

## THE FEATURES OF THE FOURIER-IR REFLECTIONSPECTRA OF $\gamma$ -IRRADIATED GALLIUM SULPHIDE

R.S. Madatov, N.N Gadzhieva, F.G.Asadov

*Institute of Radiation Problems of ANAS*

[nushaba6@mail.ru](mailto:nushaba6@mail.ru)

**Abstract:** In this paper, we investigate the features of the Fourier-IR reflection spectra of  $\gamma$ -irradiated GaS crystals in the region of absorbed doses of  $\Phi_\gamma = 30$ -200 krad at room temperature. Dispersion dependences of the real  $\varepsilon_1(\nu) = n^2 - k^2$  and imaginary  $\varepsilon_2(\nu) = 2nk$  of the parts of the dielectric constant, the function  $\text{Im}\varepsilon^{-1}(\nu) = \varepsilon_2/(\varepsilon_1^2 + \varepsilon_2^2)$ , as well as the absorption  $n(\nu)$  and refraction  $k(\nu)$  coefficients for the initial and  $\gamma$ -irradiated GaS samples were obtained and studied. The effect of gamma quanta on the optical parameters of these crystals was considered. It has been established that at relatively low doses of  $30 \leq \Phi_\gamma \leq 100$  krad, gallium sulphide crystals are radiation-resistant and at doses  $\Phi_\gamma \geq 100$  krad are not radiation-resistant.

**Keywords:** gallium sulphide, Fourier-IR reflection spectra, optical parameters, gamma irradiation

### 1. Introduction

Layered single crystals of gallium sulphide (GaS) are promising materials for radiation detectors of various types. On their basis, gamma-ray radiation detectors operating at room temperature are fabricated [1-4]. As shown in [1-3], the presence of a large number of packing defects in these layered crystals, as well as the formation of complex radiation defects under the action of  $\gamma$ -radiation in layers and interlayers, leads to a disruption in the periodicity of the structure and interaction of inter- and interlayer regions, which is accompanied by a radiation modification of their structure. Radiation effects and the radiation modification of the structure caused by gamma irradiation in these crystals were first considered and analyzed by vibrational (Fourier-IR and Fourier-Raman) spectroscopy methods in [1,2]. These studies are important and of particular interest from a practical point of view for predicting the durability of materials under the influence of ionizing radiation.

In this paper, we study the features of the Fourier-IR reflection spectra of  $\gamma$ -irradiated GaS crystals and, on their basis the effect of  $\gamma$ -quanta on the optical parameters of these crystals was examined.

### 2. Technique of experiments

Single crystals of GaS were grown by the Bridgman method. During the cultivation an excess of sulfur (1.5%) was used to determine the possibility of filling vacancies with sulfur atoms. The specific resistance of the samples obtained along and perpendicular to the C axis at room temperature was  $2 \times 10^8$  and  $3 \times 10^6 \text{ Ohm} \times \text{cm}$ , respectively.

Fourier-IR spectra of reflection and absorption of samples were recorded on a FTIR Varian 3600 spectrometer in the frequency range  $\nu = 400$ - $100 \text{ cm}^{-1}$  at room temperature. Reflection spectra were obtained at an incidence angle  $\varphi = 15^\circ$ . The optical constants of the initial and  $\gamma$ -irradiated GaS samples were determined from the reflection spectra of  $R(\nu)$ . The data are obtained by using and analyzing simple Kramers-Kronig dispersion integral equations that give the dielectric function

$$\varepsilon^1 = \varepsilon_1 + i\varepsilon_2 \quad (1)$$

$$\text{Im}(1/\varepsilon) = \varepsilon_2 / \varepsilon_1^2 + \varepsilon_2^2 \quad (2)$$

