Nonlinear response and optical limiting in inorganic metal cluster $Mo_2Ag_4S_8(PPh_3)_4$ solutions

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We describe a series of experiments on acetonitrile solutions of an inorganic cluster molecule $Mo_2Ag_4S_8(PPh_3)_4$ and compare them with data on a suspension of carbon particles in liquid (dilute ink). The optical-limiting behavior is measured by single-picosecond 532-nm pulses and nanosecond-long trains of these picosecond pulses. Nonlinear loss measurements are also performed with pulse trains at 1064 nm. Both materials show reduced transmittance for increasing fluence (energy per unit area). We also perform picosecond time-resolved pump–probe measurements at 532 nm, and we find that the observed pump–probe behavior is identical for the metal-cluster solution and the carbon-black suspension. We believe that the nonlinear mechanisms are the same for the two materials. Our previous studies of carbon-black suspension indicate that the primary nonlinear losses are due to scattering and absorption by microplasmas formed after thermionic emission from heated carbon black augmented by scattering from subsequently created bubbles. The conclusion of a similar limiting mechanism for the two materials is confirmed by time-resolved shadowgraphic images taken on both samples; however, a definitive conclusion concerning the role of microplasmas versus bubbles in either material is still under investigation. © 1998 Optical Society of America [S0740-3224(98)00905-9]

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1. INTRODUCTION

There is considerable interest in the application of the nonlinear optical properties of materials for optical limiting. An ideal optical limiter has high linear transmittance for low-input-energy laser pulses and low transmittance for high input energies in order to block the output. In addition, this ideal limiter should have rapid response (picoseconds for some applications) over a broad wavelength range (e.g., the visible spectrum) and have a large dynamic range, i.e., the ratio of the linear transmittance to the minimum transmittance occurring for the highest inputs. Of the many mechanisms tested for optical limiting, nonlinear scattering in suspensions of small particles and nonlinear absorption in reverse-saturable absorbing dyes are currently viewed with great interest. For example, Fig. 1 shows the input/output characteristics of a 1-cm-thick glass cuvette filled with a carbon-black suspension (CBS) along with a similar curve for an identical cell filled with carbon disulfide, CS_2.[1–3] The CBS sample is a suspension of carbon-black particles in a 50/50 mixture by volume of deionized water and ethylene glycol (i.e., diluted black drawing ink). The nonlinear response and the responsible mechanisms for CBS have been extensively studied. There have been a number of studies of a variety of inorganic metal-cluster compounds where reverse saturable absorption, also known as excited-state absorption, was determined to be responsible for the optical-limiting behavior.[4–6] In Ref. 6 an excited-state-absorption model using a five-level system was used to describe the nonlinear optical response of the inorganic metal-cluster compounds to nanosecond laser pulses. We extended the study by using picosecond laser pulses to study a series of 29 of these materials and found that $Mo_2Ag_4S_8(PPh_3)_4$ was the best limiting material in this series for 532-nm picosecond pulses. Figure 2 shows the limiting for $Mo_2Ag_4S_8(PPh_3)_4$ in acetonitrile with nanosecond pulses. However, the combination of data obtained with nanosecond pulses and with picosecond pulses, detailed in this paper, show that the dominant mechanism for optical limiting is not excited-state absorption, but nonlinear scattering, the same mechanism as is dominant in CBS. However, $Mo_2Ag_4S_8(PPh_3)_4$ does not limit well at 1.06 μm, unlike CBS, which has been shown to have a quite broad-band limiting behavior. This is consistent with its reduced linear absorption at longer wavelengths.

