

Optical Properties of Layered GaSe Crystals Intercalated with Hydrogen-Containing Molecules of Toluene, Water and Alcohol

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Performed in this work are low-temperature ($T = 4.5$ K) investigations of photoluminescence (PL) spectra in GaSe crystals intercalated with water, alcohol and toluene molecules. It has been ascertained that intercalation with toluene for 165 days or with water for 35 days results only in insignificant improvement of crystal quality. Essentially decreased in these cases was the intensity of emission lines for free excitons within the ranges of stacking faults of crystalline layers, while the PL intensity of the free exciton of pure ϵ -GaSe crystal was increased. Intercalation of GaSe crystals with alcohol results in practically full disappearance of emission lines inherent to free and bound excitons – present in PL spectra were only broad bands caused by radiative transitions of carriers from direct and indirect conduction bands onto the acceptor level located 70 meV above the valence band top, with participation of TO phonons. Stand that intercalation of GaSe crystal by water, alcohol and toluene molecules decreased activation energy of this acceptor level.

Keywords: Layered Crystal, Intercalation, GaSe, Photoluminescence, H_2O , C_7H_8 , C_2H_5OH .

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1. INTRODUCTION

Owing to their unique physical-and-chemical properties – a strong ion-covalent hybrid sp -bond inside crystalline layers and a weak van der Waals bond between layers, layered crystals (in particular, GaSe studied in this work) are related to low-dimensional systems allowing to easily introduce atoms or molecules into the interlayer space by using intercalation.

As shown for instance in [1 – 3], appearance of molecular hydrogen in the interlayer space results in localization of exciton motion in the plane of crystalline layers, and passivation of free radicals (both donors and acceptors) with atomic hydrogen leads to decreasing the defect level depth relatively to valence and conduction bands.

Stemming from the above facts, it seemed reasonable to study the influence of intercalated hydrogen-containing molecules (water, toluene, alcohol) on optical properties of GaSe layered crystals.

2. EXPERIMENTAL PART

Pure GaSe single crystals were grown using the Bridgman method. To study the intercalation influence on optical properties, we chipped plates with a thickness of 3 to 5 mm from GaSe ingots and then cut samples to the dimensions of 5×5 mm² from these plates.

Intercalation was performed at room temperature by using the method of dipping the samples into silica ampoules containing solutions of distilled water [H_2O], toluene [C_7H_8] or alcohol [C_2H_5OH].

Intercalation of crystals in these solutions was made for 35 and 165 days. Then, the intercalated samples were pulled out of the solutions and cleaved to prepare

fresh chip surfaces. These chips were used to measure PL spectra.

Measurements of PL were made using a 0.6-m monochromator MDR-23 with a grating of 1200 groves/mm. Investigation of PL spectra at $T=4.5$ K were made using a helium cryostat (A-255) designed at the Institute of Physics NAS of Ukraine. It was equipped with a UTRECS K-43 system allowing control over sample temperature within the range of 4.2 to 350 K with high accuracy (0.1 K).

The excitation of PL spectra was performed using a current-wave semiconductor laser with a wavelength of 532 nm and stable power at 100 mW. The photomultiplier tube FEU-79 served as radiation detector.

3. RESULTS AND DISCUSSION

Shown in Fig. 1 (a – f) are PL spectra measured at $T = 4.5$ K for GaSe crystals intercalated with toluene, water and alcohol for 35 and 165 days, as well as PL spectra of GaSe crystals (see Fig.1 g, h) both non-intercalated and that doped with Cd impurity (concentration 0.01 wt. %) and gamma-irradiated (energy of quanta was 0 to 34 MeV, dose up to 10^{14} γ/cm^2), which was studied previously in [4]. When obtaining the discussed experimental results, the spectral width did not exceed 0.25 meV.

Besides, insets in Fig. 1(b, d, f) illustrate spatial-coordination ordering the molecules: water (atomic mass - A.m. = 18, melting temperature - $T_m = 273.16$ K, hybrid ion-covalent bond - sp^4); toluene (A.m. = 92, $T_m = 178.16$ K, sp^2); and alcohol (A.m. = 46, $T_m = 159.01$ K, sp^2).

