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INFLUENCE OF γ -IRRADIATION AND ANNEALING ON FR IR-SPECTRA OF ABSORPTION OF LAYERED CRYSTALS GaS

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Abstract: In the paper it is studied the influence of gamma irradiation and annealing on optic properties of gallium sulfide in IR spectrum range (wavenumber of 4000-400 cm^{-1}). Comparative analysis of IR spectra of original, γ -irradiated and annealed samples of gallium sulfide shows that, change in temperature, annealing condition and selection of γ -irradiation (140 krad) leads to modification of the structure. The obtained data suggest that the effect of radiational change in IR absorption occurs as a result of defect reconstruction in band gap of the crystal and concentration of photosensitivity centers and their hole filling.

Key words: single crystal GaS, annealing, IR spectrum, γ -irradiation

1. Introduction

Layered single crystals GaS are promising materials for detectors of various radiations, as well as for photovoltaic devices. The most important, interesting and main area of their application is manufacture of X-ray and gamma radiation detectors, working at room temperature, based on them [1,5].

Combination of high sensitivity in a wide range with high resistance of gallium sulfide to radiation can be used for creating photoelectric detectors, operating at increased radiation conditions, and high sensitivity to flow of electron and gamma rays will allow using them as a radiation detector at room temperature. Also, application of IR-spectroscopy enables to determine directly the position and shape of intrinsic absorption edge of GaS and its shift under the influence of different types of irradiation.

In the paper it is studied the influence of gamma irradiation and annealing on optic properties of gallium sulfide in IR spectrum range [1,2].

2. Preparation of samples and experimental technique

The studied p-GaS materials were grown by Bridgman technique. When growing GaS it was used excess of sulfur (0,5%) in order to reveal the possibility of filling vacancies with sulfur atoms. Resistivity of the samples obtained along and perpendicular axis "C" at room temperature was $3 \cdot 10^9$ and $2 \cdot 10^{10}$ ohm·cm, respectively. Band gap width determined by the length of wave decay of photocurrent, was 2,52 eV which coincided with literary data [3,4]. Irradiation of the samples by γ -quanta was carried out on unit Co⁶⁰. While being irradiated the crystals were cooled in liquid nitrogen stream and their temperature did not exceed 290K. The samples were annealed at temperatures 400K—493K for 60-90 minutes in a muffle furnace in quartz ampoules pre-annealed vacuumed to a residual pressure 10^{-2} - 10^{-3} Pa. The annealing temperature was controlled with an accuracy of ± 1 K. The samples were held at the given temperature for 60-90 minutes. Fourier-IR absorption spectra of original, annealed and γ -irradiated GaS samples were recorded on Varian 640 FT-IR spectrometer at room temperature in the wavenumber of 4000-400 cm^{-1} .

3. Results and discussion

In the irradiated samples of p-GaS the photosensitivity changes slightly at small irradiation doses (up to 10 krad), that is due to high density of structural defects in original crystals. With increasing of gamma-irradiation dose up to 150 krad the photosensitivity of the samples increased but in the case of more than 150 krad it decreased.

Absorption bands registered in IR spectra are conditioned by transitions of vibrational energy levels in molecules of substance. Bands' position in IR spectrum is determined mainly by the type of connection and mass of vibrating groups; the stronger connection and less mass of atoms, the higher absorption frequency of the connection. Vibrations of bound atoms in molecules are divided into 2 main ones: valence and deformation. At valence vibrations the connections between atoms change and at deformation ones mainly bond angles.

After γ -irradiation ($D=140$ krad, at temperature no more than $T=290\text{K}$) there occurs some changes in IR spectrum of GaS, associated with the occurrence of radiation-stimulated defect formation, mainly in gallium sublattice [1,2].

Annealing (at temperature 100°C for 1 hour in vacuum) of all irradiated samples leads to recovery and improves the original optical properties of the crystals.

In figure 1 (curves a-f) it is shown Fourier IR-absorption spectra of original (a), γ -irradiated at 140 krad dose (b) and annealing in vacuum (c) and in air (d,e,f) gallium sulfide samples (GaS) at various temperatures.

