SOME OPTICAL PROPERTIES OF GaSe CRYSTALS DOPED WITH ELEMENTS OF GROUP I (Li AND K)

M. Caraman, I. Evtodiev, and E. Cuculescu

Moldova State University, 60, A. Mateevici str., MD-2009, Chisinau, Republic of Moldova
E-mail: ievtodiev@yahoo.com, elmira@usm.md

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Introduction

Alkaline solutions of the *Li*, *K,* and *Na* are used in electrical accumulators. The accumulating capacity is considerably higher comparing to technical accumulators if the principle of intercalation of the metals of group I of type $A^{III}B^{VI}$ [1, 2] of the layered semiconductor is used. Usually variations of the compound *In – Se* [3] are used as electrodes. Semiconductors *GaSe* and *GaS* are not very often used as intercalated electrodes because their electrical resistivity is much higher comparing to the semiconductors *InSe* and modifications In_2Se_3.

Table 1. Characteristics of the solutions *GaSe* and *GaS.*

Property	**GaS**	**GaSe**
Melting temperature T_t, K (°C)	1288 (1015)	1233 (960±10)
a, *b*, *c*, Å	$a = 3,585$; $c = 15,15$	$a = 3,755$; $c = 15,94$
Spatial group	$P6_3/mmc$ - D_{6h}^4	$P6_3/mmc$ - D_{6h}^4
Density of the solid phase at normal temperature *d*, g/cm^3	3,75	5,03
Temperature Debye θ_D, K	215	194
Refraction index *n*	-	n_o= 2,6975; n_e= 2,3745 (λ=10,6 μm); n_o= 2,7233; n_e= 2,3966 (λ=5,3 μm)
Width of the interdicted band at T=300 K E_g, eV	2,53 (opt.); 2,58; 3,9 (indirect transitions)	2,0 (opt.); 3,63 (indirect transitions)
Variation speed of the width of the interdicted band $(dE/dT)\cdot 10^4$, eV/grad	-7,2	-3,6
Electron effective mass m_n^*	$5m_0$	$0,51m_0$
Hole effective mass m_p^*	-	$1,34m_0$
Mobility of the electrons μ_n, cm^2/V·s	-	250
Mobility of holes μ_p, cm^2/V·s	-	10÷20

As a rule, the doping atoms are placed in the space between the chalcogen planes because the layered packages Hal-Me-Me-Hal have bonds of a relatively weak polarization nature [4]. In Tab. 1 the most important characteristics of the solutions *GaSe* and *GaS*, which determine their physical properties, are given.

Samples and experiment methodology

The GaSe monocrystals were prepared using chemical elements of high purity Ga(5N) and Se(0C) used in well proportioned quantities. Monocrystals were grown using Bridgman method [5]. The crystalline structure of the synthesized monocrystals was determined using the X-ray diffraction. The obtained crystals were monophase and of polytype ε.

Big monocrystals were split into layers with area 1.0 – 1.5 cm^2 and thickness of 0.1 – 0.3 mm. Samples were introduced in quartz containers filled with Ar. Li and K in quantities of 5.0 mg/cm^3 were also introduced in these containers. The containers were evacuated till the pressure ~1·10-5 Torr and sealed. The thermal treatment lasted for ~36 hours at the temperature 480^{o}C. The external layers of the GaSe samples were removed after the treatment with Li and K vapors. Presence of the Li and K in the prepared samples was determined using atomic emission spectra.

For analysis of the absorption spectrum films of thickness 12.5 μm and 18.2 μm were obtained using stratification of the *GaSe*(*K*, *Li*). The optical transmission was recorded using the Specord M40 spectrometer supplied with a metallic cryostat with SiO_2 windows. Samples used for measurements at low temperature were placed in nitrogen vapors at the boiling point.

Photoluminescence spectra were recorded using an installation based on a spectrophotometer with diffraction structure (600 mm^{-1}) of type MDR-2. Energetic resolution on the investigated interval did not exceed 1.5 meV. Photoluminescence of the *GaSe*(*K*, *Li*) monocrystals was stimulated with N_2 laser radiation with wave length 0.337 μm.

