# Nonlinear Optical Properties and Photoluminescence of CuCl Nanocrystals Embedded in Silica Glass

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Linear and nonlinear optical properties of CuCl nanocrystals in silica glass have been studied using low temperature absorption, degenerate four wave mixing (DFWM), and time-resolved photoluminescence spectroscopy. Assuming a spherical shape, effective radius of the CuCl quantum dots was estimated to be 2.5 nm, which is obtained from low temperature absorption data. The DFWM experiment was performed in 380-386 nm wavelength region, and the diffracted signal was measured as a function of wavelength with 1.0 nm interval. Time-resolved photoluminescence measurement was also carried out at 77 K to obtain the time response of CuCl nanocrystals. The experimental results on the large third order nonlinear optical coefficient of CuCl quantum dots are explained in terms of crystal size and oscillator strength of quantum spheres.

## Introduction

Semiconductors embedded in glass exhibit quantum confinement effects, as their crystal dimension is comparable to the bulk exciton diameter.[1~3] Those semiconductor microcrystallites can be prepared in glass by either conventional melting technique[1] or sol-gel processing.[4] The semiconductor doped glass has been widely used as color filter glasses and may have applications in optoelectronic devices due to its large optical nonlinearity. The amorphous glass matrix, in this case, serves as dielectric medium, providing a deep confinement potential in all three directions. If the size of the crystals is small enough to approach the effective Bohr radius, three dimensional confinement occurs in the electronic structure of semiconductor doped glass. In this case, the semiconductor doped glass is called quantum dot (QD) or nanocrystal, as the shape of QD is approximately a sphere and its radius is on the order of nanometer. Since the dimension of QD lies between atomic size and macroscopic bulk crystal, physical properties of QD show unique features, including large nonlinear optical effects in resonant excitation and the enhancement of oscillator strength of quantum confined excitons.[5]

Quantum confinement can be classified by two distinct categories, depending on the ratio of QD radius (R) to the effective bulk exciton Bohr radius ($a_0$). If $R/a_0 \leq 2$, strong confinement occurs and electrons and holes are individually confined, because the confinement energy is greater than Coulomb attraction. If $R/a_0 \geq 4$, weak confinement occurs and the exciton acts as a quasiparticle whose translational motion is quantized. Therefore, nanocrystals lying in this regime behave very differently, depending on their size.[6]

This work concerns the third order optical nonlinearity and time response of weakly confined cuprous chloride (CuCl) nanocrystals embedded in silica glass. Weakly confined CuCl QD has been theoretically known to give a large third order optical nonlinearity, due to its small excition Bohr radius, 0.7 nm and the large exciton binding energy, 0.2 eV.[1] To characterize mesoscopic properites of CuCl QD, the optical properties of CuCl QD were first examined using a linear absorption technique, then third order nonlinear optical coefficients were measured as a function of laser wavelength in the $Z_3$ exciton region. The degenerate four wave mixing technique with two beam configuration was employed. Finally, the steady state photoluminescence spectrum was measured at 77 K and its exciton lifetime was obtained using the time-correlated single photon counting (TCSPC) technique.[7] The third order nonlinear optical coefficient, $\chi^{(3)}$, and the time response of CuCl QD were extracted from the measured data, and comparison with theoretical prediction is made in conjunction with oscillator strength, quantum size, and zero-dimensional nature of the quantum spheres.

## Experimental

The CuCl nanocrystals used in this study were prepared by the standard two-step glass melting procedure.[8] The prepared sample containing CuCl microcrystallites was then subsequently heat treated at 550 ℃ to produce quantum dots having a few nanometer size. The thickness of the polished sample was 250 μm with *ca.* 1% QD volume fraction in the glass. To characterize CuCl quantum dots doped in silica glass, two spectroscopic methods were employed. One is the degenerate four wave mixing (DFWM) method to measure the third order nonlinear optical coefficient and the other is the time-correlated single photon counting (TCSPC) method to measure emission lifetime through photoluminescence detection.