As it is seen from figure 1a the absorption spectra of original GaS samples are characterized by the presence of absorption bands in lattice phonon region $700\text{-}400\text{ cm}^{-1}$ with frequencies 669, 635, 602, 480 and 425. The bands apparently are longitudinal and transverse vibrations of linkages Ga-S, S-Ga-S and S-S. In addition, a very broad absorption band becomes apparent in spectrum with a center of gravity at 1025 cm^{-1} which has a fine structure consisting of a set of narrow bands. The broad band is perhaps conditioned by the presence of defect states associated with growing conditions. It is not excluded that the above-mentioned area is also an integral part of the phonon and interlayer vibrations.

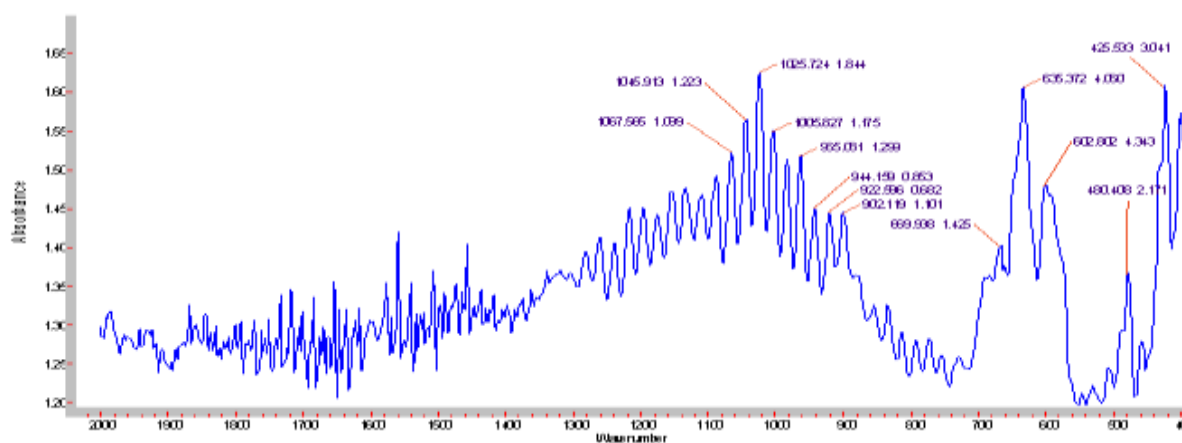


Fig. 1a. IR absorption spectrum of original single crystal GaS

Irradiation of GaS samples by γ -quanta at 140 krad dose is accompanied by the change in absorption spectra (fig. 1 b); as the intensities of absorption bands in the region of phonon lattice vibrations are redistributed; intensity of bands at 427 cm^{-1} relative bands 635 cm^{-1} increases $\sim 2,3$ times. In this case the broad band with a center of gravity 1025 cm^{-1} virtually disappears from the spectrum that indicates the change in structural defect states as a result of break in oxygen bonds.

