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# Radiation Effect on Layered Crystals of GaS and GaS <Yb>

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**Abstract:** It has been conducted the analysis of IR-absorption spectra of layered single crystals of GaS and GaS <Yb>, irradiated by gamma-quanta with subsequent annealing. It has been found that, a part of impurity atoms, introduced during the growth of crystals, as well as point defects, formed by irradiation, are located in the interlayer space, that indicates the decrease in the intensity and extension of the half-width bands 188 and 184 $cm^{-1}$ in the IR spectra. During the annealing (T = 150°C, t = 150 min.) of irradiated samples there occurs an increase of intensity and a decrease of the half-width of these bands, which is caused by partial annealing of radiation defects and the transition of a part of impurity atoms from the interlayer area in the layer.

**Keywords:** IR-Absorption, Radiation, Semiconductor, Defects, Annealing

## 1. Introduction

According to [1-7], GaS single crystals are of interest as promising materials for the formation of semiconductor detectors of elementary particles and electromagnetic radiation. The increased interest in these compounds is due to the fact that, they have a high photosensitivity to the visible, ultraviolet, X-ray and gamma-radiation, despite their strong defects. As it is shown in [7, 14], the presence of a large number of stacking faults in layered crystals, as well as the formation of complex radiation defects under radiation influence in layers and interlayers, leads to violation of structure periodicity and interaction within the layers and interlayers [10-17].

In the article [10], the characteristics of crystal structure of layered crystals of GaSe with various polytypic modifications, exposed to laser irradiation, are analyzed. It was found out the formation of the areas with a different polytypic structure and areas of residual stress after laser irradiation. The study of the nature of restructuring of the vibrational spectrum based on $A^3B^6$ type compounds provides useful information about the structural phase transitions. In addition, impurity atoms are able to form a connection with all the elements, which are part of the binary semiconductor, and thus lead to a modification of the crystal structure.

Taking into account the fact that, during the formation of defects in layered crystals by changing the binding forces within the layers, as well as interlayers, there is a restructuring of both phonon and electron subsystems of the crystal, and it is advisable to use the method of infrared absorption spectra to identify the radiation defects

Considering that, there is a correlation between the nature of the interatomic chemical bond and properties of semiconductor, then the studies of radiation effects in layered semiconductors, in particular of GaS, are promising from practical point for prediction of durability of the materials under ionizing radiation influence.

In the article it is shown the results of the study of the changes in the degree of structural disorder in layered GaS<Yb> crystals before and after influence of gamma-quanta by Fourier IR-spectroscopy.

## 2. Experimental

GaS <Yb> single crystals were grown by Bridgman technique. When growing GaS, it was used excess sulfur (1,5%) in order to determine the possibility of filling vacancies with sulfur atoms. The alloying of Yb was carried out in the growth process. Resistivity of the obtained samples, parallel and perpendicular to C axis at room temperature, was 2·108 and 3·106 Ohm·cм, respectively. Fourier IR-spectra of original and gamma-irradiated samples were registered in FTIR Varian 3600 spectrometer in frequency range of 4000-100 $cm^{-1}$ at room temperature. It was determined the ratio of optical density ($D/D_0$) of absorption bands, where $D_0$ – optical density of original, D - irradiated samples.

The samples were irradiated by gamma-quanta from $^{60}Co$ source at room temperature with dose rate $D_\gamma$=15,66rad/s. In this case the absorbed dose, determined by Fricke dosimeter, was Dγ = 30-200 krad [8].

## 3. Results and Discussions

It has been conducted Fourier IR-spectroscopic study of original, γ-irradiated, annealed crystals of GaS and GaS <Yb> in the frequency range of 4000-400 $cm^{-1}$ and the results have been shown in [19-20]. On the basis of these studies, it has been found out that, the modification of structure occurs under the influence of thermal annealing and γ-irradiation ($D_\gamma$=30-200 krad) and at the same time at the surface state of samples. Therefore, it is interesting to study the changes in the low frequency (ν = 400-100 $cm^{-1}$). It should be noted that this area is mainly connected with the interlayer vibration $A^1_{1g}$. The vibration appears at the frequency ν =188 $cm^{-1}$ and is characterized by the presence of asymmetry.

In the figure 1a, it is shown Fourier IR- absorption spectrum of interlayer vibration $A^1_{1g}$ of the crystals of GaS (a) and GaS <Yb> (b), irradiated by γ-quanta at 30 (2), 100 (3), 140 (4), 200 krad (5) doses (curve 1-unirradiated crystals) and annealed, irradiated samples of GaS <Yb> at the temperature of 100-250 C (t=150min.) (b).

