Chapter 6

Synthesis and luminescence of nanocrystalline ZnSe:Cu

A chemical synthesis is described in which ZnSe:Cu nanocrystals slowly grow to a final size that is dependent on the synthesis conditions. During particle growth, samples are extracted to study the luminescence as a function of particle size and temperature. The growth rate of the nanocrystals is strongly dependent on the synthesis temperature. For slowly growing crystals the transition from normal precursor-driven growth to Ostwald ripening could be identified. Quantum size effects are observed to influence both the ZnSe and the Cu related luminescence emissions. Temperature-dependent measurements of the luminescence intensity, lifetime and peak positions are reported and discussed.
6.1 Introduction

Nanocrystalline semiconductors showing quantum size effects are widely studied [1–6]. The change in electronic structure as a function of the particle size for the same chemical composition is of fundamental interest and may also become important for various applications (such as for low voltage electroluminescent devices [7, 8]).

Almost ten years ago research started on semiconductor nanocrystals in which luminescent dopant ions are incorporated. For dopant ions like Mn$^{2+}$ and Pb$^{2+}$ the characteristic emission of the luminescent ion is observed [4, 5, 9]. As the particle size decreases, the wavelength for excitation of the dopant emission (over the bandgap) shifts to higher energies while the emission color is unaffected. The insensitivity of the dopant emission energy to the particle size is due to the fact that an electronic transition occurring on Mn$^{2+}$ or Pb$^{2+}$ involves electronic wave functions localized on the dopant cation and the neighboring ligand anions. The localized wave functions are not influenced by quantum size effects. However, for other dopant ions emission of light may involve recombination of a delocalized charge carrier and the dopant. The emission from Cu$^{2+}$ centers in ZnS and ZnSe is assigned to recombination of a delocalized electron (in the conduction band or shallow trap) with Cu$^{2+}$ [10].

Measurements on bulk ZnSe crystals doped with copper have revealed the presence of green and red emission bands, which have been assigned to recombination of electrons in shallow traps with different Cu$^{2+}$ centers [10–12]. The Cu$^{2+}$ related emission wavelength in nanocrystalline ZnS or ZnSe semiconductor particles is expected to shift to higher energies in smaller particles. In some recent studies on ZnS:Cu this has indeed been observed [9, 13]. In this chapter the synthesis, growth and luminescence of nanocrystalline ZnSe:Cu is reported. In the synthesis procedure used, the ZnSe particles grow slowly and the luminescence properties of the ZnSe:Cu were studied as a function of particle size with samples taken at different times during the reaction. From the change in particle size as a function of time, different growth-regimes can be identified. In addition, temperature-dependent luminescence measurements are discussed. Based on the data, a model describing the luminescence mechanism is proposed.
6.2 Growth of the nanocrystals

The growth of ZnSe:Cu nanocrystals was investigated by studying the dependence of the luminescence of the nanocrystals on the synthesis time. In this way, different growth mechanisms responsible for the increasing crystal size were found in the course of the synthesis.

6.2.1 Experimental

The synthesis route that was used to prepare the ZnSe:Cu nanocrystals is similar to the well-known TOP/TOPO synthesis used for CdSe nanocrystals [14]. Hexadecylamine (HDA) was used instead of TOPO for reasons that were described in chapter 5 in some detail [15, 16]. The reactions were performed inside a glovebox in an inert dry-argon atmosphere. Chemical tests using diethylzinc and titanium tetrachloride indicated that the atmosphere contained less than 5 ppm of oxygen and less than 5 ppm of water.

A 35 g sample of hexadecylamine was heated to \( \sim 150 \, ^\circ\text{C} \) under vacuum \((<10^{-4} \text{ bar})\) for several hours to remove residual water and other contaminants that were present in the sample as received from the supplier (Aldrich). The HDA was transferred to the glovebox and heated to 270 \( ^\circ\text{C} \). In this synthesis, the HDA is used both as the solvent and as the surfactant. The copper precursor was a solution of \( \text{Cu(CH}_3\text{COO)}_2 \) in tri-\( n \)-octylphosphine (TOP). For the experiments presented in this section, \( \sim 0.8 \) mg of \( \text{Cu(CH}_3\text{COO)}_2 \) was dissolved in 12 ml of TOP. To this solution, 3 ml of a previously prepared solution of 1 M TOPSe was added. After stirring, 0.32 g of diethylzinc was added. The resulting solution was shaken and then injected into the hot HDA. The nanocrystals were grown at a constant temperature of 260 \( ^\circ\text{C} \). The synthesis was performed at this (rather low) temperature because the slower kinetics allow a more detailed investigation of the growth mechanism. At different times after the injection a \( \sim 0.5 \) ml sample of the liquid was taken. This sample was quickly poured into 5 ml of anhydrous toluene, resulting in a stable colloidal suspension. The luminescence measurements presented in this section were performed on these suspensions, immediately after the samples were removed from the glovebox.

