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Luminescence of biexcitons in CuBr quantum dots

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Abstract: In this contribution, luminescence experiments at CuBr quantum dots grown in a wide range of sizes in the weak confinement regime ($R \geq a_B$) will be presented. In intensity-dependent luminescence measurements with ns-pulses, for each dot size two peaks can be resolved and are attributed to exciton and biexciton transitions, respectively. From time-resolved luminescence after ps-excitation, we obtain additional insight into the dynamics of biexciton formation and decay. We observe a delayed onset and a faster decay of the biexciton luminescence compared to the exciton luminescence. The experimental values for the energetic difference of the exciton and the biexciton peak agree very well with recent numerical calculations for the biexciton binding energy, predicting an increase for decreasing dot sizes. An exception are very small dots where e.g. due to interface-related states these calculations can no longer be applied.

1. INTRODUCTION

For CuBr as a I-VII semiconductor with a high exciton binding energy of 108 meV, strong changes of the excitonic effects are expected with increasing quantum confinement. Of special interest for experimental as well as for theoretical works are the existence and the properties of biexcitons which have already been studied extensively in the corresponding bulk material [1-6]. Depending on the excitation conditions a biexciton binding energy around 20 meV has been derived in [1-3].

Quantum-confined I-VII structures can be realized by growing microcrystals in a glass matrix [7-10]. This paper presents results obtained by luminescence experiments on samples with sizes of the microcrystals ranging between $R = 1.4$ and 6.75 nm. As the influence of the potential barrier scales with the Bohr radius of the elementary excitation and the Bohr radius a_B of the bulk exciton is 1.25 nm, a confinement effect regarding the exciton states is expected [11]. Interesting new nonlinear-optical properties have been found based on the change in binding energy, oscillator strength and the mechanisms of exciton-exciton interaction with the onset of confinement. Large $\chi^{(3)}$ -values for CuBr [10] and CuCl quantum dots [12-14] and recently also biexciton lasing in CuCl quantum dots [15,16] have been observed.

The samples investigated were grown in two series using the following annealing procedures: the samples of one series were heated at a constant temperature of 550°C for different times ranging from 1 to 43 hours, in the other series the samples were annealed at different temperatures from 475°C to 580°C but for a constant time of one hour. For each set of samples the sizes were determined by X-ray analysis at selected samples giving a calibration curve for the size determination of all samples.

Fig. 1: Absorption spectra of CuBr quantum dots of different sizes: (1) 6.75 nm, (2) 3.8 nm and (3) 1.8 nm. The energy of the highest luminescence peak is indicated by an arrow.

Fig. 2: Intensity-dependent measurements under ns-excitation for a sample with $R = 4.4$ nm.

The confinement-induced blue-shift of the lowest exciton transition can be observed in the linear absorption spectra shown in Fig. 1. For larger dots the position of the energetically highest peak in luminescence of each sample indicated by arrows is close to the absorption maximum and follows directly the shift towards higher energies for decreasing sizes. For samples with sizes $R \leq 3$ nm, where the absorption peak shifts further with confinement, the spectral position of the luminescence converges to a lower limit and the spectral behaviour becomes similar to the luminescence obtained from the glass matrix before annealing. As for these small dots a large fraction of the atoms is situated at the glass-semiconductor interface, there seems to be a high density of states not influenced by size variation and confinement where this luminescence comes from.

2. STEADY-STATE LUMINESCENCE

For all dot sizes realized quasi-steady-state luminescence experiments were performed exciting with ns-pulses from a nitrogen laser in backscattering geometry. Fig. 2 shows the typical intensity-dependent spectra for a sample with mean radius $R = 4.4$ nm where the maximum intensity I_0 is 3 MW/cm^2 . The spectra of all samples investigated consist of two distinct peaks. The higher energetic peak can be attributed to the exciton-related transition by comparison with the corresponding absorption spectrum as mentioned in the section above. For larger dot sizes the measured energetic positions of this peak converges to the values of the transversal exciton energy observed in CuBr [2,3]. Similarly, the position of the lower energetic peak approaches the biexciton energy of the bulk material.

The two peaks show a significantly different intensity-dependence. For low excitation intensities the exciton peak dominates in the spectra (as seen in Fig. 2) whereas for higher intensities, the lower energetic luminescence increases more than linearly. This behaviour is a further strong hint to the biexcitonic nature of this peak. An ideal biexciton-exciton transition without competing recombination channels should rise with the square of the intensity. Thus, we assume that the luminescence from the lower energetic peak originates from the decay of biexcitons to the exciton ground state.

Regarding the energetic distance ΔE between the exciton and biexciton peaks, a strong size dependence has been found. ΔE increases with decreasing dot sizes as will be discussed later.

Fig. 3: Time-resolved luminescence after ps-excitation for a sample with $R = 4.4$ nm.

Fig. 4: Comparison of the biexciton binding energy observed in CuBr quantum dots from theory in [19]. The deviation at the smallest dot radii (indicated by a dashed box) is attributed to the breakdown of the confinement concept for the luminescence (see text).

3. TIME-RESOLVED LUMINESCENCE

Time-resolved experiments were performed with excitation pulses with a length of 70 ps FWHM at a photon energy of 5 eV and a streak camera as detection system. For the sample with $R = 4.4$ nm, Fig. 3 shows the decay curves measured at the exciton energy of 3.002 eV and the biexciton energy of 2.968 eV, respectively, for an excitation fluence of 1 mJ/cm^2 . We observe a delayed maximum and a faster decay of the biexciton luminescence compared to the exciton luminescence. This is the typical behaviour for a system with a high density of excited carriers formed by relaxation from free pairs. After the formation of excitons by optical absorption there is a relaxation to the biexciton state and finally excitons and biexcitons both co-exist in a quantum dot for moderate densities. Therefore, a slower rise time of the biexciton system is expected due to its finite formation time taking into account the relaxation process of the excitons to the biexciton state. As well, a faster decay time of the biexciton luminescence can be explained by the expected quantum mechanical transition probability.

These results agree very well with time-resolved measurements performed in bulk CuBr [17] where as well a delayed onset and a faster decay of the biexciton luminescence have been found.

4. CONFINED BIEXCITONS

The biexciton binding energy as defined by $E_{\text{biex}}^{\text{bind}} = 2E_{\text{ex}} - E_{\text{biex}}$ and experimentally determined by the energetic distance ΔE of the two peaks in luminescence for all samples, respectively, shows an increase for decreasing dot sizes. In Fig. 4 the experimental values for the biexciton binding energy in dependence on the dot size R are in excellent agreement with theoretical curves from [18,19]. These curves are obtained by a full numerical treatment of the Hamiltonian for one and two-pair states in quantum dots depending on the effective mass ratios of electrons and holes and on the ratio of the dielectric constants of the semiconductor and the surrounding matrix. Only for the smallest dots with radii $R \leq 3$ nm (indicated by a dashed box), where due to interface-related states the confinement concept can no longer be applied, there is a significant deviation.

In conclusion, exciton and biexciton states with increasing energetic distance for decreasing dot sizes have been found in luminescence. In time-resolved experiments the biexciton states show a slower rise time and a faster decay compared to the exciton luminescence. Our measurements also confirm the results concerning biexcitons in CuCl quantum dots presented in [20,21].

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