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Polarization dependence of optical Kerr effect in metallophthalocyanine-doped inorganic–organic hybrid materials

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ABSTRACT

Ultrafast optical Kerr effect of metallophthalocyanine-doped inorganic–organic materials was investigated using a femtosecond optical Kerr shutter at wavelength of 800 nm. Experimental results showed that the dependence of the Kerr signals on the polarization angle between the pump beam and the probe beam could be controlled by changing the pump-probe intensity ratio. The pump-intensity dependence of the polarization characters of the Kerr signals probably arose from the contribution of light induced transient grating (LITG) to the Kerr signals.

1. Introduction

Organic nonlinear optical (NLO) materials, which can yield large third-order nonlinearities, ultrafast response time and low optical losses, have been considered as promising candidates for potential application in photonic devices such as high-speed optical switching and optical limiting [1–4]. Of all these organic materials, phthalocyanine (Pc) family is one of the most attractive macrocycle systems for third-order NLO response due to its remarkable chemical and optical properties. The architectural flexibility of Pcs facilitates the tuning of photophysical and optical properties over a very broad range by changing the peripheral substituents and the central metal atom of the macrocycle. Generally, metallophthalocyanines (MPcs) with two-dimensional conjugated π-electrons delocalization exhibit large third-order NLO susceptibility $\chi^{(3)}$ due to the modified chemical and molecular structures [5–8]. Previously, much work has been carried out on MPcs which were incorporated into solution and limited ultrathin films for the applications in photonic devices. However, there is considerable interest in synthesizing bulk optical materials containing MPcs by sol–gel method to increase the laser-materials interaction length for compact-sized optical devices. Sol–gel processing is a significant technique for developing the organic–inorganic hybrid nanocomposites at low temperatures, at which organic molecules may not be decomposed. Thus, the nonresonant-type bulk materials with MPcs synthesized by sol–gel method are expected to have large NLO susceptibilities, ultrafast response time, low optical losses, and long interaction length.

In this paper, we investigated ultrafast optical Kerr effect for several kinds metallophthalocyanine-doped inorganic–organic materials using a femtosecond optical Kerr shutter (OKS) at wavelength of 800 nm. The dependence of Kerr signals on the polarization angle between the pump beam and the probe beam showed that the Kerr signals arose mainly from the photoinduced birefringence effect. We also observed the dependence of the optical Kerr signals on the polarization angle could be controlled by changing the pump power. The pump-intensity dependence of the polarization characters of the Kerr signals probably arose from the contribution of light induced transient grating (LITG) to the Kerr signals.

2. Experiments

Metallophthalocyanine (MPc)-doped inorganic–organic hybrid materials were prepared by hydrolysis condensation of the organically modified precursors vinyltriethoxysilane $H_2C{=}CHSi(OC_2H_5)_3$ (VTES) and 3-aminopropyltriethoxysilane $[NH_2{-}(CH_2)_3{-}Si(OC_2H_5)_3]_3$ (APTES) and vinyltriethoxysilane in ethanol under acid (HCl)-catalyzed hydrolysis and basic-catalyzed condensation. Details of preparation processing were described in the literature [9,10]. The MPc dye was dissolved in DMF (*N*,*N*-dimethyl formamide)/ethanol mixed solvent and sonicated for about one hour and then introduced into sol–gel precursor solution. NiPc/VTES(NiPc), PbPc/VTES(PbPc), CuPc/VTES(CuPc) and C_{60}+APTES+VTES(C_{60}) were employed in our experiments, and the weight concentrations of the MPc dye were 0.048 wt%, 0.06 wt%, 0.08 wt% and 0.12 wt%, respectively. No obvious linear absorption at 800 nm was observed in these materials.

Fig. 1 shows the experimental setup for an OKS configuration. A Ti sapphire laser amplifier operating at 800 nm was employed, which delivered 30-fs pulse with a 1 kHz repetition. The output