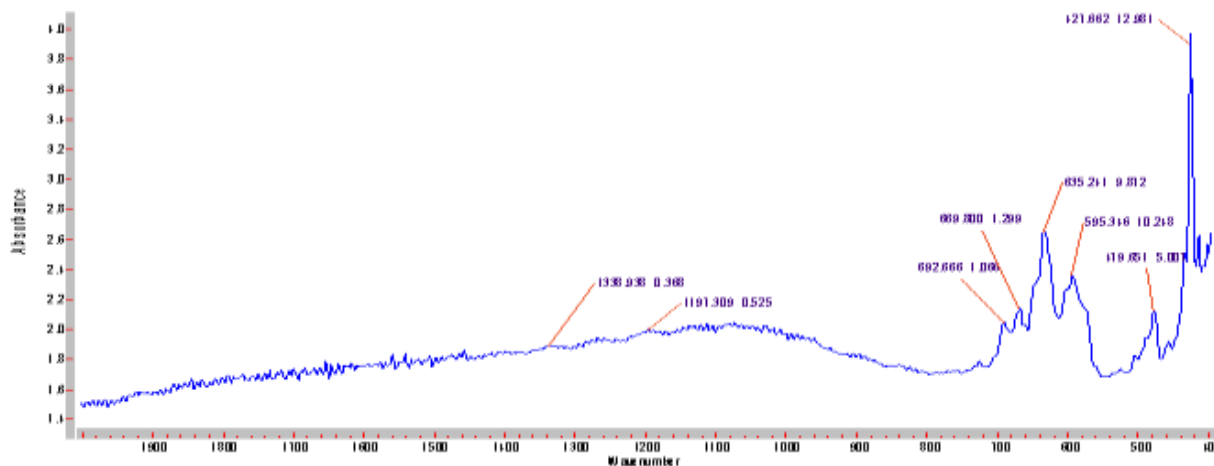


Fig. 1b. IR absorption spectrum of single crystal GaS after irradiation (140 krad)

Annealing of the samples in vacuum (fig. 1c) and (fig. 1d) at temperature 100°C leads to decrease, but annealing in air leads to increase in broad band within the range of $800\text{--}1400\text{cm}^{-1}$ with a maximum at 1025cm^{-1} . In this regard, the ratio of intensities 427 and 635cm^{-1} changes $\sim 1,5$ times. It should be mentioned that the increase in absorption of defect states within annealing in air is due to formation of linkages Ga-O and S-O.

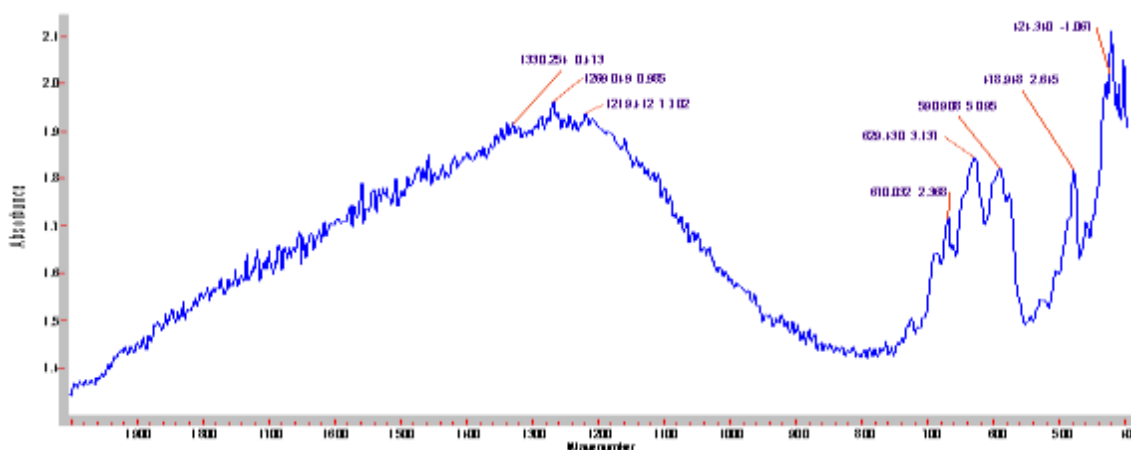


Fig. 1c. IR absorption spectrum of single crystal GaS after consequently 140 krad irradiation and annealing in vacuum (100°C , 1 hour)