The calculation formulas were used in the following form:

$$K = \frac{2\sqrt{R} \sin \theta}{(1 - \sqrt{R})^2 + 4\sqrt{R} \sin^2 \frac{\theta}{2}}, \varepsilon_1(\nu) = n^2 - k^2 \quad (3)$$

$$n = \frac{1 - R}{(1 - \sqrt{R})^2 + 4\sqrt{R} \sin^2 \frac{\theta}{2}}, \varepsilon_2(\nu) = 2nk \quad (4)$$

where  $n$  and  $k$  are the refraction and absorption coefficients, respectively,  $\varepsilon_1$  and  $\varepsilon_2$  are real and imaginary parts of the permittivity,  $\text{Im}(1/\varepsilon)$  is the dielectric energy loss characterized by the phonon interaction.

At the edges of the frequency range under study, we had a region of constant values of  $k(\nu)$ , which allowed us to use the computer-program comparison algorithm and the algorithm to calculate  $\vartheta(\nu)$  the approximation at which  $k(\nu) = \text{const}$ , at the edges of the investigated interval.

The damping constants of the oscillations  $\gamma_i$  were calculated as the half-widths of the bands of the curves  $\varepsilon_2(\nu)$  and processed using the Kramers-Kronig relations (formulas 3,4).

The optical constants of GaS were determined from the reflection spectra using the well-known dispersion formula for classical independent damped oscillators

$$\varepsilon(\nu) - n_\infty^2 = (\varepsilon_0 - n_\infty^2) \nu_0^2 / (\nu_0^2 - \nu^2 + i\gamma\nu) \quad (5)$$

where  $\varepsilon_0$  is the statistical dielectric permittivity,  $n_\infty^2 = \varepsilon_\infty$  is the asymptotic value of the permittivity in the high-frequency region, and  $\gamma$  is the phenomenological term of the damping.

The parameters  $\varepsilon_0$  and  $n_\infty^2$  satisfy the Lydden-Sax-Teller relation well [7].

$$\varepsilon_0/n_\infty^2 = (\nu_{LO}/\nu_{TO})^2 \quad (6)$$

The samples were irradiated with  $\gamma$  quanta from a  $^{60}\text{Co}$  source at room temperature with a dose rate  $d\Phi_\gamma/dt = 15.66 \text{ rad/s}$ . At the same time, the absorbed dose was  $\Phi_\gamma = 30\text{-}200 \text{ krad}$  [8].

### 3. Results and its discussion

IR spectra of reflection in the region of lattice vibrations of the initial (1) and irradiated with doses of  $\Phi_\gamma = 100$  (2) and 200 krad (3) of GaS single crystals are shown in Fig. 1. As seen from the figure, transverse  $\nu_{TO} = 315, 3 \text{ cm}^{-1}$  and longitudinal  $\nu_{LO} = 365.6 \text{ cm}^{-1}$  oscillations, which converge to the classical dispersion analysis[7]. The values of the frequencies of the longitudinal and transverse oscillations coincide with the values obtained from the Fourier-IR absorption spectra of these samples (Fig. 1, inset). The gamma irradiation of GaS samples with doses of 100 and 200 krad slightly alters (distorts) the spectra of lattice reflection. With an increase in the dose of  $\gamma$ -irradiation, the value of the reflection coefficient decreases, and the region of the residual rays also deepens. The observed singularity in the band of residual GaS rays appearing in the irradiated samples can be presumably explained with the modification of the surface state under the action of gamma radiation and the formation of quasiphonons that lie in the region of the residual rays [5,9-12]. Such surface vibrations can be surface polaritons (SP), i.e. quasiparticles arising under strong exciton-photon interaction. Gamma irradiation leads to a change in the roughness and granularity of the surface of gallium sulphide and provides the appearance of the diffraction bond required under these conditions to excite the SP by incident radiation. Indeed, the "dip" in the

reflection spectra has a "resonant" character, the appearance of which depends essentially on the method of modifying the reflecting surface.

