

STRUCTURE AND OPTICAL PROPERTIES OF GaSe-CdSe COMPOSITES DRIVEN BY Cd INTERCALATION IN GaSe LAMELLAR CRYSTALS

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Abstract

A new composite material composed of GaSe and CdSe has been obtained by treatment of GaSe single-crystal lamellas in Cd vapors at temperatures of 773–853 K and intercalation of Cd interlayers. The structure and optical properties of the GaSe-CdSe composite material have been studied. The content of CdSe crystallites was found to grow with increasing treatment temperature or with increasing duration of treatment at a constant temperature. Analysis of XRD, PL, XPS, AFM, and Raman patterns has shown that the heterogeneous composite composed of micro and nanocrystallites of CdSe in GaSe can be obtained by Cd intercalation in a temperature range of 753–853 K. On the basis of Raman spectrum, the vibrational modes of the composite have been identified. The PL of these materials contains emission bands of free and bound excitons, donor-acceptor bands, and bands of recombination via impurity levels. The PL emission spectra measured at a temperature of 78 and 300 K for the composites result from the overlapping of the emission bands of the components of GaSe doped with Cd and the CdSe crystallites.

1. Introduction

Binary A^{III}B^{VI} compounds, a typical representative of which is the GaSe lamellar semiconductor, exhibit a pronounced anisotropy of chemical bonds and optical properties [1]. An elementary lamella is composed of atomic planes arranged in the following sequence: Se–Ga–Ga–Se. The bonds between the elementary lamellas in GaSe crystals are provided by Van der Waals polarization forces, while strong ionic-covalent forces act between the atomic planes within the packets [2–3]. Weak bonds between the packets, along with saturated valence bonds on the surface, lead to the formation of plane-parallel cracks between Se atomic planes with a width of ~0.3 nm [4]. Ions, atoms, and molecules can easily penetrate these cracks; this fact expands the range of applicability of layered semiconductors. By intercalation of GaSe

crystals with Li^+ ions [5], it has been shown that this semiconductor can be applied as a solid electrolyte exhibiting characteristics superior to those of metal oxides [6]. By intercalation of GaSe single crystals with Ni, Fe, and Co, it is possible to prepare composite materials and structures with ferromagnetic properties that are promising for use in spintronics [7-9].

In this study, the structure and luminescent properties of GaSe crystals intercalated with Cd from the vapor phase have been examined. Analysis of XRD, PL, XPS, and Raman patterns has shown that a composite composed of micro and nanocrystallites of CdSe in GaSe can be prepared by intercalation with Cd in a temperature range of 753–823 K.

2. Experimental and Crystalline Structure Properties

The original material was p-GaSe single crystals grown by the Bridgman–Stockbarger method [10]. The GaSe compound was synthesized from original elements Ga (5N) and Se (5N). Plane-parallel plates with smooth surfaces at an atomic level and a thickness of 20 μm to 5 mm were prepared by splitting the grown single crystals with the crystallographic C_6 axis oriented perpendicular to the axis of the ingot. These plates were cut into rectangular samples with a surface area of 10–20 mm^2 . The samples were selected with respect to thickness and placed into quartz tubes with an internal diameter of 15–17 mm together with granules of Cd (5N) taken in an amount of 2 mg/cm^3 . After repeated evacuation (2–3 times) to a residual pressure of $\sim 5 \cdot 10^5$ Torr and sealing, the containers were subjected to heat treatment at temperatures of 75 to 823 K in an oven with a stable temperature for 6–24 h. In this temperature range, the Cd vapor pressure was in a range of 20–560 mmHg.

XRD patterns of the prepared composites were recorded on a DRON-4 diffractometer using CuK_α radiation ($\lambda = 1.5406 \text{ \AA}$) in the range of diffraction angles 2Θ of 10° – 80° with a resolution of 0.050 at a rate of $10^\circ \text{ min}^{-1}$. Photoluminescence (PL) spectra of the composites prepared by heat treatment of GaSe single crystals in Cd vapors were excited with laser radiation with Nd^{+3} ($\lambda = 532 \text{ nm}$) with an average power of 100 mW. The PL in a temperature range of 78–300 K was analyzed using a monochromator with a diffraction grating of 600 and 1200 mm^{-1} (an area of $180 \times 130 \text{ mm}^2$) and recorded using an electronic photomultiplier with a multialkali photocathode. The spectral resolution of measurements of PL and PC did not exceed 1 meV in the entire studied spectral range. Raman scattering spectra at $T = 300 \text{ K}$ were analyzed using a Raman microsystem.