The particle radius was determined using the peak broadening in the X-ray powder diffractograms, as described in section 2.3.1. Photoluminescence emission and excitation spectra were recorded with a SPEX Fluorolog spectrofluorometer. All spectra were corrected for the spectral response of the emission monochromator and the photomultiplier tube. The excitation spectra were also corrected for
Figure 6.1: Evolution of (a) the ZnSe related and (b) the Cu$^{2+}$ related photoluminescence spectra of ZnSe:Cu nanocrystal suspensions in toluene for different synthesis times: 45 minutes (■), 1 hour and 40 minutes (○), 3 hours and 9 minutes (△), 5 hours and 13 minutes (▽), 22 hours (●), 73 hours (★) and 112 hours (□). The spectra were measured at 300 K for excitation at 330 nm. All spectra were normalized on the ZnSe emission maximum.

the spectral distribution of the excitation source (xenon lamp) and the excitation monochromator. Photoluminescence lifetimes were measured using the YAG:Nd laser set-up, described in detail in the experimental section of chapter 5.

6.2.2 Results and discussion

Figure 6.1 shows the photoluminescence emission spectra for several samples of nanocrystalline ZnSe:Cu in toluene taken at different times during the synthesis. The emission spectra were all normalized on the ZnSe emission maximum. The photoluminescence spectrum shows two distinct emission bands. The first band is located at approximately 400 nm, as can be seen in figure 6.1(a); this band cor-
responds to the exciton emission of the ZnSe host lattice. The precise emission energy is found to be strongly dependent on the synthesis time. The second emission band is located at roughly 460 nm and is shown in figure 6.1(b). This peak is assigned to a copper-related dopant emission. The luminescence mechanism will be discussed in section 6.3.4.

Two important observations can be made on the basis of figure 6.1. Firstly, for increasing synthesis time, there is a clear shift of the ZnSe related emission maximum to longer wavelengths. This can be explained directly by the growth of the nanocrystals: an increase in the crystal size results in a decrease of the ZnSe bandgap, as shown in equation (1.7), and causes a red-shift of the ZnSe related exciton emission. This will be used to discuss the growth mechanism for these nanocrystals later in this section. Secondly, when a very low Cu precursor concentration is used, as was the case for the synthesis shown in figure 6.1(b), a long synthesis time is required to observe a significant Cu$^{2+}$ related photoluminescence. The Cu ions are incorporated only very slowly into the ZnSe host-lattice. The copper precursor concentration used in this synthesis was 0.17 % with respect to the zinc precursor concentration. As a result, only 0.4 (smallest crystals) to 1 (largest crystals) Cu ion is expected per nanocrystal, assuming that all copper ions are incorporated and that there is a random distribution of the ions. In section 6.3.2 evidence will be presented to show that an increased Cu precursor concentration results in a faster incorporation of the Cu ions into the ZnSe lattice and an enhanced Cu$^{2+}$ related emission intensity.

The position of the ZnSe related emission band, $E(t)$, and the half width at half maximum of this emission band, $\Delta E(t)$, have been determined from the data shown in figure 6.1(a) for different synthesis times $t$. The values were determined by fitting a Gaussian function through the emission spectrum plotted as relative emitted photon flux per constant energy interval [17]. In the remainder of this section, the synthesis time ($t$) is defined to be in minutes. Figure 6.2(a) shows the time evolution of the ZnSe related emission energy and figure 6.2(b) shows the time evolution of the half width at half maximum of this emission. It is clear from these figures that both the energy of the emission maximum and the width of the emission band for the ZnSe related emission shifts to lower values for increasing synthesis time.

Based on the known material parameters $m_e^+ = 0.17m_0$ [18], $m_h^+ = 0.60m_0$ [19], $\epsilon_s = 8.1$ [20] and $E_g = 2.8$ eV [20], together with the Brus equation [3], the particle diameter $d$ in nanometers can be calculated from the bandgap energy $E_g$ in electron
Figure 6.2: Time evolution of (a) the ZnSe related emission energy and (b) the ZnSe related half width at half maximum for the ZnSe:Cu nanocrystalline suspensions in toluene. The spectra were measured at 300 K and the excitation wavelength was 330 nm. Note the logarithmic time-axis for both plots.

\[
d(E_g) = \frac{0.32 - 3.37\sqrt{E_g - 2.79}}{2.8 - E_g}
\]

Using equation (6.1), the data in figure 6.2(a) was converted into the nanocrystal diameter as a function of the synthesis time. This data is shown in figure 6.3.