Previously we showed that nonlinear scattering dominates the transmissive losses of CBS and that the limiting is fluence dependent so that limiters based on black ink are effective for nanosecond pulses but not for picosecond pulses.[3] Additionally, the nonlinear scattering as well as the limiting behavior ceases after repeated irradiation. Both of these effects are also seen in the metal-cluster solution. For liquids, flowing eliminates the effects caused by repeated irradiation by replenishing the irradiated material after each laser firing. All the data

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obtained on CBS are consistent with a model of direct heating of the microscopic-sized carbon particles by linear absorption, with subsequent optical breakdown initiated by thermally ionized electrons. Subsequent to heating, bubbles are also formed, which further scatters incoming light. There are still questions concerning the relative importance of these two contributions to the limiting.[7] A simple calculation gives temperatures higher than the sublimation temperature at the onset of limiting. A rapid expansion of microscopic plasmas generated by optical breakdown can effectively scatter further input light. Indeed, in time-resolved experiments on CBS the trailing portion of the pulse is most heavily scattered. Time-resolved transmittance of a weak cw probe beam shows that the transmittance recovers on the time scale of $\sim 10^2$ ns,[3] which is consistent with previous measurements of the lifetime of ionized carbon.[8,9] However, rapidly expanding microbubbles would also scatter the pulse and perhaps dissipate on this time scale, provided the input is not too far above threshold. High above threshold there are clear indications of large bubbles blocking the transmittance for much longer times. Direct monitoring of the scattering by angularly resolving the scattered light for different input fluences and fitting to Mie-scattering theory shows expansion of the scattering centers with increasing fluence.[3] Additionally the complex index of refraction obtained from these studies is consistent with a plasma. Further experiments performed on samples of carbon black deposited on a glass substrate give strong evidence that microplasmas are a major contributor to the nonlinear loss.[3] The threshold fluence for limiting was nearly the same as for CBS. The temporal dependence of the transmittance of a coaxial He–Ne probe laser also showed recovery taking $\cong 10^2$ ns. Emission-spectra measurements indicate singly ionized carbon-emission lines with a hot blackbody background emission consistent with a temperature of ~4000 K with the ionized emission lasting for $\cong 10^2$ ns; however, the question has been raised as to whether this emission is from carbon or from oxygen in the air.[10]

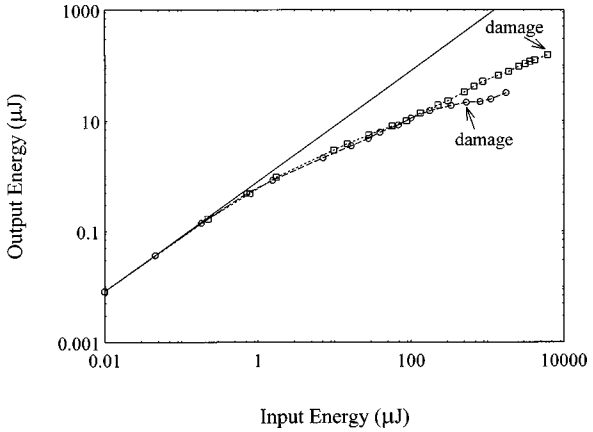

Fig. 2. Optical limiting in $Mo_2Ag_4S_8(PPh_3)_4$ in acetonitrile, 96% internal linear transmittance, with 9-ns (FWHM) pulses at 532 nm (circles for 1-mm cell, squares for 5-mm cell).