Experimental results and their explanation

a) Optical absorption and photoluminescence of the GaSe(Li) crystals

The absorption spectra at the temperature 293 K and 78 K at the edge of the intrinsic absorption band for ε-GaSe and ε-GaSe(Li) crystals are presented in Fig. 1. The maximum at 2.01 eV present for *GaSe* and *GaSe(Li)* crystals can be interpreted as exciton absorption. One argument to confirm this interpretation is that the binding energy of the electron-hole pair in *ε-GaSe* crystals is ~22 meV [1] and is of the order of the thermal energy at this temperature ~25 meV.

The presence of the Li atoms in the hexagonal crystalline structure of the modification ε-*GaSe* leads to the widening of the absorption bands by ($\Delta\nu_{GaSe(Li)} / \Delta\nu_{GaSe} \approx 1{,}4$) and to the shifting of the exciton absorption band edge towards small energies by ~15 meV when the absorption coefficient is 1000 cm^{-1}. Growing of the exciton band towards high energies is determined by the overlapping of the exciton band n>1. The integral absorption coefficient α_c of the exciton band is determined by expression (1)

$$\alpha_C(\hbar\omega) = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} \alpha(\hbar\omega - E) \frac{\Gamma}{\pi\left(E^2 + \Gamma^2\right)} dE\,, \tag{1}$$

where
$$\alpha(\hbar\omega) = \frac{(2\mu)^{3/2} e^2 f_{cv}}{n_0 c \hbar^2 m_0} \left(\sum \frac{4\pi R_0^{3/2}}{h^3} \rho(\hbar\omega - \hbar\omega_n) + \frac{2\pi R_0^{1/2} U(\hbar\omega - E_g)}{1 - \exp(-2\pi Z)} \right), \tag{2}$$

$U(\hbar\omega - E_g)$ is a continuous function, $Z = \left[\frac{R_0}{(\hbar\omega - E_g)}\right]^{1/2}$, E_g is the width of the interdicted band, and n=1,2,3,... is the number of exciton states.

Values of the contour of the integral absorption of the *GaSe*(*Li*) crystal at temperature T=293 K are presented in Fig. 1 (curve 3).

As shown in Fig. 1, the experimental curves (1-3) for crystals -*GaSe*(*Li*) near the maximum of the absorption band at T=293 K are well correlated with values calculated using expressions (1) and (2). Here the effective mass $\mu=0.145 \cdot m_0$ and the $f_{cv}=0.05$ oscillator magnitude are taken for *GaSe* [3] crystals and $R_0=21.0$ meV is the binding energy of the electron-hole pair [4].

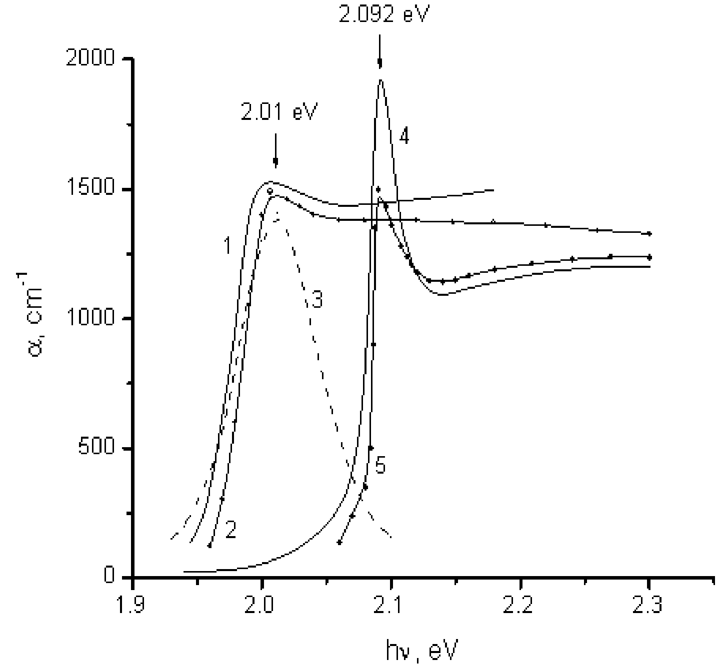

Fig. 1. The absorption spectra at the temperature 293 K and 78 K at the edge of the intrinsic absorption band for *ε-GaSe* and *ε-GaSe(Li)* crystals.