Figure 6.3(a) shows the (average) size of the nanocrystals as a function of the synthesis time. It is clear from this figure that even after 7500 minutes (more than 5 days) the nanocrystals continue to increase in size. However, the nanocrystals show only a moderate increase in size, especially after the initial growth at relatively short times. Furthermore, it is clear from this figure that two different growth-ranges exist: a (relatively) fast growth for synthesis times shorter than \(\sim1000\) minutes, followed by a slower, but persistent, growth for longer synthesis times.
6.2. Growth of the nanocrystals

Figure 6.3: (a) Time evolution of the size of the nanocrystals as calculated from the ZnSe emission energy using equation (6.1). Note the logarithmic time-axis. (b) The same data plotted as the cube of the crystal size on a linear time-axis. The lines through the data are discussed in the text.

times. This trend can also be clearly seen in figure 6.3(b), which shows the cube of the crystal diameter on a linear time-scale.

During the synthesis, the concentration of reactants decreases. As a result, it is expected that the rate of the synthesis will also decrease. This means that the growth of the nanocrystals slows down as well, which agrees with the data presented in figure 6.3(a). It is difficult to accurately explain this data because of the relatively large error and the fact that the experiment was performed only once. Therefore, the explanation presented here does not exclude other possible growth-mechanisms and further experiments need to be done to establish the growth-mechanism more firmly.

After the injection of the precursors, the rapid nucleation of the nanocrystals will quickly result in nanocrystals of a diameter \( d_0 \). On a longer time-scale, the growth of the nanocrystals begins, which is shown in figure 6.3. Here it is assumed
that this growth is concentration-driven, rather than diffusion-limited [21], and proceeds by a first order reaction. As the initial concentration of the zinc precursor is similar to the initial concentration of the selenium precursor (2.6 mM and 3 mM, respectively), is it reasonable to assume a simple, first-order reaction. In this case, the concentration \([C]\) of reactant decreases as a function of time as [22]

\[
[C] = [C_0] e^{-kt},
\]

where \([C_0]\) represents the initial concentration of the reactant, \(k\) is the reaction constant and \(t\) is the reaction time. As the increase in the volume of the nanocrystals, \(dV/dt\), is determined by the concentration of available reactants, it will be proportional to \(d[C]/dt\). When the growth of the nanocrystals is reasonably limited, one can assume that the surface area of the nanocrystals does not increase significantly. In this case, the rate of growth of the radius of the nanocrystals, \(dr/dt\), will be roughly proportional to \(d[C]/dt\) and then the diameter \(d\) of the nanocrystals at time \(t\) can be found by integration of the growth-rate. The result is

\[
d(t) = d_0 + \xi \left(1 - e^{-kt}\right).
\]

Here \(\xi\) is a constant determined by the material parameters and \(d_0\) describes the ‘initial’ size of the nanocrystals (resulting from the rapid nucleation at the time of the injection of the precursors).

Equation (6.3) is strictly speaking only valid when one assumes that the surface area of the nanocrystals does not increase significantly because a change in the surface area also changes the concentration of reactants required to add one monolayer to the nanocrystal. As a result, for a bigger crystal the decrease in the precursor concentration required to add one layer to the nanocrystal must be larger than for a small crystal. This effect is ignored because the nanocrystals only grow by a moderate amount.

The dashed line through the data in figure 6.3(a) is a fit using equation (6.3). Shortly after the injection of the precursors, the average nanocrystal radius is already \(\sim 2.3\) nm. After this fast nucleation of the nanocrystals, the subsequent growth is rather slow. Clearly, the data can be described reasonably well by this fit for synthesis times less than roughly 2000 minutes. The fact that the fit seems to be quite good is in agreement with the assumption that the mechanism responsible for the growth of the nanocrystals for the first growth stage is concentration-driven, rather than diffusion-limited or some other process. However, further experiments will be required to confirm this growth mechanism and rule out other growth-mechanisms possible.
6.3 Analysis of the luminescence

For longer synthesis times, equation (6.3) predicts a negligible growth of the nanocrystals, while a significant growth is still observed. In this long time range, Ostwald ripening is expected to be responsible for the growth of the nanocrystals, as the reagents have been depleted and there are no chemicals available for the synthesis. Figure 6.3(b) shows the cube of the average crystal diameter as a function of time on a linear time-axis. From the literature it is known that a plot of \(d^3\) as a function of time should show a straight line for pure Ostwald ripening of the nanocrystals [23, 24]. Indeed, the data for a long synthesis time can be fitted quite well by the straight line in figure 6.3(b), suggesting that this growth is due to Ostwald ripening.

Finally, a reasonable estimate of the polydispersity of the nanocrystal ensemble can be made by computing

\[
\Delta d(t) = \frac{d(E(t) - \Delta E(t)) - d(E(t) + \Delta E(t))}{2},
\]

(6.4)

which can be regarded as an approximation of the half width at half maximum of the nanocrystal size distribution.

