

# Third-order optical nonlinearities for lanthanum (Ⅲ) complexes with 1, 10-phenanthroline components

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**Abstract** The nonlinear refractive indexes  $n_2$  for the ethanol solutions of 1, 10-phenanthroline ( $2.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ), [bis(1, 10-phenanthroline) lanthanum (Ⅲ)] nitrate ( $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ), and [nitrato-fluoracil-bis(1, 10-phenanthroline) lanthanum (Ⅲ)] nitrate ( $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ) are first measured, the third-order nonlinear optical susceptibilities  $\chi^{(3)}$  and  $\langle \gamma \rangle$  are calculated, and the mechanisms of the third-order optical nonlinearities enhanced by lanthanum (Ⅲ) are discussed preliminarily.

**Keywords:** Z-scan, third-order optical nonlinearity, lanthanum (Ⅲ), 1, 10-phenanthroline.

DURING the past decades, there have been a large number of researches about the third-order optical nonlinearities of the organic polymer with a delocalized  $\pi$ -conjugated system for their possible nonlinear optical applications in view of their large and ultra-fast nonlinear optical temporal response<sup>[1]</sup>. Recently, a series of delocalized  $\pi$ -conjugated metal-coordinated molecules have been attracting a great deal of attention for their relatively large third-order nonlinear optical susceptibilities, in which there is not only a relatively largely delocalized  $\pi$ -conjugated system to offer large third-order nonlinear optical susceptibilities, but also the coordinated metal ion to enhance their third-order optical nonlinearities<sup>[1, 2]</sup>.

Rare earth metal ion with relatively high positive charges and abundant electron energy levels (especially d and f electron orbits), may be coordinated to the organic ligand with delocalized  $\pi$ -conjugated system. It will influence the electron structure of the ligand and the electron orbits will also be split into more electron energy states due to the ligand field<sup>[3]</sup>. Therefore the third-order optical nonlinearities of the material will be enhanced. Up to now, the researches have been focused on the metal-coordinated complexes with phthalocyanine or porphyrine components which have large two-dimensional  $\pi$ -conjugated system, and their third-order nonlinear optical susceptibilities, but lacking for the mechanisms of the third-order optical nonlinearities.

In this note, a series of lanthanum (Ⅲ) complexes with two-dimensional  $\pi$ -conjugated 1, 10-phenanthroline components were synthesized, the third-order optical nonlinearities were first measured by Z-scan technique, and the mechanisms of the third-order optical nonlinearities enhanced by lanthanum (Ⅲ) were discussed.

## 1 Experimental procedure and principle

According to ref. [4], [bis(1, 10-phenanthroline) lanthanum (Ⅲ)] nitrate and [nitrato-fluoracil-bis(1, 10-phenanthroline) lanthanum (Ⅲ)] nitrate were synthesized and purified by recrystallization. The pure samples were confirmed by elementary analysis and IR spectroscopic analysis, and their ethanol solutions ( $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ) were prepared for measuring the absorption spectra in the visible and ultraviolet regions and the normalized Z-scan transmittances respectively.

A Gaussian pulse laser beam (wavelength 532 nm, pulse width 35 ps and peak irradiance  $20 \text{ GW}/\text{cm}^2$ ) from a frequency-doubled Nd:YAG laser as depicted in fig. 1 is focused on a 2-mm sample cell. According to the principle of the nonlinear optics, the refractive index  $n$  of the medium can be expressed as  $n = n_0 + n_2 I(t)$ , where  $n_0$  is the linear refractive index;  $n_2$  the nonlinear refractive index, and  $I(t)$  denotes the irradiance of the laser beam. This means that the nonlinear medium can be regarded as a thin lens of variable focal length with the variable irradiance. Thereby, as the sample is moved in the  $z$  direction from prefocus to postfocus, the transmittance of the nonlinear medium through a finite aperture in the far field changes as a function of the sample position  $z$  with respect to the focal plane. A prefocal transmittance maximum (peak) followed by a postfocal transmittance minimum (valley) is, therefore, the Z-scan signature of a negative refractive nonlinearity, and positive nonlinear refraction gives rise to an opposite valley-peak configuration.