Figure 1 shows the DFWM setup used in this work. The light source consists of a tunable dye laser pumped by 355 nm from a 10 Hz Q-switched Nd : YAG laser. To cover the exciton band region, The 1 : 1 mixture of Exalite 376 and Exalite 384 dyes (Exciton, Inc.) was used. In this condition, the tunable wavelength region from the source was 370-390 nm with a few mJ pulse energy. The wavelength covers the $Z_{1,2}$ and $Z_3$ exciton band region of CuCl quantum dots. The DFWM setup shown in Figure 1 is with two beam configuration and self diffraction occurs due to the third order nonlinear effect. The laser beam from the dye laser was splitted

This paper is dedicated to Professor Woon-Sun Ahn on the occasion of his retirement.

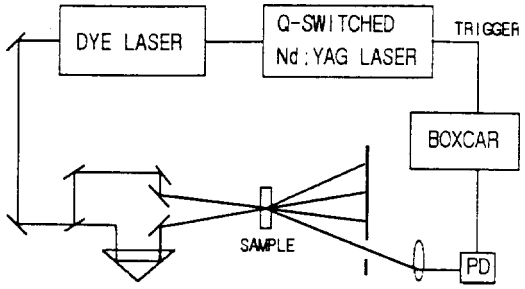


**Figure 1.** Schematic diagram for DFWM setup with two beam configuration.

by a 50/50 beam splitter. Two beams were then noncollinearly overlapped on the sample without focusing. The peak power of the dye laser pulse having 4 mm beam diameter was sufficient for DFWM experiment. In fact, tight focusing with a lens ($f$=20 cm) on the sample resulted in severe thermal damage with 1 mJ pulse energy. The diffracted signal was detected with a photodiode and subsequently sent to a boxcar integrator for signal processing. The wavelength of the dye laser output was calibrated using the third harmonic (355 nm) from the Nd : YAG laser and with a high resolution monochromator.

The steady state photoemission spectrum was measured with a spectrofluorometer and the time-resolved photoluminescence measurement was carried out using a TCSPC system from Edinburgh Instrument (Model 900CD). The TCSPC system uses a $H_2$ discharge lamp, having 40 kHz repetition rate as an excitation source and typically generates the instrument response function of *ca.* 1.0 ns. The excitation wavelength was selected by a 25 cm monochromator and focused on the sample mounted in a liquid nitrogen cryostat.

## Results and Discussion

**Linear Spectroscopic Properties.** Figure 2 is the absorption spectrum of the CuCl-doped glass. The room temperature spectrum (solid curve) shows a broad peak around 370 nm with a shoulder near 380 nm. The 370 nm peak corresponds to $Z_{1,2}$ exciton and the shoulder around 380 nm is attributable to the $Z_3$ exciton absorption. The dotted curve is the measured absorption spectrum of CuCl QD at 77 K, showing a well separated $Z_3$ band from $Z_{1,2}$ exciton band. The absorption maximum of $Z_3$ exciton is located near 381.1 nm, which is 3.6 nm blue shifted from the bulk $Z_3$ exciton peak.

The size of CuCl nanocrystals can be estimated by the following equation, as suggested by Ekimov *et al.*[1,9]

$$\hbar(Z_3)=E_b+K\frac{\hbar^2\pi^2}{2MR^2} \tag{1}$$

where $\hbar\omega(Z_3)$ is the exciton peak energy, $E_b$ is the $Z_3$ exciton energy of the bulk crystal, $M$ is the translational mass of the exciton, $R$ is the effective crystal radius, and $K$ is a numerical coefficient governed by the size distribution of microcrystals. If the distribution of QD is not known exactly, $K$ can be regarded as unity. However, it becomes 0.67, when the dispersion of microcrystallites in the matrix follows Lifshits-Slezov size distribution.[8] The $M$ value for the $Z_3$ exciton