The crystal lattice of the GaSe compound is composed of layered packets, which in turn are formed by four atomic planes of Se and Ga (Fig. 1a).

The Cd atoms of the intercalation occupy positions between the Se planes of two elementary packets neighboring to four selenium atoms from the first configuration sphere in both packets. At fairly high temperatures of $T \geq 653 \text{ K}$, at which the Se–Ga bonds are fairly weak, the bonds between Ga and Se are broken and form new compounds of the Cd–Se type, which are much more energetically stable than GaSe. Thus, during a high-temperature heat treatment at 750–830 K, CdSe clusters and condensation centers of Ga atoms are formed in the GaSe plates. Since the saturated valence bonds on the surface of the elementary packets (Se–Ga–Ga–Se) (Fig. 1b), a long-term exposure (24–30 days) to normal atmosphere leads to the formation of a nanostructured layer of oxides of the constituting elements on the outer surface of the GaSe plates [2].

Surface nanostructuring of the GaSe plates by treatment in Cd vapors at high temperatures is much more pronounced compared to a normal temperature. The surface of GaSe plates freshly

cleaved from perfect single crystals is smooth at an atomic level. The treatment in an atmosphere of Cd vapors at a temperature of $T \geq 593$ K (at 593 K, the Cd vapor pressure is 0.1 mmHg), micrometer-sized regions of different shapes are formed on the surface of the plates.

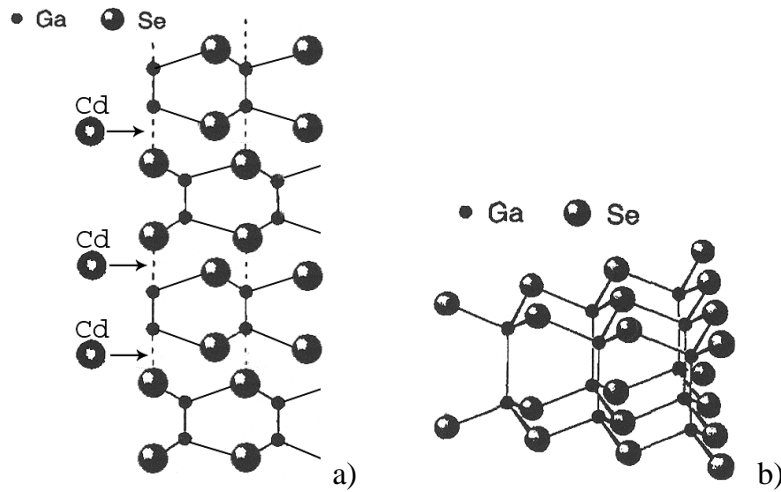


Fig. 1. Arrangement of atomic planes in ϵ -GaSe crystals.

Atomic spectrum analysis of the points, which can be easily conducted at the surface of the GaSe plates, has shown that they represent clusters of metallic Ga, which are in a liquid state at a temperature of 303 K. As noted above, GaSe single-crystal lamellas are composed of planar packets of atoms so that the plane of Se atoms is located on the surface. They can easily be combined with Cd to form layers of CdSe on the surface. This transformation results in a loss of valence bonds between the Ga atoms in the two atomic planes in the packet ...Se–Ga–Ga–Se... Figure 4 shows an AFM image of the surface of the GaSe plate subjected to heat treatment at a temperature of 833 K for 24 h. Under these conditions of formation of the composite, pyramidal and conical structures with base dimensions on the order of a few hundreds of nanometers are formed on the (001) face of the GaSe plates. The height of these structures is up to 15–20 nm, which corresponds to more than ten layered packets of the Se–Ga–Ga–Se type.

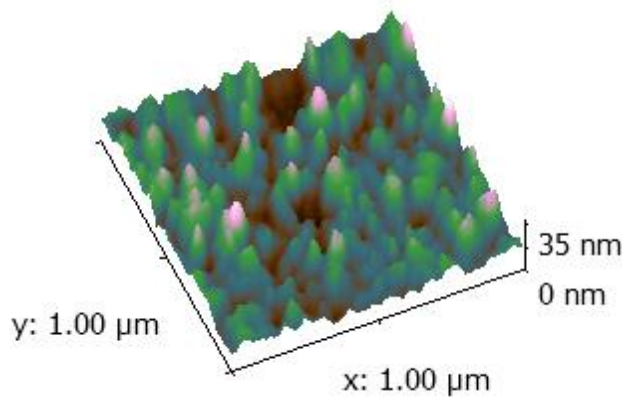


Fig. 2. AFM image of the surface of the GaSe lamella subjected to heat treatment in Cd vapors at a temperature of 833 K for 24 h.