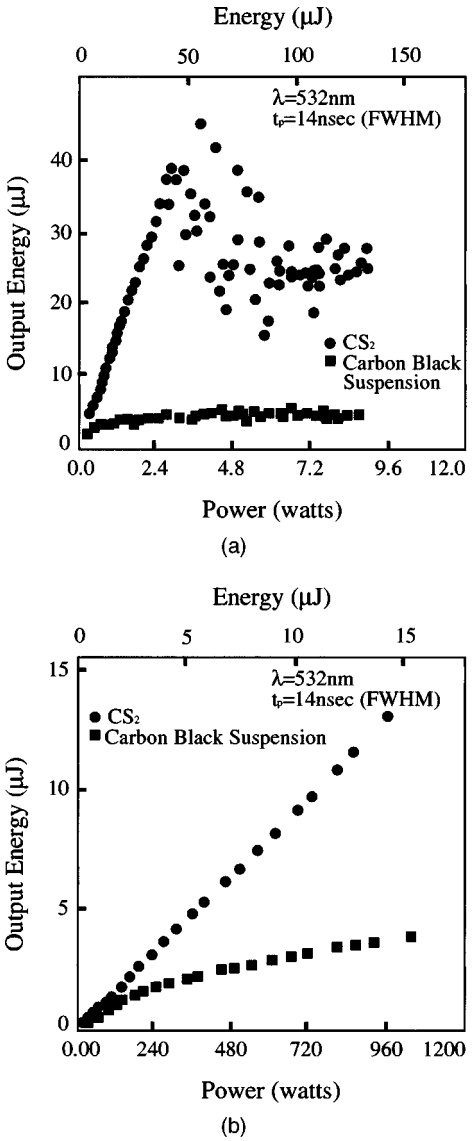

Fig. 1. Energy output for CS_2 and CBS as a function of input peak power for 14-ns (FWHM), 532-nm pulses focused to $w_0 = 3.5$ μm for input powers of (a) 1 to 12 kW and (b) 1 to 1000 W (from Ref. 3 with permission).

While we have not performed all the detailed experiments on the inorganic clusters that we performed on CBS, the results of the experiments that we have performed show a striking similarity to the results for CBS. This provides a high level of confidence that the mechanisms are the same, and we apply the above conclusions for CBS to the metal-cluster solutions. This may also suggest that the metal-cluster molecules form aggregates, although we have not been able to perform any conclusive experimental tests. However, for example, we see that after repeated irradiation, the limiting effectiveness of the cluster solution is reduced just as for CBS. The inorganic cluster samples are saturated solutions in acetonitrile with a yellowish precipitate at the bottom of the cell. If the cell sits for several days without disturbance, the limiting characteristics are degraded. Limiting for CBS is extremely broadband, since carbon particles in a suspension are "black," and the nonlinearity is initiated by linear absorption. The absorption spectrum of the metal-cluster solutions falls off toward longer wavelengths, and the limiting we measured at 1.06 μm is a factor of ~30

less effective than at 532 nm. Unfortunately the solubility of these molecules is low and the linear absorption could not be accurately measured at 1064 nm.

2. EXPERIMENTS

We performed optical-limiting and pump–probe experiments on CBS and the inorganic metal cluster, $Mo_2Ag_4S_8(PPh_3)_4$. The structure of the latter is shown in Fig. 3. In addition, we recorded shadowgraphic images of CBS with picosecond resolution.[11] An example of an optical-limiting experiment for the cluster sample using a nanosecond train of pulses at 532 nm is shown in Fig. 4. To obtain such a pulse train, the entire Q-switched envelope at 1064 nm from a hybridly mode-locked Nd:YAG laser is frequency doubled (i.e., train of picosecond pulses). This results in a train of pulses at 532 nm of FWHM 45 ns with the mode-locked pulses separated by 7 ns. The individual 532-nm pulses have a pulse width of 30 ps (FWHM). The beam was focused to a measured spot radius, $w_0 = 17\ \mu$m, into a 1-cm path-length cell. The linear transmittance of the sample at 532 nm is 96.5 $\pm$ 1.0% (not including Fresnel reflection losses from the glass cell walls). The fluence quoted is the on-axis fluence calculated at the incident surface of the liquid. The dynamic range of this single element device is >40, where the dynamic range is defined as the ratio of the linear transmittance to the minimum transmittance, which is

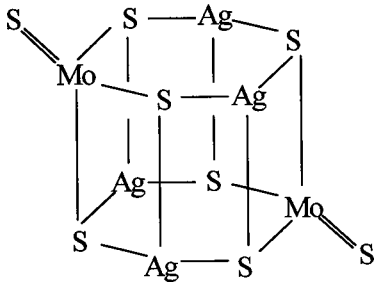

Fig. 3. Structure of the inorganic metal cluster $Mo_2Ag_4S_8(PPh_3)_4$. Each Ag is attached to a PPh_3 ion (not shown).