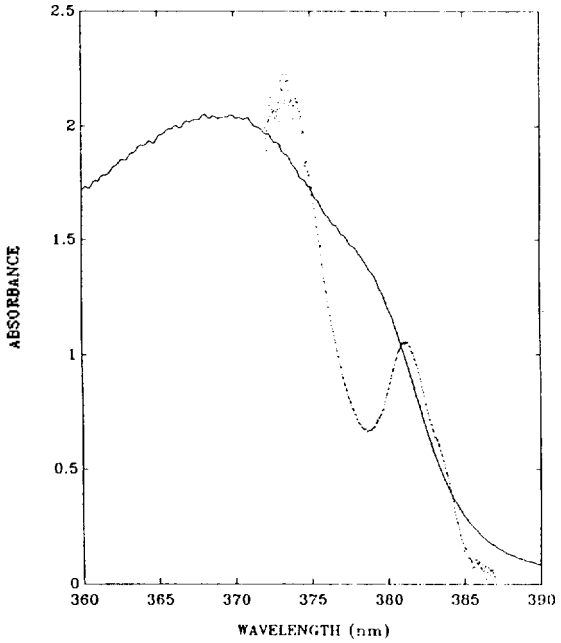


**Figure 2.** Absorption spectra of CuCl QD in silica glass at room temperature (solid curve) and at liquid nitrogen temperature (dotted curve).

was obtained as 1.9 times the electron mass by Ekimov *et al.* Since $E_b$ is known as 384.7 nm for the bulk CuCl crystal at 77 K,[1] the radius of the CuCl quantum dot is calculated as 2.5 nm from the equation. In this calculation, no assumption was made for the size distribution of QD. It should be mentioned that the real microcrystallite radius is larger than the effective radius by $a_0/2$, because of the finite exciton size.[10]

**Nonlinear Optical Properties.** Using DFWM, the diffracted signal, $I_s$, was measured as a function of the laser wavelength and the $\chi^{(3)}$ value was calculated from the following equation.[11]

$$\chi^{(3)}=\frac{n^2c}{32\pi^3}\lambda\frac{\alpha}{(1-T)\ T^{1/2}}\frac{\eta^{1/2}}{I_p} \tag{2}$$

where $n$ is the linear refractive index, $c$ is the light speed in vacuum, $I_p$ is the pump intensity, $\alpha$ is the linear absorption coefficient, and $\eta$ is the diffraction efficiency, equal to $I_s/I_p$. The transmittance, $T$, is the same as $\exp(-\alpha l)$ in which $l$ is the sample thickness. Using the DFWM setup, the diffracted signal intensity was measured as a function of wavelength to cover the $Z_3$ exciton band region. At room temperature, there is no diffracted signal observed at all even at the highest pulse energy, 5 mJ. This pulse energy corresponds to 10 MW/cm$^2$ peak intensity, considering the 4 mm beam diameter of the dye laser output. This peak intensity is too high because it forms a permanent grating in the sample, as illuminated even for a few minutes. So all the DFWM experiment was carried out with attenuated pulse energies down to factor of 30 or more. For low temperature experiment, the sample was loaded in a liquid nitrogen cryostat. At 77 K, the diffracted signal was easily seen with a UV fluorescence card. Using Eq. (2), the $\chi^{(3)}$ values of CuCl quantum dots doped in glass were calculated from the mea-

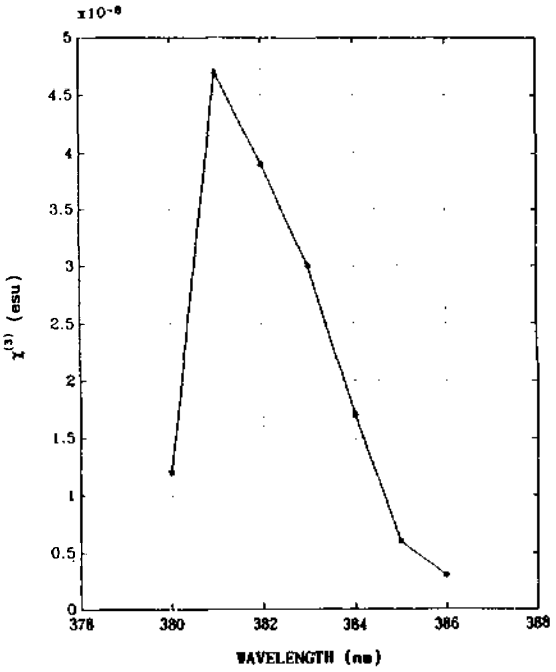


**Figure 3.** The calculated $\chi^{(3)}$ of CuCl nanocrystals, obtained from the measured diffracted signal in glass as a function of laser wavelength.

