ELSEVIER

Synthetic Metals 83 (1996) 273–276

SYNTHETIC METALS

THG from copper phthalocyanines in a sol–gel host

R. Litran [a], E. Blanco [a], M. Ramirez-del-Solar [a], A. Hierro [b], M.A. Diaz-Garcia [b], A. Garcia-Cabañes [b], F. Agullo-Lopez [b]

[a] *Departamento Fisica de la Materia Condensada, Universidad de Cadiz, Puerto Real, 11510 Cadiz, Spain*
[b] *Departamento Fisica de Materiales, Universidad Autonoma de Madrid, 28049 Madrid, Spain*

Abstract

Copper phthalocyanine molecules have been incorporated into silica xerogels at several levels of concentration. The gelation process has been monitored by optical and leachability tests. The third-harmonic (THG) susceptibilities $\chi^{(3)}$ have been measured at $\lambda = 1.064$ μm for the xerogel composites and at $\lambda = 1.064$ μm and $\lambda = 1.904$ μm after thermal treatment at 200 °C. Values up to 2.6 times higher than those of the xerogel host have been obtained for the treated samples with 10^{-4} mol/l concentration of copper phthalocyanine in the sol.

Keywords: Copper phthalocyanine; Third-harmonic susceptibilities; Sol–gel host

1. Introduction

The sol–gel method [1] offers an alternative route to the processing of materials with a great variety of structures, shapes and compositions. Basically, it consists of a two-step process. In the first stage polymerization of a suitable precursor takes place at room temperature, resulting in a porous and amorphous material, named xerogel. In the second stage, the xerogel is subjected to appropriate heat treatment for elimination of pores until densification.

One key advantage of the sol–gel technique is its low processing temperature that allows for the incorporation of organic molecules without thermal damage and to achieve high doping levels. This is particularly useful for linear and nonlinear optical applications, where one combines the useful properties of the active molecules and the transparency and stability of the glass host [2]. In fact, extensive work has been carried out on organic dyes embedded in oxide sol–gel hosts, mostly for laser and luminescence applications [3,4]. Less effort has been devoted to nonlinear optical measurements [5,6].

On the other hand, phthalocyanines are planar molecules with a large delocalized electron system [7], leading to high and fast third-order nonlinear (NLO) responses. Indeed, much work has been reported on the NLO properties of phthalocyanines in solution [8,9] and on thin films [10–12]. However, very few preliminary works have been carried out on phthalocyanines incorporated in sol–gel matrices. They involved either four-wave mixing experiments [13] or measurements of nonlinear transmission for optical limiting applications [14].

The purpose of this paper is to measure third-harmonic (THG) susceptibilities of copper phthalocyanines (CuPc) in a silica xerogel. This nonlinearity is exclusively associated with electronic mechanisms and so other third-order contributions (e.g. thermal, level population,...) are ruled out. An effort has been devoted to assure that the CuPc molecules are effectively trapped in the xerogel. THG measurements after a 200 °C annealing of the samples have also been carried out. This provides a more complete evaluation of the nonlinear behaviour and of the xerogel-composite potentialities, for nonlinear optical applications.

2. Experimental procedure

2.1. Preparation of the CuPc xerogel composite

CuPc silica sono-xerogels were prepared starting from hydrolysis and polycondensation of tetramethoxysilane (TMOS). The hydrolysis water, previously acidified with nitric acid at pH = 2, was added in a proportion of 10 acid H_2O/TMOS molar ratio. This hydrolysis water contains a certain amount of commercial copper tetra-sulfonated phthalocyanine (CuTSPc) for final concentrations of 10^{-4}, 5×10^{-5} and 10^{-5} M in the resulting sol. In order to keep the sample monolithic, a drying control chemical additive (DCCA) was added, specifically 3 mol formamide/mol TMOS, which avoids fractures during the drying process.

0379-6779/96/$15.00 © 1996 Elsevier Science S.A. All rights reserved
PII S0379-6779(96)04519-5

Once formamide and acid CuPc water have been mixed with the alkoxide, the mixture was submitted to the action of ultrasounds (20 kHz, 0.1 kJ/cm^3 energy dose) [15], leading to a blue transparent solution which was left for gelling. The resulting monolithic sonogels were aged for 1 week and dried for 3 weeks at room temperature. For comparison, an undoped silica sonogel was prepared under the same conditions, which will be referred to as the 'white' sample in the following.

The trapping efficiency has been evaluated by leachability tests and by UV–Vis absorption experiments carried out using a Hitachi V-3501 spectrophotometer.

2.2. *THG experiments*

THG experiments were carried out at 1.064 and 1.904 μm fundamental wavelengths by using the Maker-fringe technique described elsewhere [16]. The light source was a Q-switched Nd^{3+}:YAG laser, with 9 ns pulse duration, 50 mJ pulses and 10 Hz repetition rate. The 1.904 μm wavelength was obtained by Raman shifting of the fundamental emission at 1.064 μm (first Stokes radiation) in a high-pressure hydrogen cell (60 bars).

The measurements were performed in a 200 mTorr vacuum chamber on samples with thickness ranging from 1.1 to 2.2 mm. Experimental data were analysed using the simplex method to fit the theoretical Maker-fringe expression [17], and determine the magnitude of $\chi^{(3)}$. Absorption at both the fundamental and third-harmonic wavelengths was taken into account in the calculations.

3. Results

3.1. *Trapping of CuPc molecules*

CuPc xerogels were immersed in H_2SO_4/H_2O solutions for 48 h, with the aim of evaluating whether molecules are efficiently encapsulated in the xerogel pores. No evidence of CuPc absorption bands appears in the UV–Vis absorption spectra of the leachability test liquid.