Assuming that no linear and nonlinear absorptions (such as multiphoton or saturation absorption) are present, and the conditions that the on-axis phase shift at the focus  $|\Delta\Phi_0(t)| \ll 1$ , the aperture linear transmittance  $S \ll 1$  and the far-field condition for the aperture plane are satisfied, and ignoring Fresnel reflection losses, by a Taylor series expansion and the other mathematical treatment, the normalized Z-scan transmittance through a finite aperture in the far-field as a function of the sample position  $z$  with respect to the focal plane can be written as<sup>[5]</sup>

$$T(z, \Delta\Phi_0(t)) = 1 + \frac{4 \cdot \langle \Delta\Phi_0(t) \rangle \cdot x}{(x^2 + 1) \cdot (x^2 + 9)}, \tag{1}$$

where  $x = \frac{z}{z_0}$ ,  $z$  is the sample position with respect to the focal plane, and  $z_0$  the diffraction length of the laser beam.

The difference between the peak and valley of the normalized Z-scan transmittance can be calculated by solving equation  $dT(z, \Delta\Phi_0(t))/dz$ . Thus

$$\Delta T_{p-v} \approx 0.406 \langle \Delta\Phi_0(t) \rangle = 0.287 n_2 k L I_0(t), \tag{2}$$

where  $\langle \Delta\Phi_0(t) \rangle$  is the time-averaged on-axis phase shift at the focus,  $k$  is the wave vector,  $L$  the sample length, and  $I_0(t)$  is the on-axis irradiance at focus. Therefore,

$$n_2 \approx \frac{\Delta T_{p-v}}{0.287 k L I_0(t)}. \tag{3}$$

Only considering the third-order optical nonlinearities, the third-order macroscopic susceptibility can be written by

$$\chi^{(3)}(\text{esu}) = \frac{c n_0^2 n_2 (\text{cm}^2/\text{W})}{12\pi}. \tag{4}$$

The second hyperpolarizability  $\langle \gamma \rangle$  of a molecule in isotropic media is related to the third-order macroscopic susceptibility:

$$\langle \gamma \rangle = \frac{\chi^{(3)}}{L^4 N}, \tag{5}$$

where  $N$  is the number density of molecules per mL, and  $L^4$  is the local field correction factor given by  $L^4 = [(n_0^2 + 2)/3]^4$ .

2 Results and discussion

The ethanol solutions of 1,10-phenanthroline ( $2.0 \times 10^{-3}$ ), [bis(1,10-phenanthroline) lanthanum (III)] nitrate ( $1.0 \times 10^{-3}$ ), and [nitrato-fluoracil-bis(1,10-phenanthroline) lanthanum (III)] nitrate ( $1.0 \times 10^{-3}$ ) have absorption bands in the ultraviolet region of the spectrum, but no absorption bands in the visible region. Using a 532 nm, 35 ps Gaussian laser beam, we measured respectively the transmittances of the solutions through a finite aperture in the far-field as a function of the sample position  $z$  with respect to the focal plane. The normalized experimental data (open dots) and the calculated curves (solid lines) by formula (1) are shown in fig.2, and the calculated results for the third-order optical parameters of lanthanum (III) coordinated complexes with 1,10-phenanthroline components are listed in table 1.

Table 1 The third-order nonlinear optical parameters for lanthanum (III) complexes with 1,10-phenanthroline components				
Sample	$\langle \Delta\Phi_0(t) \rangle$	$n_2/\text{cm}^2 \cdot \text{W}^{-1}$	$\chi^{(3)}(\text{esu})$	$\langle \gamma \rangle(\text{esu})$
1,10-phenanthroline ( $2.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ )	0.13	$3.9 \times 10^{-16}$	$1.8 \times 10^{-14}$	$5.5 \times 10^{-33}$
[La(phen) <sub>2</sub> ](NO <sub>3</sub> ) <sub>3</sub> ( $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ )	0.30	$9.0 \times 10^{-16}$	$4.2 \times 10^{-14}$	$2.6 \times 10^{-32}$
[La(phen) <sub>2</sub> Fu(NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub> ( $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ )	0.35	$1.0 \times 10^{-15}$	$4.9 \times 10^{-14}$	$3.0 \times 10^{-32}$

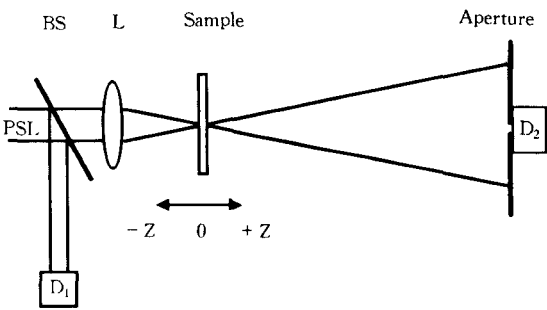


Fig. 1. Z-scan experimental setup. PSL, ps pulse laser; BS, beam splitter; L, lens; D<sub>1</sub>, D<sub>2</sub>, detectors.