At temperature 78 K besides the shifting of the absorption band edge towards high energies the contour of the exciton band is narrowing and the absorption coefficient is growing in the centre of the exciton band n=1. At the same time, at this temperature the absorption coefficient is decreasing inside the intrinsic band. But deeper inside the absorption band the characteristics $\alpha(\hbar\omega)$ at the temperature 78 K are getting close to those at the temperature 293 K. This decrease of the absorption coefficient at T=78 K is probably caused by the decrease of significance of the coefficient α of the light absorption because of free charge carriers and by the decrease of the phonon density inside these crystals. Also from comparing of the contour of the exciton band of crystals doped with *Li* atoms with those for crystals without *Li* atoms (curves 3 and 4 of Fig. 1) we can see that the width of the exciton band in *GaSe*(*Li*) crystals is quite big (~18 meV) and this difference is getting stronger when moving towards high energies. Therefore, we can conclude that the *Li* atoms having the covalent radius smaller than *Ga* and *Se* are localized not only in the space between chalcogen planes but also in the Ga vacations inside the layered package and thus increase the intensity of bands with n>1.

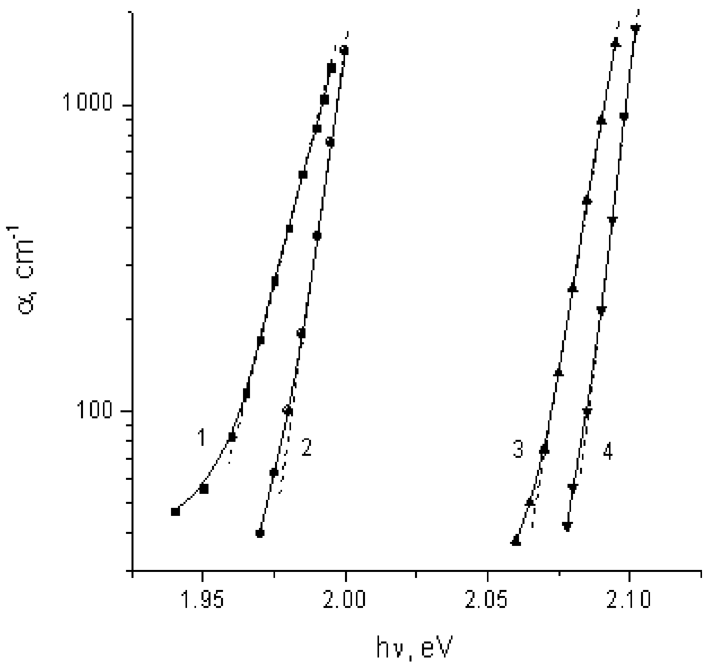

Fig. 2. Absorption coefficient for *ε-GaSe* and *ε-GaSe*(*Li*) crystals.

Figure 2 presents the $\alpha(\hbar\omega)$ characteristics in the range of low energies of the exciton band n=1 for *ε-GaSe* and *ε-GaSe*(*Li*) crystals. It can be seen that the absorption coefficient near the exciton band edge grows as an exponential function of type [1]

$$\alpha(\hbar\omega) = \alpha_0 \exp\left[-\frac{\delta(\hbar\omega_0 - \hbar\omega)}{kT}\right]. \tag{3}$$

Here δ is the energy parameter typical for this crystal, $\hbar\omega_0$ and α_0 are the energies and absorption coefficient near the absorption band in the maximum of the exciton band.