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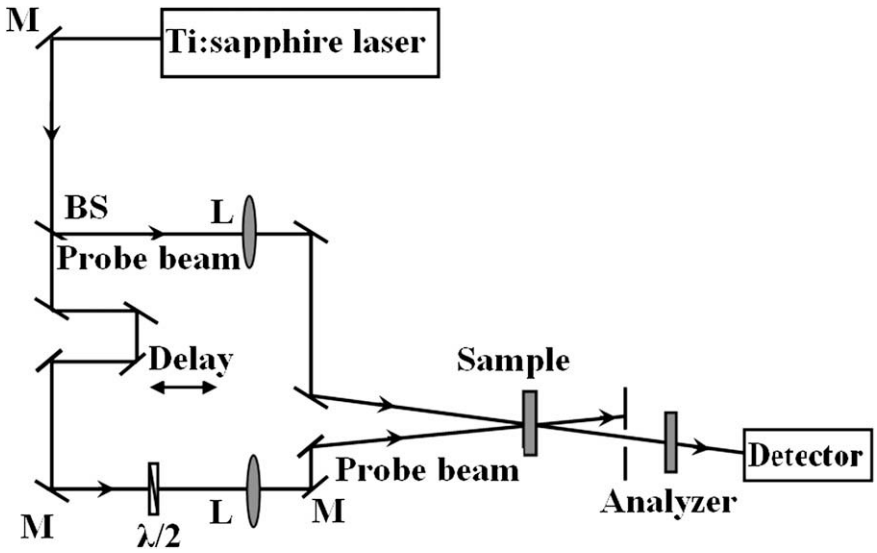

Fig. 1. Experimental setup for OKS using femtosecond laser at 800 nm. BS, beam laser; F, filter; L, lens; and M, mirror.

laser beam was split into a strong pump beam and a weak probe beam. The pump beam passed through a time-delay device and a $\lambda/2$ plate to control the path length and polarization of the beam, respectively. These two beams were focused on the same spot of the sample. The angle between the two beams was about 10.7°. The sample was placed between a polarizer and an analyzer in a cross Nicole polarizer configuration. The polarization of the pump beam was rotated 45° with respect to the polarization of the probe beam, so that the probe beam could not pass the analyzer without the pump beam. The response time of the optical Kerr signals was measured by delaying the pumping beam. The Kerr signals were detected by a photomultiplier tube.

3. Results and discussions

Using the OKS setup, we measured the dependence of optical Kerr signal intensity on delay time between the pump and probe pulses in the MPc-doped glasses and a standard quartz reference sample. The results are showed in Fig. 2. The signal intensities for these materials are normalized by their peak intensities. The solid curve that refers to the quartz reference sample is symmetrical, and the full width at the half-maximum (FWHM) of the time-resolved Kerr signals measured for the quartz sample is about 93 fs indicating that the nonlinearity of quartz arose from electronic processes. From Fig. 2, we can see that the OKS response for all of the PbPc, CuPc, NiPc and C_{60} materials are slower than that of the quartz sample, and the curves have asymmetrical decay tails response, which are estimated to be about 190 fs, 167 fs, 175 fs and 222 fs, respectively. The slow decay probably arose from the population-relaxation process of the excited-states in molecules after the multiphoton induced excitation. This decay is different from the slow response process of CS_2. The inset of Fig. 2 shows the response time of CS_2 and quartz to confirm the results in Fig. 2. The solid curve refers to CS_2 with an asymmetrical decay tail approximately 1.6 ps response originating from the molecular reorientation relaxation process, which was agree well with the previous reports [11].

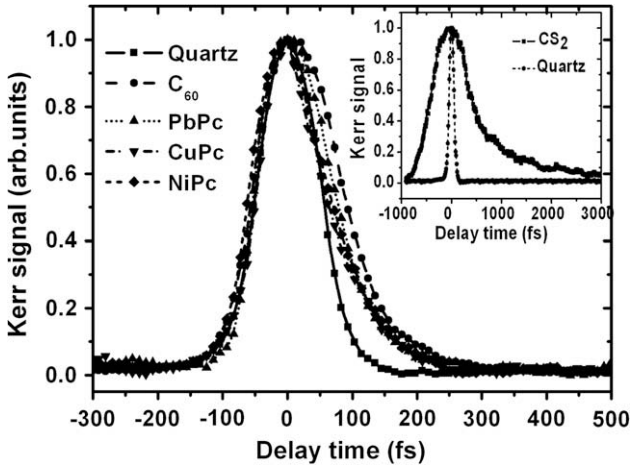

Fig. 2. Time-resolved measurements of the OKS signal intensity for MPc-doped glasses, C_{60}-doped glasses, and quartz. The solid, shot dash, short dot, short dash dot and shot dash refer to quartz, C_{60}, PbPc, CuPc and NiPc, respectively. The inset figure shows the time-resolved OKS singles of CS_2 and quartz.