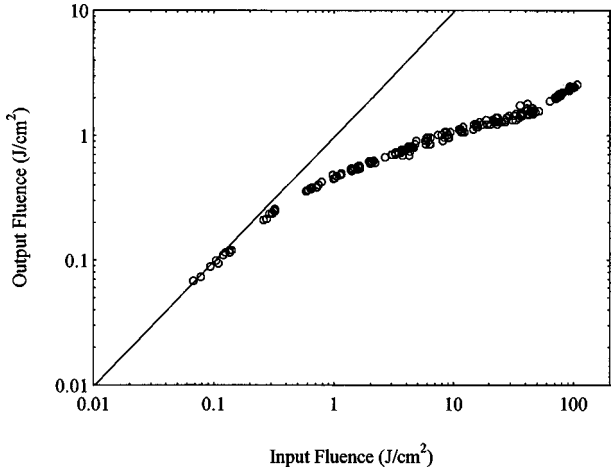

Fig. 4. Limiting in $Mo_2Ag_4S_8(PPh_3)_4$ with a 45-ns pulse train of 30-ps (FWHM) pulses at 532 nm.

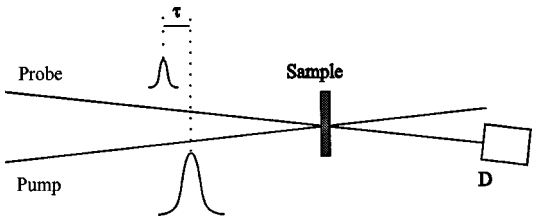

Fig. 5. Pump–probe experimental setup.

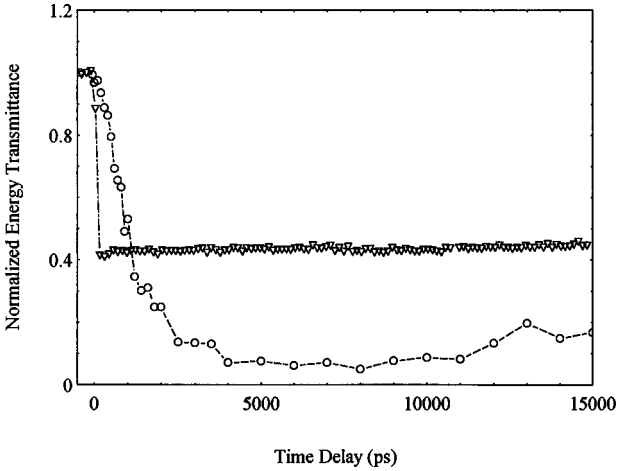

Fig. 6. Normalized transmittance of the probe as a function of time delay for a pump energy of 50 μJ in TBP (squares) and in the metal cluster $Mo_2Ag_4S_8(PPh_3)_4$ (circles).

obtained for an input fluence just below the threshold fluence for damage to the surface of the optical cell.

We next performed pump–probe experiments at 532 nm using the apparatus shown schematically in Fig. 5. This is a standard pump–probe arrangement where the probe peak irradiance is approximately 1% of the pump irradiance. In addition, the probe is focused to a spot size approximately one fourth as large as the pump, to reduce spatial averaging effects while sampling the largest nonlinearity. The pump and probe are orthogonally polarized to aid separation with polarizers and are incident at an angle of 3° with respect to each other. Figure 6 shows a plot of the normalized probe transmittance as a function of temporal delay between pump and probe. A typical signal for an excited-state absorber is the response of zinc tetra (p-methoxyphenyl) tetrabenzporphyrin (TBP), which has a turn-on time shorter than the 30-ps pulse width and a long lifetime for the nonlinear absorption.[12] The inorganic metal cluster, however, has a different response. The turn-on time of the nonlinearity is much slower, with effectively all of the nonlinear response occurring well after the 30-ps excitation pulse is gone. Although the response is much slower than for TBP, the nonlinear transmission loss for the inorganic metal cluster is much higher. The energy dependence of the pump–probe signal for $Mo_2Ag_4S_8(PPh_3)_4$ can be observed in Fig. 7. As the pump energy increases, the limiting performance improves both in increased maximum loss and in reduced turn-on time. Figure 8 shows a comparison of pump–probe results for the inorganic clusters and CBS (these experiments had not previously been performed for CBS). The coincidence of the data for differ-