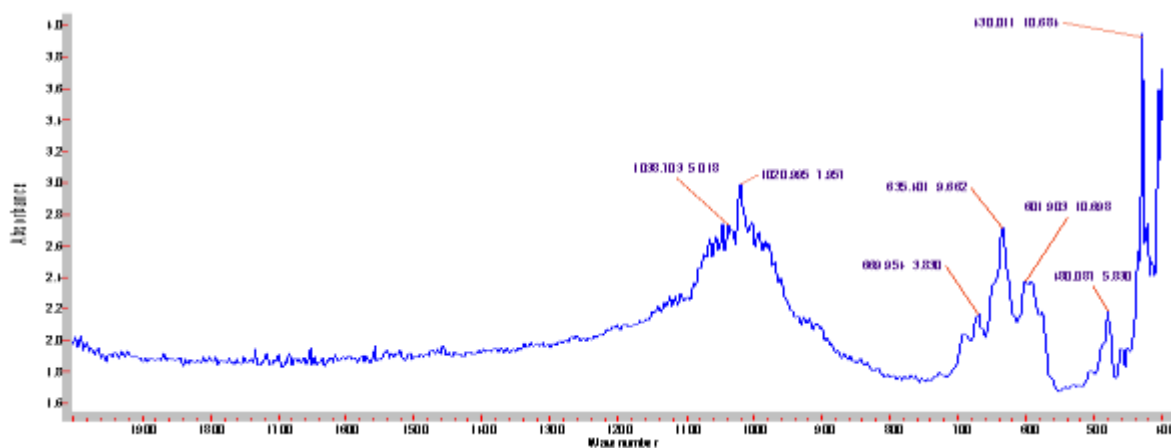


Fig 1d. IR absorption spectrum of single crystal GaS after consequently 140 krad irradiation and annealing in vacuum (100°C , 1 hour) and open air (100°C , 1 hour)

The most interesting results were obtained at sequential annealing of GaS samples at temperatures 150 °C and 200 °C for 1 hour. As it is seen from figure 1 (curve f) thermal treatment of the samples leads to change in bands 635 cm⁻¹, contraction and decrease in its intensity with respect to band 427cm⁻¹. In this case the area of defect states 800-1400 cm⁻¹ disappears as a result of their healing during diffusion and implantation of oxygen atoms in the volume of crystal lattice. In these conditions the spectral area becomes transparent.

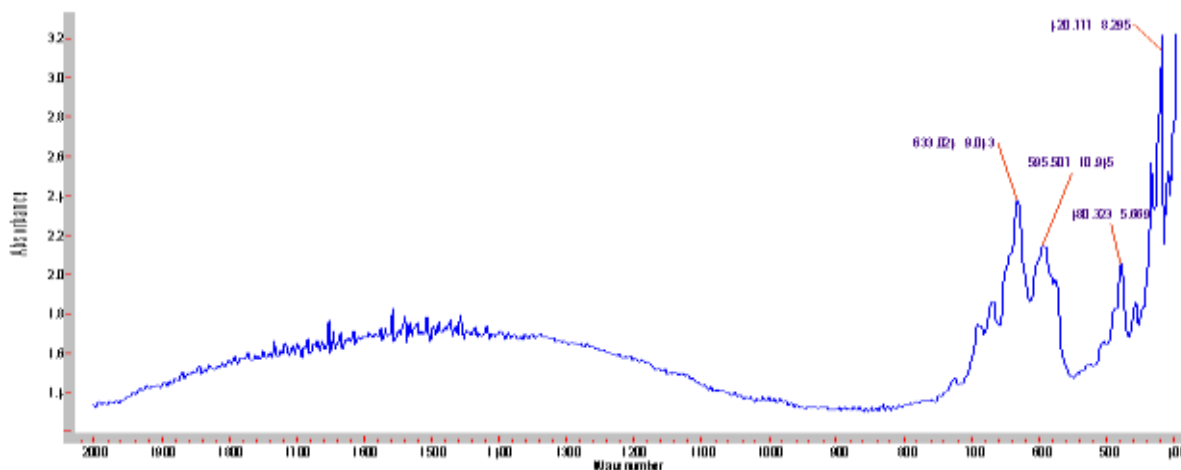


Fig. 1e. IR absorption spectrum of single crystal GaS after consequently 140 krad irradiation and annealing in vacuum (100 °C, 1 hour), open air (100 °C, 1 hour), open air (130 °C, 1 hour) and open air (150 °C, 1 hour)