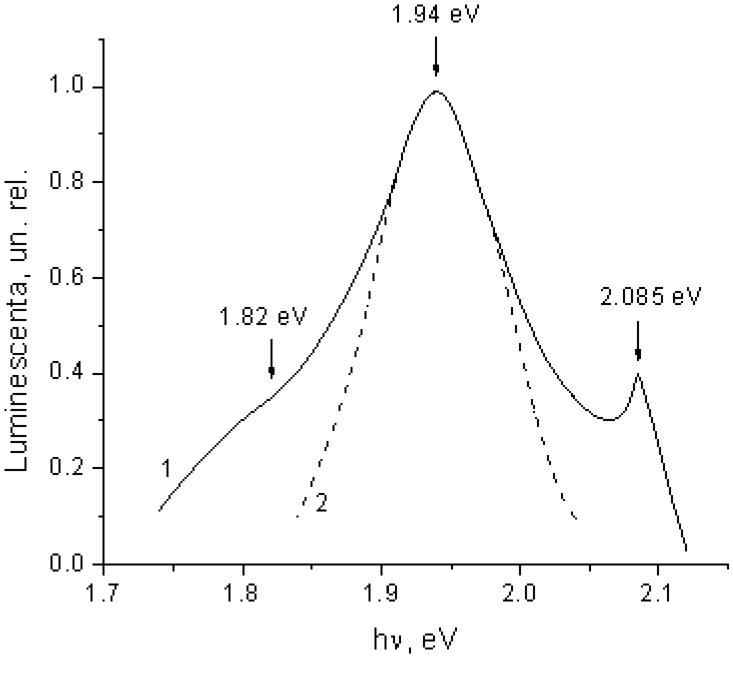

Fig. 3. Photoluminescence spectrum of the *ε-GaSe*(*Li*) crystals at the temperature 78 K.

The experimental results correlate very well with expression (3) if σ = 1.7 and 3.5, respectively, for *GaSe*(*Li*) and *GaSe* crystals. The good correlation between experimental results and calculations using expression (3) can serve a criterion that the absorption band edge in the *ε-GaSe* and *ε-GaSe*(*Li*) crystals is formed by free excitons interacting with optical phonons.

Photoluminescence (PL) spectrum of the *ε-GaSe*(*Li*) crystals at the temperature 78 K is presented in Fig. 3. It can be seen that the PL spectrum has a large band with maximum localized at 1.940 eV. For high energies on this band there is a maximum at 2.085 eV, but for low energies there is a threshold for 1.820 eV.

The absorption line of the free exciton corresponds to the energy 2.092 eV and it is by ~7 meV higher than the energy of the PL band from the absorption band edge. This way we can admit that the band is obtained as a result of the luminescence emission of the excitons bound around the ionized centers, which can be the Li ions.

In order to find the nature of the 1.940 eV the contour of luminescence band was analyzed by recombination inside an ionized centre. The contour of the luminescence band $L(\hbar\omega)$ obtained using one absorption-recombination centre is described by a function of the Gauss type [1]

$$L(\hbar\omega) = L(0)\exp\left[-\frac{(\hbar\omega-\hbar\omega_0)^2}{2\delta^2}\right], \tag{4}$$

where $L(0)$ and $\hbar\omega_0$ are the intensity and energy in the maximum of the PL band, and δ is the parameter that determines the width of the band.

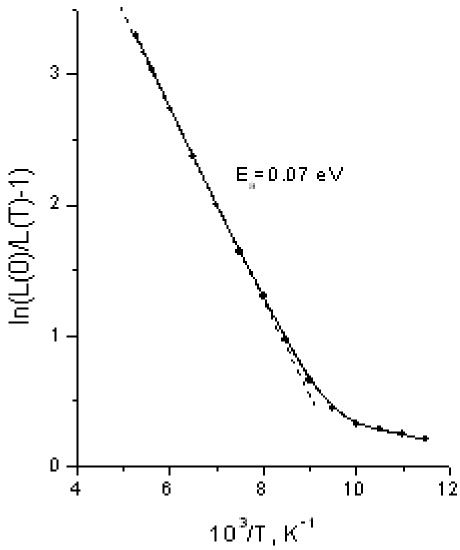

Fig. 4 Thermal attenuation of the PL band for *ε-GaSe(Li)* crystals.

As we can see for $\delta = 0{,}02$ eV the experimental curve is close to the one calculated using formula (4) only near the upper part of the PL band. We have to mention that the absorption coefficient of the light at 1.950 eV is bigger than 20 cm^{-1}. These results show that the band 1.940 eV, as well as the threshold 1.820 eV, is of a recombination nature and is obtained as a result of recombination of the donor-acceptor pairs.

When the temperature grows from 78 K to ≈120 K one can observe a narrowing of the 1.940 eV band, which rapidly disappears for temperatures T>125 K. As we can see in Fig.4, in the domain of thermal attenuation of the PL band its intensity *L(T)* can be analytically described using an exponential function of type [2]

$$L(T) = L(0)\left[1 + a\exp\left(-{E_a}/{kT}\right)\right], \tag{5}$$

where E_a is the activation energy of the thermal narrowing process of the PL band, *a* is the parameter typical for this material, *k* is the Boltzmann constant.

