Broad Band Luminescence Of *Β*-ZnP_2 Single Crystals

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Abstract. The results of the experimental study of the temperature dependences of the photoluminescence (PL) spectra of β-ZnP_2 single crystals are presented. Under the band-to-band excitation, besides the well-known excitonic emission an infrared broad spectral band was found. The origin of this vibronic band is associated with a deep centre due, presumably, to the presence of an intrinsic defect in the β-ZnP_2 crystal.

Keywords: β-ZnP_2, broad band luminescence, excitons, deep levels.

I. Introduction

Zinc diphosphide crystals (ZnP_2) belong to the family of II-V compounds that can have two structurally different forms: a red tetragonal form α-ZnP_2 and a black monoclinic one β-ZnP_2. The β-ZnP_2 crystals have a direct energy gap E_g=1.603 eV (T=2K, [1]) and show strong anisotropy that govern the dependence of optical properties of these crystals on light polarization [2]. At low temperature, an excitonic series was observed in these crystals, which was the subject of many research papers over a long period of time [3-8].

In the present study, we have investigated the dependence of photoluminescence (PL) spectra of β-ZnP_2 single crystals as function of temperature. An infrared (IR) broad band has been revealed and the processes of radiative recombination are discussed.

II. Experimental Results

This paper deals with β-ZnP_2 single crystals with typical dimensions of several mm^3, obtained from the gaseous phase. PL measurements in the temperature range T =10–120K (over each 10 degrees) were performed with a grating monochromator coupled to a cooled photomultiplier with a S1 photocathode, or an InGaAs photodetector. Optical intrinsic excitation of the samples was provided by a He-Ne laser (λ_{L1}=632.8nm, P_{L1}~1W/cm^2) and a second harmonic emission of a *cw* operating YAG:Nd laser (λ_{L2}=532nm, P_{L2}~10W/cm^2).

The steady-state PL spectra of the β-ZnP_2 samples investigated in the energy range $\hbar\omega_{PL}$=1.2÷1.6eV (λ_{PL}~0.8÷1.04μm) contain two distinct spectral regions (Fig. 1): the well-known *excitonic region*, consisting of several sharp lines located at about 0.05eV below the direct band gap [1, 5] and their phonon replica; the *vibronic broad band* located in the near IR region, with the temperature dependent half-width band $\Delta\hbar\omega \approx$ 0.15÷0.20eV. The presence of these two spectral regions demonstrates the existence of two radiative recombination channels of the charge carriers, i.e. an excitonic recombination channel and a recombination via a deep level.

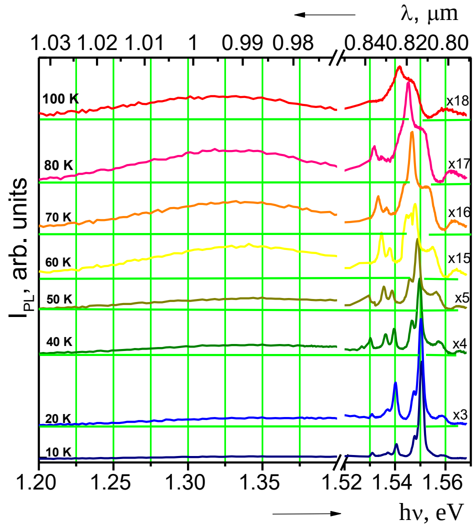


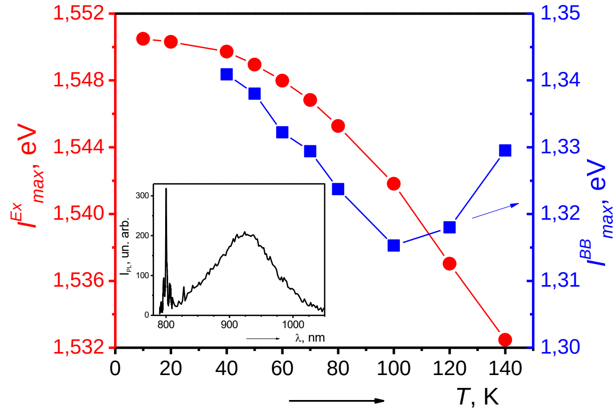
Fig. 1 PL spectra evolution of β-ZnP2 (λL2=532 nm) single crystal as function of temperature.

The PL maxima position at different temperatures for both, excitnic $I^{Ex}_{max}(T)$ and broad band $I^{BB}_{max}(T)$ regions, are plotted in Fig. 2a. The experimental temperature dependences of the integral intensities of the excitonic $I^{Ex}(1/T)$ and broad band $^{BB}(1/T)$ spectral regions are presented in Fig. 2b.