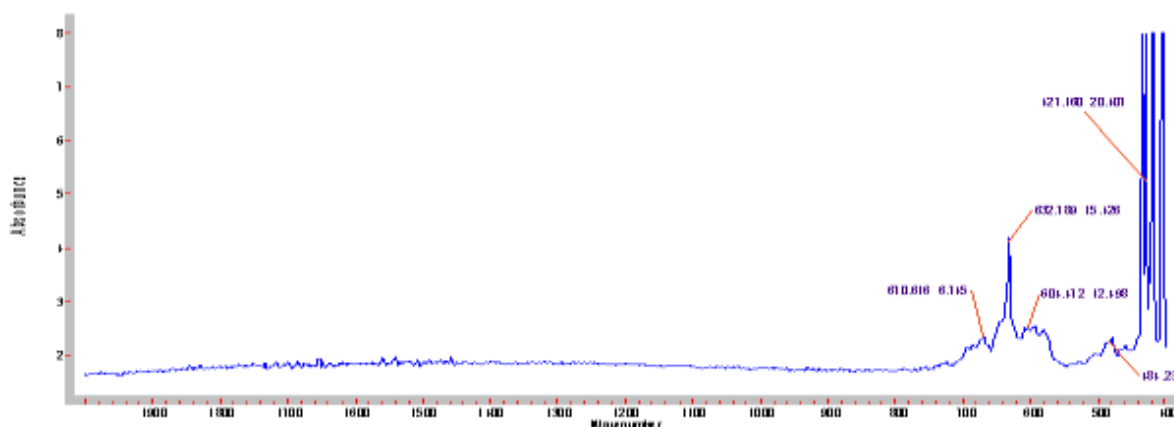


Fig. 1f. IR absorption spectrum of single crystal GaS after consequently 140 krad irradiation and annealing in vacuum (100 °C, 1 hour), open air (100 °C, 1 hour), open air (130 °C, 1 hour) and open air (200 °C, 1 hour)

Thus, comparative analysis of IR spectra of original, γ -irradiated and annealed samples of gallium sulfide shows that, change in temperature, annealing condition and selection of γ -irradiation (140 krad) leads to modification of the structure.

The data for GaS samples are proof of a significant transformation of defects of the structure in crystals at thermal treatment, which is also confirmed by measurements of IR absorption spectra. Thus, it can be concluded that the annealing after γ -irradiation of single crystal GaS causes a considerable complementary absorption within 595-600cm⁻¹, whereas within 1400-2000 cm⁻¹ their IR spectra change little at used irradiation modes up to 150 krad.

The obtained data suggest that the effect of radiational change in IR absorption occurs as a result of defect reconstruction in band gap of the crystal and concentration of photosensitivity centers and their hole filling [4].

Acknowledgment

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ВЛИЯНИЕ γ -ОБЛУЧЕНИЯ И ОТЖИГА НА ФРИК –СПЕКТРЫ ПОГЛОЩЕНИЯ СЛОИСТЫХ КРИСТАЛЛОВ GaS

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Резюме: В данной работе исследовано влияние гамма облучения и отжига на оптические свойства сульфида галлия в инфракрасной области спектра (в области волновых чисел $4000-400\text{ см}^{-1}$). Сравнительный анализ ИК-спектров исходных, γ -облученных и отожженных образцов сульфида галлия показывает, что изменение температур в условия отжига и выбора дозы γ -облучения (140 крад) приводит к модификацию структуры. Полученные данные позволяют сделать вывод о том, что эффект радиационного изменения ИК поглощения обусловлен как результат перестройки дефектов в запрещенной зоне кристалла и концентрации центров фоточувствительности, так и их дырочного заполнения.

Ключевые слова: монокристалл, отжиг, ИК спектр, γ -облучения.

γ -ŞÜALANMANIN VƏ DƏMLƏMƏNİN GaS LAYLI KRİSTALIN FR İQ SPEKTRLƏRİNƏ TƏSİRİ

N.İ. Hüseynov, N.N. Hacıyeva, F.G. Əsədov

Xülasə: Qamma şüalanmanın və dəmləmənin Qalium Sulfid monokristallarının infraqırmızı oblastda optik xassələrinə təsiri tədqiq edilmişdir. İlk, γ -şüalanmış və dəmləmənin müqayisəli İQ optik udulma spektrlərin analizindən məlum olmuşdur ki, γ şüalanma bu kristalda struktur dəyişikliklər yaradır.

Açar sözlər: GaS, monokristal, dəmləmə, İK spektr, γ -şüalanma.