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Femtosecond laser-induced birefringence and transient grating in lead(II) phthalocyanine-doped hybrid silica gel glasses

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Abstract

Ultrafast nonlinear optical properties of lead(II) phthalocyanine (PbPc)-doped silica gel glasses were investigated using a femtosecond optical Kerr shutter (OKS) setup at wavelength of 800 nm. The nonlinear response time of the PbPc-doped silica gel glasses was measured to be less than 90 fs. Measurements for the dependence of Kerr signals on the polarization angle between pump and probe beams showed that the Kerr signals induced by 30-fs pulses arose mainly from photoinduced birefringence effect and not from a laser-induced transient grating as observed when using a 200-fs pulse laser.

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 nonlinear optical (NLO) susceptibility $\chi^{(3)}$ due to the modified chemical and molecular structures [5–7]. 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 addition, optical Kerr effects can be used to measure NLO response of materials. When the pump and probe beams with equal wavelength are in optical Kerr shutter

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(OKS) experiments, optical Kerr signals originate from the photoinduced birefringence effect [8] or laser-induced transient gratings (LITG) [9,10], which depends on the NLO mechanism of the materials used in the experiments. Some studies have shown that when a femtosecond laser whose pulse width is about 200 fs is used to OKS experiments for some organic molecular systems [9,10], Kerr signals result mainly from self-diffraction of the pump beam by the LITG. In the process, the interference of the pump and probe beams leads to the transient population gratings, so the temporal behavior of the Kerr signals measured using the OKS setup is the field correlation time of the two pulses between the pump and probe beams, and not the NLO response time of the materials. Therefore, it is difficult to measure the NLO response of materials using the OKS setup described above.

In this paper, we measured the ultrafast nonlinear optical properties of lead phthalocyanine (PbPc)-doped silica gel glasses using a femtosecond optical Kerr shutter (OKS) setup, in which a 30-fs femtosecond laser at wavelength of 800 nm was used. The response time was measured to be less than 90 fs. The measurements for the dependence of Kerr signal intensity on the intersecting angle between the polarization of the pump and probe beams indicated that when a 30-fs pulse laser was used, the Kerr signals resulted mainly from the photoinduced birefringence effect and not resulted from a laser-induced transient grating (LITG) observed when using a 200-fs pulse laser.

2. Experiments

The PbPc-doped bulk material was prepared by hydrolysis condensation of the organically modified precursors vinyltriethoxysilane $H_2C = CHSi(OC_2H_5)_3$ (VTES) in ethanol under acid (HCI)-catalyzed hydrolysis and basic-catalyzed condensation. Details of preparation processing were described in the literature [11]. The PbPc dye was dissolved in DMF (*N*,*N*-dimethyl formamide)/ethanol mixed solvent and sonicated for about 1 h and then introduced into sol–gel precursor solution at different initial concentration of 1.25×10^{-4} mol/l corresponding to 0.06 wt.%. The derived PbPc-doped gel glasses were yellowish and cylindrical transparent materials with 0.6 mm in thickness and 20 mm in diameter. No obvious linear absorption at 800 nm was observed [12].

The femtosecond OKS experimental setup used in the PbPc was shown in Fig. 1. Two Ti:sapphire laser amplifier systems operating at 800 nm were employed separately, which delivered 30-fs pulses at 1 kHz and 200-fs pulses at 200 kHz, respectively. The output laser beam was split into a strong pump beam and a weak probe beam with relative intensities of 10:1. 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. The two beams were focused on the same spot of the sample at an angle of 7.5°. The diameter of the two beams at the sample was about 100 μm. A polarizer was positioned behind the sample in a cross-Nicol configuration, so that the probe beam could not pass through the polarizer without the pump beam. The polarization of the pump beam was rotated 45° by $\lambda/2$ plate from that of the probe beam to optimize the intensity of Kerr signals. The pump pulses induced transient birefringence in the nonlinear sample and caused the polarization change of the probe beam when the two beams overlapped spatially and temporally on the sample. An attenuator was used to vary the pump power in order to obtain the appropriate probe light transmittance. The response time of the OKE was measured by adjusting the time-delay device. The Kerr signals were detected by an optoelectronic diode.