In OKS experiments using pump and probe beams with equal wavelength, optical Kerr signals usually originate from the self-diffraction effect related to the LITG [12,13] or the photoinduced birefringence effect [14]. The LITG is due to the interference of the pump beam and the probe beam, in which the Kerr signals are dominated from the self-diffraction. Part of the pump beam will be diffracted into the direction of the probe beam by the LITG, and is detected as Kerr signals. Some studies have showed that when 200 fs laser was used, the self-diffraction dominated the Kerr signals [15,16]. In the photoinduced birefringence effect, the pump beam incident on the nonlinear optical materials induces an optical anisotropy in the medium, which can cause a partial depolarization of the probe beam so that part of the probe beam passes through the analyzer and is detected as Kerr signals. In this case, the Kerr signal intensity is given as [13]:

$$I = I_0 \sin^2(2\theta) \sin^2(\Delta\phi/2) \quad (1)$$

where θ is the intersecting polarization angle between the probe and pump beams, $\Delta\varphi$ is the phase shift. $\Delta\varphi$ holds constant, when the pump power is invariable. The Kerr signal intensity I depends on the polarization angle θ, and reaches to its maximum value at 45° and minimum value at 0°. The period is 90°.

To understand the mechanisms of the Kerr signals observed in our experiments, we measured the dependence of the Kerr signal

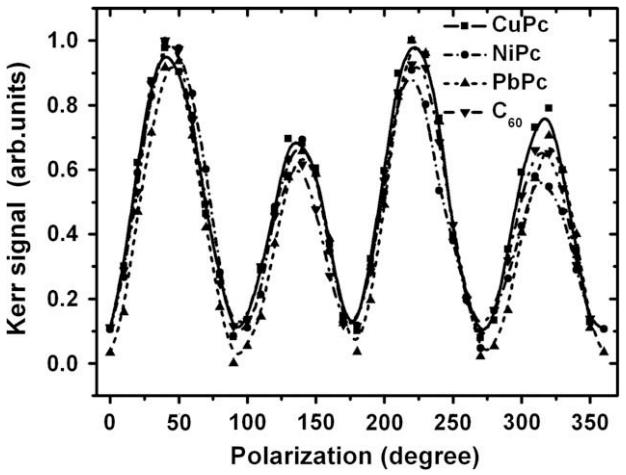

Fig. 3. Dependence of the Kerr signal intensity on the polarization angle between the pump beam and probe beam for the MPc-doped glasses and C_{60}-doped glasses. The intensity ratio of the pump beam to the probe beam was 10:1.

intensity on the polarization angle between the pump beam and probe beam. The pump-probe delay time for all measurements was set at 0 fs. The intensity ratio of the pump beam to the probe beam was 10:1. From Fig. 3, we can see that the polarization angle θ between the two beams should be set at $\pi/4 + n\ \pi/2$ ($n = 0, 1, 2,\ldots$) to attain the maximum probe transmittance, and the period of the relation curve is $\pi/2$. Comparing the results with Eq. (1), we can conclude that the photoinduced birefringence effect was responsible for the Kerr signals of the MPc-doped and C_{60}-doped glasses.

From Fig. 3, we can see that the maximum values of the Kerr signals at the polarization angle of $\pi/4 + n\pi(n = 0, 1, 2,\ldots)$ are different from those of the Kerr signals at $3\pi/4 + n\pi(n = 0, 1, 2,\ldots)$. In order to investigate the cause of this difference, we measured the dependence of the Kerr signal intensity on the polarization angle of PbPc for different intensity ratios of the pump beam to the probe beam. The results are showed in Fig. 4, in which the average power of the probe beam was set at 7.8 mW and only the pump power was changed. From Fig. 4, we can see that when the intensity ratios of the pump beam to the probe beam were increased, the maximum value of the Kerr signals at $\pi/4 + n\pi(n = 0, 1, 2,\ldots)$ decreased while the maximum value at $3\pi/4 + n\pi(n = 0, 1, 2,\ldots)$ increased. When the intensity ratio was changed to 1:1.75, all of the peak values became equal. So, by varying intensity ratio, we were able to control the difference in the peak values of the Kerr signals for the polarization dependence curve. The pump-intensity dependence of the polarization characters of the Kerr signals probably arose from the contribution of LITG to the Kerr signals. As we know, the period of the polarization dependence for LITG is π, with the maximum values of the signals occurring at $n\ \pi(n = 0, 1, 2,\ldots)$, and the minimum values occurring at $\pi/2 + n\pi(n = 0, 1, 2,\ldots)$ [8], which is different from the optical Kerr effect described above. In addition, we have found the contribution of the self-diffraction effect in CS_2 to the Kerr signals increased with increase of the pump intensity [13].