Figure 6.4 shows the estimate of the polydispersity of the nanocrystal ensemble determined from equation (6.4). As can be seen from the data, the polydispersity decreases for increasing synthesis times, which is especially clear for the synthesis times shorter than 1000 minutes. As diffusion-limited growth of the nanocrystals would result in a decrease of the polydispersity for increasing crystal size (i.e. synthesis time) [21], this result suggests that the reaction may be diffusion-limited to some extent.

6.3 Analysis of the luminescence

In this section the luminescence and the luminescence mechanism of nanocrystals of ZnSe doped with Cu is considered in detail. The temperature dependence of the photoluminescence and luminescence lifetimes are determined and an estimate of the temperature-induced shift of the conduction band edge is made. Furthermore, a model is presented that describes the luminescence processes.

6.3.1 Modified synthesis

The synthesis route that was used to prepare the ZnSe:Cu nanocrystals for this part is almost identical to that discussed in the first part of this chapter. The only dif-
ferences are the precursor concentrations, the synthesis temperature and the precipitation of the nanocrystals. As a result of the significantly higher synthesis temperature, the reaction is much quicker and the growth of the nanocrystals is faster. Furthermore, due to the higher Cu precursor concentration, more copper is expected to be incorporated into the nanocrystals.

The reactions were performed in the dry-argon atmosphere of a glove-box. A sample of 45 ml of HDA was heated to 290 °C. A solution of 4.8 mg Cu(CH₃COO)₂ in 12 ml TOP was prepared and to this solution 3 ml of a 1 M solution of TOPSe was added. After stirring, 0.32 g of diethylzinc was added. The resulting solution was shaken and then added to the hot HDA. The nanocrystals were grown at a constant temperature of 290 °C. A ~1 ml (liquid) sample was taken at different times after the injection. The nanocrystals in each of the samples were precipitated by adding 5 ml of anhydrous 1-butanol. The precipitate was redissolved in 1-octanol for measurements on a suspension of nanocrystals, or washed with methanol and dried in a vacuum desiccator for powder measurements. The powders had a slightly grey color.

Figure 6.4: Time dependence of the polydispersity of the nanocrystal ensemble as determined from equation (6.4). Note the logarithmic time-axis.
6.3. Analysis of the luminescence

Figure 6.5: Normalized luminescence spectra of ZnSe:Cu suspensions in octanol for different synthesis times. The spectra were measured at 300 K for an excitation wavelength of 330 nm.

6.3.2 Results and discussion

Figure 6.5 shows photoluminescence spectra of ZnSe:Cu nanocrystals of different sizes. The near band edge emission shifts from 380 nm to 430 nm as the particles grow from a radius of about 1.7 nm to 3.4 nm. The sizes indicated in figure 6.5 were determined from the peak broadening in the powder X-ray diffractograms. A comparison with the data shown in figure 6.1 or figure 6.3(a) shows that the higher synthesis temperature results in a significantly enhanced growth rate of the nanocrystals, but that the initial size of the nanocrystals (due to the nucleation) is smaller. The higher growth-rate can be expected, because the rate of the chemical reaction increases exponentially with temperature (Arrhenius behavior) [22]. Furthermore, the final size of the nanocrystals in this experiment is larger than that found in the previous section. This is also expected due to the higher growth-rate at higher temperature.

For the larger particles, the longer wavelength emission band (assigned to the Cu$^{2+}$ dopant as before) becomes visible between 400 and 500 nm. This emis-
Figure 6.6: Excitation spectra of a ZnSe:Cu sample with a radius of 1.7 nm in octanol. Measured at 4 K for the emission wavelengths indicated in the figure. Relative intensities of the two spectra cannot be compared.

The emission band also shifts to longer wavelengths as the particle size increases. Because for this synthesis the crystal size is increasing quite rapidly, the shift of the Cu\(^{2+}\) related emission to longer wavelengths is much more pronounced than in figure 6.1(b). Due to the strong overlap of the ZnSe and Cu\(^{2+}\) related emission bands, it is difficult to determine accurately the position of the maximum of the Cu\(^{2+}\) emission band. The relative increase of the Cu\(^{2+}\) photoluminescence suggests that the Cu concentration in the ZnSe nanocrystals grows with synthesis time. This agrees with the data shown in figure 6.1(b). As a result of the much higher copper precursor concentration used in this synthesis (1.1 % compared to 0.17 % in section 6.2), the relative contribution of the Cu\(^{2+}\) related photoluminescence to the total luminescence is also much higher.

