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OPTICAL PROPERTIES OF ZnS SINGLE CRYSTALS DOPED WITH COBALT

ZnS:Co single crystals were obtained by diffusion-related doping with cobalt. An optical density spectra in the region of 4-0.38eV are investigated. It is established, that at cobalt doping of crystals, the absorption edge is displaced in lower energy region. Analogy of ZnS:Co and ZnTe:Co crystals optical absorption spectra is established. The investigated lines of ZnS:Co absorption are caused by electrons optical transitions from Co^{2+} ion basic condition level $^4A_2(F)$ on the excited states $^4T_1(P)$, $^4T_1(F)$ and $^4T_2(F)$ levels split with spin-orbit interaction.

1. INTRODUCTION

Zinc chalcogenide crystals doped with cobalt and chromium are of interest due to the fact that they can be employed as the active media of lasers that emit in the middle infrared (IR) spectral region. These lasers are used in medicine, biology, and other application-oriented fields. Presently the structure of absorption spectra of the ZnSe crystals doped with cobalt and chromium is studied in detail [1—3]. Doping of ZnS crystals with cobalt and chromium is limited by the small diffusion coefficients of these metals.

We suggested the diffusive-related doping method of ZnS single crystals with cobalt. The results of investigation of ZnS:Co crystals optical absorption spectra in the visible, near and middle IR-region of spectrum are presented. The structure of ZnS:Co optical absorption spectrum is studied and identified in the visible, near and middle IR-region. It is established that ZnS crystals absorption edge shifts to the lower energy region at doping by cobalt.

The purpose of this study is to develop the procedure of diffusion cobalt doping of ZnS crystals and to identify of ZnS:Co optical absorption spectra.

2. EXPERIMENTAL

ZnS:Co crystals under study were obtained by diffusion doping of originally undoped ZnS single crystals with cobalt. The undoped crystals were obtained by free growth method. This method was described in detail, along with a report of primary characteristics for the obtained crystals, in [4]. The choice of temperature profiles and design of growth chamber precluded any contact between the crystal and chamber walls. The dislocation density in the crystals under study was no higher than 10^4 cm^{-2}.

Doping of ZnS crystals by cobalt was carried out by the method of impurity thermal diffusion from the endless source. ZnS crystal, powdered cobalt and zinc sulfide in the correlation 1:5 was loaded in a quartz ampoule. Choice of correlation for powdered ZnS and Co is stipulated by the fact that there is the intensive etching of crystal in cobalt powder at large cobalt concentrations. Annealing of crystals was carried out in the evacuated quartz cells at temperatures 1223 and 1273K during 5h. After annealing, ZnS:Co crystals became turquoise unlike the clear ZnS crystals. Estimation in the highest concentration of cobalt was determined by comparison of optical absorption spectra with present data [2]. The highest cobalt concentration in the obtained crystals is estimated 10^{18} cm^{-3}.

For comparison, the crystals ZnTe:Co were obtained by the similar method. The temperature of annealing for these crystals was 1123K. After annealing, ZnTe:Co crystals became umber unlike red-brown color of the undoped ZnTe crystals.

The spectra of optical density were measured by SF-46 diffraction spectrophotometer working within the range 4.1-1.0 eV and MDR-6 monochromator with the diffraction grating 600 grooves/mm and 325 grooves/mm. The first of them was used to analyze absorption spectra within energy range 1.2-0.6eV, and second — within the range 0.6-0.3eV. As the recorder of light stream in the middle IR-region was used PbS photoresistor working in the mode of alternating current recording. The optical density spectra were measured at 77 and 293 K.

3. OPTICAL-DENSITY SPECTRA OF ZnS:CO CRYSTALS IN THE ABSORPTION EDGE REGION

Figure 1 shows the absorption spectra of ZnS and ZnS:Co crystals in the absorption edge region. The absorption spectra of undoped ZnS crystals are characterized by absorption edge on 3.58eV (fig. 1, curve 1) at T=77K. In the range of the energies 3.58—0.40eV no features are observed for undoped crystals.

