

Optical absorption and photoconductivity of ZnSe:Co single crystals

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Influence of cobalt impurity on the optical absorption and photoconductivity spectra of zinc selenide crystals has been considered. Basing on optical and electrophysical studies results, the scheme of electronic transitions in the investigated crystals is presented.

Рассмотрено влияние примеси кобальта на спектры оптического поглощения и фотопроводимости кристаллов селенида цинка. На основании результатов оптических и электрофизических исследований представлена схема электронных переходов в исследуемых кристаллах.

The interest to research of wide-band semiconductors of the A_2B_6 group is increased considerably during last few decades in connection with the development of ZnSe-based semiconductor light emitting diodes and lasers for the green-blue spectral region. Moreover, the study of A_2B_6 group compounds doped with transition elements (Cr, Co, Ni, Fe, etc.) is an actual task today. This is due to the fact that the intracenter transitions in unoccupied 3d shells of those atoms are typical of such crystals, namely, the absorption and luminescence having a spectrum in medium IR range (1 to 5 μm) and a high quantum yield. The absorption and luminescence spectra under study are rather close to one another and the Stokes loss is minimal in this case. The crystals being studied may be used as active media for compact lasers with tunable IR emission wavelength. Such lasers are applied in medicine, biology, optical communications as well as in various spectroscopic investigations, e.g., for optical identification of chemicals. In particular, laser generation in chromium-doped ZnSe crystals has been re-

ported [1]. The transmission of ZnSe:Co, Fe crystals in IR region is nonlinear. That is why these crystals are used as passive gates for IR lasers. The interest in such lasers is due to the fact that the emission of those lasers is believed to be safe for sight. Therefore, those can be used in range-finders [2].

The purpose of this work is to study the effect of cobalt dopant on the absorption and photoconductivity spectra of zinc selenide crystals as well as to define the nature of optical transitions therein.

The ZnSe:Co crystals were obtained using the diffusion method where powdered cobalt metal was used as the dopant source [3]. The undoped ZnSe crystal and the cobalt powder were placed into a quartz ampoule that was then evacuated down to 10^{-5} Torr, then filled with argon and evacuated again. The diffusion process was carried out at 1173–1273 K for 5 to 10 h. The optical density spectra were measured using an SF-46 diffraction spectrophotometer (in visible region) and an MDR-6 monochromator with 600 lines per millimeter grating (or 325 lines per millimeter in IR region of 1 to

3 μm). The optical density spectra were measured at 77 and 293 K. To study the photoconductivity spectra, indium contacts were applied onto the crystal surface by vacuum burning-in at about 600 K.

The doping of ZnSe crystals with cobalt results in a shift of the absorption edge towards lower energy from 2.76 eV for undoped crystals down to 2.33 eV for those annealed at 1273 K. Such a considerable absorption edge shift (by 0.43 eV) evidences the formation of a $\text{Zn}_{1-x}\text{Co}_x\text{Se}$ solid solution having a narrower band gap. When interpreting the optical transitions in ZnSe:Co, the calculated energy spectrum data for cobalt [4] were used. In the low-energy wing of ZnSe:Co absorption edge, a series of weak absorption lines have been found at 2.36, 2.43, and 2.55 eV (referred to as *L*, *M*, *N* lines). The same series has been revealed in the ZnS:Co absorption spectra, although those being shifted by 0.18–0.19 eV towards higher energies as compared to the *L*, *M*, *N* lines in ZnSe:Co crystals; at the same time, the difference in energy values corresponding to the band gap for the crystals amounts about 0.8 eV. This suggests that the *L*, *M*, *N* lines in both ZnS and ZnSe crystals are due to intracenter transitions ${}^4\text{A}_2(\text{F}) \rightarrow {}^2\text{T}_1(\text{H})$ occurring within cobalt ion. At the same time, the *L*, *M*, *N* lines were not observed at the low-energy wing of ZnTe:Co spectra. This is due to the fact that the position of the fundamental absorption edge in ZnTe corresponds to an energy lower than that of optical transitions for the *L*, *M*, *N* lines.