ent energies for the CBS and clusters is remarkable. This indicates that the nonlinear phenomena are the same. Also, it is interesting to note in Fig. 8 that changing the sample thickness does not change the nonlinear behavior. This is what occurs in bulk laser-induced breakdown of transparent optical materials. The small extra feature that can be seen around zero delay in Fig. 8 for CBS is the contribution of the solvent (toluene), and it is due to transient energy transfer via stimulated Rayleigh wing scattering.[13] Of course, these data only show that the phenomena are the same for picosecond inputs. Previous data on CBS, however, showed that the nonlinear response for picosecond and nanosecond pulses were similar when the same fluence is used. Thus we can expect that the nonlinear mechanisms remain the same for longer pulses owing to the similarity of response for optical limiting with longer pulses for these materials.

At 1064 nm the nonlinear loss is approximately the same at a fluence of 1.5 J/cm^2 as it is at 532 nm for an input fluence of 0.13 J/cm^2 as determined by Z scans.[14,15] This implies an order of magnitude reduced limiting effectiveness at 1064 nm, which may be attributed to a reduction in the linear-absorption coefficient that initiates the heating.

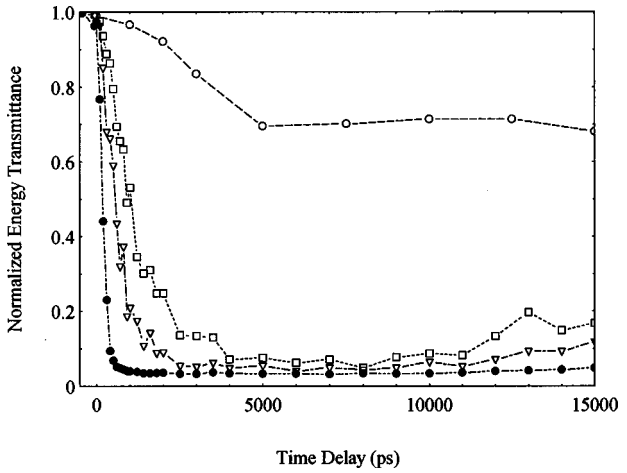

Fig. 7. Normalized probe transmittance as a function of time delay for the inorganic metal cluster $Mo_2Ag_4S_8(PPh_3)_4$, for pumping energies of 14 (open circles), 50 (squares), 100 (triangles), and 200 μJ (filled circles).

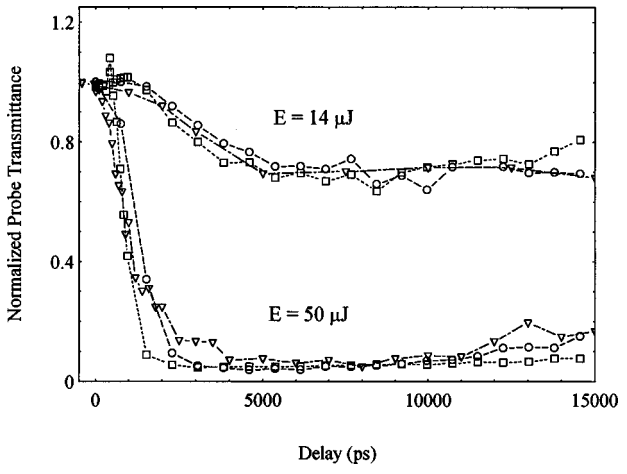

Fig. 8. Normalized probe transmittance as a function of time delay for the inorganic cluster $Mo_2Ag_4S_8(PPh_3)_4$ in a 1-mm cell (triangles), CBS in a 1-mm cell (circles) and CBS in a 5-mm cell (squares).

The transmittance of the metal-cluster solution is determined by its solubility, which is quite low. In experiments on CBS at a low concentration to give similar loss, the response at 532 nm is still the same as for the metal-cluster solution at 532 nm. Both CBS and the metal-cluster solution work quite well even with high internal transmittance ($\cong$96%). This is related to the nonlinear mechanism. As long as the density of particles in CBS is high enough that there are particles in the focal volume, optical limiting will be initiated at the same input fluence.