sured diffraction intensity. Figure 3 shows the values of CuCl quantum dots as a function of laser wavelength. The third order nonlinear optical coefficients of CuCl quantum dots closely resemble the linear absorption spectrum at 77 K. The obtained $\chi^{(3)}$ values are $0.3\text{-}4.7\times10^{-8}$ esu in the 380-386 nm wavelength region. The largest $\chi^{(3)}$ appeared at 381 nm which is the absorption maximum of the linear spectrum at 77 K. This indicates the $\chi^{(3)}$ value of CuCl QD is proportional to oscillator strength in resonant condition.

The nonlinear optical property of CuCl QD in silica glass has been studied by Musumoto *et al.*,[12] and later by Campillo and coworkers,[13] both using the absorption saturation method. They recorded the saturated absorption spectra of CuCl QD at 77 K, and, applying the Kramers-Kronig transformation, obtained the nonlinear refrative index change in the $Z_3$ exciton region. The direct $\chi^{(3)}$ measurement for CuCl QD, using DFWM, was first performed by Nogami *et al.*[4] who prepared the QD sample by sol-gel processing. Our maximum $\chi^{(3)}$, $4.7\times10^{-8}$ esu, is somewhat larger than their reported value ($1.1\times10^{-8}$ esu). However, the direct comparison between the measured $\chi^{(3)}$ values of different samples need some caution, because $\chi^{(3)}$ depends on the QD volume fraction in the matrix.

The $\chi^{(3)}$ values also strongly depends on the QD size. The third order susceptibility of quantum-confined structure is determined by two volume-dependent factors; the enhanced oscillator strength and the interaction between excitons. The enhanced oscillator strength is proportional to $R^3$ at or near resonance. On the other hand, the interaction energy between excitons is inversely proportional to QD volume. Therefore, due to these two counteracting effects, it is anticipated that there should exist an optimum nanocrystal size which exhibits the maximum $\chi^{(3)}$ value.[13] The optimum radius for CuCl QD in silica glass has been predicted to be *ca.* 7 nm.[14] The size of our CuCl QD is smaller than the optimum, so it may be possible to obtain larger $\chi^{(3)}$ values, if the QD size is optimized during preparation.