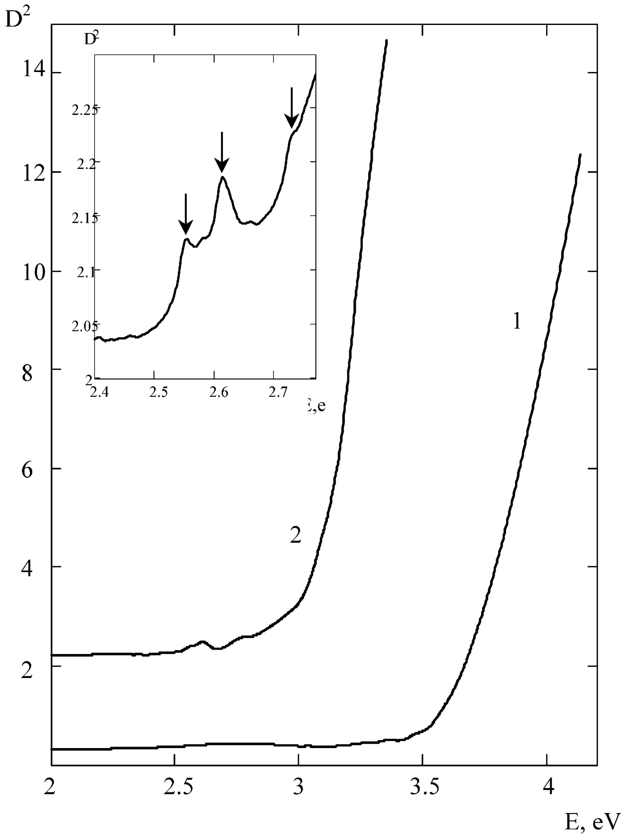

Fig. 1. Absorption spectra of ZnS(1) and ZnS:Co(2) crystals. T = 77 K. The fragment of curve 2 in the region of low absorption energies is shown in the inset

Doping of crystals with cobalt results in shift of absorption edge to the lower energy region, and the change of crystals coloring testifies this. This shift raises with annealing temperature increasing. For ZnS:Co crystals, obtained by annealing at temperature 1223 K, the absorption edge is characterized by the energy 3.03e V (fig. 1, curve 2). The shift of absorption edge in the lower energy region at doping with cobalt was observed in ZnTe:Co crystals and was 0.68eV.

The careful analysis of ZnS:Co crystals absorption edge showed the presence wildly resolving absorption lines on 2.73, 2.61 and 2.55eV (shown by arrows in the inset in Fig.1) at 77 K.

The similar spectral lines were observed [3] on the low energy region of ZnSe:Co crystals absorption edge on 2,55, 2,43 and 2,36eV. These lines are shifted in relation to L,M,N-lines, observed in ZnS:Co crystals, on the magnitude of 0,18 ÷ 0,19eV toward the lower energies. This confirms the suggestion that L,M,N-lines in ZnS:Co crystals, as well as in ZnSe, caused by the intracenter transitions $^4A_2(F) \rightarrow {}^2T_1(H)$, taking place within the limits of cobalt ion. Thus the level $^2T_1$ is split on three sublevels due to spin-orbit interaction.

At the same time L,M,N- lines of absorption were not observed on the lower energy ranges for ZnTe:Co spectra. It is caused to those that the energy of ZnTe absorption edge falls on the energy that is lower the energy of optical transitions for L,M,N-lines.

4. OPTICAL DENSITY SPECTRA OF ZnS:CO CRYSTALS IN IR REGION

In the near-IR spectral region at T = 77K there were the characteristic series of the ZnS:Co absorption lines at 1.86, 1.80 and 1.73eV (Fig. 2, curve 1). In crystals ZnTe:Co, the similar lines series on 1.53, 1.47 and 1.38eV is in the lower energy region of absorption edge.