The optical absorption of ZnSe:Co crystals in the near IR region is characterized by lines at 1.64, 1.71, and 1.77 eV (Fig. 1). The 1.64 eV line is due to ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$ transitions within cobalt ion. Other two

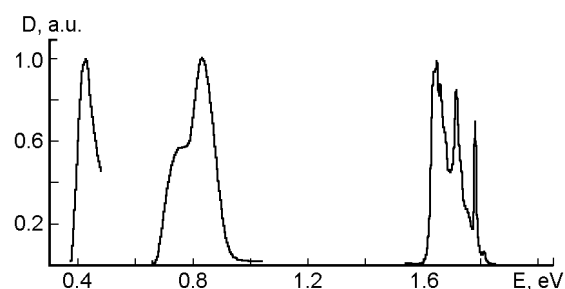


Fig. 1. Optical absorption spectra of ZnSe:Co crystals in IR region.

lines have been observed by us for the first time. Perhaps those are due to transitions onto split ${}^4\text{T}_1(\text{P})$ states of cobalt ion resulting from the spin-orbit interaction. In the medium IR region, the absorption bands are observed in two ranges referred to conventionally as the medium-1 and medium-2, the maxima of those bands being at 0.83, 0.75 and 0.43 eV (Fig. 1). The two first bands correspond to the ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$ transitions within cobalt ion while the third one, to the ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_2(\text{F})$ transition between the ground ${}^4\text{A}_2(\text{F})$ and the nearest excited ${}^4\text{T}_2(\text{F})$ states of cobalt ion. Similar absorption lines were observed in ZnS:Co and ZnTe:Co crystals.

The spectral analysis results for ZnS:Co, ZnSe:Co, ZnTe:Co crystals are summarized in Table. The Table presents the values of optical transition energy corresponding to specific absorption lines as well as the lattice constants (*a*), band gap widths (E_g) for the samples studied, and radii (*R*) of anions surrounding cobalt ion in the semiconductor crystal lattice. The changes in elemental composition of the semiconductors under study is seen to result in a spectral shift of the absorption lines in all the observed

Table. Spectral positions (eV) of cobalt absorption lines in ZnS, ZnSe and ZnTe crystals at 77 K

Crystal		ZnS			ZnSe			ZnTe		
Absorption edge ${}^4\text{A}_2(\text{F}) \rightarrow {}^2\text{T}_1(\text{H})$		2.73	2.61	2.55	2.55	2.43	2.36	–		
IR re- gion	Near ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$	1.86	1.80	1.73	1.78	1.71	1.64	1.53	1.47	1.38
	Medium-1 ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$	0.86 0.76			0.83 0.75			0.73 0.67		
	Medium-2 ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_2(\text{F})$	0.43			0.43			0.43		
<i>a</i> , nm		0.541			0.567			0.610		
E_g , eV (300 K)		3.78			2.68			2.28		
<i>R</i> , nm		0.184			0.191			0.211		

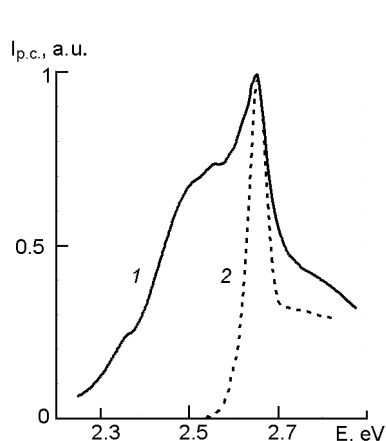


Fig. 2. Photoconductivity spectra of ZnSe:Co (1) and ZnSe (2) crystals.

wavelength ranges. In particular, the absorption lines are shifted towards lower energy in the anionic sequence S–Se–Te. That shift cannot be due to changes in the band gap width, since the E_g variation in ZnS, ZnSe, ZnTe crystals exceeds considerably the low-energy shift of the spectral lines. Moreover, the consideration of absorption spectra shows clearly that the spectra are due to intracenter transitions. At the same time, for the intracenter absorbing and emitting transitions, there are two possible reasons for the spectral line shifts depending on the crystal elemental composition [5]. First, it is known that the covalence factor decreases in the S–Se–Te series, that should result in a high-energy shift of the absorption bands, while just a low-energy one is observed ZnS, ZnSe, ZnTe crystals. Second, the line shift might be influenced by a geometry factor taking into account the crystal field change resulting from increasing radius of anions surrounding the Co^{2+} ion. In the ZnS, ZnSe, ZnTe sequence, that factor should cause a low-energy shift of the spectral lines, just the same being observed in experiment. Thus, the observed dependence of the spectral position for cobalt absorption lines on the elemental composition of ZnS, ZnSe, ZnTe crystals is explained by increasing anion radius in the S–Se–Te sequence. This conclusion is confirmed by the fact that the ZnTe:Co absorption line shift as compared to ZnSe:Co exceeds appreciably that of ZnS:Co in relation to ZnSe:Co. This is consistent with the ratio of ionic radii for sulfur, selenium, and tellurium.

