

## Influence of the chromium and ytterbium co-doping on the photoluminescence of zinc selenide crystals

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**Abstract:** The luminescent properties of ZnSe, ZnSe:Cr (0.05 at.% Cr), ZnSe:Yb (0.03 at.% Yb) and ZnSe:Cr:Yb (0.05 at.% Cr, 0.05 at.% Yb) crystals, doped during the growth process by the chemical vapor transport method, were studied within the temperature interval of 6–300 K. At the 6 K temperature in the visible spectral range 2 bands were observed: a band in the excitonic spectral region and a band of self-activated luminescence. It was shown that co-doping of zinc selenide crystals with the chromium and ytterbium led to the combination of the impurities influence on the photoluminescent properties. At the liquid helium temperature in the middle infrared range of the spectra of the ytterbium and chromium co-doped crystal a band with the maximum localized at 1.7  $\mu\text{m}$  was observed, which was overlapped with a complex band in the middle-IR spectral range, characteristic for the chromium doped ZnSe crystals. On the basis of obtained data an interaction mechanism of the chromium and ytterbium co-doping impurities was proposed. Guided by the existent model of the ytterbium ion incorporation in the selenide sublattice of the ZnSe crystals, an assumption about stabilization of single charged chromium ions in the zinc sublattice crystal nodes, by means of formation of the local charge compensating clusters, was made. It was assumed that the resonant energy transfer from one chromium ion to another, which led to the concentration quenching of the IR emission in the ZnSe:Cr PL spectra, would lead to the broadening of the IR emission in the spectra of ytterbium and chromium co-doped zinc selenide crystals.

**Keywords:** ZnSe; luminescence; co-doping; defects; Cr; Yb; rare earths

In the end of 1960's and beginning of 1970's the active study of the rare-earth element (REE) doped materials was started<sup>[1–5]</sup>. The interest in such materials was predominantly fundamental, for example, the interaction between REE ion 4f-electrons with the free charge carriers or bulk crystal lattice recombination centers was studied. Absence of the free charge carriers in the purely ionic crystals allows to suppose that such effects may be observed only in II-VI semiconductors<sup>[4]</sup>. This context has significantly stimulated research on the optical and magnetic properties of the wide band-gap semiconductors doped with f-element ions<sup>[2–5]</sup>.

Nowadays REE-doped materials are of renewed interest<sup>[6–8]</sup>, mostly because of their potential application as solid-state laser active media<sup>[9,10]</sup>. Particular interest to Yb<sup>3+</sup> is caused by its relatively simple energy diagram (electronic structure of [Xe]4f<sup>13</sup> type), presented by one excited state <sup>2</sup>F<sub>5/2</sub> and a ground <sup>2</sup>F<sub>7/2</sub> state lying ~1.2 eV below, absence of the line widening and absorption on the excited state<sup>[10,11]</sup>.

In the past years chromium doped materials were largely used as the Q-switching constructive elements of some optical systems<sup>[12,13]</sup>. Co-doping of laser crystals

with chromium and REE allows to combine functionality of the active media and Q-switching into the single functional element of the laser system, this opens large perspectives to the development of compact solid state lasers<sup>[14]</sup>. These reasons lead to the detailed study of YAG<sup>[9,12]</sup> and GGG<sup>[10]</sup> crystals co-doped with chromium and ytterbium. Study of the luminescent spectra of the YAG:Yb:Cr and GGG:Yb:Cr showed that the intensity of the Yb ions emission decreases in ~6 and ~5 times respectively, compared to crystals doped only with ytterbium<sup>[14,15]</sup>. Decreasing of the intensity and life time of the Yb<sup>3+</sup> emission in most cases are considered to be caused by the background absorption of the chromium ions<sup>[16]</sup>, which allows the conclusion that there is no interaction between transition metal (TM) and REE ions. However, it was observed that the emission cross-section of the Yb<sup>3+</sup> ions becomes larger in the case of co-doping with the chromium ions<sup>[9]</sup>, also a resonant energy transfer between Yb<sup>3+</sup> and Cr<sup>4+</sup> ions was assumed<sup>[12]</sup>. The last agrees well with the decrease of emission intensity of the Yb ions. It was shown that the efficiency of the energy transfer depends on the impurity concentration and may be as high as 54%<sup>[12]</sup>.

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Fundamental possibility of the resonant energy transfer between REE and TM ions may also be interesting from another point of view. It is known that Zn and Cd chalcogenides doped with TM ions, for example  $\text{Cr}^{2+}$  and  $\text{Fe}^{2+}$ , are prospective materials for the mid-IR tunable lasers<sup>[17,18]</sup>. One of the most studied TM doped zinc chalcogenides is ZnSe:Cr. The spectroscopic properties of this material, close to one quantum efficiency at room temperature and absence of significant absorption on excited state in middle-IR spectral range, make it a valuable source of coherent emission in middle-IR spectral range<sup>[18–20]</sup>. Because of the impurity ions interaction, co-doping of the zinc selenide with TM and REE may improve pumping techniques of the laser systems based on ZnSe:Cr, and also extend the spectral interval of tunability. In this work PL properties of the ZnSe, ZnSe:Cr, ZnSe:Yb and ZnSe:Cr:Yb crystals were studied within a large temperature interval, with the aim to determine the reciprocal influence of the doping impurities on the luminescent properties of the zinc selenide crystals. The possible energy transfer mechanisms were evaluated.