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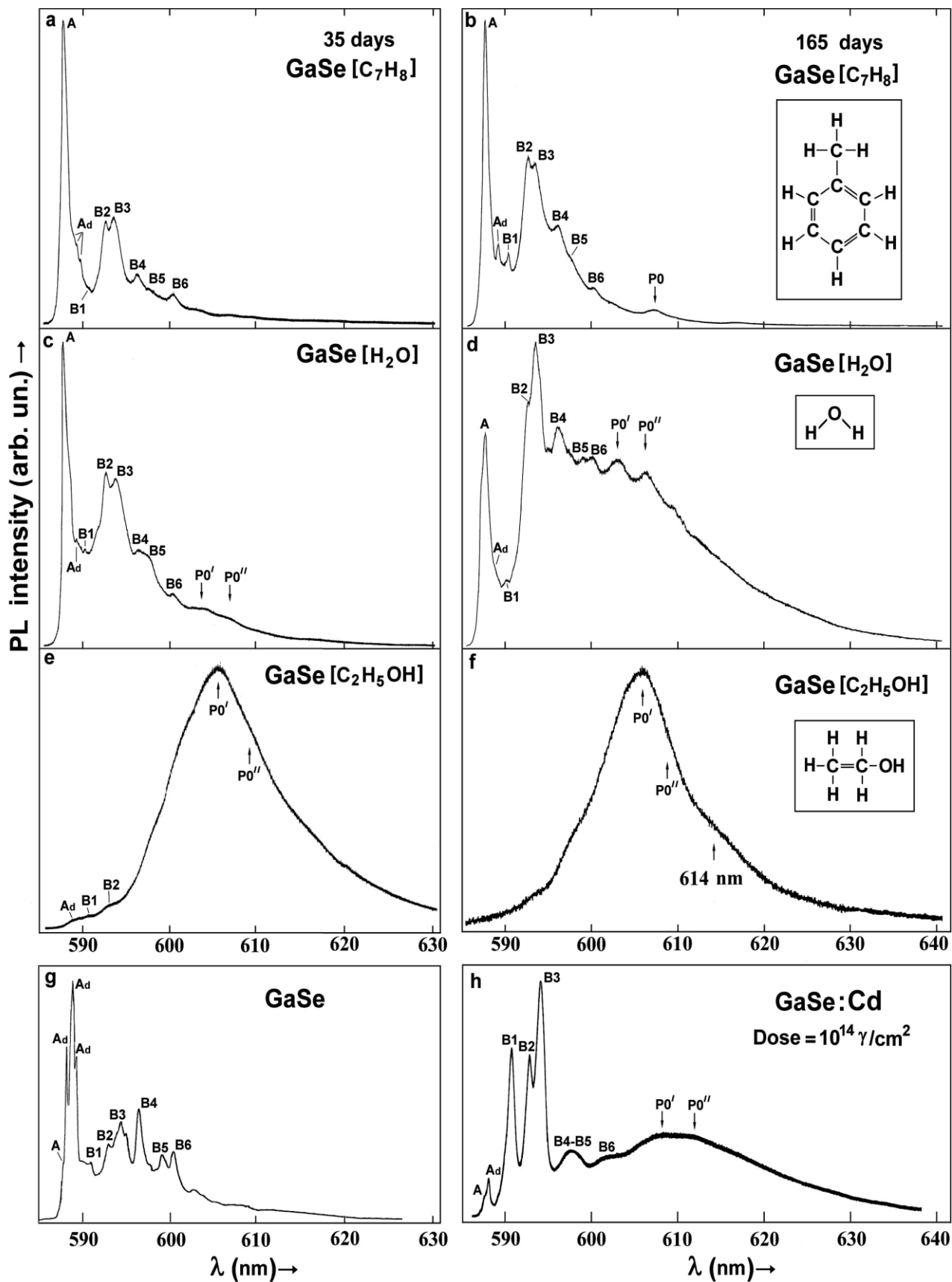


Fig. 1 – PL spectra at T = 4.5 K for crystals: a,b - GaSe[C₇H₈]; c,d - GaSe[H₂O]; e,f – GaSe[C₂H₅OH], intercalated for 35 and 165 days, respectively; g – GaSe; and h – GaSe:0.01Cd

