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Properties of MBE-Grown ZnBeSe: Study of Be Isoelectronic Traps and of Dopant Behavior

I.L. KUSKOVSKY[1] (a), Y. GU (a), M. VAN DER VOORT (a), C. TIAN (a), B. KIM (a),
I.P. HERMAN (a), G.F. NEUMARK (a), S.P. GUO (b), O. MAKSIMOV (b),
and M.C. TAMARGO (b)

(a) Department of Applied Physics and Applied Mathematics, Columbia University, New York, NY 10027, USA

(b) Chemistry Department, City College of CUNY, New York, NY 10007, USA

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In this paper we present studies on undoped, Cl-doped, and N-doped ZnBeSe using photoluminescence (PL). We show that the dominant PL from undoped samples is "effective mass" type and suggest that it is of isoelectronic origin. We also show that the binding energy of both donor and acceptor impurities increases with Be concentration.

Introduction II–VI wide bandgap semiconductors are of high interest for fabricating devices emitting light in the green and blue spectral regions. However, such devices have short "lifetimes" [1]. The use of Be in ZnSe based alloys (i.e. $Zn_{1-x}Be_xSe$ ternary alloy) has been suggested [2] to improve the hardness of the material [3, 4], and as a result the device lifetime. In this paper we present PL studies of both undoped and doped ZnBeSe that shed some light on the nature of the luminescent transitions of these materials.

Undoped ZnBeSe Our samples are nominally undoped, grown by molecular beam epitaxy (MBE). For the details of the growth procedure see Guo et al. [5]. The dominant feature in all samples consists of a strong, fairly sharp line (sometimes consisting of two peaks, with a splitting less than 3 meV) in the near band edge region with several weaker lines on the low-energy side, and, at least in samples with less than 6% Be, two lines on the high-energy side [6]. (Samples with Be concentrations higher than 6% do not show these two peaks due to larger lattice mismatch.) We attributed the dominant line to bound excitons, the peaks on the low energy side to phonon replicas of the main peak(s), and the high energy peaks to free excitons [6], with their location giving the excitonic bandgap.

To further understand the possible origin of the dominant PL features, we performed PL temperature (T) and pressure (P) studies. We plot in Figs. 1a and b the peak energy as a function of temperature and pressure, respectively. The temperature dependence was fitted to Varshni's formula, $E(T) = E(0) - \alpha_{PL}T^2/(\beta_{PL} + T)$ (see Ref. [7]), giving $\alpha_{PL} = 9.0 \times 10^{-4}$ eV/K and $\beta_{PL} = 365$K, which are very close to values obtained earlier for the ZnSe [8, 9] bandgap. The pressure dependence was fitted to a quadratic formula, $E(P) = E(1\text{ atm}) + \alpha_P P + \beta_P P^2$, where α_P and β_P are the linear and quadratic

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[1] Corresponding author; Tel.: 1-212-854-1580; Fax: 1-212-854-8257; e-mail: ik29@clumbia.edu

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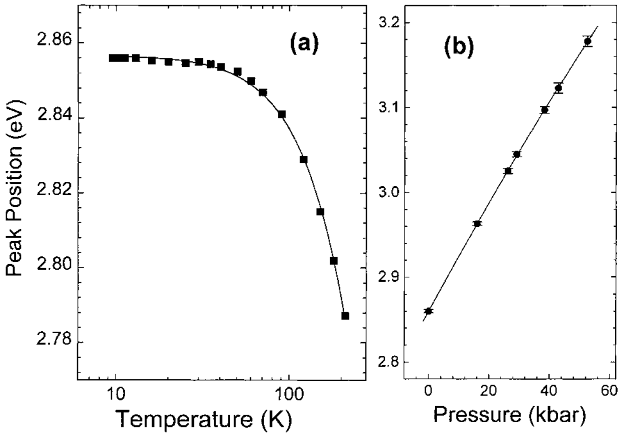

Fig. 1. Peak position of the dominant PL from undoped ZnBeSe as a function of a) temperature; b) pressure

pressure coefficients, respectively. This resulted in $\alpha_P = 6.61$ meV/kbar and $\beta_P = -1.1 \times 10^{-2}$ meV/(kbar)^2, i.e. values which are very close to those obtained for the pressure shift of the ZnSe bandgap [10, 11]. These two observations mean that the defect responsible for the PL is of "effective mass" nature, since it is well known that in the "effective mass" approximation all relevant states are formed from the band wavefunctions and, thus, all energy levels follow the band edge with temperature and pressure.