The crystalline structure of the new components of the composite prepared by heat treatment of GaSe single-crystal plates in Cd vapors was studied by X-ray diffraction and Raman scattering. Figure 3 shows XRD patterns of two samples prepared by treatment of GaSe plates with a thickness of 0.3 and 1.2 mm in Cd vapors at a temperature of 753 (Fig. 5a) and 833 K (Fig. 5b) for 24 h.

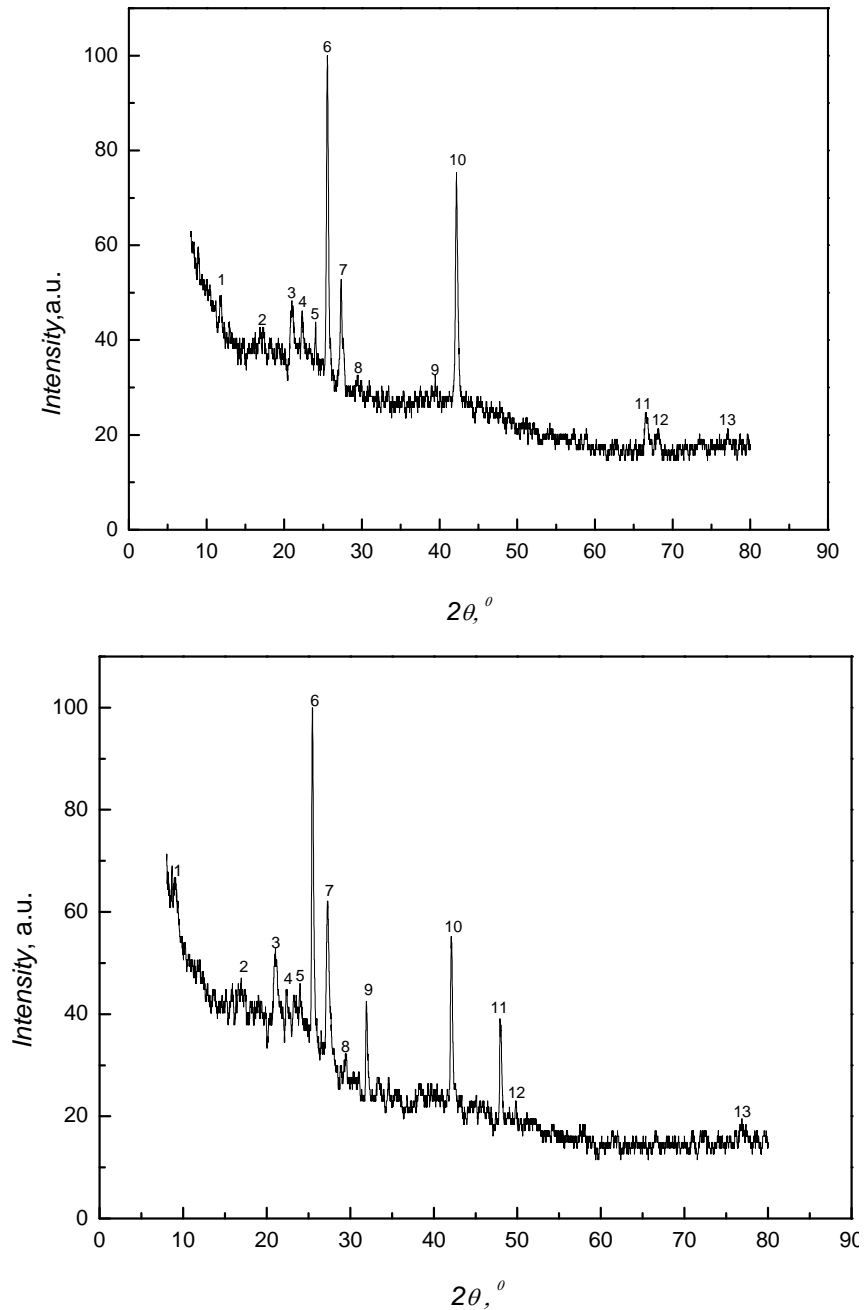


Fig. 3. XRD pattern of the GaSe lamella treated in Cd vapors at a temperature of (a) 753 and (b) 833 K for 24 h.