## 1 Experimental

Four samples of the zinc selenide crystals (ZnSe; ZnSe:0.05 at.%Cr; ZnSe:0.03 at.%Yb; ZnSe:0.05 at.%Cr:0.05 at.%Yb), doped with the TM and REE during the growth process of the CVT method using iodine as the transportation agent were studied. The selection of the concentration range was determined by the fact that IR emission efficiency of the doubly charged chromium ions decreases sharply at increase of impurity concentration. Earlier, it was established that for practical applications concentration of the chromium impurity in zinc selenide should be smaller than  $1.4 \times 10^{19} \text{ cm}^{-3}$  ( $\sim 0.063 \text{ at.}\%$ )<sup>[21]</sup>.

Synthesis from the elements and crystal growth was performed in high vacuum pumped ( $<0.1 \text{ Pa}$ ) silica ampoules. Iodine amount introduced in ampoules was  $5 \text{ mg/cm}^3$ . Chromium concentrations in the samples considered in the paper correspond to chromium amount in the source material. During the synthesis, an ampoule with the materials was placed for 2–3 days in zone of reverse gradient, i.e. temperature in the source zone was lower than in the growth zone, such position prevents substance transport and allows synthesis of zinc selenide. Synthesis was performed at temperatures of  $\sim 1020 \text{ K}$ . After the synthesis, the ampoule was placed in the growth position with direct gradient (temperature in the source zone was 10–15 K higher than in the growth zone), in which it was maintained during the whole crystal growth time (8–14 days depending on the crystal dimensions). After the growth, the ampoule was rapidly cooled to the room temperature, at the same time the sample-free end of the ampoule was cooled quicker to guarantee solidification of the transport agent in it.

Grown crystals were washed in boiling ethanol to remove iodine from their surfaces. For study of optical and luminescent properties single-crystal blocks were cut out from the bulk samples by wire-saw, and the surface damaged by cutting was mechanically polished. The growth face, used for PL study was not polished neither mechanically nor chemically.

Luminescence in 420–800 nm range was excited by radiation of pulsed nitrogen SRS NL100 laser with 337.1 nm wavelength, pulse energy of  $\sim 170 \mu\text{J}$ , and registered by a Hamamatsu R943-02 photomultiplier tube, connected to the SRS gated integrator and boxcar averager. In middle-IR spectral range (800–3000 nm) a solid state YAG:Nd<sup>3+</sup> laser (532 nm,  $\sim 300 \text{ mW}$ ) and photoresistance Hamamatsu P394A on PbS basis were used. Spectra were analyzed with an MS257 diffraction grid monochromator, with resolution better than 1.3 nm. The input slit was covered with corresponding spectral filter to prevent registration of higher orders of the diffraction grids. The studied samples were mounted on the cold finger of the open cycle helium cryostat Janis Research ST-100.

## 2 Results and discussion

### 2.1 PL in the visible spectral range

The PL spectra in the visible spectral range of ZnSe, ZnSe:Cr, ZnSe:Yb and ZnSe:Cr:Yb crystals at  $T=6 \text{ K}$  are presented in Fig. 1. The emission spectrum of undoped crystal shows a relatively broad band of edge emission (full width at half maximum (FWHM) is 46.4 meV) with maximum localized at 444.4 nm at liquid helium temperature. Considering the large FWHM of the band, it may be assumed that it is not elementary, also the temperature dependence of its maximum position repeats with high accuracy the shape of free exciton maximum position temperature dependence, calculated by Varshni equation<sup>[22,23]</sup>. This reveals the band's excitonic nature and allows the conclusion that the band consists of free exciton emission overlapped with few bound-exciton emission lines. The conclusion is also confirmed by the

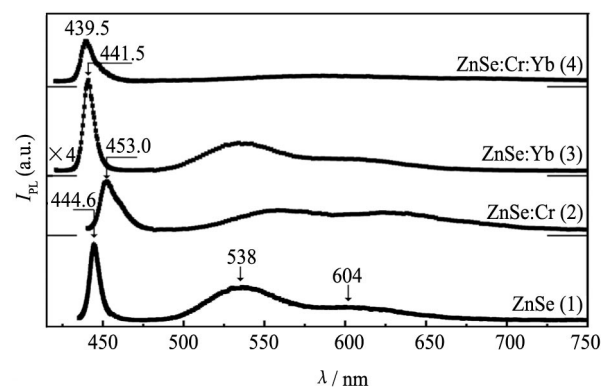


Fig. 1 PL spectra of ZnSe (1), ZnSe:Cr (2), ZnSe:Yb (3) and ZnSe:Cr:Yb (4) crystals in the visible spectral range at  $T=6.5 \text{ K}$

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