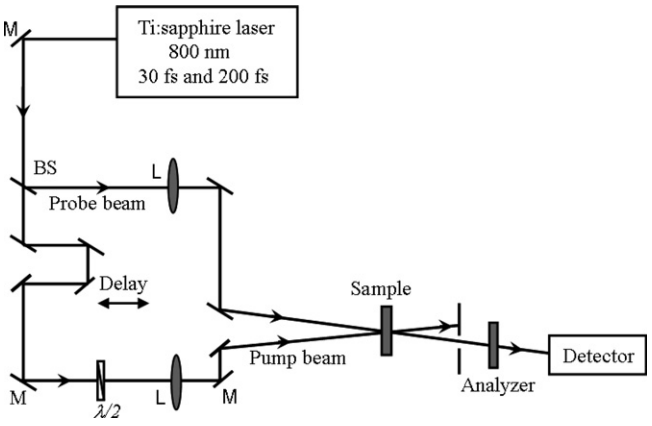

Fig. 1. Experimental setup for OKS using femtosecond laser pulses at 800 nm. BS: beam splitter; F: filter; L: lens; M: mirror.

3. Results and discussion

Using the OKS setup, we measured the dependence of Kerr signal intensity on delay time between the pump and probe pulses in the PbPc-doped gel glass and a standard CS_2 reference sample using 30-fs pulses. The pump power was set at 20 mW. The results are shown in the Fig. 2, in which the autocorrelation measurements of the 30-fs laser pulses is also shown. The liquid CS_2 was situated in a quartz cell with 3.0 mm in thickness. The curve has an asymmetrical decay tail with over 1 ps response originating from the molecular reorientation relaxation processes, which was agreement well with the previous reports [13]. Under the same experimental conditions, the full width at half-maximum of the pulse correlation for the Kerr signals of the PbPc sample was measured to be about 90 fs, corresponding to the laser pulse width of 90 fs at the sample. From Fig. 2, we can see that the OKS response for PbPc consists of two components, an ultrafast response process faster than 85-fs and a slow decay that corresponds to the delay tail of the response curve. The ultrafast response process, which was the dominative contribution to the OKE signals, originated essentially from the purely electronic distortion. The slow decay probably arose from the slow population-relaxation process of the sample after the multiphoton induced excitation. The dependence of Kerr signals on the pump

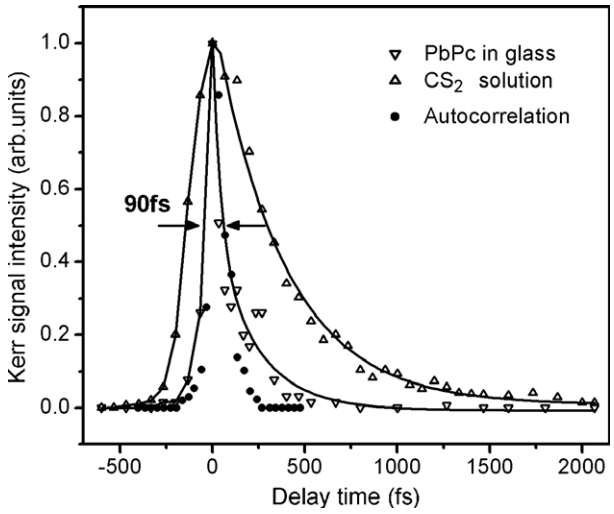

Fig. 2. Time-resolved measurements of the OKE signal intensity in gel glass and CS_2. The signal intensity is normalized by the peak intensity. The solid lines are guides to the eye. The solid circles indicate the autocorrelation measurements of the 30-fs laser pulses.