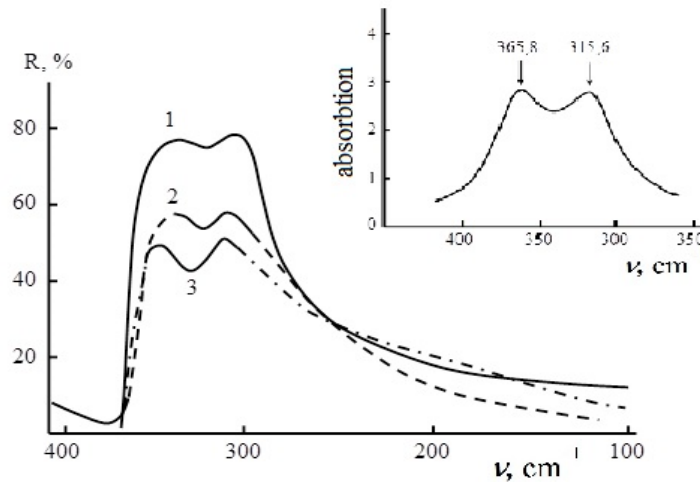


Fig. 1. FT- IR reflection spectra of the initial (1) and  $\gamma$ -irradiated with doses of 100 (2) and 200 (3) krad of GaS samples obtained at room temperature. The inset shows the absorption spectrum of the initial GaS

Dispersion dependences of the real  $\epsilon_1(\nu) = n^2 - k^2$  and imaginary  $\epsilon_2(\nu) = 2nk$  of the parts of the dielectric constant, the function  $\text{Im } \epsilon^{-1}(\nu) = \epsilon_2 / (\epsilon_1^2 + \epsilon_2^2)$ , and the absorption  $n(\nu)$  and refraction  $k(\nu)$  coefficients for the initial (1) and  $\gamma$ -irradiated doses of 100 (2) and 200 krad (3) of GaS samples are presented in Figures 2 and 3. The frequencies and the damping constants of longitudinal and transverse optical phonons of samples of gallium sulphide are determined from the curves  $\epsilon_2(\nu)$  and  $\text{Im } \epsilon^{-1}(\nu)$ . The values of the statistical dielectric permittivity  $\epsilon_0$  of the initial and gamma-irradiated GaS samples are also determined, which are equal to 10.4, 9.7 and 9.2 respectively.

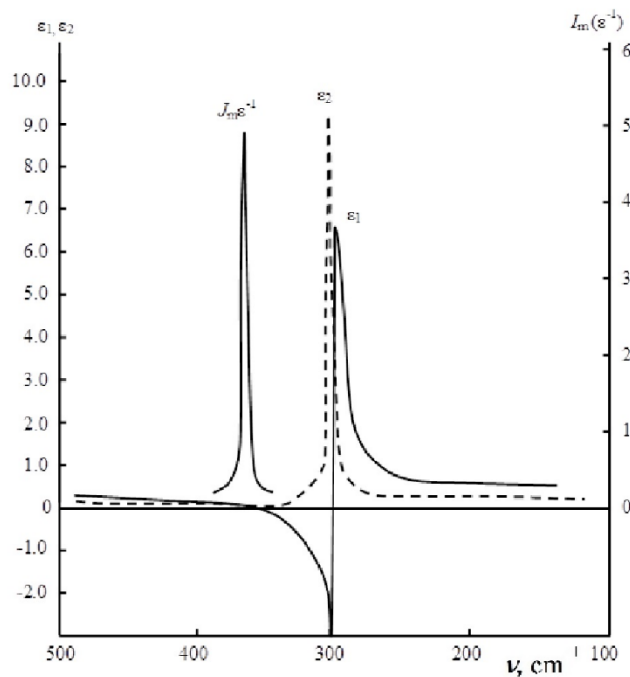


Fig.2. Dispersive curves of the initial (1) and  $\gamma$ -irradiated with doses of 200 krad (2) absorption (a) and refraction coefficients (b) of GaS samples.