Thus, both temperature and pressure studies show "effective mass" behavior, even though the exciton has a larger ionization energy. According to Ref. [12] ZnBeSe is a completely miscible system and we do not believe that the same atom can both change the bandgap and also create a localized level. Thus, we suggest that a complex of Be introduces an isoelectronic trap, and therefore the observed PL is due to isoelectronic bound excitons. Since the Be atom is substantially smaller than Zn, it is quite probable that Be will introduce a short-range potential which would lead to the formation of an isoelectronic trap [13]. Moreover, since the ionization energy of Be is slightly smaller than that of Zn, according to the theory of Hopfield et al. [14] this would lead to having the trap capturing a hole first, with an electron subsequently captured via the Coulomb attraction, i.e. there is formation of an isoelectronic donor. Such a donor is expected to be effective mass like [14], and the observed effective mass behavior in our experiments confirms that this is indeed the case.

Doped ZnBeSe Figure 2 shows PL data from three typical ZnBeSe:Cl samples. It is plausible to assume that the observed PL is due to neutral donor (Cl) bound excitons. It is interesting to compare the peak positions of the bound excitonic line with reported ZnBeSe bandgap values. There are several reports on the dependence of the ZnBeSe direct bandgap, e.g. [15] or the excitonic bandgap, e.g. [6, 12, 16] on Be concentration. (We would like to note that the data in Ref. [12] are referred to as the bandgap; however, the ZnSe data-point of 2.80 eV clearly suggests that the obtained dependence provides the excitonic bandgap.) In Refs. [12, 16] similar dependences of the bandgap on composition of 23 and 24 meV per %, respectively, were reported. In Ref. [15] the bandgap values were obtained at room temperature via absorption experiments and have only four data-points. The best fit of these data can be obtained if a quadratic

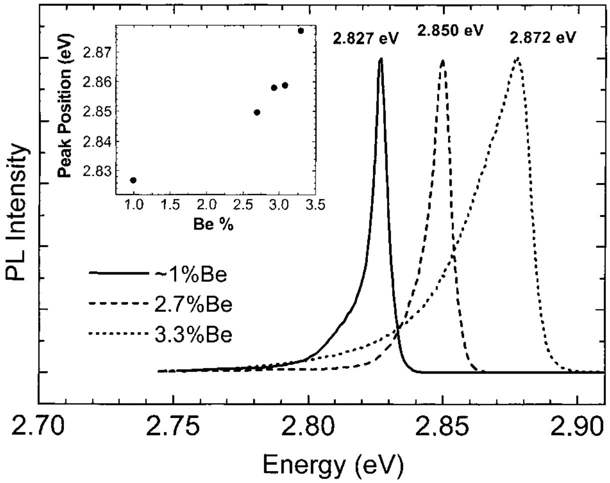

Fig. 2. Low temperature PL from three ZnBeSe:Cl samples; the inset show the peak position as a function of Be concentration for all investigated samples

dependence on the Be composition is assumed. Similarly, a quadratic dependence was reported in Ref. [6].

Since Refs. [15, 16] pertain to bulk crystals, for our comparison we shall use only data from Refs. [6, 12] corrected for the binding energy of the ZnSe free exciton (20 meV).

The peak position for the sample with 1% Be is about 2.827 eV, while the corresponding bandgap values are 2.845 eV with use of [12] and 2.857 eV with [6]. Thus, the PL peak is below the edge of the bandgap by 18 meV if we use Ref. [12] and by 30 meV if we use Ref. [6]. Clearly, 18 meV is an unrealistic number since it is smaller than the free exciton binding energy (20 meV in ZnSe); on the other hand, 30 meV seems quite realistic (the position of the Cl bound exciton is 25–26 meV below the ZnSe band edge); moreover, one expects an increase of the excitonic binding energy in ZnBeSe due to a decrease of the dielectric function. Indeed, the binding energy of a hydrogenic impurity would increase as the dielectric constant decreases with the increase of the bandgap due to the higher Be concentration. (A simple theory, see e.g. [17], predicts that dielectric constant decreases as a square of the bandgap.) When we consider the 3.3% Be sample, the peak here is at 2.877 eV while the bandgaps values reported are 2.898 eV [12] and 2.916 eV [6]. Again, the separation calculated using the first value is 21 meV, which appears too small, while the second value gives 40 meV, which we believe is more likely. (Both approaches give a larger binding energy for the 2.7% Be sample, which admittedly we find puzzling.)