Table 1 lists the 2θ diffraction angles corresponding to the diffraction lines, the intensity of the lines, the identification of a lot of the planes in which X-ray diffraction occurs, and the respective

compound.

Table 1. Identification of the GaSe-CdSe composite according to XRD patterns

No.	753 K		Identification	833 K		Identification
	2 θ	I (a.u.)		2 θ	I (a.u.)	
1	22.35	46.1	[002] <i>GaSe</i>	20.96	51.7	[002] <i>GaSe</i>
2	25.56	100	[101] <i>CdGa₂Se₄</i>	25.49	100	[002] <i>CdGa₂Se₄</i>
3	27.33	52.8		27.27	62.1	
4	42.17	75.3	[004] <i>GaSe</i>	31.93	42.5	[004] <i>GaSe</i>
5	66.5	24.7		42.08	55.2	
6	8.93	59.65	[002] <i>CdSe</i>	47.93	39.1	[002] <i>CdSe</i>
7	11.85	49.05	[001] <i>CdSe</i>	9.05	66.48	[101] <i>CdSe</i>
8	17.34	42.25		16.97	46.24	
9	20.99	47.44	[103] <i>CdSe</i>	22.46	44.23	[103] <i>GaSe</i>
10	22.32	45.43		57.91	17.80	[110] <i>CdSe</i>
11	29.53	32.24		76.93	19.19	[222] <i>CdGa₂Se₄</i>
12	39.39	31.22	[210] <i>GaSe</i>			[310] <i>CdGa₂Se₄</i>
13	68.14	20.40				[210] <i>GaSe</i>
14	73.5	20.00				
15	76.93	20.00				

It is evident from Fig. 3 and Table 1 that the diffraction lines of the ensembles of planes of both the GaSe-based composite and the crystallites composed of CdSe are clearly detected. Along with XRD reflections of crystalline clusters of CdSe in GaSe, both at 753 and 833 K, reflections from the ensemble of the [101] plane of the CdGa₂Se₄ compound are clearly recorded. A change in the intensity ratio of the XRD reflections with an increase in the treatment temperature from 753 to 833 K (with a respective increase in the Cd vapor pressure) is indicative of an increase in the concentration of CdSe crystallites in the composite. Narrow contours of reflections of the ensembles of the [002], [101], and [110] planes can be used as a criterion of high perfection of CdSe crystallites, while a considerable broadening of the contour of the diffraction lines from the [004] and [210] atomic planes of the hexagonal network of gallium monoselenide is indicative of the degradation of the base material (GaSe single crystal). Comparison of Figs. 5a and 5b shows that an increase in the concentration of Cd atoms in the composite upon switching from 753 to 833 K leads to a significant increase in the content of both CdSe and CdGa₂Se₄.

3. Optical Properties

The presence of micrometer-sized regions of different shapes on the surface of the plates in the form of circular dots with unordered areas is clearly evident in reflected light and much more pronounced in a polar field of monochrome light in reflection and luminescence (Fig. 4).

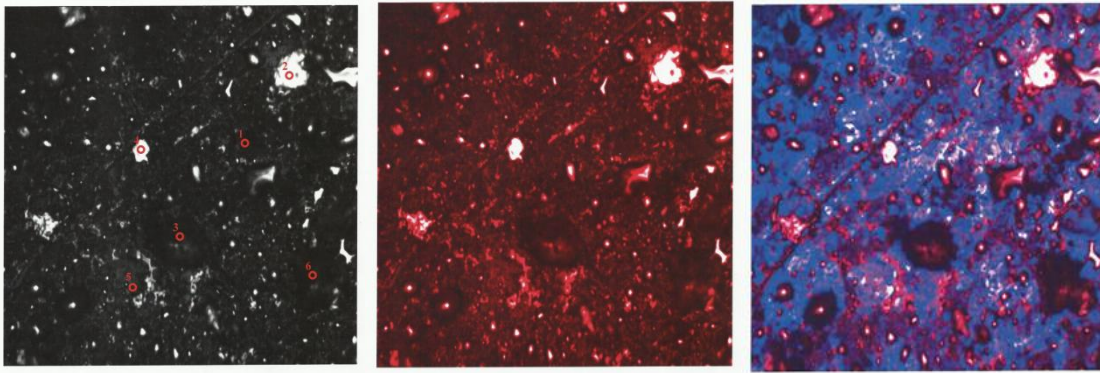


Fig. 4. Microscopic image in reflected light and luminescence on the surface of the GaSe lamella subjected to treatment in Cd vapors at a temperature of 823 K for 24 h. The recorded area is $193.3 \times 193.3 \mu\text{m}^2$.

