Optical nonlinearities of excitons in CuCl microcrystals

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Nonlinear optical properties of excitons in CuCl microcrystals in NaCl host crystals were studied by the absorption saturation method. Prominent absorption saturation of excitons was observed together with a blue shift. Optical nonlinearity was found to increase with an increase in the size of the CuCl microcrystals. The observed nonlinearities are very large compared with those in bulk CuCl crystals and GaAs quantum wells.

Recently optical properties of semiconductor microcrystals (quantum dots) have attracted much interest. This is because semiconductor microcrystals are expected to have novel optical properties in a way similar to semiconductor quantum wells. Also, semiconductor microcrystals are expected to have high optical nonlinearity. Therefore, they have a potential for becoming novel optoelectric devices which are useful in optical information processing. In this sense, the search for new materials including semiconductor microcrystals which have a high optical nonlinearity is important. So far, many authors have reported the quantum size effects for excitons in semiconductor microcrystals. Based on the classification made by Ekimov *et al.*, the quantum size effects are classified into two categories: electron or hole confinement and exciton confinement.[1] Hanamura expects high optical nonlinearity for excitons in semiconductor microcrystals where exciton confinement takes place.[2,3] The quantum size effect for excitons in CuCl microcrystals is a typical example of exciton confinement. Therefore, excitons in CuCl microcrystals are expected to give a high $\chi^{(3)}$ (the third-order nonlinear susceptibility). The purpose of this letter is to examine optical nonlinearity as a function of the size of CuCl microcrystals by means of nonlinear absorption, and to examine Hanamura's prediction.

Samples of CuCl microcrystals in NaCl host crystals are grown from high quality, zone-refined CuCl and vacuum-distilled NaCl. The transverse Bridgman method was used for the growth followed by various heat treatments. The heat treatment determines the size distribution of CuCl microcrystals. We determined the size of the CuCl microcrystals by the absorption peak energy of Z_3 excitons at 77 K following the method established by Itoh.[4] The molar fraction of CuCl was determined by the inductively coupled plasma optical emission spectroscopy. The spectroscopy analyzes chemically the concentration ratio of Cu and Na ions. The five samples used in this study are listed in Table I. For the transmission experiments, samples were directly immersed in bubble-free liquid nitrogen. We used an incandescent lamp for the weak-limit absorption experiments and a dye laser pumped by a nitrogen laser (600 kW, 10 ns) for the nonlinear absorption experiments. A dye solution, BBQ in dioxane, was used as the active medium. The pulse duration was 7 ns and the pulse energy was measured by using a pyroelectric energy detector (Gentec, ED100A and ED-X). The size of the excitation spot was measured under a microscope. The transmitted laser light was detected directly by a photomultiplier (Hamamatsu R453) with a calibrated set of neutral density filters. A boxcar integrator was used for averaging.

In the weak-limit absorption spectra, all the samples (1–5) show clear absorption peaks ascribed to Z_3 and $Z_{1,2}$ excitons at 77 K. The absorption peak positions of Z_3 excitons of samples 2, 3, 4, and 5 shift toward higher energies compared with the Z_3 exciton energy of bulk CuCl. Itoh studied both the Z_3 exciton energy and the size of CuCl microcrystals. The size was measured by means of small-angle x-ray scattering. On the basis of his study, the Z_3 exciton energy E_{ex} is best expressed by the formula

$$E_{ex} = E_{ex}(\text{bulk}) + (\pi\hbar)^2/[2M(a + 0.5a_{ex})^2],$$

where E_{ex} (bulk) means the Z_3 exciton energy of bulk CuCl crystals, $M(=2.3m_0)$ is the Z_3 exciton translational mass, a is the average radius of CuCl microcrystals, and a_{ex} ($=0.68$ nm) is the Z_3 exciton Bohr radius. The equation can give values of a from the values of E_{ex}. Thus the average radii of CuCl microcrystals in samples 2, 3, 4, and 5 as determined are shown in Table I. The shift of the Z_3 exciton absorption peak in sample 1 is much smaller than the absorption linewidth, so that the shift is not definitely obtained. Therefore, the radius of CuCl microcrystals in sample 1 is judged to be larger than 10 nm.

In Fig. 1, nonlinear absorption spectra around Z_3 excitons in CuCl microcrystals are shown. The absorption coefficient α is calculated by the formula $\alpha = -\ln(T)/fd$, where f is the volume fraction of CuCl in samples, d is sample thickness, and T is the transmittance of the laser light intensity. The absorption spectra under the lowest density laser exciton almost agree with the weak-limit absorption spectra. With the increase of the excitation density, the absorption peak decreases prominently together with a blue shift. These nonlinear absorption features are similar to those observed in semiconductor quantum wells.[5–8] The excitation intensity

TABLE I. List of samples. d is the sample thickness, f is the volume fraction of CuCl in samples, and E_{ex} is the Z_3 exciton energy at 77 K observed in the absorption spectra. Size means the average radius of CuCl microcrystals.

