EFFECT OF ANNEALING OF ZnSe:Cr CRYSTALS IN Bi(Zn) MELT ON THE INTENSITY OF RADIATION BANDS OF Cr IONS

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(Received 22 March 2010)

Abstract

The photoluminescence in visible and near-IR spectral range of ZnSe:Cr as-grown and annealed in Bi(Zn) melt crystals was investigated at room temperature. It was established that heat treatment of the crystals in Bi melt does not lead to chrome extraction, but their annealing in Zn melt results in partial extraction into melt of chrome and some other shallow impurities.

1. Introduction

In the majority of cases, it is necessary to satisfy rigid requirements related to the uniform distribution of impurities over the crystal while doping semiconductor compounds. This also holds true for ZnSe:Cr crystals promising as laser materials emitting in the middle IR spectral range [1]. Moreover, the purity and perfection of crystals exert a strong influence on the efficiency of lasers. It was shown [2, 3] that annealing of ZnSe crystals in Bi(Zn) melts leads to a partial cleaning of the material from various uncontrolled impurities and improves stoichiometry owing to annealing in Bi melt. Taking the aforesaid into account, and with the aim to evaluate the ability of extraction of chromium impurities in the annealing media, in this research work, we studied the radiative properties of ZnSe:Cr crystals thermally treated in Bi(Zn) melts.

2. Experimental details

Single-crystaline ZnSe:Cr samples (10^{-2} at %) with a thickness of 1.5 mm cut from the same ingot were placed into a quartz ampoule together with Zn weight, additionally purified by vacuum sublimation, or with Bi (99.999%) weight; the weight was calculated so that the volume ratio of Bi or Zn to ZnSe amounted to 10. The ampoules were evacuated to a pressure of 10^{-4} torr, sealed, and placed in a furnace. The thermal treatment of the samples was carried out at a temperature of 1180 K for 120 h. Below 880 K, the ampoules were cooled at a rate of 70 K/hr. Then the samples were separated from the melt, and the further cooling occurred in air.

The luminescence measurements were carried out using a MDR-23 monochromator; the cleaved sample surfaces were excited by a nitrogen (λ = 337.1 nm) or YAG:Nd^{3+} laser. Photomultipliers with cesium potassium sodium-antimony photocathode (type FEU-79) or with oxygen silver caesium photocathode (type FEU-62) and PbS photoresistance were used as photodetectors.

3. Experimental results and discussion

The radiation spectra of ZnSe:Cr crystals at 300 K are shown in Fig. 1 for the initial material (curve *1*) and for crystals annealed in Zn (curve *2*) and Bi melt (curve *3*). In the near and middle IR region, all the studied samples exhibit emission bands with maxima near 1000 and 2050 nm. The thermal treatment does not change the structure of the bands. However, annealing of ZnSe:Cr crystal in Zn melt leads to a reduction in the intensity of the observed bands. At the same time, annealing of this crystals in Bi melt increases the intensity of radiation of the same bands by up to two times.