Additional information about the nature of the structures formed on the surface of GaSe plates is provided by luminescent emission spectra measured at room temperature. Figure 5 shows PL spectra recorded at $T = 300$ K in bright (point 1) and dark regions (point 3). It is evident from the comparison of these curves that the PL intensity at the bright points (1, 5) is about 5–6 times higher than at the dark points. However, at points 1 and 5, the PL band peak is shifted by ~ 20 meV to higher energies and is indicative of splitting into two subbands peaking at 1.818 and 1.797 eV.

It can be assumed that the PL bands of the GaSe–CdSe composites prepared by heat treatment of GaSe crystals in Cd vapors are formed by overlapping of the respective bands of the constituting compounds GaSe and CdSe.

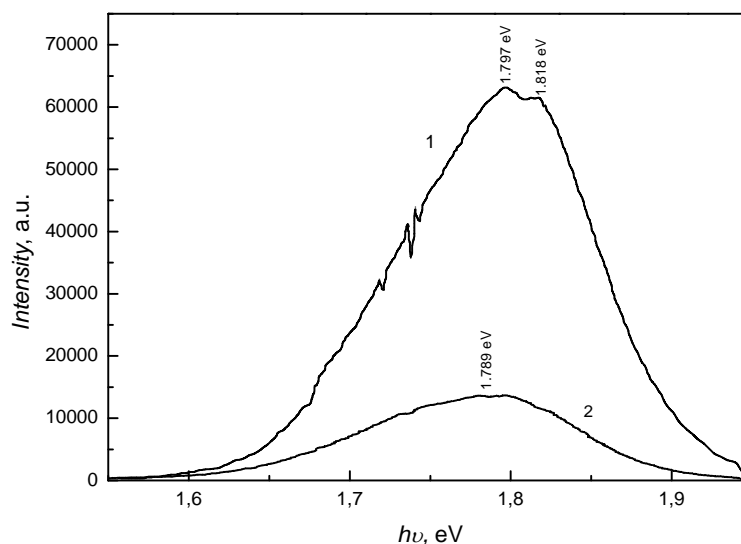


Fig. 5. PL spectra of the composite prepared by a heat treatment of GaSe crystals in Cd vapors at a temperature of 773 K for 24 h: (curve 1) bright points on the surface (1, 5) and (curve 2) dark points (3, 4).

Figure 6 shows the Raman scattering spectrum of the GaSe–CdSe composite prepared by heat treatment of GaSe single-crystal plates in Cd vapors at a temperature of 773 K for 6 h. The spectra exhibit vibration bands of the crystal lattice of the original material (GaSe) and the newly formed compound (CdSe). The wave numbers and intensities of the bands of Raman scattering in the GaSe–CdSe compound are shown in Table 2.

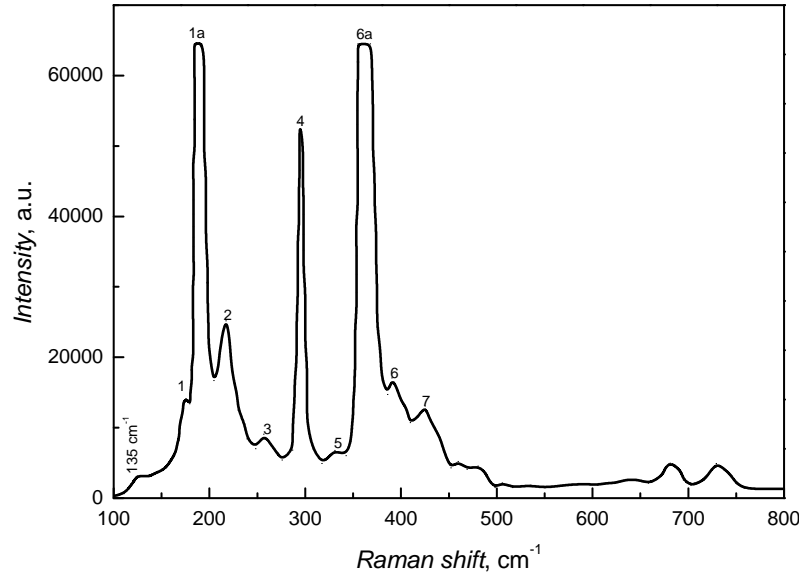


Fig. 6. Raman spectrum of the GaSe lamella subjected to treatment in Cd vapors at a temperature of 773 K for 6 h.

