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# Determinations of the transient thermal lensing effect in metal cluster Polymer $\{WS_4Cu_4I_2(bpe)_3\}_n$ solution by the use of the Z-scan

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ABSTRACT

The nonlinear optical (NLO) properties of a novel cluster Polymer $\{WS_4Cu_4I_2(bpe)_3\}_n$ solution are studied by using Z-scan technique with laser pulses of 4.5 ns pulse-width at a wavelength of 532 nm. The results show that the cluster solution possesses strong nonlinear absorption and refraction. Nonlinear refraction of the cluster is composed of third-order nonlinear refraction and transient thermal effect. The thermal effect is mainly due to the strong nonlinear absorption. Numerical simulations obtained by solving simultaneously photo-acoustic and electromagnetic wave equations, agrees basically with experimental results.



## 1. Introduction

Materials that possess nonlinear optical (NLO) properties have been investigated extensively for their potential applications in optical fibers, data storage, optical computing, optical switching, and optical limiting [1–3]. Recently, metal clusters [4–8] have received much attention and been demonstrated to be a new kind of the excellent optical limiting (OL) molecule. Such metal clusters can have various kinds of architectures, which may change or enhance the optical nonlinearities and thus can be optimized for each photonic application. The heterothiometallic W(Mo)/Cu/S clusters have been widely studied due to their excellent third-order NLO properties during the last decade. In the previously reported clusters, few flexible ligands were chosen to construct Mo(W)/Cu/S cluster-based compounds and only four similar polymers was synthesized [9].

Thermally induced refractive index changes caused by the absorption of light in a material have been repaid attention recently because of their potential applications in optical limiters in different time scale [10–20]. Brochard et al. [13] have reported the experimental and theoretical study of thermal effect in the transient regime using a 5 ns pulse laser and Z-scan technique. But they considered the thermally induced nonlinear refraction which only caused by linear absorption. There is almost no experimental data and theory reported on thermal refractive nonlinearity induced by nonlinear absorption in several ns laser pulses because of the complicated model. For the theoretical investigation of thermally induced refractive index change, Kovsh et al. [13,14] developed a numerical modeling of thermal refraction by solving simultaneously acoustic and electromagnetic wave equations. With the rapid development of low-cost computer technology, numerical modeling of pulsed laser beam propagation through nonlinear optical materials is becoming a powerful tool to investigate the interaction of light with matter [14–19].

In this letter, the NLO properties of a novel cluster compounds, $\{WS_4Cu_4I_2(bpe)_3\}_n$, is investigated by using Z-scan technique [21] with nanosecond pulse. Experimental results show that the cluster solution exhibits strong nonlinear absorption and nonlinear refraction under nanosecond pulse excitation. We mainly investigate the thermal effect caused by the strong nonlinear absorption by the nanosecond Z-Scan experiment. Numerical simulations obtained by solving simultaneously photo-acoustic and electromagnetic wave equations. The result of theoretical simulation is in good agreement with the experimental result of $\{WS_4Cu_4I_2(bpe)_3\}_n$ solution.

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## 2. Sample preparation and experiment

Synthesis of compound $\{WS_4Cu_4I_2(bpe)_3\}_n$: a well-ground mixture of $[NH_4]_2[WS_4]$ (0.5 mmol), CuI (2.0 mmol) and 1,2-bis(4-pyridyl)ethane (2 mmol) was added to a mixture of DMF and $CH_3CN$ (15 mL; v/v 2:1) under a purified nitrogen atmosphere. After stirring for 10 h, the filtrate was layered with diethyl ether. Red block-shaped single crystals suitable for X-ray diffraction were obtained several days later in 22%. Compound crystallizes in tetragonal space group *P*4(2). Compound consists of the saddle-shaped $[WS_4Cu_4I_2]$ SBUs. Each SBU of the compound is bound by six nitrogen atoms from six bridging 1,2-bis(4-pyridyl)ethane (bpe) ligands and two iodine atoms. The five metal atoms are nearly coplanar. The four Cu(I) centers in the SBU are linked by six bpe ligands in a trans conformation and form a 2D layer network. The chemical details of the cluster Polymer $\{WS_4Cu_4I_2(bpe)_3\}_n$ will be reported elsewhere.

The NLO of the cluster in DMF solution is measured with a Nd: YAG laser (Continuum), which produces 4.5 ns laser pluses at 532 nm with a repetition rate of 1 HZ, by the Z-scan method. The spatial distribution of the pulse is nearly a Gaussian profile. The pulse energy is about 68 uJ. The sample solution is placed in quartz cells of 2 mm thickness. The quartz cells with these three samples were placed on a translation stage controlled by a computer that moved the sample along the z-axis with respect to the focal point of a 400 mm focal lens .the beam waist radius in the focal plane was about 25 μm. The transmittance of the samples is measured with and without an aperture in the far-field. The linear transmittance of the aperture is 0.13. The laser pulses adjusted by an attenuator are separated into two beams by using a splitter. The two beams were simultaneously measured by using two energy detectors (Rjp-735 energy probe) linked to energy meter (Rj-7620 Energy Ratiometer, Laserprobe Corp.). A personal computer is used to collect and process data coming from energy meter through IEEE-488 interface.

