel) was used as a light source.

The transmission measurements were carried out under perpendicular incidence of light to the natural layer plane surface of $TlGaSe_2$. The slit width was kept at 1 mm and all the measurements were performed at heating rate at ~ 1 K/min. The incident light beam was unpolarized.

The light from the lamp was collimated and focused on the entrance slit of monochromator and the transmitted light was again collimated and focused on detector. As a detector Hamamatsu R-1527 photomultiplier tube was used. The transmittance was measured using the sample-in/sample-out method which consisted of measuring the intensity transmitted by the sample and normalizing it to the intensity transmitted by a transparent plate.

The following measurement procedure was employed in investigating the effect of temperature annealing. At first, the sample was cooled to 15 K and held at this temperature for ~ 30 min (this condition ensured the disappearance of the non-equilibrium states in the C-phase) and then measurements of the optical parameter of $TlGaSe_2$ were performed in heating regime up to room temperature. After that, the sample was cooled to 15 K, held at this temperature for ~ 30 min, and then heated to T_{ann}. It was annealed at this temperature for about 5 h and cooled again to 15 K. The temperature dependence of the indicated physical parameter of $TlGaSe_2$ was recorded during the heating regime of the sample from 15 to 300 K.

3. Experimental results

Fig. 1 demonstrates the transmission spectra of $TlGaSe_2$ crystal registered at different temperatures before and after the annealing procedure. Two unusual effects are clearly detected: strong increase in the transmission coefficient with temperature and strong influence of annealing on this dependence, Fig. 1a and b, respectively. It can be seen that the long absorption tail in $TlGaSe_2$ extends beyond 1.77 eV. Note, that in several papers, optical energy gap (E_g) of $TlGaSe_2$ was detected to vary from 2.0 eV to 2.23 eV [21]. So, the observed effects are probably due to some defects near the absorption edge. As it is seen from Fig. 2a, the transmission coefficient increases with the temperature in the region of $T<150$ K and the slopes of curves are positive and approximately equal for all the wavelengths, except for $\lambda = 580$ nm. The $\lambda = 580$ nm curve is very close to the band gap energies. The temperature variation of the transmittance is rather impressive; at high temperatures the intensity of the transmitted light is ~ 4 times higher in magnitude than at low temperatures.

Fig. 2b illustrates the temperature variations of the light intensities transmitted through $TlGaSe_2$ after crystal annealing within INC-phase at $T_{ann} = 113$ K for 5 h. The extremely large rice of the crystal transparency for almost all wavelengths after sample annealing was revealed. Just only the intensity of the transmitted light with $\lambda = 580$ nm varies with temperature in the same way as that before annealing.

Another interesting effect seen in Fig. 2b is the four peaks appeared in the transmission spectra after crystal annealing within the INC-phase. The peaks in transmission light intensities represent good regularity for almost all wavelengths. It is very important to note that positions of these peaks fully coincide with positions of impurity peaks registered in photo-induced current transient spectroscopy (PICTS) spectra of $TlGaSe_2$ crystals recently [22].

Fig. 3 demonstrates another feature of annealing effect on absorption edge: it is clearly seen that before annealing the expected temperature shift of the absorption edge with temperature is negligible. On the other hand, this shift becomes apparent after the annealing and corresponds to usual values of band edge shifts with temperature $\sim 2 \times 10^{-4}$ eV/K.