Table 2. Vibration modes of the crystal lattice of the GaSe–CdSe composite obtained from the Raman spectrum

No.	$\tilde{\nu}$, cm^{-1}	Intensity (a.u.)	Compound	Vibration symmetry
	135.0	3000	<i>GaSe</i>	A_1
1	174.4	14000	<i>CdSe</i>	E(TO)
1a	188.9	>60000	<i>GaSe</i>	
2	217.5	25000	<i>GaSe</i>	E(TO)
3	256.8	8000	<i>GaSe</i>	E'(LO)
4	295.4	52000	<i>GaSe</i>	
5	329.9	6000	<i>GaSe</i>	
6	361.6	>60000		
6a	393.9	16000	<i>CdSe</i>	
7	426.8	12000	<i>CdSe</i>	

It is evident from Table 2 that, along with the monophononic vibration modes in the GaSe crystals, the vibration bands of the crystal lattice of the CdSe compound are also clearly pronounced. The lower intensity of the diffusion bands in the CdSe crystallites compared to GaSe corresponds to the percentage composition of the composite prepared at a temperature of 733 K.

These results are consistent with the data on the intensity of the XRD reflections from the planar systems in the GaSe and CdSe crystals shown in Table 1.

Both the classification of vibration modes by the type of symmetry and the energy shifts of the Raman bands associated with combination of different vibration modes are well known for GaSe single crystals [12–13]. The reduced intensity of resonance vibration modes E(TO) (267.5 cm^{-1}) and E'(LO) (256.8 cm^{-1}) compared to the bands (188.9 and 361.6 cm^{-1}) can be attributed to the fact that the formation of the composite is accompanied by the degradation of the crystal lattice of the original GaSe compound.

The PL spectra of GaSe and CdSe crystals are also well known at low temperatures of $T \leq 78\text{ K}$. The PL of these materials contains emission bands of free and bound excitons, donor–acceptor bands, and bands of recombination via impurity levels [14]. Figure 7 shows the PL spectra of the GaSe and CdSe crystals measured at temperatures of 300 and 78 K and the spectra of the compounds prepared by heat treatment at temperatures of 753 and 833 K for 20 and 24 h. The PL spectrum of the GaSe crystals at a temperature of 300 K exhibits a donor–acceptor band peaking at 2.00 eV and an impurity band at 1.94 eV. At a temperature of 78 K, the PL spectrum exhibits an emission line of localized excitons ($h\nu = 2.092\text{ eV}$), a donor–acceptor emission band ($h\nu = 2.072\text{ eV}$), and an intrinsic impurity band peaking at 1.920 eV. Figure 7 (curves 5, 6) shows that the PL spectrum of the CdSe single-crystal compound at temperatures of 300 and 78 K exhibits an emission band with a symmetrical contour peaking at 1.720 and 1.790 eV, respectively. The PL spectra measured at $T = 300\text{ K}$ for the GaSe–CdSe composite prepared by treatment in Cd vapors at temperatures of 823 and 853 K exhibit a broad band without pronounced characteristic features with two low-intensity peaks at 1.78 and 1.72 eV, respectively.