Activation energy determined byhe slope of the linear segment from Fig. 4 is equal to 0.07 eV. Thus, we may consider that inside the *ε-GaSe* crystals *Li* atoms form acceptor states localized at 70 meV from the maximum of the valence band.

b) Light absorption and photoluminescence of the ε-GaSe(K) crystals

The absorption spectrum of the *ε-GaSe*(*K*) crystals at the temperature 293 K and 78 K is presented in Fig. 5a. The absorption coefficient in the energy interval from 1.92 eV to 1.98 eV grows from ~120 cm^{-1} to 1400 cm^{-1}. Also for energies $\hbar\omega > 2{,}0\,\text{eV}$ there is a small growth of the absorption coefficient, which can be associated with the growth of the density of the states inside the valence band of the *GaSe*(*K*) crystal. K atoms form localized states in the *GaSe* crystals screening the exciton bonds at normal temperature.

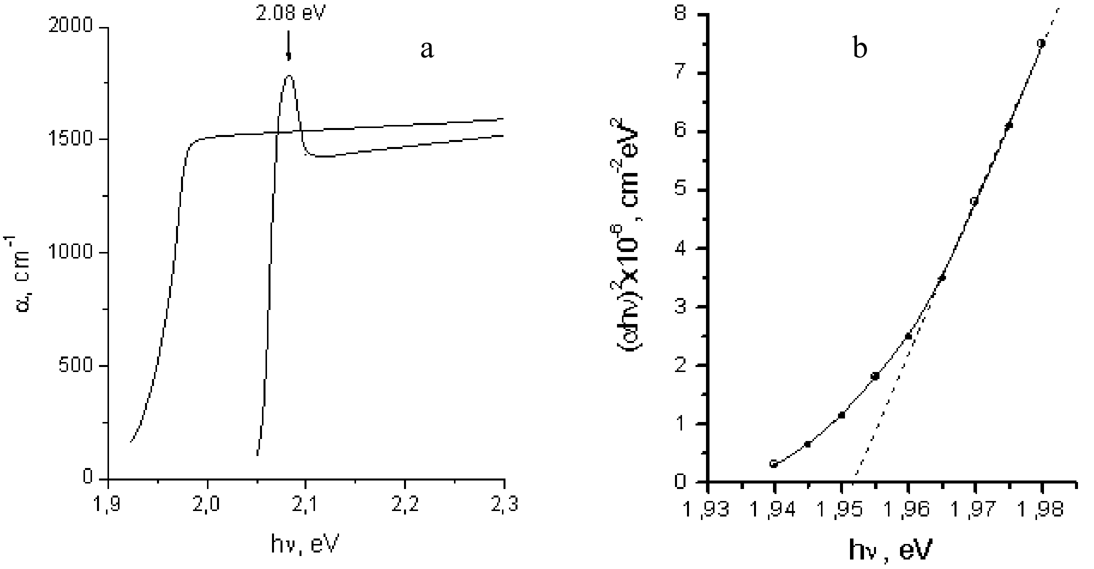

Fig. 5 Absorption spectrum of the *ε-GaSe*(*K*) crystals at the temperature 293 K and 78 K.

The spectral dependence of the absorption coefficient in the region of the band edge is determined by the direct optical transitions of electrons from the valence band to the conduction band and is described by relation (6)

$$\alpha(\hbar\omega)\cdot\hbar\omega = a(\hbar\omega - E_g)^{1/2} \tag{6}$$

Here a is the parameter typical for the material irrespective of the photon energy, E_g is the width of the optical band. As we can see in Fig. 5b, in the domain of the absorption band edge the $\alpha(\hbar\omega)$ characteristic satisfies relation (1), which indicates that in *ε-GaSe(K)* crystals direct optical transitions are realized. The width of the optical band determined by extrapolation of $(\alpha\hbar\omega)^2 = f(\hbar\omega)$ line segment towards $\alpha\hbar\omega = 0$ is equal to 1.95 eV.

For the temperature 78 K the size of the absorption band of the *GaSe(K)* crystals is determined by direct optical transition with formation of excitons in state n=1.

