Journal of Luminescence 145 (2014) 237–243

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Influence of annealing medium on photoluminescence and optical properties of ZnSe:Cr crystals

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ARTICLE INFO

Article history:
Received 2 April 2013
Received in revised form
20 June 2013
Accepted 10 July 2013
Available online 19 July 2013

Keywords:
ZnSe
Photoluminescence
Transmission spectra
Cr impurity
Annealing

ABSTRACT

Modification of photoluminescence (PL) and optical properties of ZnSe:Cr crystals caused by annealing in medium of Zn or Se vapors are investigated. Possibility to modify the intensity of infrared (IR) impurity PL (~1 μm and 2 μm) and optical absorption spectra by several orders of magnitude, reversibility of the observed modifications of crystal properties, influence of co-doping with Cr and Cl impurities on radiative and optical properties of ZnSe are discussed. Models that explain both disappearance of Cr^{2+}_{Zn} centers responsible for the IR emission due to crystal enrichment with Zn and formation of Cr_2Se_3 precipitates against the background of crystal enrichment with Se are suggested. Complex PL bands in the IR and edge spectral ranges are analyzed for ZnSe:Cr crystals.

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1. Introduction

Wide band gap II–VI semiconductors have been intensively investigated due to perspectives of their utilization in optoelectronics. IR PL spectra of ZnSe:Cr crystals consist of two bands localized at 0.95–1 μm and 1.95–2.47 μm [1–3]. The last band is attributed to emission transitions between the ground ($^5T_2$) and the first excited (^5E) states of Cr^{2+}_{Zn} ions and determines the prospects for utilization of this material as an active element for IR lasers [4–6].

Many papers deal with investigation of luminescence properties of ZnSe:Cr crystals, however, there are questions still open to discussion. For example, the essential discrepancy in localization of PL bands in the near- and mid-IR spectral ranges, which depends on preparation methods, is observed, in particular, the mid-IR band is reported to be localized at 1.95 [7], 2.1 [8], 2.25 [9], and 2.47 μm [10]. The band localized near 1 μm is attributed either to emission transitions with participation of Cr^+ ions [11] or to transitions between the ground and the second excited ($^3T_1$) states of Cr^{2+}_{Zn} ions [3]. Identification of the center responsible for the emission in the visible spectral range (band at 2.2 eV [12]) and edge spectral range, where the emission of donor–acceptor pairs is registered, which is usually attributed to non-controlled impurity and not to Cr impurity [10,13], is also of question. At the same time, we consider that there is limited information about the influence of annealing in various media on PL and optical properties of the similar crystals, while this information may help to resolve the above-mentioned problems. This work deals with investigation of PL and transmission spectra modifications caused by annealing of ZnSe:Cr crystals in Zn and Se media.

2. Experiment

The PL spectra in the range from 350 to 3000 nm and transmission spectra in the range from 460 to 6000 nm are analyzed for both as-grown ZnSe single crystals and the samples preliminary doped with Cl donor impurity, doped afterwards with Cr thermal diffusion. The doping by thermal annealing of the samples of 1 mm thickness was carried out in quartz ampoules evacuated down to 10^{-4} Torr in the atmosphere of both rarefied Zn vapors (100 Torr) and lower chrome selenide (CrSe). Annealing temperature was 1050 °C, doping level was varied by varying the annealing duration from 12 to 200 h. After doping, ZnSe:Cr samples were annealed in saturated Zn vapors at 920 and 1050 °C or Se vapors (3 atm.) at 920 °C. The duration of annealing was varied from 48 to 150 h. Ampoules were extracted from the furnace within a period of 30 s, without quenching.

Edge PL was excited by a nitrogen laser (337.1 nm (3.68 eV), ~10 mW/mm², 103 Hz, pulse width of 10 ns). Luminescence in IR and long-wavelength (LW) visible spectral ranges was excited by Nd^{3+}:YAG laser (532 nm (2.32 eV), ~130 mW/mm², 64 Hz, pulse width of 8 ms). IR PL and transmission spectra were registered

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http://dx.doi.org/10.1016/j.jlumin.2013.07.018

using PbS detector, and PL in visible range was registered using a photomultiplier detector. Luminescence was measured at 110 and 300 K and transmission spectra were measured at 300 K.

3. Results

3.1. Influence of Cr concentration

The doping with chrome impurity leads to appearance of two IR PL bands: the A band centered near 2 μm (0.6 eV) and attributed to intracenter transitions within the Cr_{Zn}^{2+} centers (or Cr_{Zn}^{2+}-based complexes), and the B band at 0.96 μm (1.3 eV) (Fig. 1). Variation of doping duration has no essential influence on intensity of the IR PL bands (Fig. 1, inset (b)). LW emission increases in the edge PL spectra of lightly doped samples at low temperature (110 K) and a shoulder at 454 nm appears in the spectra of heavily doped samples (Fig. 1, inset (a)). The emission at 454 nm was investigated in detail in Ref. [14]. A slight increase of LW part of the A band with increasing doping level also attracts our attention (Fig. 1, inset (c)).