Sample No.	d(mm)	f(%)	E_{ex} (eV) at 77 K	Size (nm)
1	0.44	0.12	3.219	$\geqslant$10
2	0.34	0.12	3.223	5.7
3	0.60	0.12	3.225	5.0
4	0.55	0.12	3.236	3.3
5	0.52	0.12	3.240	3.0

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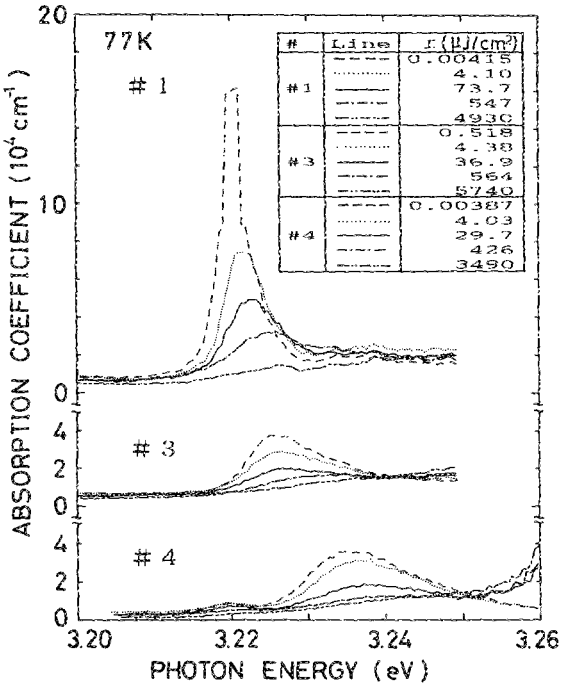

FIG. 1. Nonlinear absorption of Z_3 excitons in CuCl microcrystals in NaCl host crystals (1, 3, and 4). The sample temperature is 77 K. The excitation densities corresponding to various lines are shown in the inset table.

dependence of the absorption intensity is well described by the absorption saturation formula $\alpha = \alpha_1/(1 + I/I_s) + \alpha_2$ (shown in Fig. 2), where α_1 and α_2 are fitting parameters and I and I_s are the laser light density and saturation density, respectively. In Fig. 2, various symbols indicate experimental points and lines least-squares-fitted results. The experimental points are well expressed by the formula except in the highest power density region. The saturation density thus obtained is plotted as a function of the size of the CuCl microcrystals in Fig. 3. Here, the CuCl microcrystals are assumed to be spheres and the size means the radius of the spheres, a.[4] Figure 3 shows that the saturation density decreases with an increase of the size of the microcrystals. The relation between I_s and a is best expressed by $I_s \propto a^{-2.6}$. The saturation density I_s can be related to the third-order nonlinear susceptibility $\chi^{(3)}$, when we consider the low-density excitation limit. The relation is written by

$$\mathrm{Im}\chi^{(3)} = -\frac{\epsilon_0 n_0^2 c^2 \alpha_1 fd(\alpha_1 + \alpha_2)}{\omega I_s\{1 - \exp[-(\alpha_1 + \alpha_2)fd]\}},$$

where ϵ_0 is the dielectric constant in vacuum, n_0 the linear refractive index, and c the light velocity in vacuum.[9] The third-order nonlinear susceptibility $\chi^{(3)}$ increases with the increase of the size of CuCl microcrystals, because it is inversely proportional to I_s. The results almost agree with Hanamura's expectation of the a^3 dependence.

A more detailed analysis for sample 2 is shown in Fig. 4, where we derive the experimental changes in the absorption $\Delta\alpha(\omega)$ and the corresponding refractive index $\Delta n(\omega)$. The

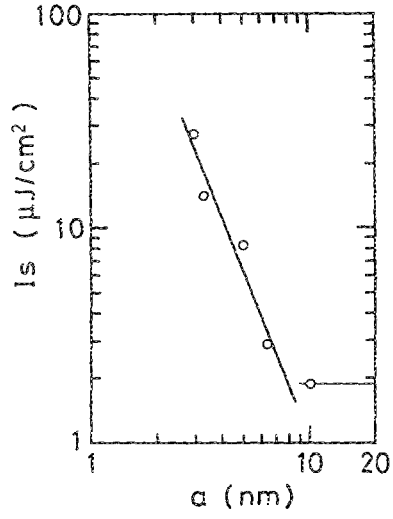

FIG. 3. Saturation density as a function of the average radius a of the CuCl microcrystals. A solid line shows the $a^{-2.6}$ dependence.