PL spectra of the *ε-GaSe(K)* crystals at the temperature 78 K represent a weakly shaped band with an absolute maximum at 1.91 eV. Also two thresholds are present: one towards high energies from the central band at 2.09 eV and the other at 1.80 eV. The 2.09 eV threshold is probably obtained as a result of the exciton emission, but the 1.80 eV particularity can be determined by the recombination of the electrons inside the conduction band through a deep acceptor level formed by the *K* atoms.

The activation energy of thermal suppression of the band 1.91 eV is determined by the slope of the characteristic $\ln\left(\frac{L(0)}{L(T)} - 1\right) = f\left(10^3/T\right)$ and it is equal to 60 meV.

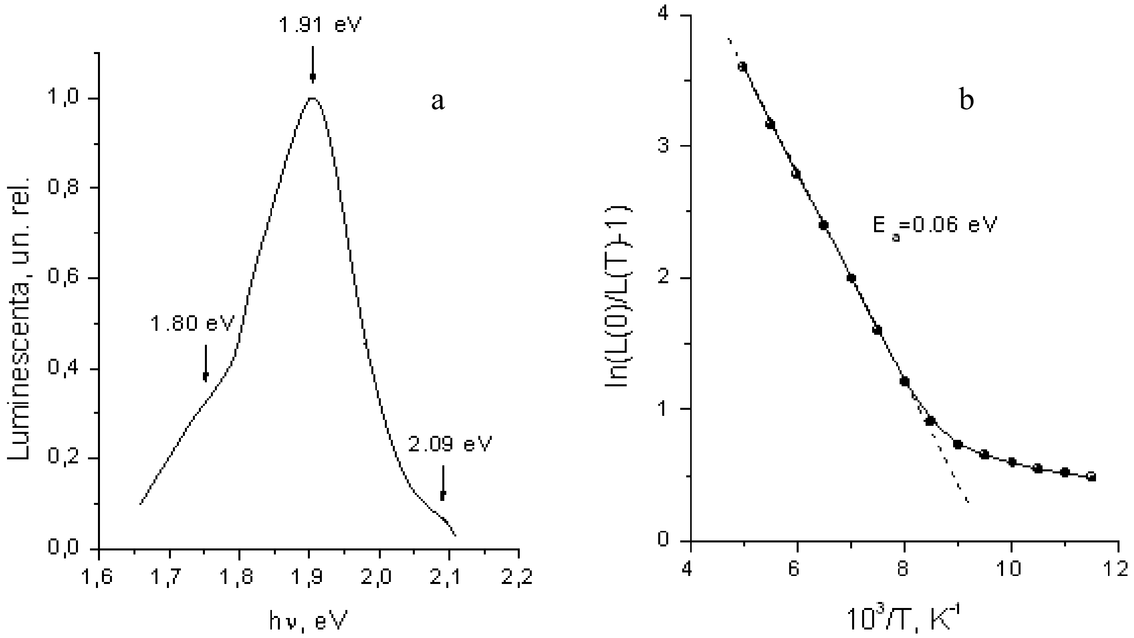

Fig. 6. PL spectra of the *ε-GaSe(K)* crystals at the temperature 78 K (a). Thermal attenuation of the PL band for *ε-GaSe(K)* crystals (b).

Conclusions

The growth of the absorption band of the *ε-GaSe(Li)* crystals is determined by optical transitions with formation of excitons with state n=1.

Inside the *ε-GaSe* crystals *Li* atoms form acceptor states localized at 70eV from the maximum of the valence band.

The absorption line of the free exciton corresponds to the energy 2.092 eV and it is by ~7 meV higher than the energy of the PL band from the absorption band edge. The band is obtained as a result of the luminescence emission of the excitons bound around the ionized centers, which can be the Li ions.

K atoms form localized states in *GaSe* crystals screening the exciton bonds at normal temperature.

For temperature 78 K the size of the absorption band of the *GaSe(K)* crystals is determined by direct optical transition with formation of excitons in state n=1.

The 2.09 eV threshold is probably obtained as a result of the exciton emission, but the 1.80 eV particularity can be determined by the recombination of the electrons inside the conduction band through a deep acceptor level formed by the *K* atoms in *GaSe* crystals.

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