

STUDY OF IMPURITIES-DEFECTIVE LUMINESCENCE IN ZnSe:Cr AND ZnSe:Fe IN THE RED AND NEAR INFRARED RANGE

I.I. ABBASOV

Azerbaijan State Oil and Industry University
Azadlig ave., 34, Baku

In this work, the impurity-defect luminescence in the red and near-infrared ranges has been studied for ZnSe:Cr⁺ and ZnSe:Fe⁺ crystals. Shown, that the mechanism of radiative recombination, which forms emission lines in the spectral range of 0.7-1 μm , is associated with intracenter radiative transitions of the iron and chromium atom, included in the complex defect as Fe²⁺ and Cr²⁺.

Key words: polycrystalline CVD (chemical vapor deposition) ZnSe, iron and chromium impurities, ZnSe:Cr and ZnSe:Fe crystals, high isostatic pressure(HIP).

PACS: 535.37

INTRODUCTION

Recently, interest has increased in the study of the effect of transition metals, including Cr²⁺ and Fe²⁺ ions, on the electronic structure of zinc chalcogenides [1-8]. Interest in these impurities was related mainly to the fact that they can be used to reduce the luminescence yield in the visible region of the spectrum and to improve the use of these materials as a working medium for IR lasers with a wide tuning band and the ability to operate at room temperature (at $T=300\text{K}$) due to the formation deep energy levels in the forbidden zone [1, 4,6,7]. Therefore, the study of the effect of iron and chromium ions on the optical properties of ZnSe in the red and near-infrared wavelength range is very relevant.

EXPERIMENTAL AND RESULTS

In this work, using a Cary Eclipse (Varian) spectrofluorimeter in the range of 0.7-1 μm at room temperature, we studied the spectral composition of the luminescence of two CVD (chemical vapor deposition) ZnSe samples doped with a chromium impurity and two doped with an impurity of iron.

On both sides of the CVD ZnSe samples, a film of Cr⁺ and Fe⁺ was deposited by electron beam evaporation, then diffusion doping was carried out in the HIP (hot isostatic pressure) treatment diffusion doping in the first ZnSe:Cr⁺ sample was carried out at 1000 *atm.*, 1423K for 72 hours, and in the second at

1000 *atm.*, 1423K for 76 hours. And diffusion doping in the first ZnSe:Fe⁺ sample was carried out at 1000 *atm.*, 1423K for 66.5 hours, and in the second at 1000 *atm.*, 1523K for 26 hours. The maximum concentration of chromium and iron impurities, determined by the shift of the absorption edge in the ZnSe:Cr⁺ and ZnSe:Fe⁺ samples, is respectively $6.1 \cdot 10^{19} \text{cm}^{-3}$ and $4.65 \cdot 10^{19} \text{cm}^{-3}$ in ZnSe:Cr⁺ samples, and in ZnSe:Fe⁺ it is equal to $7.27 \cdot 10^{18} \text{cm}^{-3}$ and $9.83 \cdot 10^{18} \text{cm}^{-3}$, respectively. The band gap is 2.34eV and 2.4eV for ZnSe:Cr⁺, and 2.6eV and 2.62eV for ZnSe:Fe⁺.

1. ZnSe:Cr⁺

The excitation of the samples was initially carried out by light with a wavelength $\lambda_{\text{ex}}=620\text{nm}$, and in the luminescence spectrum the maxima in both samples were observed at wavelengths 697nm and 824nm, and in the second sample its LO or 2LO phonon repetitions (713nm, 731nm) were added to the maximum at 697nm (Fig.1,2,3). The excitation spectrum of maxima at a wavelength of $\lambda=824\text{nm}$ in both samples is similar, but they have a completely different structure: both samples contain maxima at a wavelength of 604nm, i.e. In both samples, the luminescence spectrum with a maximum of $\lambda=824\text{nm}$ is more efficiently excited by light with $\lambda=604\text{nm}$. According to the structure, the excitation spectrum of the first sample has only one maximum ($\lambda=604\text{nm}$), while the second one covers the wavelength range of 586-675nm from several maxima.