As it is seen from figure 1a, original, unirradiated, unalloyed GaS crystals are characterized by the presence of narrow absorption bands with half-width $\nu_{1/2}$ =25 $cm^{-1}$ (Curve 1). Irradiation of samples by γ-quanta at $D_\gamma$=30-200 krad dose leads to the decrease of vibration band $A^1_{1g}$ by ~3 times (from 25 to 80 $cm^{-1}$). In this case, the position of the band maximum does not change.

The introduction of impurity Yb into the GaS leads to a weak change of the maximum of vibration band $A^1_{1g}$ (ν = 184 $cm^{-1}$) (figure 1b, curve 1). In this case half-width of the original unirradiated GaS <Yb> crystal increases by 5 $cm^{-1}$, ie $\nu_{1/2}$ = 30 $cm^{-1}$. Irradiation dose of Dγ = 30-200 krad increases the half width by ~ 4.5 times ($\nu_{1/2}$ =135$cm^{-1}$) (figure 1b, curves 2-5). Intensity of the absorption band becomes very weak when the absorbed dose is Dγ = 200 krad. Figure 1b shows the IR-spectra of vibration band $A^1_{1g}$ for irradiated GaS <Yb> samples after thermal annealing. As it is seen from figure 1 (curve 1-5), the change of intensity of band $\nu_{max}$=184 $cm^{-1}$ in spectrum of irradiated GaS<Yb> samples after annealing at 100÷250 C (t = 0-100 min.) undergoes the following changes:

1. Band maximum is shifted to $\triangle\nu_{max}$=2,5 $cm^{-1}$ compared with the band of unannealed sample.
2. Intensity increases by ~1,5 times, herewith half-width of bands increases by $\triangle\nu_{1/2}$=50 $cm^{-1}$. Due to these changes, the spectral parameters show that, annealed samples of GaS<Yb> close to its original state, characteristic to the GaS during irradiation.

***Table 1.*** *The changes of spectral parameters ($\nu_{max}$ and $\nu_{1/2}$) of vibration band $A^1_{1g}$ depending on the temperature of annealing.*

| № | samples | $\nu_{max}$ at dose of 200 krad | $\nu_{1/2}$ at dose of 200 krad |
|---|---|---|---|
| 1 | GaS | 188 | 56 |
| 2 | GaS<Yb> | 184 | 64,5 |
| 3 | GaS<Yb> annealed at T=100°C | 185 | 62 |
| 4 | GaS<Yb> annealed at T=150°C | 186,5 | 53 |
| 5 | GaS<Yb> annealed at T=200°C | 187 | 54,5 |

In the table it is shown the change of the value of spectral parameters at irradiation doses of $D_\gamma$ = 200 krad, depending on thermal annealing. The most effective one was at T=150°C among the selected annealing temperature (100, 150, 200 and 250°C).

In the figure 2, It has been shown dose dependence of half-width of interlayer vibration band $A^1_{1g}$ of GaS (curve 1) and GaS<Yb> (curve 2) at ν= 188 and 184 $cm^{-1}$. As it is seen from the figure, both dependences have linear characteristics in considered area of absorption doses ($D_\gamma$=30-200 krad). In this case inclination of dependence for the crystals of GaS<Yb> is twice more than the crystal of GaS, that indicates the increase of half- width band by 184 $cm^{-1}$ (interlayer vibration) with the addition of Yb atom, as well as with irradiation.

The figure 3 shows the dependence of relative optical density of absorption band of original and gamma-irradiated layered crystals of GaS (curve 1) and Gas <Yb> (curve 2) at irradiation dose of $D_\gamma$=30, 100, 140 and 200 krad. It is seen from figure 3 that, the nature of dependencies consist of linear ($D_\gamma \leq$100 krad) and stationary ($D_\gamma \geq$200 krad) areas. Comparison of the rate of change of dependence, determined from inclination of the curves, shows that in the case of crystals GaS <Yb>, it is 1.5 times higher than for the crystals of GaS.

The observed radiation effects in spectra and spectral parameters ($\nu_{max}$, $\nu_{1/2}$ and $D/D_0$) in layered crystals of GaS and GaS<Yb> connected with restructuring of initial defects.