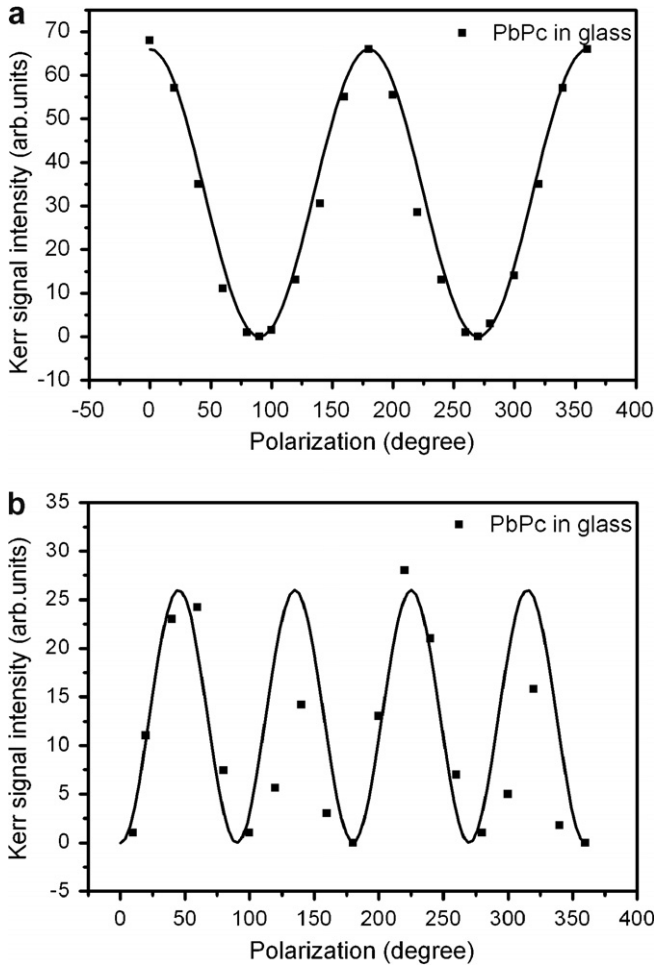

Fig. 3. Dependence of Kerr signal intensity on the pump power.

power was also measured, and the results are given in Fig. 3, from which we can see that the Kerr signals increase with the increase of the pump power.

In OKS experiments using pump and probe beams with equal wavelength, optical Kerr signals usually originate from the photoinduced birefringence effect [8] or the self-diffraction effect related to the LITG [9]. In the photoinduced birefringence effect, the pump beam incident on the NLO materials induces an optical anisotropy in the medium, which can cause a partial depolarization of the probe beam so that the probe beam passes through the analyzer and is detected as Kerr signals. In this case, the Kerr signal intensity is given as [8]:

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

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

In some NLO materials whose optical nonlinearities result from photoinduced excited-state population, the Kerr signals observed in OKS experiments using 200-fs laser result mainly from self-diffraction of the pump beam by the LITG. In the self-diffraction effect [9,10], the LITG related to the population grating is formed due to the interference of the pump and probe beams with equal wavelength. Part of the pump beam will be diffracted into the direction of the probe beam by the LITG, and is detected as Kerr signals. When the intersecting angle θ between polarization of the probe and pump beams is changed, the LITG modulation varies, and reaches to the maximum and minimum values at 0° and 90°, respectively. Therefore the optical Kerr signal intensity is the strongest at 0°, while it is the weakest at 90°. And the period should be 180°.

To understand the mechanisms of the Kerr signals of the PbPc samples observed in our experiments, we measured the dependence of Kerr signal intensity on the polarization angle between the probe and pump beams using 200-fs and 30-fs pulses, respectively. The pump–probe delay time for all measurements was set 0 fs. When the 200-fs pulse laser was used, the pump power was set at 200 mW, and the results are shown in Fig. 4a. From Fig. 4a, we can see that the intersecting polarization angle θ between two beams should be set at $n\pi$ ($n = 0, 1, 2, \ldots$) to attain the maximum probe transmittance, and the period of the curve is π. These results indicate that when the 200-fs pulse laser was used, the LITG generated in the PbPc-doped gel glass was responsible for Kerr signals. Fig. 4b shows the experimental results for the 30-fs pulse laser, in which the pump power was set at 20 mW. From Fig. 4b, we can see that when 30-fs pulse laser was used, the maximum probe transmittance occurred at $\pi/4 + n\pi/2$ ($n = 0, 1, 2, \ldots$), and the period was found to be $\pi/2$. Comparing the results showed in Fig. 4b with Eq. (1), we can conclude that the photoinduced birefringence effect was responsible for Kerr signals of the PbPc sample when the 30-fs pulse laser was used. In order to confirm the results shown in Fig. 4b, the dependence of Kerr signal intensity on the polarization angle