Figure 2 and table 1 show that the third-order nonlinear optical susceptibility increases in turn from 1, 10-phenanthroline to [bis(1, 10-phenanthroline) lanthanum (III)] nitrate to [nitrato-fluoracil-bis(1, 10-phenanthroline) lanthanum (III)] nitrate. Among them, 1, 10-phenanthroline has relatively large third-order optical nonlinearity. As rare earth metal ion  $\text{La}^{3+}$  coordinated with 1, 10-phenanthroline, the two dimensional  $\pi$  conjugated electron system may be distorted by the positive charges of lanthanum (III), and two 1, 10-phenanthroline in a complex may be coupled. Moreover, the interaction between the singlet states and the multiplet states may also be enhanced. Therefore it results in the enhancement of the third-order optical nonlinearities. Thus, the third-order nonlinear optical susceptibilities of [bis(1, 10-phenanthroline) lanthanum (III)] nitrate and [nitrato-fluoracil-bis(1, 10-phenanthroline) lanthanum (III)] nitrate are larger than that of 1, 10-phenanthroline. Besides, due to the ligand field, the electron energy levels of lanthanum(III), especially d and f electron orbits, may be split into more mixed energy states for one-photon and multi-photon allowed transitions. The larger and more complicated the ligand field is, the more complicated the produced energy states are, which may enhance one-photon-off-resonance and two-photon-near-resonance for the third-order optical nonlinearities. In [nitrato-fluoracil-bis(1, 10-phenanthroline) lanthanum (III)] nitrate, lanthanum (III) is coordinated with not only 1, 10-phenanthroline, but also with nitrate and fluoracil. So the third-order nonlinear optical susceptibility of [nitrato-fluoracil-bis(1, 10-phenanthroline) lanthanum (III)] nitrate is slightly larger than that of [bis(1, 10-phenanthroline) lanthanum (III)] nitrate.

According to the above results and discussion, it is confirmed that lanthanum (III) may effectively enhance the third-order optical nonlinearities of 1, 10-phenanthroline, the new type of rare-earth-metal-coordinated  $\pi$ -conjugated compounds may open the way for nonlinear optics applications.

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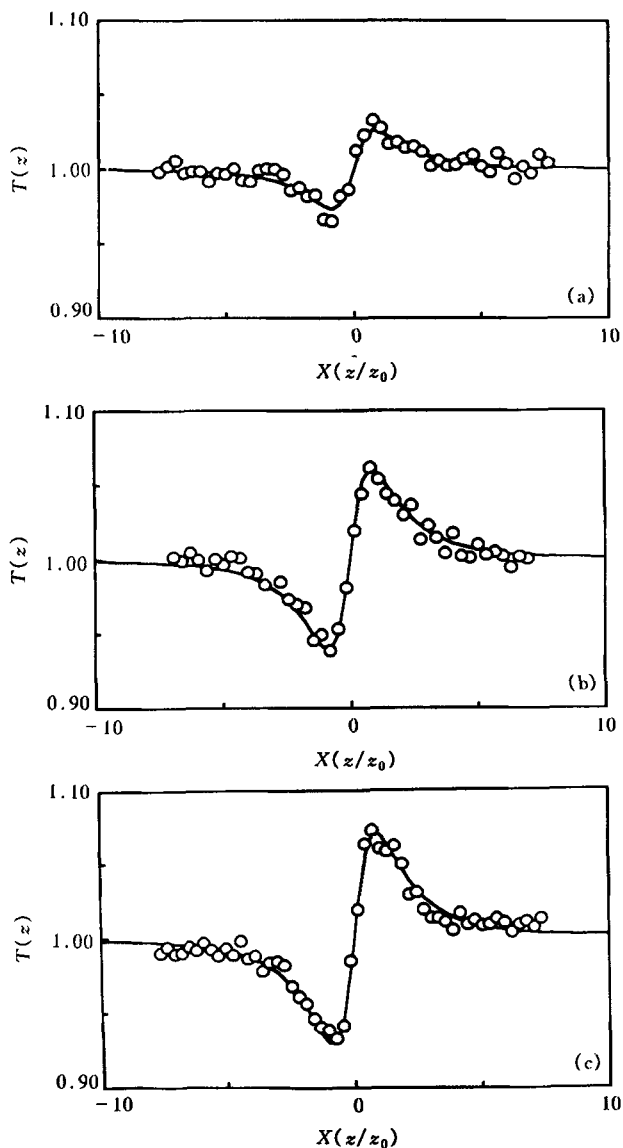