In figure 6.6 the excitation spectra of the low-temperature luminescence of ZnSe:Cu particles with a radius of 1.7 nm is shown. Here, \(\phi\) denotes the photon flux per constant wavelength interval. The ZnSe related emission is at 370 nm, while the Cu\(^{2+}\) emission has a maximum at 421 nm at 4 K. The excitation spec-
6.3. Analysis of the luminescence

The excitation spectrum shows that the Cu\(^{2+}\) photoluminescence (measured at 421 nm) can also be excited via the bandgap of the ZnSe host lattice. Furthermore, an additional excitation band is observed at 355 nm. A similar sub-bandgap excitation band is also observed in the excitation spectra of the Cu\(^{2+}\) emission in bulk ZnSe:Cu crystals and this band has been assigned to the direct excitation of the Cu\(^{2+}\) dopant [10, 11]. The energy difference between the maxima of the bandgap and the Cu\(^{2+}\) excitation bands in the different excitation spectra is between 0.3 and 0.4 eV. The same energy difference is observed between the emission maxima of the near band edge and the Cu\(^{2+}\) emission bands. This energy difference indicates that the Cu\(^{2+}\) level is located in the bandgap about 0.3 – 0.4 eV above the top of the valence band. This has also been reported previously for the green Cu\(^{2+}\) emission in bulk ZnSe [10]. This shows that the Cu\(^{2+}\) emission in the ZnSe:Cu nanocrystals is analogous to the well-known green emission from bulk ZnSe:Cu. Due to the quantum confinement the conduction band edge shifts to higher energies and therefore the green emission shifts to shorter wavelengths as the particle size decreases.

6.3.3 Temperature dependence and luminescence lifetime

In figure 6.7 the emission spectra of a powder consisting of ZnSe:Cu nanocrystals with a radius of 3.4 nm are shown as a function of temperature. At 4 K the Cu\(^{2+}\) related emission is the dominant spectral feature. The mechanism involved in the temperature dependence of the emission intensities will be discussed below. Both the Cu\(^{2+}\) and the ZnSe related emission bands shift to shorter wavelengths as the temperature is decreased. In figure 6.8 the position of the emission maximum is plotted as a function of temperature for both emission bands. In chapter 5, dealing with the luminescence of 3.5 nm diameter ZnSe:Mn\(^{2+}\) nanocrystals, it was shown that the shift of the ZnSe related emission can be described by the Varshni equation [25] which has been derived to describe the temperature dependence of the
bandgap of bulk semiconductors. This expression states that

$$E_g(T) = E_0 - \frac{\alpha T^2}{T + \beta},$$

where $E_0$ represents the bandgap at 0 K and $\alpha$ and $\beta$ are fitting parameters. It is known from the literature that $\beta$ is of the order of the Debye temperature of the semiconductor. This equation takes into account both the temperature-induced change in the lattice parameter and the temperature dependence of the electron-lattice interaction.

Figure 6.8 shows the temperature-dependence of the emission energy of the ZnSe and the Cu$^{2+}$ related photoluminescence signals. The nanocrystals have a radius of 3.4 nm and the measurements were performed on a powder sample. The reported emission energies were found by fitting a Gaussian lineshape through the data using the relative emitted photon flux per constant energy interval as a function of energy. Similar results were also found for the smaller particles. For temperatures above 150 K (when the Cu$^{2+}$ related photoluminescence is quenched), the
6.3. Analysis of the luminescence

Figure 6.8: Temperature dependence of the ZnSe (●) and Cu$^{2+}$ (□) related photoluminescence emission energies for a powder sample of ZnSe:Cu nanocrystals with a radius of 3.4 nm. The lines through the data are fits using the Varshni equation (6.5).

determination of the Cu$^{2+}$ peak position becomes increasingly difficult. Because of the large uncertainties, these data are not shown in figure 6.8 and will be omitted in the further discussion. The lines through the data are fits using the Varshni equation as shown in equation (6.5). The values of the parameters that were obtained from these fits are shown in table 6.1.

The change in the ZnSe related emission energy (i.e. the bandgap energy) between 4 K and 300 K is about 0.12 eV, as is seen from the filled circles in figure 6.8. The small shift of the ZnSe emission to higher energy between 4 K and 50 K will be discussed in section 6.3.4. From an extrapolation of the Varshni fit the shift of the Cu$^{2+}$ related emission (i.e. the conduction band) is calculated to be 0.09 eV between 4 K and 300 K. This means that the shift of the bandgap is dominated by the shift of the conduction band and that the shift of the valence band seems to be relatively small.

Due to the rather large error in the fit parameters (as shown in table 6.1), it is difficult to draw quantitative conclusions from these results. Furthermore, the
Table 6.1: Values for \(\alpha\) and \(\beta\) as were obtained by fitting equation (6.5) to the ZnSe and Cu\(^{2+}\) related luminescence data shown in figure 6.8. The literature values for bulk ZnSe are included for comparison.