In a final series of pump–probe experiments we modified the apparatus of Fig. 5 to perform time-resolved shadowgraphic imaging of the irradiated sample region. In this new configuration the probe is expanded and collimated and directed at a 90° angle with respect to the pump so that the cell is illuminated from the side. The transmitted probe is then imaged after magnification onto a two-dimensional CCD detector array. Details of this geometry are given in Ref. 11 and the accompanying paper. Here the pump is at 532 nm and the probe is at 1064 nm to facilitate blockage of any scattered pump radiation. What is observed is a confirmation of the data of Fig. 6. Near zero time delay, no changes in transmittance are detectable. Near 100-ps probe delay for a pump energy of approximately 110 μJ, a dark line along the beam develops, which becomes darker with increasing time delay up to approximately 500 ps. This line remains dark, but with a perceptible reduction in contrast, up to the longest time delay of 15 ns. No discernible structure within or outside of this darkened region is observed. Unfortunately, these data also do not give a definitive answer to the question of the relative roles of microplasma and bubble formation.

3. CONCLUSION

We conclude that the dominant nonlinearity leading to limiting in the inorganic metal cluster $Mo_2Ag_4S_8(PPh_3)_4$ and CBS are the same. This conclusion is further substantiated in Refs. 11 and 12, accompanying papers that show a series of shadowgraphic images of both CBS samples and metal-cluster solutions at various times after irradiation with nanosecond pulses along with photographs of radiant emission. The images for the metal-cluster solutions and CBS are qualitatively similar. That study shows images at time delays up to microseconds. The formation and growth of bubbles can be clearly tracked in time in those images. While the limiting mechanisms are the same, on short time scales we cannot make a definitive conclusion as to the dominant mechanism beyond being some combination of the effects of microplasma and microbubble formation.

The early portions of the pulse rapidly heats the metal clusters or carbon particles. Subsequently these ionize or vaporize forming microplasmas or bubbles or both. Later portions of the input pulses are absorbed and scattered by microplasmas and/or scattered by bubbles. Line-emission spectra and time-resolved fluorescence measurements on carbon deposited on glass substrates

were consistent with previous measurements of plasma production using carbon targets.[16] Angularly resolved scattering measurements on CBS showed growth of scattering centers with increasing fluence with complex indices of refraction consistent with plasmas. The limiting threshold and temporal response of limiting for CBS and carbon deposited on glass were similar. The disappearance of the limiting effect after a single irradiation of carbon on glass and after multiple-pulse irradiation of a single site in CBS (before the liquid can be replenished) also confirms the fact that the carbon particles or metal clusters are destroyed (atomized) and are no longer useful for optical limiting. Therefore, for protection against multiple-pulse irradiation the liquids must be flowing.

Well above threshold this vaporization causes bubbles to be formed that do not dissipate.[17,18] These are readily observable on longer time scales, as reported in Ref. 18 for CBS and observed in shadowgraphic images in Ref. 11, and can cause problems for high-energy limiting and/or for high-repetition-rate limiting applications.

The fluence dependence for CBS was confirmed in Ref. 3 by focal-spot-size dependence measurements with collimated beams and by pulse-width dependence measurements with nanosecond and picosecond irradiation. However, we showed there that, if a tight focusing geometry is used where the depth of focus is shorter than the sample thickness, the fluence dependence is masked, and the response becomes energy dependent (i.e., independent of focusing). This also manifests itself as an independence on sample cell length for small losses, as seen in Fig. 2 for the metal clusters. As shown there, the nonlinear transmittance is nearly the same for two different cell lengths of 1 mm and 5 mm with the same focusing geometry. These relationships are important to consider in optical-limiting applications.

The spectral dependence for CBS is known to be broadband owing primarily to the flat linear-absorption spectrum. For the inorganic clusters the linear absorption drops at longer wavelengths, and we see a concurrent reduction in the effectiveness of limiting at 1064 nm.

The fact that the inorganic clusters of $Mo_2Ag_4S_8(PPh_3)_4$ give identical results to CBS at 532 nm is intriguing and may lead us to find methods for lowering its limiting threshold.

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