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Polar enhancement of the nonlinear optical properties of Fe_2O_3 microcrystallites

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Abstract

The dependence on surface environment of laser-induced luminescence and the nonlinear optical response of Fe_2O_3 microcrystallites is studied. The luminescence is decreased, the third-order susceptibility enhanced, the excited state relaxation time is decreased and the reverse saturable absorption enhanced. These phenomena are analyzed in terms of the surface effect.

1. Introduction

The size dependence of the nonlinear optical properties of microcrystallites (MC) has attracted considerable attention recently. For MC in such a small regime, a large percentage of atoms is on or near the surface [1]. By modifying this interface by coating the surface with a layer of organic molecular, dodecyl benzene sulfonic acid sodium salt (DBS), we find that we can alter the optical properties greatly. With Fe_2O_3 as example, the laser-induced luminescence intensity decreases by 2 orders of magnitude; the reverse saturable absorption is enhanced; the third-order susceptibility is increased by 2 orders of magnitude and the excited state relaxation time is decreased greatly in a coated Fe_2O_3 MC. We will clarify in this paper how strongly the nonlinear optical response is modified when the surface is coated with a layer of organic molecules.

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2. Surface effect on luminescence and excited state relaxation

2.1. Experimental results

To investigate the luminescence of naked and coated Fe_2O_3 MC, we use 488 nm Ar^+ laser for excitation. Figures 1 and 2 show the luminescence of naked and coated Fe_2O_3 MC with radius of 10 nm. It shows that coating with a layer of DBS decreases the luminescence by 2 orders of magnitude.

To further investigate the optical process of the naked and coated Fe_2O_3 MC, the excited state relaxation time is measured as 9 ps for naked and as

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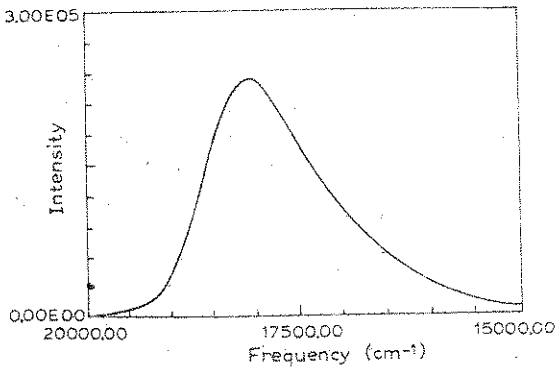

Fig. 1. Laser-induced luminescence of naked Fe_2O_3 microcrystallites.

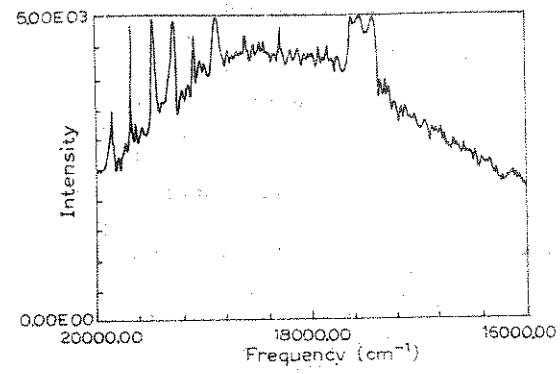

Fig. 2. Laser-induced luminescence of coated Fe_2O_3 microcrystallites.

less than 70 fs for coated Fe_2O_3 MC, using time-delayed four wave mixing with incoherent light. The surface state relaxation time of naked and coated Fe_2O_3 MC is measured in the nanosecond regime using the pump–probe technique with a mode-locked 514.5 nm Ar^+ laser, with a pulse width of 200 ps and repetition rate of 82 MHz.

2.2. Discussion

We will discuss how the luminescence intensity and the excited state relaxation time depend upon the surface environment. The excitons are sometimes trapped at defects on the interface between the MC and the surrounding medium. When the Fe_2O_3 MC is coated with a layer of organic molecules, the molecules could coordinate with the Fe^{3+}, forming a strong coordinate bond. Hence electronic processes can be greatly changed under the strong interaction of the polar field. For materials in the nanometer regime, the excited state relaxation time is mainly determined by the creation and subsequent scattering at the surface of the exciton, and can be described by [2]

$$\tau = R^2/\pi^2 D, \tag{1}$$

where R is the radius of the Fe_2O_3 MC and D is the scattering rate. For naked Fe_2O_3 MC, $R \sim 10$ nm, $D \sim 100\,\mathrm{cm}^2/\mathrm{s}$, $\tau \sim 7$ ps, agreement with our experimental results. For coated Fe_2O_3 MC, the exciton is scattered and trapped at the surface very rapidly by the large polar field of the surface coordinate band, so that nonradiative relaxation is enormously enhanced. This is the reason why the excited state relaxation time decreases greatly, accompanied by a reduction in luminescence.