<table>
<thead>
<tr>
<th></th>
<th>ZnSe</th>
<th>Cu(^{2+})</th>
<th>Literature [26]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha) ([10^{-4} \text{ eV K}^{-1}])</td>
<td>8.8 ± 0.3</td>
<td>5.8 ± 0.7</td>
<td>7.5</td>
</tr>
<tr>
<td>(\beta) ([10^2 \text{ K}])</td>
<td>2.8 ± 0.5</td>
<td>2.6 ± 1.5</td>
<td>2.95</td>
</tr>
</tbody>
</table>

expected shift of the conduction band and valence band edges as a function of the temperature has been theoretically or numerically calculated for many cases and no consensus about the expected trends has been reached. Fan claims that the shift should be proportional to \((m^*)^{-3/2}\) for nonpolar crystals and to \(\sqrt{m^*}\) for polar crystals, while the intermediate case (which would be expected for ZnSe) is not treated [27]. On the other hand, Gopalan et al. show calculations in which the shift is almost independent of the effective mass for the (somewhat polar) semiconductor GaAs [28]. Finally, Shen et al. have recently shown experimental data for PbSrSe indicating that the shift can be linear in the effective mass [29]. Seiwert proved that, for single crystal CdS, the temperature dependence of the lattice parameter must be responsible for less than 15% of the experimentally observed shift in the bandgap energy [30]. This means that the majority of the shift must be due to the electron-phonon interaction. Now one interesting observation about the data shown in figure 6.8 can be made as the temperature-induced shift of the conduction band is (much) larger than that of the valence band. This indicates that the electron-phonon interaction in the conduction band is stronger than the electron-phonon interaction in the valence band for these ZnSe:Cu nanocrystals. A stronger electron-phonon coupling for the charge carrier with the smaller effective mass is expected (note that for ZnSe \(m_e^* = 0.17m_0\) and \(m_h^* = 0.60m_0\)) since the wave function of that charge carrier will be more delocalized allowing for more wave function overlap with a phonon.

Figure 6.9 shows the time dependence of the Cu\(^{2+}\) related photoluminescence signal for a powder of 3.4 nm radius ZnSe:Cu nanocrystals after a \(\sim 10\) ns excitation pulse. The inset shows the same data on a logarithmic intensity axis. The thick line in the inset is a single-exponential fit to the data with a lifetime of \(\tau = 0.97\) \(\mu\)s, which fits the data reasonably well. However, the decay is not single-exponential and a longer lifetime component can be identified in the tail of the plot. The thin line through the data in both plots is a double-exponential fit with a fast lifetime of
6.3. Analysis of the luminescence

Figure 6.9: Time dependence of the Cu$^{2+}$ related photoluminescence signal for a powder sample of ZnSe:Cu nanocrystals with a radius of 3.4 nm. The line through the data is a double-exponential fit. Pulsed excitation was at 355 nm and the measurement was performed at 4 K. Inset: The same data using a logarithmic intensity axis. The thick line is a single-exponential fit and the thin line is the double-exponential fit.

$\tau_f = 0.97 \, \mu s$ and a slow lifetime of $\tau_s = 3.1 \, \mu s$. The contribution of the fast lifetime to the total luminescence signal was about 90% at 4 K,

$$
\int dt \, I_{PL}(\tau_f) \approx 9 \cdot \int dt \, I_{PL}(\tau_s) .
$$

(6.6)

At higher temperatures the lifetime decreases, as will be shown below. Furthermore, the contribution of the fast lifetime to the total time-trace decreases as well, down to about 75% at room temperature.

The temperature dependence of the lifetime of the Cu$^{2+}$ related photoluminescence is shown in figure 6.10 together with the temperature dependence of the integrated photoluminescence for this emission. At low temperatures the Cu$^{2+}$ emission is strong and from the single exponential decay curve of the emission intensity a luminescence lifetime of 0.97 $\mu s$ is derived. There is no data available
on the lifetime of the green Cu$^{2+}$ emission in bulk ZnSe:Cu for comparison. The near band edge emission (at 400 nm) has a single exponential decay with a 3.6 ns lifetime at 4 K, as was shown in the previous chapter.

As the temperature is increased above 50 K the Cu$^{2+}$ emission intensity starts to decrease. The quenching temperature, defined as that at which the integrated emission intensity has dropped to 50% of the value at 4K, is about 130 K. This value is very similar to the quenching temperature of 140 K reported for the green Cu$^{2+}$ emission in bulk ZnSe:Cu [12], providing further support for the assignment of the blue/green emission presented above. The luminescence lifetime of the emission decreases at the same rate as the emission intensity. This behavior is expected if the luminescence quenching is induced by a thermally activated non-radiative decay channel, which depopulates the excited state from which emission occurs. The quenching mechanism may be thermally activated deopposition of trapped electrons from shallow electron traps close to the Cu$^{2+}$ dopant, competing with radiative recombination with Cu$^{2+}$. For such a thermally activated process,
an Arrhenius dependence of the emission intensity and the emission lifetime on the
sample temperature is expected,

\[ A(T) = \frac{A_0}{1 + C \exp \left( \frac{-\Delta E}{k_B T} \right)}, \]  \hspace{1cm} (6.7)

where \( A_0 \) represents the value (of either the lifetime or the emission intensity) at 0
K and \( C \) is a fitting parameter.