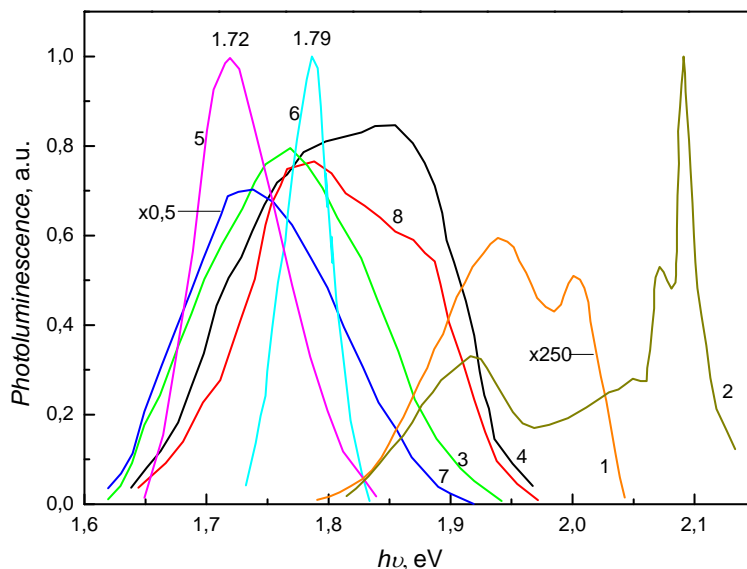


Fig. 7. PL emission spectra of the ϵ -GaSe and CdSe crystals and the GaSe–CdSe composite at temperatures of 78 and 300 K: (1, 2) the GaSe single crystal at temperatures of 300 and 78 K; (3, 4) GaSe annealed in Cd vapors at a temperature of 823 K for 20 h; (5, 6) the CdSe single crystal at temperatures of 300 and 78 K; and (7, 8) GaSe annealed in Cd vapors at a temperature of 853 K for 24 h.

An increase in the duration of intercalation from 20 to 24 h, along with an increase in temperature from 823 to 853 K, results in a shift of the emission peak to lower energies by ~60 meV and, simultaneously, to an increase in the PL band intensity by about 2 times. Comparison of the PL spectra of GaSe subjected to intercalation with Cd (curve 1) and CdSe (curve 5) clearly shows close agreement between the peaks of the respective bands. The extension of the PL band contour to high energies results from the overlapping of the impurity PL bands of the GaSe lamellas and CdSe crystalline clusters of the composite. Note that a decrease in the temperature of the sample from 300 to 78 K results in a more than 200 times increase in the intensity of the PL spectrum of the GaSe lamellas, which leads to an increase in the fraction of GaSe crystals in the intensity distribution of the emission band of the GaSe–CdSe composite. Figure 7 shows the PL emission spectra measured at a temperature of 78 (curves 4, 8) and 300 K (curves 3, 7) for the GaSe lamellas treated in Cd vapors at a temperature of 823 and 853 K, respectively. It is evident that the PL band contour has a complex structure, which probably results from the overlapping of the impurity emission band of GaSe with an absolute maximum at 1.920 eV and the emission band of the CdSe compound peaking at 1.79 eV. Treatment of the GaSe single-crystal plates in Cd vapors at high temperatures, along with the intercalation of Cd atoms between the elementary packets and the formation of CdSe crystallites, leads to doping of the residue of GaSe with Cd, while the newly formed CdSe crystals are doped with Ga. The PL spectra of GaSe crystals doped with Cd in a concentration of 0.01–0.1 at % that were measured at a temperature of 78 K have been thoroughly studied in [15]. The Cd concentrations in GaSe higher than 0.01 at % lead to the formation of defects and screening in the exciton binding and, simultaneously, to the formation of a dominant emission band with a weak peak shifted to lower energies: 1.95 eV at $C = 0.01$ at % and 1.75 eV at $C = 0.05$ at %. Therefore, we can assume that the PL spectra shown in Fig. 6 by curves 4 and 6 at $T = 78$ K and by curves 3 and 7 at $T = 300$ K are the result of the overlapping of the PL bands of the GaSe compound doped with Cd in concentrations of less than 0.05 at % and the CdSe crystallites formed during intercalation at temperatures of $T \geq 753$ K.

4. Conclusions

- (i) A new composite material composed of GaSe and CdSe microcrystals has been prepared by treatment of GaSe single-crystal lamellas in Cd vapors at temperatures of 773–853 K. The content of the CdSe crystallites increases with increasing treatment temperature or with increasing duration of treatment at a constant temperature.
- (ii) XRD patterns and Raman spectra have shown that the CdSe crystallites of the composite are fairly perfect, while the remaining GaSe is composed of strongly deformed and structurally imperfect crystals.
- (iii) New micro- and nanostructures composed of GaSe and CdSe crystallites are formed on the surface of the GaSe lamellas subjected to treatment at 833 K for 24 h.
- (iv) The PL emission spectra measured at a temperature of 78 and 300 K for the composite prepared by the intercalation of Cd atoms in GaSe at a temperature of 773–823 K result from the overlapping of the emission bands of the components of GaSe doped with Cd and the CdSe crystallites.

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