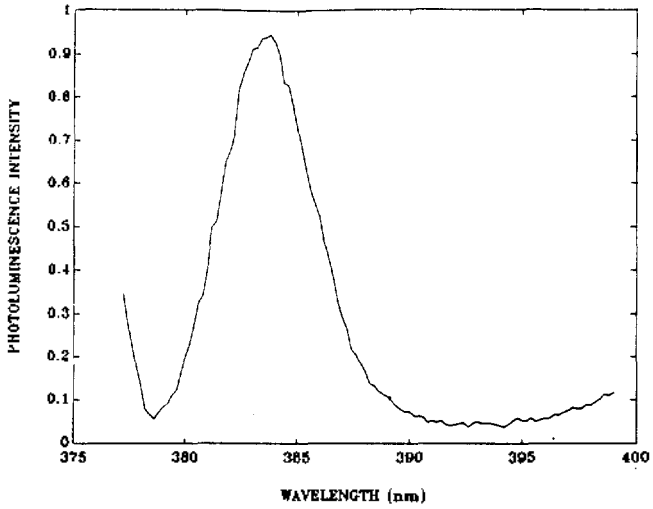


**Figure 4.** Photoluminescence spectra of CuCl QD at 77 K. The excitation wavelength is 370 nm.

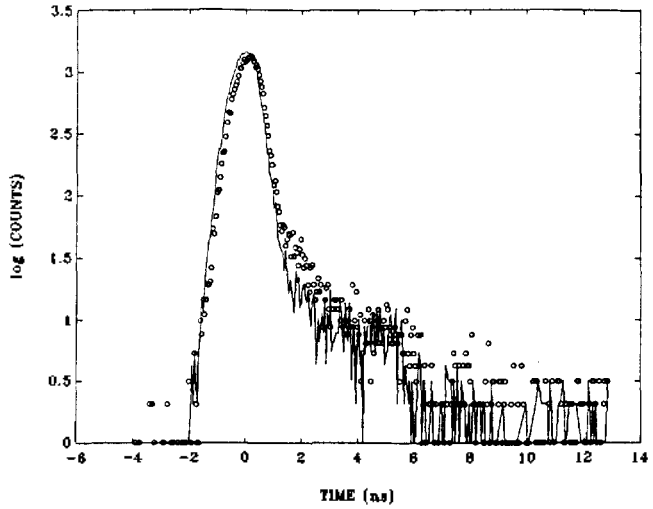


**Figure 5.** The measured luminescence decay profile (open circles) of CuCl nanocrystals embedded in glass. The excitation wavelength and detection wavelength are 370 nm and 384 nm, respectively. The solid curve is the instrument response function obtained by scattering from the excitation beam.

**Photoluminescence and Time Response.** The response time of nonlinear optical materials can be measured either pulsed DFWM or time-resolved photoluminescence spectroscopy.[10,15] The laser pulses used in DFWM experiment is *ca.* 5 ns, which is too broad for the response time measurement for CuCl QD sample. To measure the time response of CuCl QD through photoluminescence, the emission spectra were first recorded using a scanning monochromator and a photon counter. Figure 4 shows the photoluminescence spectra of CuCl QD doped in silica glass at 77 K. The excitation wavelength was chosen as close as the $Z_3$ exciton band.

However, the emission intensity was very weak, so the 370 nm from a xenon lamp light source appears to be the optimum wavelength for sample excitation. To block the excitation beam, a 380 nm cutoff filter was used to record the emission spectra. This may affect the emission spectra in the short wavelength side and make the peak position somewhat unclear. Although the sample was excited at $Z_{1,2}$ exciton band, the photoluminescence occurs in the $Z_3$ exiton state, implying ultrafast relaxation from the $Z_{1,2}$ excition state to the $Z_3$ exciton state.

Figure 5 shows the time profile of the photoluminescence of the CuCl QD doped in glass at 77 K. The excitation wavelength is 370 nm and the detection wavelength is 384 nm respectively. As shown in the figure, the photoluminescence decay curve is very close to the instrument response function (FWHM = 1.0 ns). Therefore, a careful deconvolution procedure was necessary to extract the CuCl QD lifetime. A nonlinear curve fitting procedure gives a single exponential lifetime of *ca.* 200 ps.

However, due to the low emission quantum yield, it was not possible to apply multiexponential fitting procedure. So, the lifetime which we obtained with the 1 ns instrument response function may represent an average lifetime of many decay components, arising from the broad size distribution of quantum dots. It is expected that relaxation of the photoexcited exciton to the ground state is strongly dependent upon the sample temperature, because the lifetime of CuCl QD is in the picosecond regime at 77 K, but no emission was observed at room temperature. It may be interesting if one measure the CuCl QD lifetime as a function of temperature with better time resolution.

## Conclusion

We have measured the third order optical nonlinear coefficient and time response of CuCl quantum dots embedded in silica glass. The radius of CuCl quantum dots was estimated to be 2.5 nm, which was obtained from low temperature absorption data. The $\chi^{(3)}$ values was strongly dependent on the resonant wavelength, ranging from $0.3\times10^{-8}$ esu to $4.7\times10^{-8}$ esu in the 380-386 nm wavelength region. The largest $\chi^{(3)}$ was observed at the peak of absorption maximum, indicating the optical nonlinearity is associated with the oscillator strength. No photoemission was detected from CuCl nanocrystals at room temperature, but weak luminescence was observed upon photoexcitation at 77 K. The $Z_3$ exciton lifetime of the CuCl QD has been measured as about 200 ps. The results indicate that both quantum confinement and temperature strongly affect the decay processes of photoexcited CuCl quantum dots.

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