Equation (6.7) fits the data rather well, as can be seen from the line through
the data. Using both sets of data shown in figure 6.10, a value for the activation
energy of \( \Delta E = 20 \text{ meV} \) was found. This value does not agree with the position of
the copper state in the ZnSe bandgap, as discussed before (about 0.3 eV above the
top of the valence band). Therefore, it seems unlikely that this activation energy
is due to hole detrapping from the copper ion. As a result, it is concluded that
this activation energy is related to electron detrapping as will be shown in the next
section.

From the data presented in figure 6.7 it is concluded that at 300 K the \( \text{Cu}^{2+} \)
emission is quenched to 10% of the intensity at 4 K. The quenching of the lumines-
cence is a drawback for a potential application of ZnSe:Cu in (electroluminescent)
devices. The quantum efficiency of the total emission was determined for a powder
of ZnSe:Cu nanocrystals by comparing the light output with that of a commercial
phosphor under identical measuring conditions. The details of this procedure were
discussed in section 5.3.2. At room temperature a luminescence quantum effi-
ciency between 2 and 4% was found. The relatively low quantum efficiency is
largely due to the thermal quenching of the \( \text{Cu}^{2+} \) emission, which is the dominant
spectral feature at 4 K.

From the ratio of the integrals of the photoluminescence at room temperature
and at 4 K the quantum efficiency at 4 K is estimated to be 30%. Similar high quantum
efficiencies for undoped nanocrystalline semiconductor particles have been ob-
tained for CdSe synthesized with a similar method. If the quenching temperature
for the \( \text{Cu}^{2+} \) emission can be increased, the material is promising for application
in electroluminescent devices. This could possibly be achieved if one is success-
ful in introducing a deeper electron trap in the ZnSe lattice, such as \( \text{Cl}^- \) on \( \text{Se}^{2-} \)
sites. Further investigation of this, as well as the introduction of other electron
traps might yield a material efficiently luminescing at room temperature.
6.3.4 Description of the luminescence mechanism

After the excitation of the ZnSe host-lattice \((h\nu_{\text{ex}} \geq E_g)\), three possible processes can occur. First of all, non-radiative recombination of the electron and the hole may take place. This is a loss-process and obviously undesirable. As most defect-states will be on the surface of the nanocrystal, a good surface passivation (possibly also using another type of (wider bandgap) semiconductor, such as ZnS) will reduce the probability for non-radiative recombination. The second and third processes, both radiative, are schematically depicted in figure 6.11.

Immediately after the creation of the exciton, the electron can be trapped in a shallow trap-state which is delocalized over (nearly) the entire ZnSe nanocrystal. When the recombination of this electron with a hole in the ZnSe valence band occurs, indicated by process (1) in figure 6.11, the blue ZnSe related emission is observed,

\[
(1) \quad e^- + h\nu_{VB} \rightarrow h\nu_{\text{ZnSe}}.
\]

As the electronic trap-state is close in energy to the bottom of the conduction band,
the emission from this level can be regarded as the excitonic emission of the nanocrystal. At low temperature, most of the exciton emission will result from recombination of a shallowly trapped electron with a hole in the valence band. When the temperature is increased, some of the electrons will detrap to the conduction band. This results in a shift of the emission energy to higher energies, agreeing with the data shown in figure 6.8 between 0 K and 50 K. From the temperature range in which this effect occurs, a rough estimate of the energy separation between the delocalized electron-level (indicated by the dashed line in figure 6.11) and the bottom of the conduction band results in about 5 meV. A similar value has been reported in chapter 3 for the ZnS related luminescence in nanocrystalline ZnS.

In order to assign the Cu\(^{2+}\) related luminescence, the initial energy level of the electron must first be determined. This can be done using the low-temperature emission spectrum shown in figure 6.7. From this data an extrapolation of the emission bands to higher energy can be made, resulting in an estimate of the zero-phonon energy for the ZnSe and Cu\(^{2+}\) related emissions. The result is \(~370\) nm for the ZnSe related emission and \(~400\) nm for the Cu\(^{2+}\) related emission. In figure 6.6 the excitation spectra of the Cu\(^{2+}\) related emission was shown, indicating that the Cu\(^{2+}\) has an energy level located about 0.3 eV above the bottom of the valence band. This value agrees quite well with the difference in energy between the (extrapolation of) the zero-phonon energy for the ZnSe and Cu\(^{2+}\) related emissions. As a result, the initial energy level of the electron must be the delocalized electron-level (indicated by the dashed line in figure 6.11), about 5 meV below the bottom of the conduction band. However, as long as the electron is in this energy level, the close proximity of the conduction band will mean that the electron has mainly a conduction band character. Therefore, an intermediate step is required so that the electron will be bound to the copper resulting ultimately in the Cu\(^{2+}\) related emission.