## 3. Results and discussion

Fig. 1 shows the Z-scan results of the cluster solution. Under nanosecond laser pulse excitation, the solution shows strong nonlinear absorption and nonlinear refraction. The NLO absorption component is evaluated under an open-aperture configuration. The NLO refractive property is assessed by dividing the normalized Z-scan data obtained under the closed-aperture configuration by the normalized Z-scan data obtained under the open-aperture configuration. Under the strong nonlinear absorption, the purely refractive effect can not be obtained by dividing the closed aperture normalized Z-scan by the one with open aperture, but we can simply acquire the important information of the nonlinear refraction sometimes, and we can perform a detailed fitting of the experimental data to estimate the value of nonlinear absorption and nonlinear refraction. Assuming a sample which have large effective third-order nonlinear absorptive and nonlinear refractive coefficient, Fig. 2 shows the results of numerical simulation, which include the nonlinear absorptive curve and the divided nonlinear refractive result. It shows that under the strong nonlinear absorption, compared with the case of the purely refractive effect, the peak of the divided refractive curve is enhanced and the valley is suppressed. However, our experimental result is obviously difference of the general case, the peak of the divided results is suppressed and the valley is enhanced. We think that there must be another mechanism under the nanosecond pulse excitation.

Previous studies of thermally induced refractive change almost focus on the problem of thermal lensing produced inside the material on microsecond longer time scales. Thermal effects have been

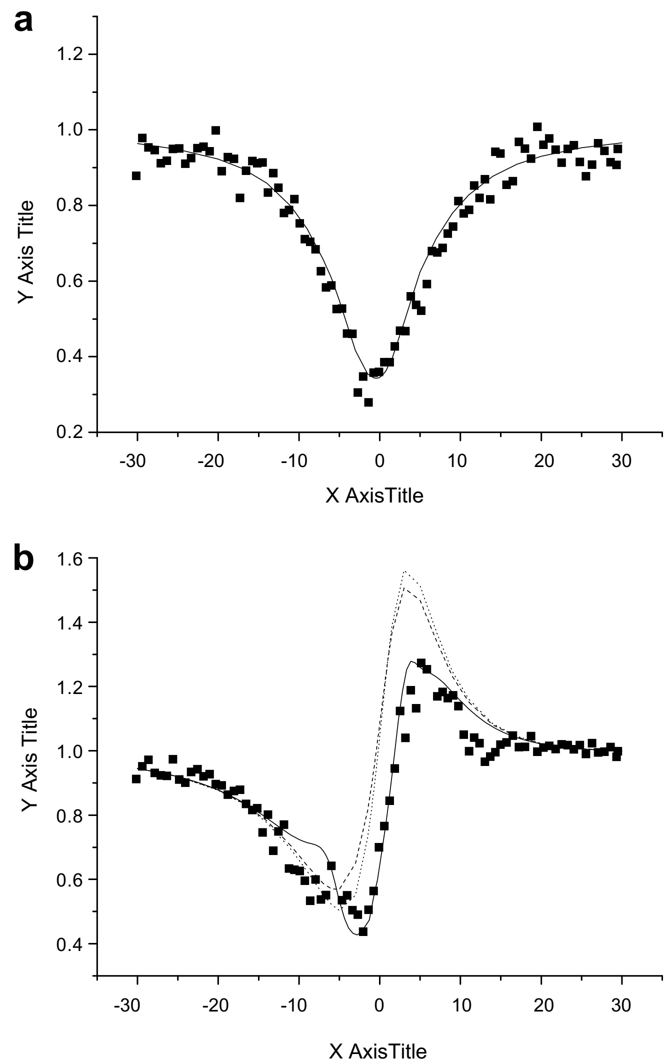


**Fig. 1.** (a) Open aperture Z-scans curve of the solution for 4.5 ns pulse width and (b) divided Z-scan curve of the solution for 4.5 ns pulse width. Dot line: the simulation results no thermal effect. Dash line: the simulation results including thermal effect only caused by linear absorption. The squares represent experimental data, and the solid lines are theoretical fitting curves.

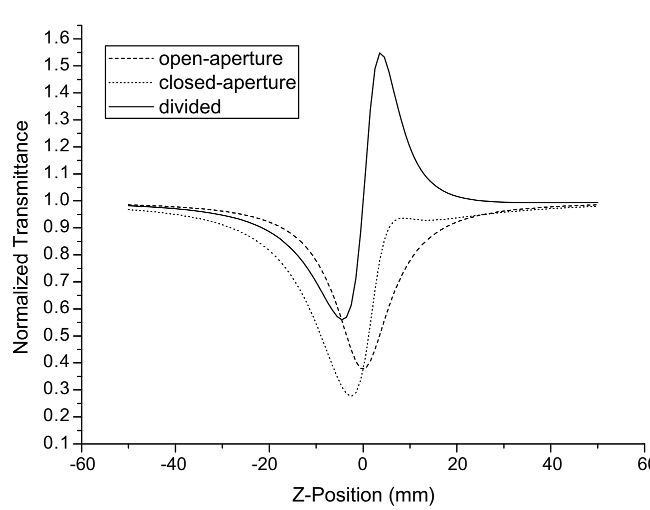


**Fig. 2.** The theory simulation results of Z-scan experiment only considering the pure third-order nonlinear optical properties.