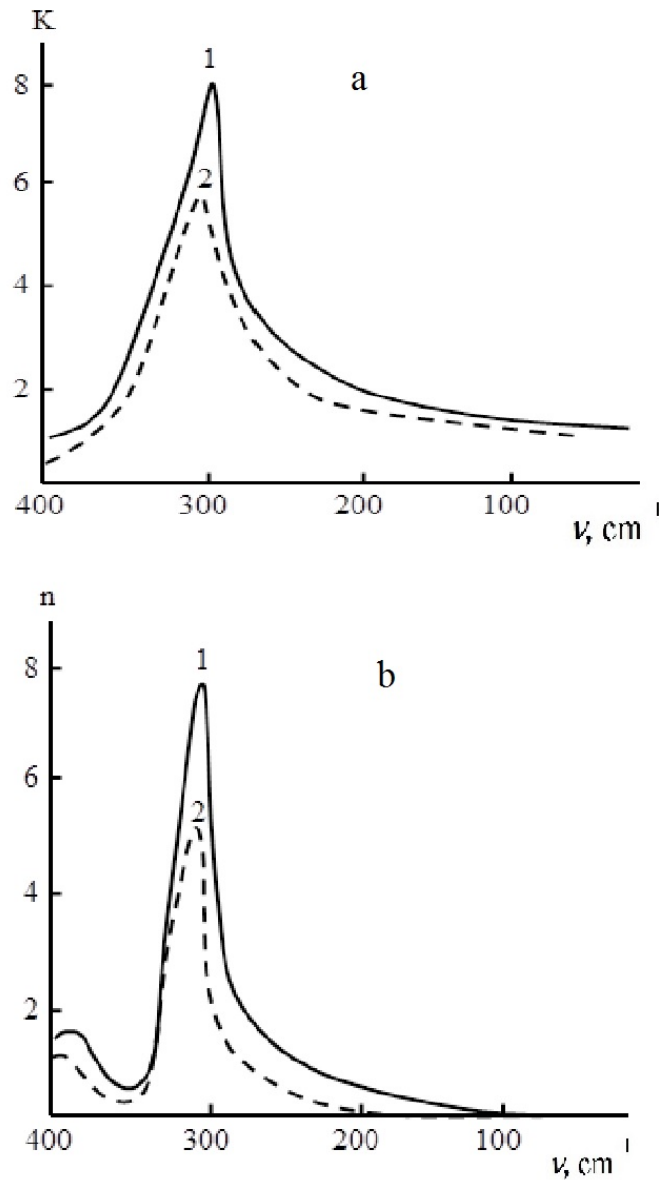


Fig.3. Dispersive curves of real  $\varepsilon_1(\nu) = n^2 - k^2$ , imaginary  $\varepsilon_2(\nu) = 2nk$  parts and loss of dielectric permittivity  $Im \varepsilon^{-1}(\nu)$  of GaS samples.

The dispersion dependence of the real part of the dielectric permittivity  $\varepsilon_1(\nu)$  of the initial gallium sulphide is characterized by the presence of a frequency region with a pronounced minimum of about  $300 \text{ cm}^{-1}$ , in which  $\varepsilon_1(\nu) < -1$  (Fig. 2,3). The irradiation of GaS with a dose of  $100 \Phi_\gamma \leq 200 \text{ krad}$  leads to an insignificant shift of the SP region towards the short waves by  $\sim 6\text{-}10 \text{ cm}^{-1}$  and its broadening.

The effect of the dose of  $\gamma$ -irradiation on the position of the frequencies and the value of the damping constant of the longitudinal and transverse optical GaS phonons is studied. It is revealed that the frequencies of the optical phonons of gallium sulphide do not undergo displacement. At the same time, the damping constants of optical phonons ( $\gamma$ ) calculated as half-widths of the curves ( $\nu_{1/2}$ ) increase with increasing absorbed radiation dose (Table).