The Cu\(^{2+}\) related luminescence mechanism begins when a hole from the valence band is trapped in a localized Cu\(^{+}\) level, forming Cu\(^{2+}\) in an excited state or in the ground state. At sufficiently low temperature, a (delocalized) electron can be trapped in the potential well of the bound hole through the Coulomb interaction. This electron-hole pair can subsequently recombine via the Cu\(^{2+}\) ion, resulting in the characteristic green Cu\(^{2+}\) related emission. These processes can be
schematically written as

\[
\begin{align*}
(1') & \quad \text{Cu}^+ + h_{VB}^+ \rightarrow \text{Cu}^{2+}, \\
(2') & \quad \text{Cu}^{2+} + e^- \xrightarrow{\Delta E} \text{Cu}^{2+} + e_{\text{trap}}^-, \\
(3') & \quad \text{Cu}^{2+} + e_{\text{trap}}^- \rightarrow \text{Cu}^+ + h\nu_{\text{Cu}}. 
\end{align*}
\]

These processes, denoted by (1'), (2') and (3'), are also schematically shown in figure 6.11. The transfer of the hole to the copper may result in Cu\textsuperscript{2+} in the \textsuperscript{2}E excited state or in the \textsuperscript{2}T\textsubscript{2} ground state. If the Cu\textsuperscript{2+} is in the \textsuperscript{2}E excited state, it will most likely return quickly (either non-radiatively, or through infra-red emission) to the \textsuperscript{2}T\textsubscript{2} ground state. The Cu\textsuperscript{2+} related luminescence observed in this chapter is exclusively due to the recombination with the Cu\textsuperscript{2+} in the ground state as only one emission band is observed. At elevated temperature, the bound electron-hole pair, created in step (2'), can dissociate, requiring an energy \( \Delta E \). When this happens, the electron-hole pair is lost and the Cu\textsuperscript{2+} related luminescence is quenched.

Note that the energy levels of the copper ion are fixed in the ZnSe bandgap. This implies that the energy of the Cu\textsuperscript{2+} related emission will change when the energy of the conduction band edge changes (e.g. through a change in the crystal size or a change of the sample temperature). This agrees with the data shown in figure 6.5.

The thermally-activated quenching of the copper emission intensity and lifetime can now be understood: at elevated temperatures the electron-hole pairs dissociate (with activation energy \( \Delta E = 20 \text{ meV} \)) and some of the electrons that are released may now recombine non-radiatively or generate ZnSe related luminescence. Because these processes compete with the radiative recombination from the copper ion, the lifetime of the Cu\textsuperscript{2+} related emission decreases, as shown in figure 6.10. This can therefore explain the decrease of the Cu\textsuperscript{2+} emission intensity in the temperature regime where the Cu\textsuperscript{2+} lifetime is reduced. When the electron-hole pair dissociates, the ZnSe related photoluminescence can still occur. As a result, the Cu\textsuperscript{2+} related photoluminescence is expected to quench at lower temperature than the ZnSe related luminescence, which is in agreement with the data shown in figure 6.7. The quenching temperature of the Cu\textsuperscript{2+} related emission can be increased by introducing a deeper electron trap into these ZnSe nanocrystals. As a result, efficiently luminescing ZnSe:Cu nanocrystals at room temperature may be achieved.
6.4 Conclusions

In conclusion, the dependence of the luminescence properties of suspensions and powders of nanocrystalline ZnSe:Cu on the particle size and the sample temperature is described. From measurements on the growth of the nanocrystals two distinct growth ranges are identified. In the first period a concentration driven chemical reaction may explain the observed trend. The data in the second period agree with Ostwald ripening behavior.

Size-dependent measurements show that the color of the Cu$^{2+}$ emission is influenced by quantum confinement effects and can therefore be tuned by varying the size of the nanocrystals. Both the near band edge ZnSe emission and the Cu$^{2+}$ emission shift to shorter wavelengths as the temperature decreases. This temperature dependence is well described by a theory derived for bulk semiconductors. The shift of the Cu$^{2+}$ emission energy only reflects the temperature induced shift of the conduction band edge. The low quenching temperature of the Cu$^{2+}$ emission ($\sim 130$ K) is a serious drawback for potential application of ZnSe:Cu nanocrystals in (electroluminescent) devices. It is possible that the quenching temperature can be increased by incorporating a deeper electron-trap in the ZnSe lattice such as Cl$^{-}$ on Se$^{2-}$ sites.

References