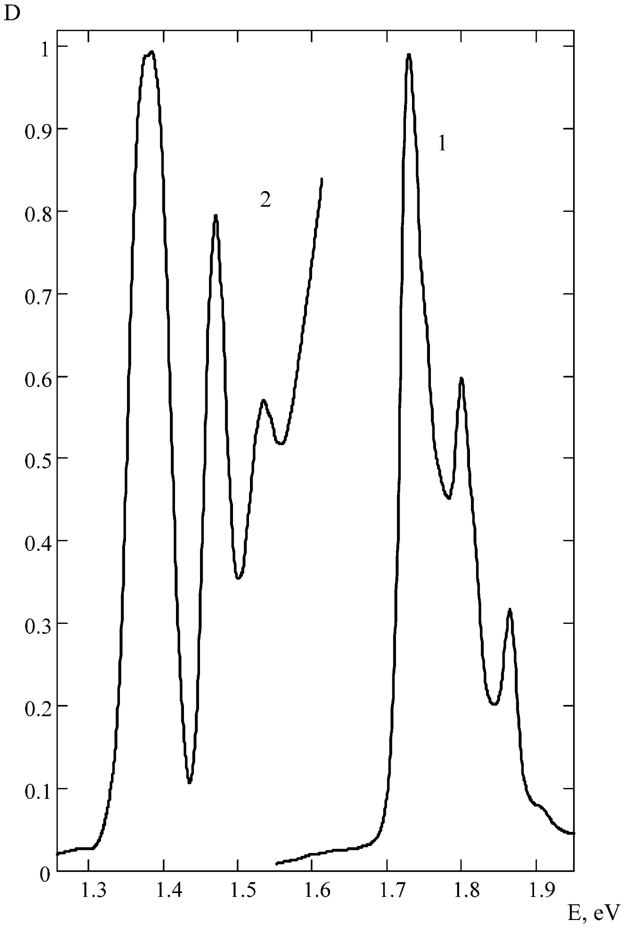

Fig. 2. Optical-density spectra in the near-IR region for ZnS:Co(1) and ZnTe:Co(2) crystals. T = 77K

It is established that intensity of these lines increases considerably with annealing temperature raise. At the same time, position of these lines remains unchanged. The position spectral lines remain unchanged at increasing of crystals temperature from 77 to 300 K too. The obtained results allow to assume that observed absorption lines are caused by intracenter optical transitions within the limits of cobalt ion. The line at 1.86eV was observed before [2], and was bonded with the intracenter transitions $^4A_2(F) \rightarrow {}^4T_1(P)$ within the limits of Co_{Zn}^{2+} cobalt ion. The second and third lines were not observed before in ZnS:Co crystals. Probably, they are caused by transitions to $^4T_1(P)$-state of cobalt ion split as a result of spin-orbit interaction.

The similar absorption line in the ZnTe:Co crystals on 1.53eV bonds with the intracenter transitions $^4A_2(F) \rightarrow {}^4T_1(P)$ within the limits of Co_{Zn}^{2+} cobalt ion. An absorption lines on Co_{Zn}^{2+} 1.47 and 1.38eV caused by transitions to 4T1(P)-state of cobalt ion split as a result of spin-orbit interaction.

In middle-IR region characteristic absorption in two ranges was observed. In higher-energy region ZnS:Co crystals were characterized by two broad lines at 0.86 and 0.73eV (Fig. 3, curve 1). The position of these absorption lines did not change with crystal temperature change. In ZnTe:Co crystals, the similar lines are displaced in relation to the lines ZnS:Co toward the lower energies at 0.09-0.13eV and located at 0.73 and at 0.67eV (Fig. 3, curve 2). The absorption line was observed earlier [5] at 0.76eV in ZnS:Co crystals, that corresponds to intracenter transition from the basic state $^4A_2(F)$ in the excited $^4T_1(F)$ state of Co_{Zn}^{2+} ion. Consequently, the absorption line on 0.67eV in ZnTe:Co is due to the similar transition $^4A_2(F) > {}^4T_1(F)$. The presence of line at 0.73eV in ZnTe:Co crystals as well as lines at 0.86eV in ZnS:Co crystals are obviously caused by the spin-orbit splitting of excited state $^4T_1(F)$ level. The obtained results evidences that the observed absorption lines of ZnS:Co and ZnTe:Co crystals are caused by transitions from the basic state $^4A_2(F)$ in the excited $^4T_1(F)$ states that are split due to spin-orbit interaction.