**Table.** Dependence of the optical and dielectric parameters of the optical phonon  $\nu_{TO} = 315.4 \text{ cm}^{-1}$  on the dose of  $\gamma$ -irradiation of GaS

№	GaS samples	$\epsilon_0$	$\nu_{TO}, \text{ cm}^{-1}$	$\nu_{LO}, \text{ cm}^{-1}$	$\gamma$	$\epsilon_\infty$	$(\nu_{LO}/\nu_{TO})^2$
1	initial	10,4	315,3	365,6	54	8,4	1,34
2	$\gamma$ -irradiated with a dose of 100 krad	9,7	315,3	365,6	60	8,2	1,34
3	$\gamma$ -irradiated with a dose of 200 krad	9,2	315,3	365,6	75	8,0	1,34

The broadening of the bands is apparently due to a structural change in the interlayer (most defective) regions, which is confirmed by the IR absorption spectra of gamma-irradiated GaS (Fig.1, inset). Since the half-widths of the bands of interlayer vibrations increase as a function of the irradiation dose in the 1.2- 1.5 times. The increase in the amorphous phase due to recrystallization processes leads to the observed broadening of the half-widths of the optical phonons. On the basis of the analysis of dispersion dependencies, it can be concluded that at relatively low doses of  $30 \leq \Phi_\gamma \leq 100$  krad, gallium sulfide crystals retain radiation resistance, and at doses of  $\Phi_\gamma \geq 100$  krad are not radiation-resistance.

#### 4. Conclusion

In this paper, we study the features of the Fourier-IR reflection spectra of  $\gamma$ -irradiated GaS crystals in the region of absorbed doses of  $\Phi_\gamma = 30$ -200 krad at room temperature. The effect of gamma quanta on the optical parameters of these crystals was considered. It was found that at relatively low doses of  $30 \leq \Phi_\gamma \leq 100$  krad, gallium sulphide crystals retain radiation resistance, and at doses of  $\Phi_\gamma \geq 100$  krad are not radiation-resistant.

#### References

1. N.I. Huseynov, N.N. Gadzhieva, F.G. Asadov, Journal of Radiation Research, p.11-15. vol.2, 2015, Baku
2. R.S.Madatov, N.N. Gadzhieva, A.I. Nadjafov, N.I. Huseynov, F.G. Asadov, A.A.Abdurrahimov, D.J. Askerov. Radiation Effect on Layered Crystals of GaS and GaS<Yb>.Colloid and Surface Science.Vol.2, No. 1, 2017. pp. 43-46.
3. A.Z. Abasova, RS Madatov, V.I. Stafeev. Radiation-stimulated processes in chalcogenide structures. "Baku. ELM, 2010 "p.352.
4. R.S. Madatov, T.B. Tagiyev, A.I. Najafov, I.F. Gabulov, Sh. P. Shekili. Semicond.Phys.Quantum Electronics Optoelectronics., 9, №2, p.8-11, (2006)
5. Allahverdiev K.R., NaniR.Kh., SalayevE.Yu.,Tagiev M.M. Vibrational spectrum and optical properties of GaS and GaSe single crystals. // Proceedings of the Academy of Sciences of Azerbaijan. SSR. Series of physico-technical and mathematical sciences.1976, №4, p. 19-25.
6. Belenky G.L., Stopachinsky V.B. Electronic and vibrational spectra of layered semiconductors of the  $A^3B^6$  group // UFN, 1983, v.140, is. 2, pp.233-236
7. Lucazeau G. Vibrational spectra of GaS single crystals.//Sol.State Commun., 1976,v.18,p.917-922.
8. Pikayev A.K. Modern radiation chemistry.Radiolysis of gases and liquids.
9. Gadzhieva N.N., Aliev M.M., AbdullaevaKh.I. IR spectra of reflection of thermally treated beryllium oxide / J. Applied Spectroscopy, 1991, v.54, №1, p.163. The article was deposited at VINITI.27.07.90. №4304-B-90.