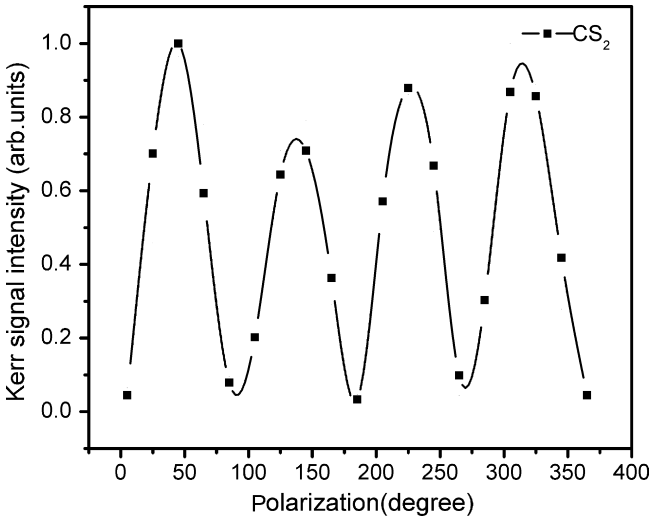

Fig. 4. Dependence of Kerr signal intensity on polarization angle between the pump beam and probe beam for PbPc samples using different femtosecond lasers: (a) for 200-fs pulse laser. (b) for 30-fs pulse laser. The solid lines are guides to the eye.

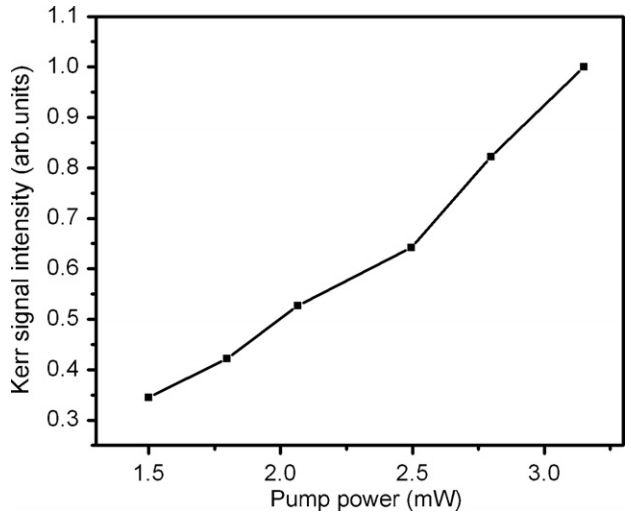

Fig. 5. Dependence of Kerr signal intensity on polarization angle between the pump beam and probe beam for CS_2 using the 30-fs pulse laser. The solid line is guides to the eye.

for the CS_2 sample was measured under the same experimental condition, and the results are shown in Fig. 5. Comparing Fig. 5 with Fig. 4b, one can see that the PbPc sample showed the similar polarization dependence as the CS_2 sample. It is well known that OKS signals of CS_2 originate from the photoinduced birefringence related to the molecular reorientation [13], so these results indicate further that the OKS signals of the PbPc sample for the 30-fs pulse laser resulted mainly from the photoinduced birefringence effect and not from LITG.