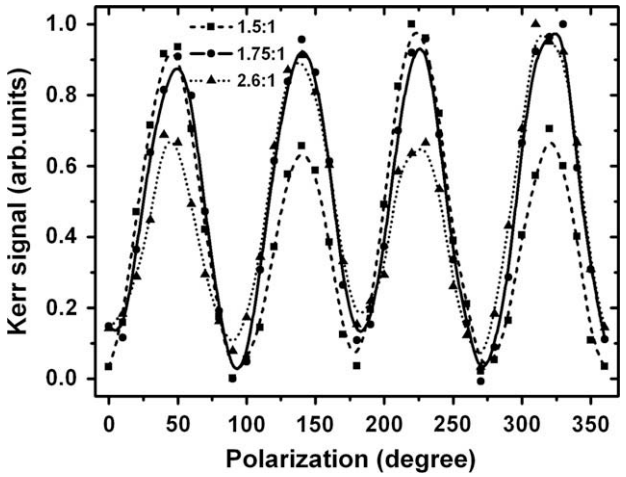

Fig. 4. Dependence of the Kerr signal intensity on the polarization angle between the pump beam and the probe beam for the PbPc-doped glass for different intensity ratios of the probe beam to pump beam.

The pump-intensity dependence of the polarization characters of the Kerr signals may have influence on the measurements of the optical nonlinearities of materials. Therefore, we suggest that a proper pump-probe intensity ratio, which makes all of the peak values equal, should be chosen for measuring the optical nonlinearities of materials by using OKS. If we assume that the probe beam is polarized along x and the pump beam is polarized at 45° to it, then the presence of the pump beam will induce a y component in the probe beam which can be detected after passing the probe beam through a crossed polarization. The photoinduced anisotropy in the susceptibility $\Delta\chi$ is showed as the equation [17]:

$$\Delta\chi^{(3)} = (\chi^{(3)}_{xyxy} + \chi^{(3)}_{xyyx})|E(\omega)|^2 = \chi^{(3)}|E(\omega)|^2 \tag{2}$$

where $\chi^{(3)}$ is the effective third-order susceptibility. χ_{xyxy} and χ_{xyyx} are the tensor component of the $\chi^{(3)}$. $E(\omega)$ is the strength of the light electric field.

The following equation was employed to calculate the third-order nonlinear optical susceptibilities $\chi^{(3)}_R$ of the samples [12]:

$$\chi^{(3)}_S = \chi^{(3)}_R \left(\frac{I_S}{I_R}\right)^{\frac{1}{2}} \left(\frac{n_S}{n_R}\right)^2 \tag{3}$$

where the subscripts of the S and R indicate for the sample and the reference sample of quartz, respectively. I is the OKS signal intensity and n is the refractive index. The nonlinear refractive-index $\chi^{(3)}_R$ of fused quartz was 1.73×10^{-13} esu [18], which was used as a calibration standard. The values of $\chi^{(3)}_S$ for PbPc, CuPc, NiPc and C_{60} were about 2.58×10^{-13} esu, 2.81×10^{-13} esu, 3.29×10^{-13} esu, and 4.56×10^{-13} esu, respectively. In the calculation, the contribution of the matrix to $\chi^{(3)}$ was neglected because it was much smaller than that of the samples in our experiments. It should be indicated that the $\chi^{(3)}$ of the samples is not only from the contribution of the real part of $\chi^{(3)}$ related to the photoinduced birefringence, but also from the contribution of the imaginary part of $\chi^{(3)}$ due to the two-photon absorption at the wavelength of 800 nm.

4. Conclusion

In summary, we investigated the ultrafast nonlinear response of MPc-doped hybrid materials using a femtosecond OKS setup. The experimental results for the dependence of the Kerr signal intensity on the polarization angle between the two incident beams showed that the Kerr signal resulted mainly from photoinduced birefringence effect. We also demonstrated the dependence of the optical Kerr signals on the polarization angle could be controlled by changing the intensity ratio of the pump to the probe beam.

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