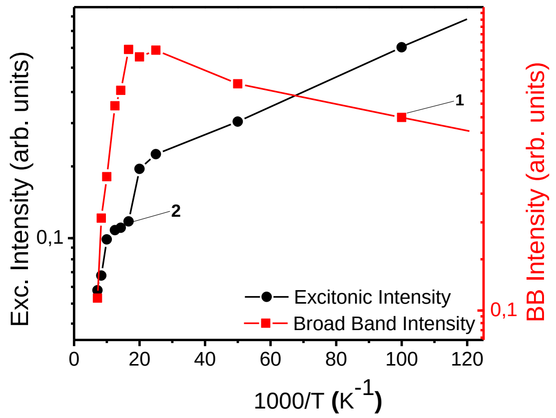
III. Discussions

The analysis of the PL spectra evolution as function of temperature (Fig. 1 and Fig. 2) shows, that the raise of temperature results in the redistribution of excitonic lines intensity located within 1.53 ÷ 1.56eV range, and in their attenuation at T >50K. The thermal quenching of the excitonic luminescence at high temperatures is due to the increase of vibronic energy and, respectively, of the probability of nonradiative transitions.

In order to properly interpret the radiative recombination processes in β-ZnP_2 in the frame of the potential curves model [9] a single coordinate diagram was constructed (Fig. 3). The temperature dependence of the PL integral intensity for the broad band (curve 1, Fig. 2b) is characterized by two regions: in the first one, (up to T ≈50 K) the increase of the integral intensity takes place on the account of the overcoming of a potential barrier E_{qx} by nonequilibrium carriers (Fig. 3), which, in effect, reduces the PL integral intensity of the excitonic radiative recombination (curve 2, Fig. 2b).



a)



b)

Fig. 2 Temperature dependences of the spectral maxima position (a) and of the PL integral intensity (b) for excitons (circles) and the broad band emission (squares).

At temperatures T >50K the PL quenching process occurs due to the lattice-relaxation multiphonon emission. The transfer of electrons from the deep level T into valence band V over the potential barrier with the activation energy E_T (Fig. 3) results in their nonradiative recombination (curved arrows) with the excited holes. This process takes place under conditions of strong electron-vibronic interaction. The temperature dependent efficient recombination channel via the deep level (trap) T should lead to the decrease of the PL intensity, caused by the excitonic recombination channel. Indeed, this relatively slow decrease of the excitonic spectrum intensity $I^{Ex}(1/T)$ is observed up to the temperatures of about 50K (Fig. 2b), i.e. until the advent of a thermal quenching of PL. One can assume that the broad spectral band, observed in the energy range 1.2 ÷ 1.4 eV, is caused by an unidentified intrinsic defect of the lattice that acts as the recombination channel T (Fig. 3). Results of chemical analysis of β-ZnP_2 crystals obtained by the X-ray energy dispersion (EDX) method do not revealed a deviation from the stoichiometry composition, however this does not exclude the presence of structural defects in the lattice, or of a small amount of impurities, that could explain the origin of the deep level T.

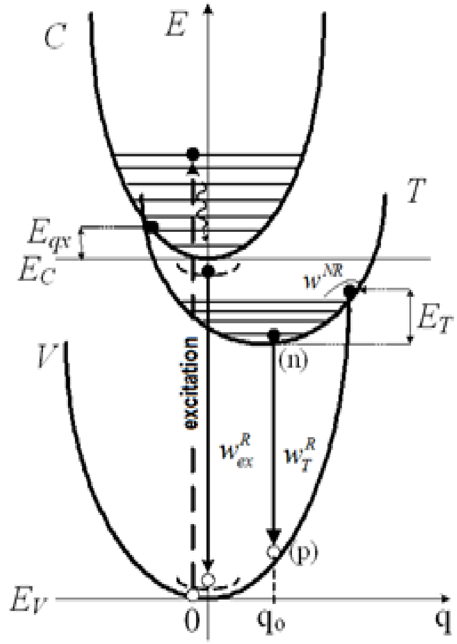


Fig. 3 Single coordinate diagram qualitatively describing the recombination of photo-excited carriers in β-ZnP_2

IV. Conclusions

A broad band emission has been revealed in the PL spectral characteristics of β-ZnP_2 crystals. Taking into account the temperature behavior of this band, as well as of the excitonic emission spectrum, the presence of the recombination channel via a deep center has been identified. For the qualitative description of the recombination processes in β-ZnP_2 crystals, a single coordinate configuration diagram has been proposed.

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V. References

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