Generally, the LITG is due to interference of the two coherent incident femtosecond pulses [14], so the mechanism responsible for Kerr signals should depend on the coherence of the incident femtosecond pulses. As we know, femtosecond lasers have a broad spectrum distribution and the spectrum width increases with the decrease of the pulse width of femtosecond lasers, so the time-coherence of 30-fs pulses were much worse than that of 200-fs pulses. In order to explain the dependence of the LITG on the coherence of femtosecond lasers, we made numerical simulation of the interference modulation degree of the 30-fs and 200-fs femtosecond laser pulses, respectively. The results are shown in Fig. 6a and b, where the x-axis indicates the cross-section of the pump and probe beams. In the simulation, the spectrum widths for the 30-fs and 200-fs pulse lasers are chosen as 40 nm and 6 nm, respectively, and both central wavelengths are chosen as 800 nm. From Fig. 6a and b, it can be seen that when 30-fs laser pulses are used the modulation degree decreases with deviating from $x = 0$, the central position of the cross-section of the two incident beams. The interference of 200-fs pulses shows nearly the same modulation degree in the cross area of the two incident beams. Therefore, when the 30-fs pulse laser was used the modulation of the

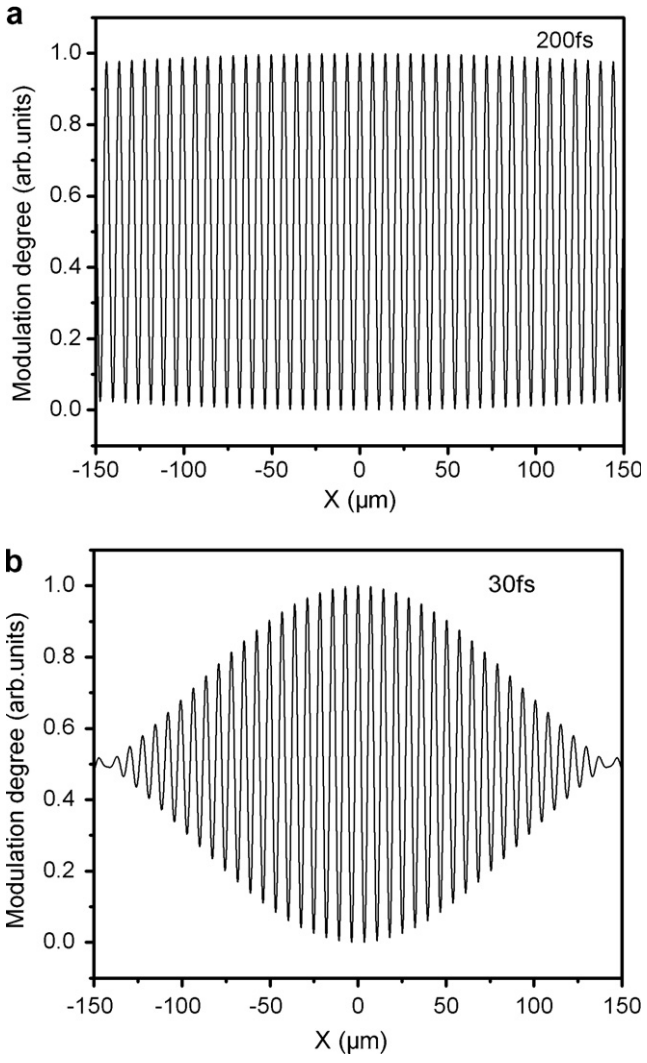

Fig. 6. The numerical simulation of the interference modulation degree of femtosecond laser pulses: (a) for 200-fs pulse laser (b) for 30-fs pulse laser. The x-axis indicates the cross-section of the pump and probe beams.

LITG generated by the interference of the pump and probe beams was much weaker than that of the LITG generated by the 200-fs pulse laser, and the contribution of the photoinduced birefringence effect to the Kerr signals became dominant.

4. Conclusion

We investigated the ultrafast nonlinear optical properties of the PbPc-doped silica gel glasses using a femtosecond OKS setup at 800 nm. The NLO response time for the fast component was measured to be less than 90 fs. The experimental results for the dependence of Kerr signal intensity on the polarization angle between two incident beams showed that the OKS signals for 30-fs pulse and 200-fs pulse lasers resulted from photoinduced birefringence effect and LIGT, respectively. This may help us understand the photoinduced transient behavior in the NLO materials by femtosecond lasers with different pulse widths.

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