Table 1 – Position of a free and bound exciton PL peaks at T=4.5 K for non-intercalated and intercalated GaSe crystals

Crystal	Wave length of emission line and band peaks (nm)								
	A, Ad		B1	B2	B3	B4	B5	B6	P0
GaSe	587.8, 588.1, 588.6, 589.3		590.9	592.6	594.1	596.5	599.1	600.4	
GaSe[C ₇ H ₈] – 35 days	587.8, 588.0, 588.9, 589.7		590.5	592.6	593.7	596.4	597.6	600.5	
GaSe[C ₇ H ₈] – 165 days	587.9, 589.2		590.4	592.5	593.5	596.1	597.5	600.2	607.2
GaSe[H ₂ O] – 35 days	587.9, 589.5		590.3	592.1	593.2	596.2	597.4	600.3	603.5, 606.9
GaSe[H ₂ O] – 165 days	587.9		590.1	592.6	593.7	596.3	599.0	600.1	603.1, 606.3
GaSe[C ₂ H ₅ OH] – 35 days	588.9		590.7	593.0					605.8
GaSe[C ₂ H ₅ OH] – 165 days									606.0
GaSe:0.01Cd (dose = 10 ¹⁴ γ/cm ²)	587.6, 588.5			591.5	593.6			600.4	608.0, 612.0

It is known [5 – 7], that single crystals grown by the Bridgman method possess four polytypes (β -, δ -, ϵ - and γ -) varying between each other in the sequence of crystalline layer stacking. GaSe single crystals are of ϵ -polytype. These belong to hexagonal crystalline structure (spatial group D_{3h}^{13}), the unit cell of which consists of two Ga₂Se₂ molecules located within two crystalline layers.

As seen from Fig. 1, PL spectra at T = 4.5 K for GaSe crystals intercalated with toluene and water as well as for those crystals non-doped or doped with Cd consist of emission lines inherent to free excitons (A-line, $\lambda = 587.8$ nm), excitons localized within the ranges of stacking faults of crystalline layers (A_d-lines), bound excitons (B1 – B6-lines) as well as broad doublet band P0', P0'' caused, as it was shown in [4] using the samples of GaSe:0.01Cd crystals, by radiative recombination of carriers from direct (DCB) and indirect (ICB) conduction bands at the acceptor level located 70 meV higher than the top of the valence band (VB). In accord with [4], these transitions occur under participation of TO phonons. The energy positions of peaks for A, A_d, B1-B6 lines and doublet P0 band are summarized in Table 1.

Intercalation of GaSe crystals with toluene and water for 35 days, as seen from Fig. 1, results in noticeable changes in PL spectra within the ranges of free and bound excitons as compared to those in non-intercalated GaSe crystals: the intensity of A-line for free exciton radiation inherent to ϵ -GaSe is increased, while the intensity of A_d-lines inherent to radiation of excitons localized within the ranges of stacking faults of crystalline layers is decreased.

It is indicative of increasing the lifetime and, respectively, free path for the exciton as a result of decreasing amount of point and spatial defects where its scattering takes place. It should be noted that similar phenomena were observed in [4] when doping the GaSe crystals with Cd and Zn impurities with the concentration 0.01 wt. %, as well as after “annealing” them with gamma-quanta. In accord with [4], it is caused by “curing” the Schottky and Frenkel defects, respectively. However, the effect of growing intensity in A-line emission and that of decaying intensity in A_d-lines observed in intercalates GaSe[H₂O] and GaSe[C₇H₈] are consid-

erably clearer pronounced than in the case of Cd-, Zn-doped or “annealed” with gamma-quanta GaSe crystals.

Further growth in duration of intercalation with these solutions up to 165 days results in the increase of radiation intensity within the range of P0 band. Despite the fact that this effect is clearer pronounced in GaSe[H₂O] intercalates than in GaSe[C₇H₈] ones, the integrated intensity of radiation spectra inherent to GaSe[H₂O] and GaSe[C₇H₈] crystals intercalated for 165 days remains the same as in crystals treated for 35 days.