The crystals under study were photosensitive in the light quantum energy range of

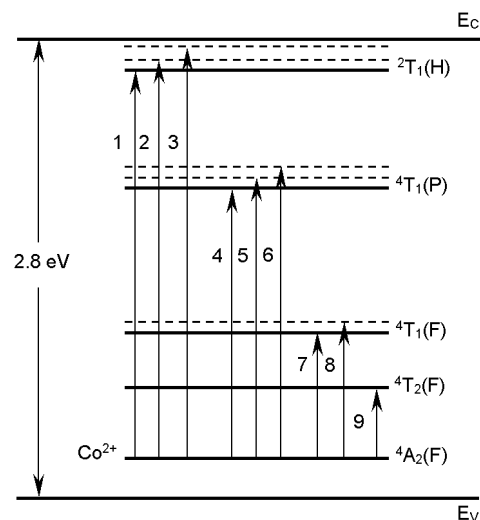


Fig. 3. Scheme of optical transitions within Co^{2+} ion in ZnSe:Co crystals.

2.3 to 2.8 eV. The photoconductivity (PC) spectrum of ZnSe:Co crystals is shown in Fig. 2 along with that of undoped ZnSe. The undoped crystals have shown a single photoconductivity band peaked at 2.65 eV at 300 K (Fig. 2, curve 2). That band is due to interband optical transitions. As is seen in Fig. 2, introduction of cobalt results in an additional PC band positioned in the same spectral region as the L, M, N absorption bands (2.30 to 2.55 eV). It is worth to note that the PC band typical of cobalt is essentially unobservable at 77 K. These results evidence that the photoconductivity in the 2.30–2.55 eV range is due to optical transitions of electrons from the ground state $4A_2(F)$ levels of cobalt to the excited state $2T_1(H)$ levels followed by thermal transitions from the levels of split excited states to the conductivity band.

Basing on the optical and electrophysical studies, the scheme of electron transitions in the crystals under study has been presented (Fig. 3). The L, M, N absorption bands of cobalt are connected with the 1–3 transitions of electrons from the ground state $4A_2(F)$ to the split levels of the excited state $2T_1(H)$. The absorption lines in the near IR region are associated with the transitions 4–6 from the ground state levels to the split levels of the excited state $2T_1(P)$. The absorption lines at 0.75 and 0.83 eV are due to the transitions 7 and 8 from the ground state levels to the split levels of the excited state $2T_1(F)$. The absorption band in the farthest IR region at 0.43 eV is caused by the transition 9 from

the ground state to the nearest excited one, $^4T_2(F)$.

The photoconductivity of ZnSe:Co in the 2.30–2.55 eV range is due to optical transitions of electrons from the ground state $^4A_2(F)$ levels of cobalt to the excited state $^2T_1(H)$ levels followed by thermal transitions from the levels of split excited states to the conductivity band.

Thus, the absorption studies within a wide spectral range carried out on ZnS:Co, ZnSe:Co, ZnTe:Co crystals have revealed the spectral absorption lines of the same type in those crystals. The observed shift of those lines is due to increasing anion radius in the S–Se–Te sequence. The ZnSe:Co crystals exhibit a photoconductivity when irradiated with light of 2.3 to 2.8 eV quantum energy. The photoconductivity is due to optical transitions from the ground state

$^4A_2(F)$ level of Co^{2+} ion to the excited state $^2T_1(H)$ levels near the C band followed by thermal transitions of electrons to the conductivity band. A scheme of electron transitions in the studied crystals has been presented that illustrates the absorption and photoconductivity processes.

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Оптичне поглинання та фотопровідність монокристалів ZnSe:Co

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Розглянуто вплив домішок кобальту на спектри оптичного поглинання та фотопровідності кристалів селеніду цинку. На підставі результатів оптичних і електрофізичних досліджень представлено схему електронних переходів у кристалах, що досліджувалися.