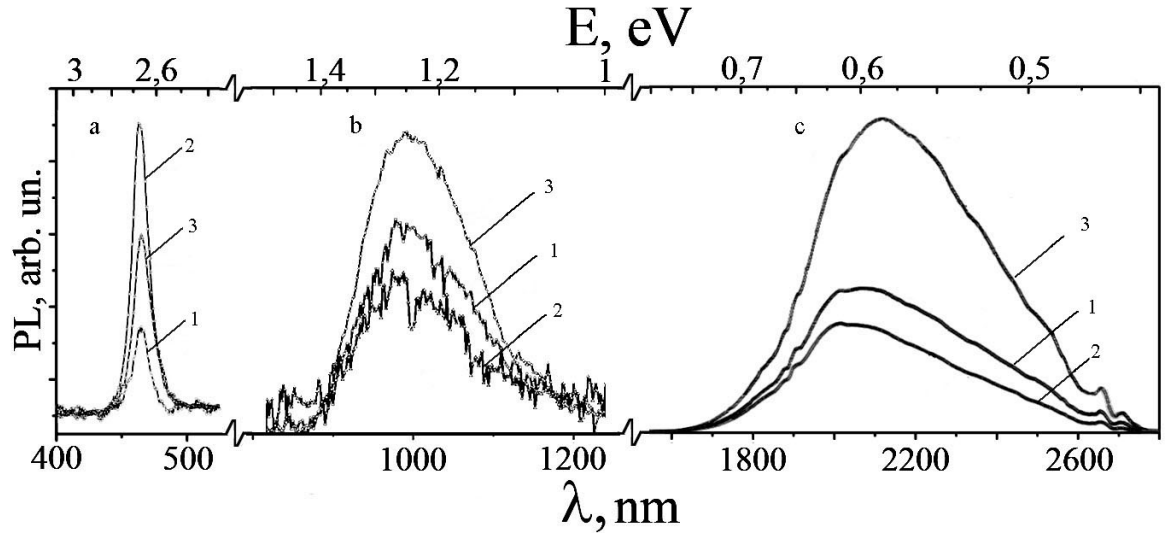

Fig. 1. Photoluminescence spectra of ZnSe:Cr single crystals measured at room temperature: *(1)* initial crystal, *(2)* sample annealed in Zn melt, and *(3)* sample annealed in Bi melt.

The photoluminescence spectrum of the samples in visible region consists of a single band with a maximum near 460 nm (Fig. 1a). After the heat treatment, the intensity of this band increases, and the increase is more pronounced for the sample annealed in the Zn melt.

According to [4], the position of Cr^{+} and Cr^{2+} ions relative to the bottom of the conduction band in ZnSe:Cr crystals amounts to 1.24 and 2.26 eV, respectively. Therefore, we can assume that radiative electron transitions from the conduction band to the Cr^{+} levels are responsible for the emission band with maximum near 1000 nm. The emission band with maximum near 2050 nm is due to the radiative transitions between $^5E \rightarrow {}^5T_2$ states split by zinc selenide crystal field [5]. The intensity of bands at 1000 and 2050 nm in the photoluminescence spectra of ZnSe:Cr crystals after their annealing in Zn melt decreases either due to the partial extraction of Cr impurities into the melt or because Zn substitutes Cr^{2+} ions in the lattice sites. However, the fact that the edge band at 460 nm significantly increases after annealing gives an evidence of partial chromium extraction into Zn melt. Actually, the intensity of the edge luminescence increases when the crystal becomes cleaner.

In the case of annealing of ZnSe:Cr crystals in Bi melt, the intensity of Cr^{+} and Cr^{2+} bands increases significantly rather that decreases (Figs. 1b, 1c). This fact indicates that there is no appreciable extraction of chromium into Bi melt. The increase of the edge luminescence intensity for these samples (Fig. 1a) can be attributed to a partial extraction of background impurities into the melt as well as some reduction of the concentration of centers of nonradiative recombination and improvement of stoichiometry.

4. Conclusions

As a result of the research, it was shown that

- There are no extraction of chromium impurities into the melt during the thermal treatment of ZnSe:Cr crystals in Bi melt, and the intensity of Cr^{+} and Cr^{2+} bands significantly increases.
- The thermal treatment of ZnSe:Cr crystals in Zn melt leads to a partial purification of samples from chromium as well as from several other background impurities, and the intensity of Cr^{+} and Cr^{2+} bands decreases.

References

[1] D. DeLoach, H. Hage, D. Wilke, A. Payme, and F. Knipke, IEEE J. Quantum Electronics, 32, 6, 885, (1996).
[2] K.D. Sushkevich, A.V. Simashkevich, A.V. Koval, and O.S. Coschug, in: Proc. 16th Annual Semiconductors Conf. CAS-93, 513, (1997).
[3] M. Aven, J. Appl. Phys., 2, 3, 1204, (1971).
[4] S. Bhaskar, P. S. Dobal, B. K. Rai, R. S. Katiyar, H. D. Bist, J. O. Ndap, and A. Burger, J. Appl. Phys., 85, 439, (1999).
[5] J. Kreissl and H.J. Schulz, J. Cryst. Growth., 161, 239, (1996).