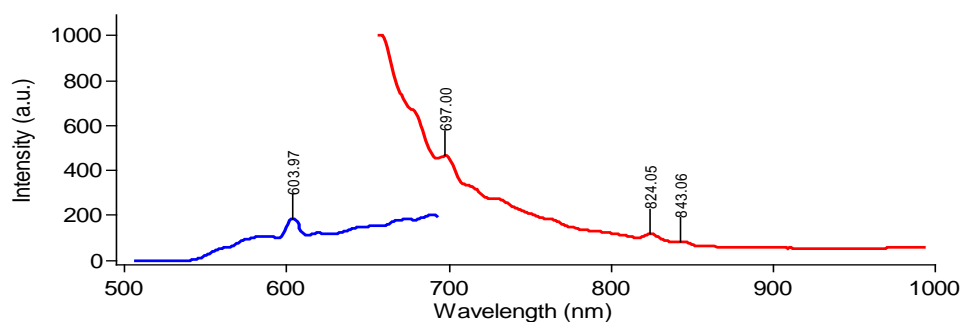


Fig. 1. PL spectrum of polycrystalline CVD ZnSe: Cr⁺ (1-sample) upon excitation with a xenon lamp ($\lambda_{\text{ex}} = 620\text{nm}$) - red line; blue - excitation spectrum of maximum 824nm.

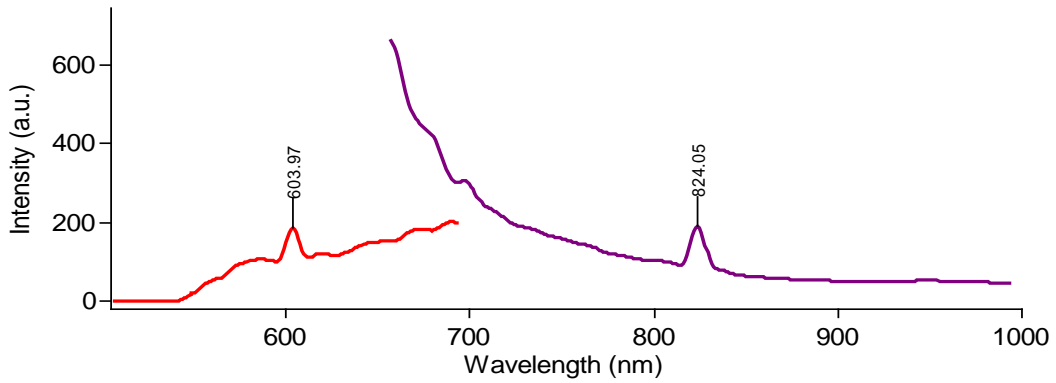


Fig. 2. PL spectrum of polycrystalline CVD ZnSe: Cr⁺ (1-sample) upon excitation with a xenon lamp ($\lambda_{ex}=604nm$) - violet line; red - excitation spectrum of maximum 824nm

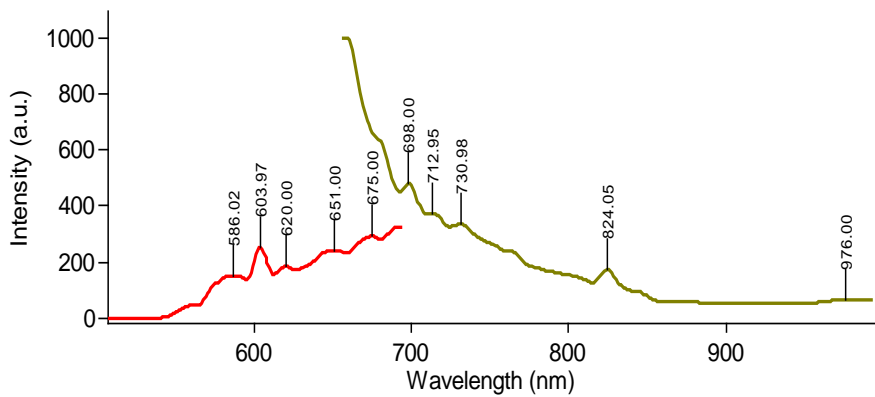


Fig. 3. PL spectrum of polycrystalline CVD ZnSe: Cr⁺ (2-sample) upon excitation with a xenon lamp ($\lambda_{ex}=604nm$)-green line; red-excitation spectrum of maximum 824nm.

2. ZnSe:Fe⁺

In this case, the excitation of the samples was also initially carried out by light with a wavelength of $\lambda_{ex}=620nm$, and in the luminescence spectrum, the maxima in the first sample were observed at wavelengths of 697 and 824nm, and in the second sample only at 825nm and equidistant maxima with LO repetition (Fig.4,5,6). The excitation spectrum of the peaks in the samples at $\lambda=824nm$ is completely

different from each other, and for the first sample it covers the wavelength range of 530-780nm with a maximum at $\lambda=604nm$, and for the second sample only with a maximum at $\lambda=604nm$. The presence in both samples of the same maximum in the excitation spectrum at $\lambda=604nm$ shows that the luminescence spectrum with a maximum at $\lambda=824nm$ in both samples is more efficiently excited by light with a wavelength of $\lambda=604nm$.