The increase of chrome impurity concentration in ZnSe samples leads to the decrease of optical transparence both in the visible and IR spectral ranges (Fig. 2) that is characteristic of materials having impurity precipitates. Increasing doping level also leads to more pronounced local minimum near 0.7 eV (Fig. 2(a)), which is attributed to intracenter absorption within the isolated Cr_{Zn}^{2+} ions. Concentration of Cr_{Zn}^{2+} in the samples is estimated by the ratio of transparence coefficients at 0.7 and 0.6 eV (Fig. 2, inset) [15]. With increasing doping level, absorption (dispersion) by impurity precipitates increases both in the visible range (in particular, in green spectral range corresponding to PL excitation source) and IR region at 2 μm, which corresponds to intracenter impurity emission (A band). It is considered to be a reason of the absence of apparent dependence of the A band intensity on doping level, despite the increase of Cr_{Zn}^{2+} concentration (Fig. 1).

3.2. Influence of medium composition of post-doping annealing on PL and optical properties of ZnSe:Cr crystals

3.2.1. Annealing in Se vapors

Annealing of lightly doped samples (12 h) in Se vapors slightly decreases the A band intensity (Fig. 3, inset) that is caused by extraction of impurity from thin near-surface doped layer. The same intensity decrease is observed for annealing in neutral medium. For the samples with longer doping duration (80–200 h), a more pronounced decrease of the A band intensity is observed. The intensity decrease is also observed in the near-IR spectral range (B band), while the edge PL intensity increases (Fig. 3).

As a result of annealing in Se vapors, the band of intracenter impurity absorption (~ 0.7 eV) in the transmission spectra of heavily doped samples becomes less pronounced and optical transparency of the samples decreases both in the visible and IR spectral ranges (Fig. 4). This fact may indicate growing number of impurity precipitates in the samples and, consequently, decreasing concentration of isolated Cr_{Zn}^{2+} centers. Slow cooling (about 6 h), which has to promote greater number of precipitates, leads to an additional decrease of the A band intensity.

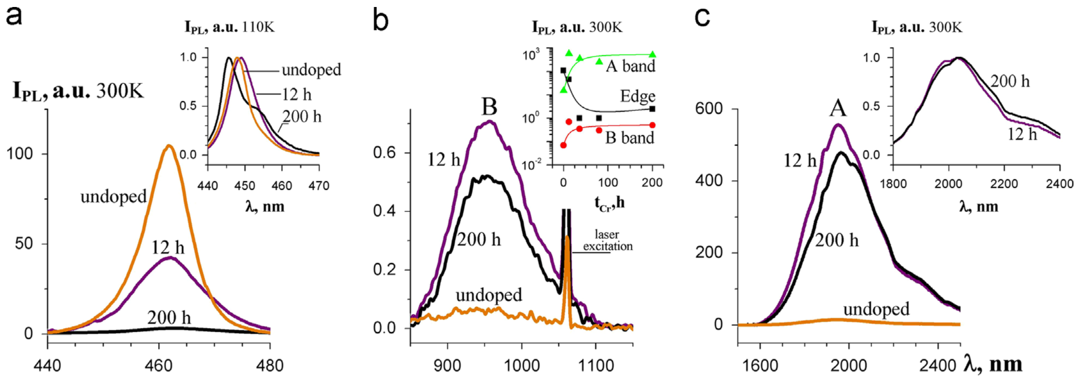

Fig. 1. PL spectra of undoped and doped ZnSe:Cr samples during 12 and 200 h, $T=300$ K. Insets: (a) normalized edge band spectra at 110 K; (b) dependence of impurity and edge PL band intensities on annealing duration at Cr doping, 300 K; and (c) normalized impurity band of doped samples, 300 K.

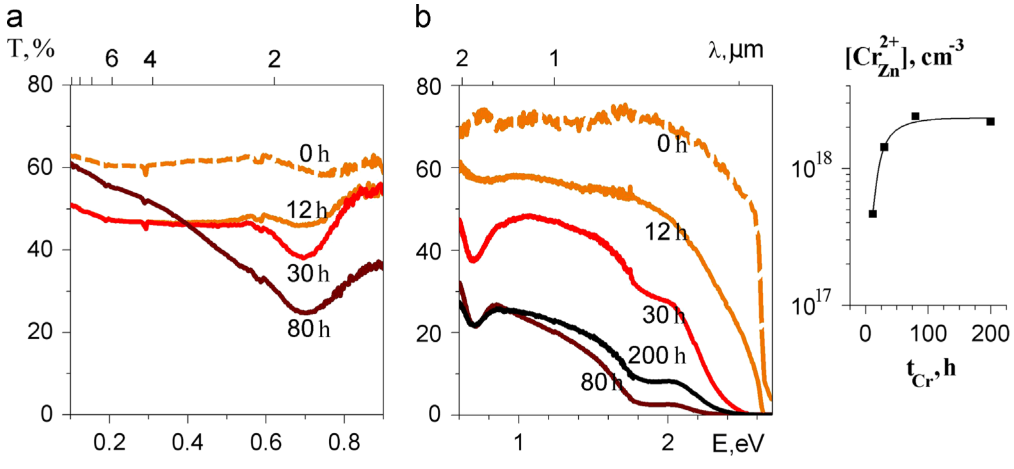

Fig. 2. Transmission spectra in IR (a) and near IR–visible (b) spectral ranges for ZnSe samples doped with chrome during indicated time (in hours). Inset: concentration of Cr_{Zn}^{2+} centers versus annealing duration at doping, 300 K.

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