10. Noritaka Kuroda, Yuichiro Nishina, Davydov splitting of degenerate lattice modes in the layer of compound GaS, Physical Review B Volume 19, Number 2 15 January 1979.
11. N.M.Gasanly, Aydinli A., Ozkan H., Kocabas C., "Temperature Dependence of the First-Order Raman Scattering in GaS Layered Crystals", Solid State Commun., 116: 147-151 (2000).
12. K. Allakhverdiev, T. Baykara, S. Ellialtioglu, F. Hashimzade, D. Huseinova. Materials Research Bulletin, 41, Issue 4, pp. 711-763 (2006)

## ОСОБЕННОСТИ ФУРЬЕ - ИК СПЕКТРОВ ОТРАЖЕНИЯ $\gamma$ -ОБЛУЧЕННОГО СУЛЬФИДА ГАЛЛИЯ

Р.С. Мадатов, Н.Н. Гаджиева, Ф.Г. Асадов

**Резюме:** В настоящей работе исследованы особенности Фурье-ИК спектров отражения  $\gamma$ -облученных кристаллов GaS в области поглощенных доз  $\Phi_\gamma=30-200$  крад при комнатной температуре. Получены и изучены дисперсионные зависимости реальной  $\epsilon_1(\nu)=n^2-k^2$  и мнимой  $\epsilon_2(\nu)=2nk$  частей диэлектрической проницаемости, функции  $\text{Im}\epsilon^{-1}(\nu)=\epsilon_2/(\epsilon_1^2+\epsilon_2^2)$ , а также коэффициентов поглощения  $n(\nu)$  и преломления  $k(\nu)$  для исходных (1) и  $\gamma$ -облученных образцов GaS. Рассматривалось влияние  $\gamma$ -квантов на оптические параметры этих кристаллов. Установлено, что при сравнительно малых дозах  $30\leq\Phi_\gamma\leq 100$  крад кристаллы сульфида галлия являются радиационно-стойкими, а при дозах  $\Phi_\gamma\geq 100$  крад - не радиационно-стойкими.

**Ключевые слова:** сульфид галлия, Фурье-ИК спектры отражения,  $\gamma$ -облучение, оптические параметры

## $\gamma$ -ŞÜALANMIŞ QALLIUM SULFİDİN FURYE-İQ ƏKSETMƏ SPEKTRLƏRİNİN XÜSUSİYYƏTLƏRİ

R.S. Mədətov, N.N. Hacıyeva, F.Q. Əsədov

**Xülasə:** Təqdim edilmiş işdə  $\gamma$ -şüalanmış GaS kristallarının  $\Phi_\gamma=30-200$  krad udulma dozası oblastında və otaq temperaturunda Furye-İQ əksetmə spektrlərinin xüsusiyyətləri öyrənilmişdir. İlkin və  $\gamma$ -şüalanmış GaS nümunələrinin udulma  $n(\nu)$  və sındırma əmsallarının  $k(\nu)$ , eyni zamanda dielektrik nüfuzluğunun həqiqi  $\epsilon_1(\nu)=n^2-k^2$  və xəyalı  $\epsilon_2(\nu)=2nk$  hissələrinin,  $\text{Im}\epsilon^{-1}(\nu)=\epsilon_2/(\epsilon_1^2+\epsilon_2^2)$  funksiyasının dispersiya ayrılırları alınmışdır.  $\gamma$ -kvantların bu kristalların optik parametrlərinə təsirinə baxılmışdır. Müəyyən edilmişdir ki, dozanın nisbətən kiçik  $30\leq\Phi_\gamma\leq 100$  krad qiymətlərində GaS kristalları radiasiyaya davamlıdır, dozanın  $\Phi_\gamma\geq 100$  krad qiymətlərində isə radiasiyaya davamsızdır.

**Açar sözlər:** qallium-sulfid, Furye-İQ əksetmə spektrləri,  $\gamma$ -şüalanma, optik parametrlər