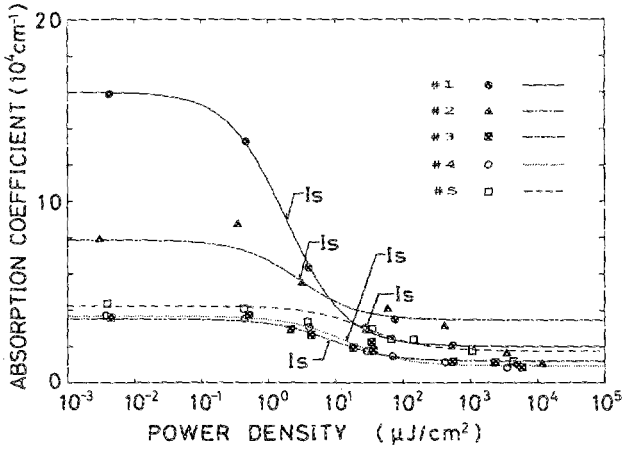

FIG. 2. Absorption coefficient α of Z_3 exciton absorption peak of samples (Nos. 1–5) as a function of laser power density I. Symbols show experimental values. Lines are least-squares fitted results by the equation $\alpha = \alpha_1/(1 + I/I_s) + \alpha_2$, where α_1 and α_2 are fitting parameters. Saturated density is shown by I_s.

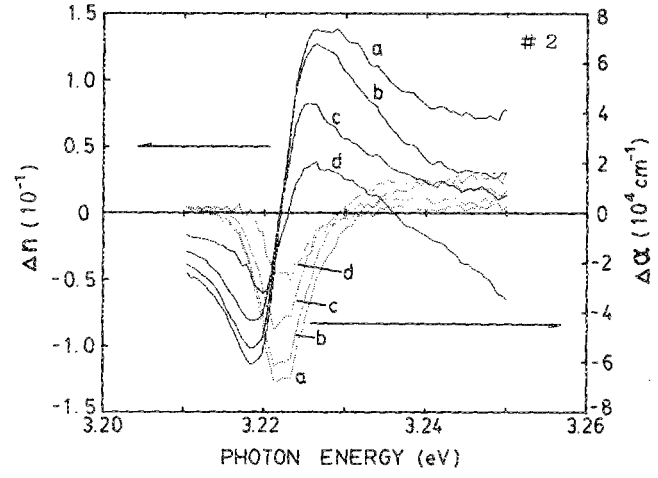

FIG. 4. Absorption change $\Delta\alpha(\omega) = \alpha(\omega, I) - \alpha(\omega, 3.1\times10^{-3}\,\mu\mathrm{J/cm^2})$ and the corresponding refractive index $\Delta n(\omega)$ for sample 2 ($a = 5.7$ nm). Dotted and solid lines show $\Delta\alpha(\omega)$ and $\Delta n(\omega)$, respectively. The excitation densities corresponding to a, b, c, and d are 11 800, 3430, 406, and 3.19 μJ/cm^2, respectively.

change in the refractive index $\Delta n(\omega)$ is obtained by the Kramers–Kronig transformation[10]:

$$\Delta n(\omega) = \frac{c}{\pi} P \int_0^\infty \frac{d\omega' \Delta\alpha(\omega')}{\omega'^2 - \omega^2}.$$

Practically, we used the data of $\alpha(\omega, I) - \alpha(\omega, 3.1\times10^{-3}\,\mu\text{J/cm}^2)$ for $\Delta\alpha(\omega)$. The change in the refractive index $\Delta n(\omega)$ is 4.0×10^{-2} under an excitation density of 3.2 μJ/cm^2 (0.46 kW/cm^2) and increases to 1.4×10^{-1} under an excitation density of 11.8 mJ/cm^2 (1.7 MW/cm^2). The obtained $\Delta n(\omega)$ is larger than that observed in bulk CuCl by two orders of magnitude.[11] Figure 3 indicates that the saturation densities for samples 1 and 2 are 1.9 μJ/cm^2 (270 W/cm^2) and 2.9 μJ/cm^2 (420 W/cm^2), respectively. The saturation density is smaller than that reported in GaAs quantum wells,[7,12] indicating larger optical nonlinearity.

In conclusion, we experimentally demonstrated optical nonlinearity as a function of the size of CuCl microcrystals for the first time. Optical nonlinearity increases with an increase of the size of CuCl microcrystals. The observed nonlinearities are very high compared with those in bulk CuCl crystals and GaAs quantum wells. With a further increase of the size of CuCl microcrystals, a reduction of optical nonlinearity is expected. Testing the validity of this statement is necessary for a complete understanding of the optical nonlinearity due to excitons in CuCl microcrystals and remains to be studied in the future.

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$$\alpha = \alpha_1 + \alpha_2 + \frac{\text{Im}\,\chi^{(3)}\omega I\{1 - \exp[-(\alpha_1 + \alpha_2)fd]\}}{\epsilon_0 n_0^2 c^2 fd(\alpha_1 + \alpha_2)}$$

by expanding Maruani's expression [see IEEE J. Quantum Electron. **18**, 558 (1980)]. Then the I-dependent terms in both expressions are equated.
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