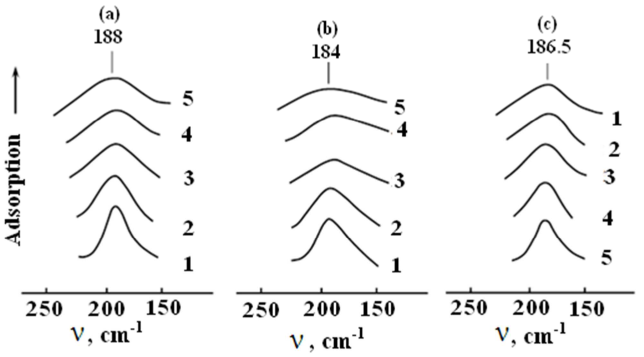


***Fig. 1.*** *Fourier IR- absorption spectra of interlayer vibration $A^1_{1g}$ of GaS (a) and GaS<Yb> (b) crystals, irradiated by γ-quanta at 30 (2), 100 (3), 140 (4), 200 krad (5) doses; 1-non-irradiated samples and irradiated GaS<Yb> samples after thermal annealing (140 krad) at temperatures of 1-0; 2-250; 3-200; 4-100; 5-150°C (t=1hour) (b).*

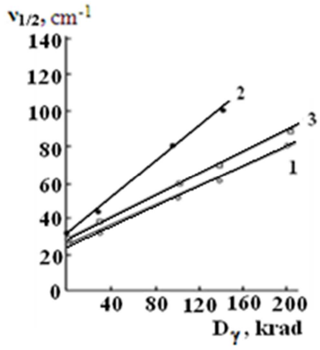


***Fig. 2.*** *Dose dependence of half-width of the band ($\nu_{1\backslash 2}$) of interlayer vibration $A^1_{1g}$ of layered GaS (1) and GaS<Yb> (2) crystals and annealed GaS<Yb> crystals after irradiation by 140 krad dose at T=150°C (3).*

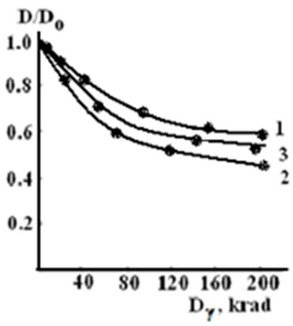


***Fig. 3.*** *Dose dependence of the ratio of optical density of absorption band (D / $D_0$) of interlayer vibration $A^1_{1g}$ of layered GaS (1), GaS <Yb> (2) crystals and GaS <Yb>(3), annealed at T = 150°C.*

It is known that, layered crystals are formed from layers, containing four atomic planes. Bond has ionic-covalent nature inside layers, and the interaction is mainly carried out by van der Waals forces with a small amount of Coulomb forces, between the layers. Anions and cations are located in planes, perpendicular to the crystal axis – C in sequence of S-Ga-Ga-S. The arrangement of atoms within a layer corresponds to the space group $D_{(sh)}^1$ [3-6].

It is shown in the article [11-17] that, the presence of a large number of stacking faults in layered crystals (~ $10^{17}$ $cm^{-3}$), as well as the formation under the radiation influence in the layers and interlayers leads to the violation of structure periodicity and the change of force within the layers and interlayer interaction. The obtained results show that, the intensity of the bands $A^1_{1g}$, as well as their half-width slightly increase at ν=188 and 184 $cm^{-1}$ in GaS spectrum (figure 1) within the alloying of Yb (~1%), that indicates the partial recovery of structure periodicity. The intensity and half-width of the bands do not change within the gamma irradiation at dose up to 50 krad, but at higher doses the intensity decreases and the half-width increases, which is due to the increase of tension of interlayer space. A similar result was observed in [9], where it was studied spectra by resonance Raman in layered GaSe under pressure. It is shown that, the character of the change of band intensity under pressure is associated with the formation of local fields with residual voltage in crystal volume. The analyses of spectra of annealed samples of GaS <Yb> after irradiation at different doses (figure 1c) show that, previous behavior of change of the intensity and half-width of the bands at ν=188 $cm^{-1}$ and 184 $cm^{-1}$ is partially recovered with annealing. It is due to the fact that, the presence of radiation and impurity defects in interlayer space leads to an increase in the intensity of interlayer space, as a result of which the crystal is deformed, and defects are partially annealed at annealing of the irradiated samples. Violation of structure periodicity in the direction of the axis C is associated with the increase of intensity in the crystal in the field of residual voltage.

Thus, it can be assumed that a part of impurity atoms introduced in single-crystal growth process, as well as radiation defects generated under gamma-irradiation are partially located in interlayer space, as evidenced by the decrease of intensity and extension of half-width of the bands with 188 and 184 $cm^{-1}$ in IR-spectrum. Within annealing (T=$150^0$ C, t= 150 min.) of the irradiated samples there occurs an increase in intensity and decrease in half-width of these bands, which is due to the partial annealing of radiation defects and transition of a part of impurity atoms from interlayer regions to the layer.

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