Fig. 2. Measured Z-scan of a 2-mm thick ethanol solution for the lanthanum (III) complexes with 1, 10-phenanthroline components ( $\circ$ ), and the calculated results with formula (1) (—). (a) The ethanol solution of 1, 10-phenanthroline ( $2.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ); (b) the ethanol solution of [bis(1, 10-phenanthroline) lanthanum (III)] nitrate ( $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ); (c) the ethanol solution of [nitrato-fluoracil-bis(1, 10-phenanthroline) lanthanum (III)] nitrate ( $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ).

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## Anisotropic propagation of flare-induced shocks

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**Abstract** It is demonstrated that the fastest propagation direction of a flare-induced shock deviates eastwards by about  $4^\circ$  at 1 AU relative to the flare normal if the shock introduced at 0.1 AU propagates along the local magnetic field, whereas it deviates westwards by about  $1^\circ$  if the introduced shock propagates in the radial direction instead.

**Keywords:** solar flare, MHD shock, interplanetary dynamics.

INTERPRETATION of spaceborne observations and interplanetary scintillation data shows that the fastest propagation direction of flare-induced shocks deviates from the flare normal, being to the east in the equatorial plane and drifting towards the heliospheric current sheet in the meridional plane<sup>[1,2]</sup>. Such a propagation asymmetry still survives even if the convection effect of the ambient solar wind is deducted<sup>[3]</sup>. However, previous simulation studies of flare-induced shocks in the equatorial plane created the fastest propagation direction of these shocks which was almost parallel to the flare normal<sup>[4]</sup>, in conflict with observations. This note will demonstrate that the eastward deviation of the fastest propagation direction may be obtained if the manner of introducing shock disturbances at the lower boundary is properly modified.

Since the source of a solar flare rotates with the Sun, it is convenient to adopt the corotating coordinate system. In this system, the ideal MHD equations for two-dimensional planar flows are as follows:

$$\frac{\partial \rho}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \rho v_r) + \frac{\partial}{\partial \varphi} (\rho v_\varphi) = 0, \quad (1)$$

$$\begin{aligned} \frac{\partial}{\partial t} (\rho v_r) + \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \left( p^* + \rho v_r^2 - \frac{B_r^2}{\mu} \right) \right] + \frac{1}{r} \frac{\partial}{\partial \varphi} \left( \rho v_r v_\varphi - \frac{B_r B_\varphi}{\mu} \right) \\ = \frac{1}{r} \left( 2p^* + \rho v_\varphi^2 - \frac{B_\varphi^2}{\mu} - \frac{\rho GM}{r} \right) + \rho \Omega^2 r + 2\rho \Omega v_\varphi, \end{aligned} \quad (2)$$

$$\begin{aligned} \frac{\partial}{\partial t} (\rho v_\varphi) + \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \left( \rho v_r v_\varphi - \frac{B_r B_\varphi}{\mu} \right) \right] + \frac{1}{r} \frac{\partial}{\partial \varphi} \left( p^* + \rho v_\varphi^2 - \frac{B_\varphi^2}{\mu} \right) \\ = \frac{1}{r} \left( \frac{B_r B_\varphi}{\mu} - \rho v_r v_\varphi \right) - 2\rho \Omega v_r, \end{aligned} \quad (3)$$

$$\frac{\partial B_r}{\partial t} + \frac{1}{r} \frac{\partial}{\partial \varphi} (v_\varphi B_r - v_r B_\varphi) = 0, \quad (4)$$

$$\frac{\partial B_\varphi}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} [r(v_r B_\varphi - v_\varphi B_r)] = 0, \quad (5)$$

$$\begin{aligned} \frac{\partial E}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 (E + p^*) v_r - \frac{r^2 B_r}{\mu} (v_r B_r + v_\varphi B_\varphi) \right] \\ + \frac{1}{r} \frac{\partial}{\partial \varphi} \left[ (E + p^*) v_\varphi - \frac{B_\varphi}{\mu} (v_r B_r + v_\varphi B_\varphi) \right] = \rho v_r \left( \Omega^2 r - \frac{GM}{r^2} \right), \end{aligned} \quad (6)$$