We, however, note that the range of our data is for samples with relatively low Be concentrations, since at higher Be content the binding energy of free excitons is expected to increase, and the observed bending [6] of the excitonic bandgap would not represent a real bandgap value. Thus we suggest that an extension of this investigation toward higher Be content material is needed.

Next we show in Fig. 3a low temperature PL from a typical uniformly doped $Zn_{0.966}Be_{0.034}Se:N$ sample at different excitation intensities (normalized and shifted along intensity axis for convenience). The high excitation intensity spectrum consists of a dominant peak at 2.769 eV and a shoulder at 2.746 eV as well as a small high energy peak at 2.844 eV. It is clear that the peak at 2.746 eV is not a phonon replica of the

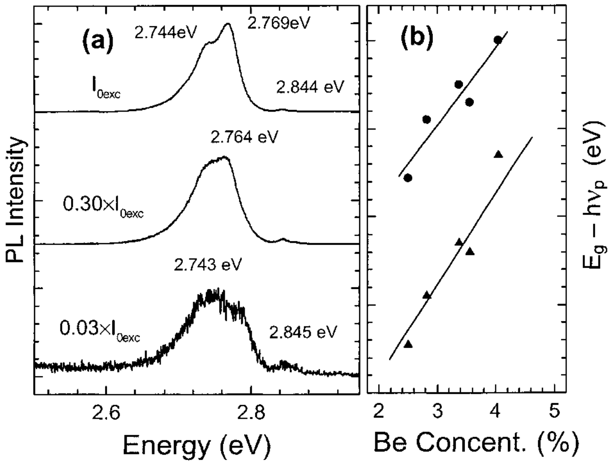

Fig. 3. a) Intensity dependence of the PL from a typical ZnBeSe:N sample; b) energy separation of the dominant peak from the bandgap calculated using Ref. [6] (circles) and Ref. [12] (triangles)

dominant transition as it does not scale with the intensity of the 2.769 eV peak; moreover, it becomes dominant at lower excitation intensities. In Fig. 3b we show the energy difference between the dominant peak energy and the bandgap calculated according to Refs. [6] and [12]. In both cases the binding energies of the relevant impurities increase with Be content. This corresponds to hydrogenic nature of the impurities as has already been mentioned above. Note that in the similar case of ZnMgSe:N such a behavior was not observed, but rather several discrete values for N acceptor were reported, depending on the number of surrounding Mg atoms [19].

If we extrapolate these data to ZnSe values we obtain the following values: 81 meV if we use Ref. [12] and 105 meV if we use Ref. [6]. We note that previously this PL was attributed to a donor–acceptor pair (DAP) recombination [6, 18]. Therefore, we can estimate a sum of the activation energies of acceptors and donors, $(E_A + E_D)$, by adding to the above values the Coulomb shift. We take a Coulomb shift of about 25 meV, which is appropriate for a shallow donor in ZnSe [20]. With this Coulomb shift we obtain $(E_A + E_D) \approx 106$ meV, using Ref. [12] and $(E_A + E_D) \approx 130$ meV, using Ref. [6]. It is clear that the latter values are closer to those expected for ZnSe ($(E_A + E_D) \approx 137$ meV for a 111 meV acceptor and a 26 meV donor).

Therefore, giving the results for Cl and N doped samples, the bandgap values reported in Ref. [12] seem too low to explain the observed PL, at least in the case of low Be concentrations. We, therefore, postulate that the bandgap of ZnBeSe first increases superlinearly, but then it may well become a linear function of Be concentration, as reported elsewhere [12].

Summary We have investigated the behavior of undoped and doped ZnBeSe alloy system with Be concentrations less than 6%. We have found that the dominant radiative transition in undoped material is of isoelectronic nature. Also, from a donor bound excitonic PL as well as a lower energy DAP band, we conclude that the impurity activation energies increase with Be concentration according to the "effective mass" approximation. Our data also suggest that the behavior of ZnBeSe bandgap as a function of Be composition requires further investigation.

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