3. Surface enhancement of $\chi^{(3)}$

3.1. Theoretical analysis of $\chi^{(3)}$

The model of our electronic system to be considered is as follows: a ground state g, a single-exciton state n, and a two-exciton state m. The exciton in n can relax nonradiatively into the trapped state T under the influence of the surface. The trapped electron in T is connected to the higher excited surface state M by a one-photon transition. Effects of the surface and phonon field are taken into account by longitudinal and transverse relaxation rates. The density matrix $\rho(t)$ of the electronic system obeys the following equation of motion [3]:

$$\partial\rho/\partial t = \frac{1}{i\hbar}[H_0 + H', \rho(t)] + [\partial\rho/\partial t]_{\mathrm{relax}}. \tag{2}$$

where H_0 denotes the Hamiltonian of the electronic system and H' describes the interaction between the external field and the electronic dipole moment. Expanding to third order in H' under the rotating

wave approximation, we have the third-order optical susceptibility with a number density N_c as

$$\chi_{ex}^{(3)}(\Omega;\Omega,-\Omega,\Omega)$$

$$= N_c|P_1|^4\left\{\frac{1}{\hbar^3(\Omega-\omega+i\Gamma)^2(\Omega-\omega-i\Gamma)}\right.$$

$$\left.-\frac{1}{\hbar^3(\Omega-\omega+i\Gamma)(\Omega-\omega-i\Gamma)[\Omega-\omega-\omega^{int}+i(\Gamma+2\gamma)]}\right\}$$

$$\times\left\{\frac{2(\gamma+\gamma')}{\gamma}-\frac{(\Omega-\omega-i\Gamma)}{(\Omega-\omega-\omega^{int}+i\Gamma)}\right\}, \quad (3)$$

$$\chi_s^{(3)}(\Omega;\Omega,-\Omega,\Omega)$$

$$=\frac{N_c|P_1|^4\Gamma_{n\to T}\Gamma}{\hbar^3\Gamma_{T\to g}\gamma(\Omega-\omega+i\Gamma)(\Omega-\omega-i\Gamma)}$$

$$-\frac{N_c|P_{TM}|^2|P_1|^2\Gamma_{n\to T}\Gamma}{\hbar^3\Gamma_{T\to g}\gamma[(\Omega-\omega)^2+\Gamma^2](\Omega-\omega_{MT}+i\Gamma_{MT})}. \quad (4)$$

Here $\Gamma=\gamma+\gamma'$ is the transverse relaxation rate, γ' the phase relaxation rate, 2γ the decay rate of the exciton, $\Gamma_{n\to T}$ and $\Gamma_{T\to g}$ the longitudinal decay rates from n to T and from T to g, respectively, Γ_{MT} and P_{MT} the transverse relaxation rate and the dipole moment between T and M, respectively. P_1 is the mesoscopic dipole moment as described in [4]. $\hbar\omega^{int}$ denotes the interaction energy of two excitons. Equation (3) and (4) describe the contributions of the exciton and of the surface, respectively.

3.2. Results and discussion

The absolute value of $\chi^{(3)}$ is found to be $\sim 10^{-11}$ esu for naked and $\sim 10^{-9}$ esu for coated Fe_2O_3 MC by DFWM using a Q-switched YAG laser with frequency doubled 10 ns pulses. Thus the third-order susceptibility is increased by 2 orders of magnitude when coated with a layer of organic molecules. As far as the exciton is considered as an ideal boson, it cannot contribute to the nonlinear optical response. Here, however, three factors make the excitons in MC deviate from an ideal boson: (1) two excitons interact with each other through the repulsive interaction $\hbar\omega^{int}$, (2) the longitudinal decay rate of the exciton 2γ, and (3) the transverse decay rate $\Gamma=\gamma+\gamma'$ with the pure phase constant γ'. In our case, mesoscopic excitonic enhancement contributes little to the enhancement of $\chi^{(3)}$, and the main contribution arises from the effect of the surface. In some cases, the trapped electron has a long decay time. While the electron is in the trapped state, this electron is missing from the ground state and the trapped electron is polarizable to the higher excited surface states. Both of these processes contribute to the third-order optical susceptibility and enhance it by the factor $\Gamma_{n\to T}/\Gamma_{T\to g}$ as described by the first and second terms of Eq. (4). We find that the nonradiative relaxation time is on the order of several picoseconds for naked Fe_2O_3 MC, on the order of several tens of femtoseconds for coated ones, and the trapped state relaxation time is on the order of nanosecond. If these estimates are correct, $\chi^{(3)}$ should be enhanced by a factor of $\Gamma_{n\to T}/\Gamma_{T\to g}\sim 10^3$ for naked Fe_2O_3 MC and $\sim 10^5$ for coated ones: i.e. by 2 orders of magnitude when coated, as observed. These results show that the enhancement mainly arises from the contribution of the surface state. We see that the experimental results are nearly in agreement with the theory. Note that the imaginary part of the second term of Eq. (4) has a sign opposite to that of the first term, implying reverse saturable absorption. For coated Fe_2O_3 MC, more electrons are trapped at the coated surface, and the trapped electrons transit into the higher excited surface state under excitation, which results in enhanced reverse saturable absorption, in agreement with our experiment.

4. Conclusions

We have studied the dependence on surface environment of the laser-induced luminescence and the nonlinear optical responses of Fe_2O_3 microcrystallites. We find that when the Fe_2O_3 MC are coated with a layer of polar organic molecules, laser-induced luminescence is decreased, third-order susceptibility enhanced, excited state relaxation time is decreased, and reverse saturable absorption is enhanced. These results clearly demonstrate the

surface enhancement of the nonlinear optical response of Fe_2O_3 MC.

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