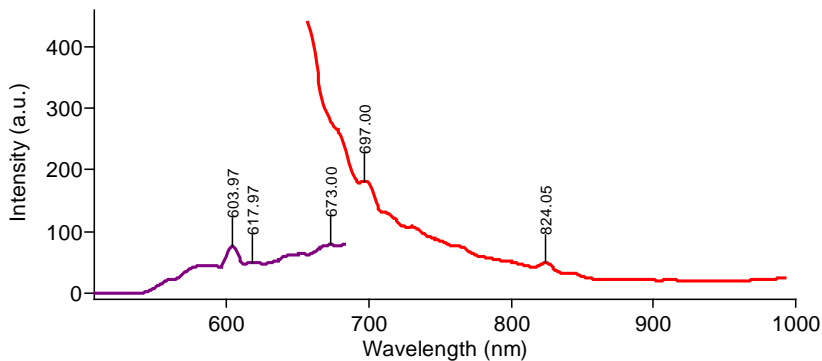


Fig. 4. PL spectrum of polycrystalline CVD ZnSe: Fe⁺ (1-sample) upon excitation with a xenon lamp ($\lambda_{ex}=620nm$)-red line; violet - excitation spectrum of maximum 824nm.

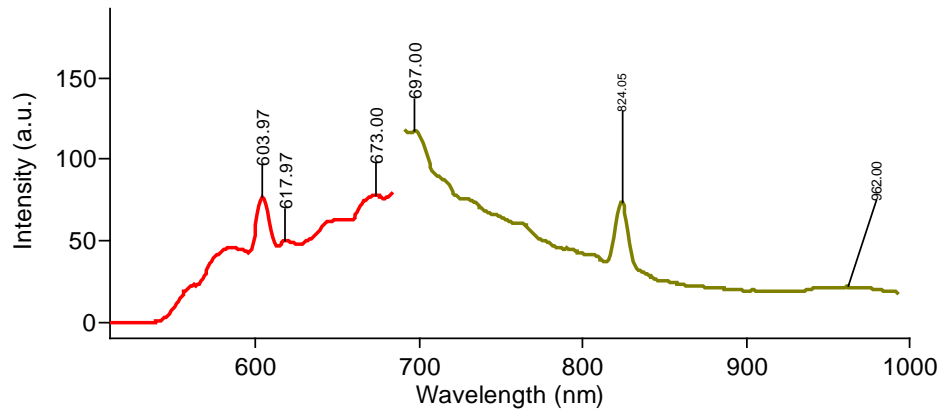


Fig. 5. PL spectrum of polycrystalline CVD ZnSe: Fe⁺ (1-sample) upon excitation with a xenon lamp ($\lambda_{ex}=604nm$)-green line; red-excitation spectrum of maximum 824nm.

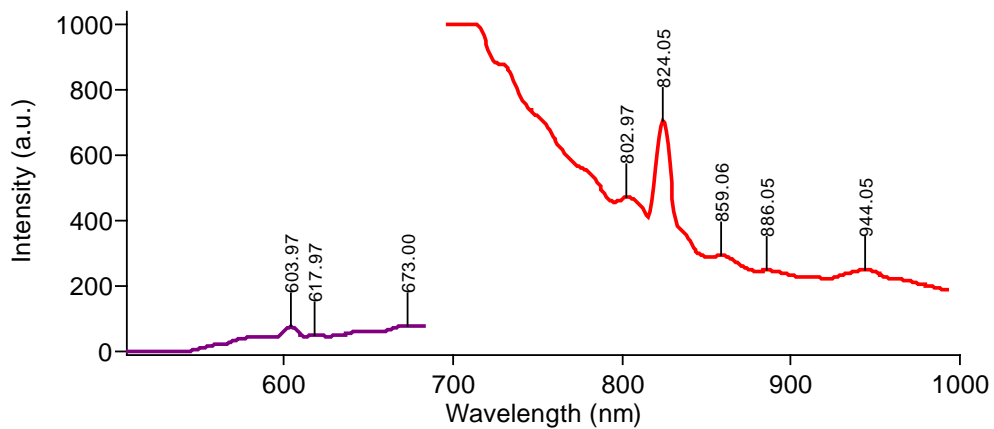


Fig. 6. PL spectrum of polycrystalline CVD ZnSe: Fe⁺ (2-sample) upon excitation with a xenon lamp, ($\lambda_{ex}=604nm$ - red line); violet-excitation spectrum of maximum 824nm.