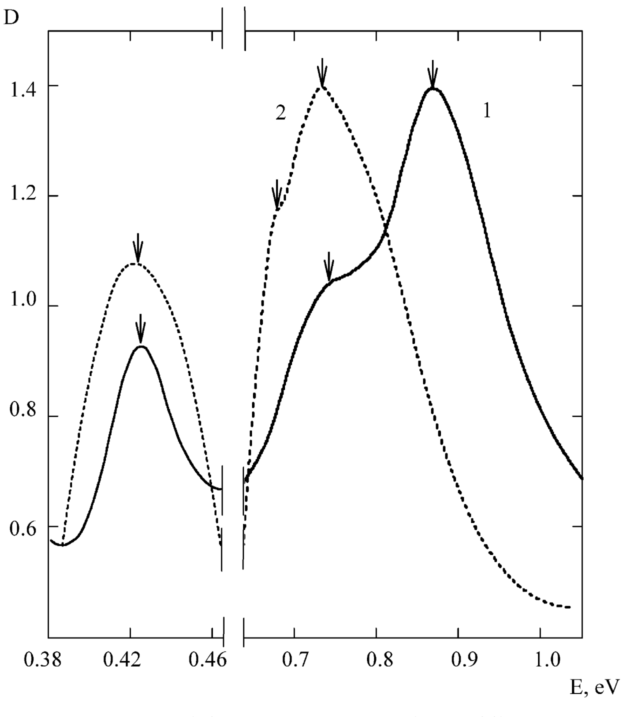

Fig. 3. Optical-density spectra in the middle-IR region for ZnS:Co(1) and ZnTe:Co(2) crystals. T = 77K

The shift of ZnTe:Co crystal absorption lines to the lower energy region in comparison with ZnS:Co crystal absorption lines are explained by a geometrical factor. This geometrical factor takes into account the crystalline field change in radius increase of anion surrounded Co^{2+} ion. This factor for the sequence of anion S → Te must result in shift of spectral lines toward the lower energies that was observed in the experiment.

In the lower energy range of middle-IR region in the absorption spectra of the ZnS:Co and ZnTe:Co crystals the unique line at 0.43eV (Fig. 3) is observed. In accordance with [5] in ZnS:Co crystals this line is caused by the transitions $^4A_2(F) \rightarrow {}^4T_2(F)$ between basic $^4A_2(F)$ and the nearest excited state $^4T_1(F)$. These transitions are resonant and are observed both in absorption spectra and in emission spectra. The energy of these transitions does not change depending on the material of explored semiconductor. The analogy of absorption spectra of the ZnS:Co and ZnTe:Co crystals allow to consider that the nature of optical transitions in these crystals is identical.

5. CONCLUSION

The studies carried out allow us to conclude the following.

1. A procedure for diffusion doping with Co of the ZnSe crystals has been developed. The highest Co impurity concentration in the crystals obtained is estimated as 10^{18} cm^{-3}.
2. It is shown that doping of ZnS crystals with cobalt results in shift of absorption edge in the lower energy region.
3. The analogy of absorption spectra for ZnS:Co and ZnTe:Co crystals is established. Shift of absorption spectral lines in ZnTe:Co crystals in relation to similar lines in ZnS:Co crystals are caused by the increase in anion (S, Te) ionic radius.
4. It is shown that observed ZnS:Co crystals absorption lines are caused by electrons optical transitions from Co^{2+} ion basic state $^4A_2(F)$ level to the excited states $^4T_1(P)$, $^4T_1(F)$ and $^4T_2(F)$ levels split by spin-orbital interaction.

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ОПТИЧЕСКИЕ СВОЙСТВА МОНОКРИСТАЛЛОВ ZnS, ЛЕГИРОВАННЫХ КОБАЛЬТОМ

Монокристаллы ZnS:Co получены методом диффузионного легирования кобальтом. Исследованы спектры оптической плотности в области 4-0.38эВ. Установлено, что при легировании кристаллов кобальтом край поглощения смещается в низкоэнергетическую область. Установлена аналогия спектров оптического поглощения кристаллов ZnS:Co и ZnTe:Co.

Исследуемые линии поглощения ZnS:Co объясняются оптическими переходами электронов с уровня основного состояния $^4A_2(F)$ иона Co_{2+} на расщепленные спин-орбитальным взаимодействием уровни возбужденных состояний $^4T_1(P)$, $^4T_1(F)$ и $^4T_2(F)$.

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ОПТИЧНІ ВЛАСТИВОСТІ МОНОКРИСТАЛІВ ZnS, ЛЕГОВАНИХ КОБАЛЬТОМ

Монокристали ZnS:Co отримані методом дифузійного легування кобальтом. Досліджено спектри оптичної густини в області 4-0.38еВ. Встановлено, що при легуванні кристалів кобальтом край поглинання зміщується в низькоенергетичну область. Встановлена аналогія спектрів оптичного поглинання кристалів ZnS:Co і ZnTe:Co.

Досліджені лінії поглинання ZnS:Co пояснюються оптичними переходами електронів з рівня основного стану $^4A_2(F)$ іона Co^{2+} на розщеплені спін-орбітальною взаємодією рівні збуджених станів $^4T_1(P)$, $^4T_1(F)$ и $^4T_2(F)$.