We assume that the observed redistribution of radiation intensities into the long-wave range is caused by participation of carriers from DCB and ICB recombining at the **a1** acceptor level with further recombination radiation promoted by TO phonons. As it has been shown in [4], in GaSe:0.01Cd crystals this level is located near 70 meV above the VB top. However, it follows from Fig. 1 and Table 1 that the energy position of P0 band in the case of GaSe[H₂O] and GaSe[C₇H₈] intercalates is shifted to the high-energy range.

Availability of this short-wave shift is indicative of passivation observed for free radicals (acceptors, in this case), which is provided by water and toluene molecules. As the molecules of water, toluene and alcohol have hydrogen in their composition, the latter passivates point defects and lowers the energy depth of defect levels (both donors and acceptors) relatively to conduction and valence bands, respectively. It was demonstrated in [8] using the samples of InSe crystals intercalated with hydrogen.

In accord with the data adduced in Table 1, one can show that, the energy depth of the acceptor level is 70 meV higher than the VB top in pure GaSe crystals, but this value in intercalates GaSe[C₇H₈], GaSe[C₂H₅OH] and GaSe[H₂O] is lowered by 2.7, 6.7 and 15.8 meV, respectively.

Intercalation of GaSe crystals with alcohol (Figs 1e and 1f) leads to practically full degradation of emission lines for free exciton and excitons localized near stacking faults of crystalline layers, and those bound to crystal point defects as well. In the PL spectrum, in this case one can observe only wide weakly structured band with the radiation peak at 606.0 ± 0.5 nm and a shoul-

der near 614 nm.

At the same time, the integrated intensity of PL spectra remains practically the same as in GaSe crystals intercalated with water and toluene. The energy position of the peak for this band, as mentioned above, allows to associate it with recombination radiation of carriers from DCB and ICB at the **a1** acceptor level located in this case near 63 meV above the VB top, with account of TO phonon participation.

Unfortunately, discussion of the nature of the band at 614 nm is out of the frames of these considerations and requires performing some additional investigations.

CONCLUSION

The performed low-temperature ($T = 4.5$ K) investigations of PL spectra inherent to GaSe crystals intercalated with hydrogen-containing molecules of water, alcohol and toluene, as well as juxtaposition of the obtained results with those for GaSe crystals non-intercalated and doped with Cd and Zn impurities (concentration 0.01 wt. %) showed that:

Intercalation with these hydrogen-containing compounds does not result in a noticeable decrease in the integrated radiation intensity.

By contrast, in crystals intercalated with toluene and water, the effect of growing the intensity of A-line emission inherent to free exciton and decay of A_d -lines for excitons localized at the stacking faults of crystalline layers is pronounced much clearer than in the case of doping the crystals with Cd and Zn impurities or "annealing" with gamma-quanta.

By analogy, like to the case of doping the crystals with Cd and Zn impurities or with increasing the dose of their gamma-irradiation, one can observe redistribution of the intensity between emission caused by transitions from free and bound excitonic states into the

valence band and that of the emission caused by transitions of carriers from direct and indirect conduction bands onto the acceptor level **a1**.

When transferring from non-intercalated GaSe crystal to those intercalated with hydrogen-containing molecules along the row \rightarrow toluene \rightarrow alcohol \rightarrow water, the energy position of the acceptor level **a1** is decreased in the sequence $70 \rightarrow 67 \rightarrow 63 \rightarrow 56$ meV.

The intensity of radiation related with transitions of DCB and ICB carriers onto the acceptor level **a1** increases both with intercalation duration and when transferring in the direction of changes in intercalate composition: toluene \rightarrow water \rightarrow alcohol.

Despite the fact that water molecules, as it has been shown by the performed investigations, provide the most efficient passivation of the acceptor (i.e., defect of crystalline lattice) and, respectively, results in lowering the position of the acceptor level **a1**, their influence on free exciton behavior is not so considerable as in the case of intercalation with alcohol molecules.

Intercalation of these crystals with alcohol leads to practically full disappearance of emission lines inherent to free and bound excitons; only broad bands related with radiation caused by transitions of DCB and ICB carriers onto the acceptor level **a1** remain.

This discussion, the drawn conclusions, as well as our previous investigations of hydrogen intercalates of GaSe enable us to assume that hydrogen-containing molecules of water, alcohol and toluene are mainly located in the interlayer space and passivate both point and spatial defects in this crystal.

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