DISCUSSION

As can be seen from fig. 1–6, with a decrease in the concentration of chromium and iron in ZnSe, the structure and the number of maxima in the excitation spectrum change, and we believe that this change is a consequence of the nonelementarity of the observed long-wavelength photoluminescence bands in the samples under study. It is known [9] that in doped crystals, light from the fundamental absorption region weakly excites luminescence, and in our case, it is more efficiently excited by light with $\lambda=604nm$, where there corresponds a long-wavelength shift of hundreds of meV from the absorption edge for pure ZnSe.

In [10] it was shown that the energy levels of Fe²⁺ in ZnSe are located at a distance of 1.1eV above the ceiling of the valence band, and in the case of Cr²⁺ - 1.9eV. In addition, it is known [11] that in ZnSe the

total content of background impurities is within $<10^{16}-10^{17}cm^{-3}$ (Cu $\sim 10^{16}cm^{-3}$). Cu⁺ interstitials participate in the formation of an acceptor complex located 0.8eV above the ceiling of the valence band, and emission in the red regions of the spectrum is due to the transition of free electrons to this acceptor level [12]. We believe that in our case, the maximum in the emission spectrum at $\lambda=697nm$ is also associated with the transition of electrons from the conduction band to this acceptor level, and the maximum at $\lambda= 826nm$ with the transition of electrons from shallow levels to the Fe²⁺ and Cr²⁺ levels.

In conclusion, we can say that the mechanism of radiative recombination, which forms emission lines in the spectral range of 0.7–1 μm , is associated with intracenter radiative transitions of iron and chromium atoms entering into a complex defect in the form of Fe²⁺ and Cr²⁺.

[1] V.V. Fedorov, S.B. Mirov, A. Gallian and et al. IEEE J. Quant. Electron. 2006, v.42, pp. 907.
 [2] D.C. Harris. Development of Hot-Pressed and Chemical-Vapor-Deposited Zinc Sulfide and Zinc Selenide in the United States for Optical

Windows; Tustison, R.W., Ed.; SPIE: Bellingham,WA, USA., 2007, pp. 654502.
 [3] S.D. Velikanov, V.P. Danilov, N.G. Zakharov. Quantum. electron., 2014, T.44, pp.141.

I.I. ABBASOV

- [4] *S. Mirov, V. Fedorov, D. Martyshkin and et al.* IEEE J. Sel. Top. Quant. Electron., 2015, v. 21. pp.1.
- [5] *D.V. Martyshkin, D.V. Fedorov, M. Mirov et al.* CLEO: 2015, OSA Technical Digest SF1F. 2. 2015.
- [6] *S.D. Velikanov, N.A. Zaretskii and E.A. Zotov.* Quant. Electron., 2016. T.46. pp.11.
- [7] *M.P. Frolov, Yu.V. Korostelin, V.I. Kozlovsky, Y.P. Podmarkov, Y.K. Skasyrsky.* Laser Optics (LO), International Conference R1-10., 2016.
- [8] *V.I. Kozlovsky, Y.V. Korostelin, Y.P. Podmarkov, Y.K. Skasyrsky, M.P. Frolov.* J. Phys. Conf. Ser. 2016, v.740, pp. 012006.
- [9] *L.L. Kulyuk and et al.* Physica 2010, B 405, 4330.
- [10] *M. Surma, M. Godlewska, T. Surkova.* Iron and chromium impurities in ZnSe as centers of nonradiative recombination. Phys Rev B Condens Matter. 1994, Sep 15, 50(12):8319-8324. doi: 10.1103/physrevb.50.8319.
- [11] *I.I. Abbasov, M.A. Musayev, J.I. Huseynov, L.A. Aliyeva, S.Q. Nuriyeva, A.V. Sharifova, R.Sh. Rahimov, J.I. Ismayilov, N.N. Hashimova.* Funct. Mater., 2022, 29, 3, pp. 331.
- [12] *G.N. Ivanova, V.A. Kasiyan, D.D. Nedeoglo and S.V. Oprya.* 32, No. 2: 171, 1998, Semiconductors, DOI: 10. 1134/1.1187337 Corpus ID: 97853527

Received: 11.10.2022