Fig. 1 shows the absorption spectra corresponding to a CuPc xerogel at different moments during gelation, ageing and drying processes. They show the Q band of CuPc with peaks at 692 and 614 nm, corresponding to different aggregated species. The spectra are very similar to those observed in evaporated samples, where X-ray diffraction analysis confirms the presence of crystallites (α and β phases) [18]. The characteristic phthalocyanine absorption bands in the ultraviolet region, B, N, L and C bands, are difficult to study because they are screened by silica absorption.

The Q-band position, which is dependent on the aggregation state and the crystalline phases present, exhibits no changes with time. However, an important increase in the optical density is observed as gelation proceeds. This behaviour indicates that organic concentration in the gel increases during sample shrinkage because of the elimination of residual liquid.

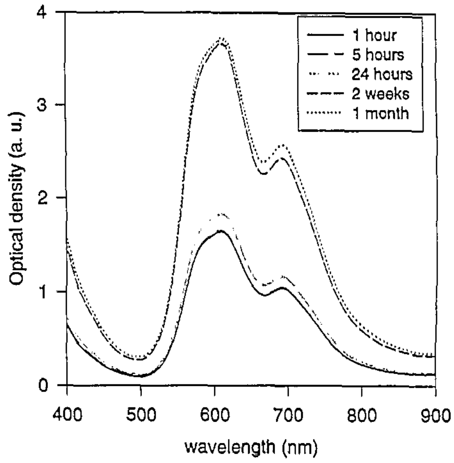

Fig. 1. Visible absorption spectra of a 10^{-4} M CuPc composite at different processing steps.

Consequently, we infer that guest molecules remain in the sample and, therefore, that effective trapping takes place in the xerogel matrix.

Fig. 2 shows the comparison between the absorption spectra (in the wavelength range from 350 to 2000 nm) of a composite at room temperature and the same sample treated at 200 °C. A very strong band at about 1960 nm, associated with the formamide, has been largely reduced by the annealing treatment. At the same time, a marked rise in the UV absorption below 500 nm is observed. The phthalocyanine Q band is not substantially modified except for a clear decrease in its magnitude. The enhancement in the UV absorption has been also measured in 'white' xerogel samples (not containing phthalocyanine) and may be attributed to light scattering. Moreover, compounds arising from the decomposition of formamide absorb at much shorter wavelengths.

3.2. *THG results*

For the sake of clarity the results for untreated and annealed xerogel samples will be separately described. In fact, the strong effect of annealing in the optical spectra (see Fig. 2) may imply different nonlinear responses. In some cases, Maker fringes are not too well defined due to the roughness of the xerogel surface.

3.2.1. *Data for untreated samples*

The experiments at 1.06 μm yield $|\chi^{(3)}|$ values between 2.1 and 2.4 times those obtained for the undoped xerogel host (see Table 1). On the other hand, this host shows a nonlinear susceptibility $\chi^{(3)}{}_{\text{host}} = 1 \times 10^{-14}$ e.s.u. The very similar values of $\chi^{(3)}$ for the two extreme concentrations may suggest some strong effects of molecular aggregation (see Discussion).

For the untreated samples it was not possible to obtain THG data at 1.904 μm due to the strong absorption at about

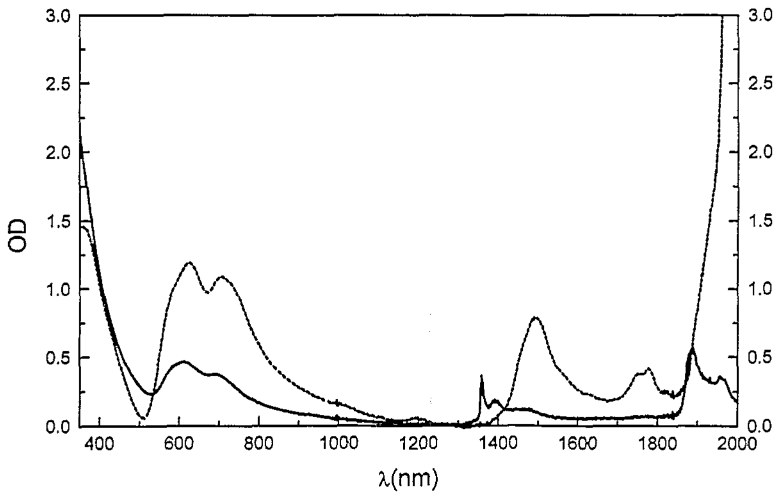

Fig. 2. Absorption spectra for a treated (———) and untreated (- - -) 10^{-4} M CuPc-xerogel sample.

Table 1
THG susceptibilities for CuPc-xerogel samples. All concentrations refer to the sol

Sample	Concentration (mol/l)	$\lvert\chi^{(3)}\rvert / \lvert\chi^{(3)}\rvert_{\text{xerogel host}}$	
		$\lambda = 1.064$ µm	$\lambda = 1.904$ µm
Untreated	10^{-4}	2.4	
	5×10^{-5}	2.3	
	10^{-5}	2.1	
Treated	10^{-4}	2.6	1.4
	5×10^{-5}	2.6	1.2

2 µm (see Fig. 2). This caused marked damage of the samples during laser illumination.

3.2.2. Data for annealed samples

For these samples the $\lvert\chi^{(3)}\rvert$ values at 1.064 µm are slightly higher than those obtained for untreated samples. $\lvert\chi^{(3)}\rvert$ susceptibilities at 1.904 µm have been now obtained and show slightly lower values. Data for the two excitation wavelengths and two concentrations are included in Table 1.

3.3. Discussion

The $\chi^{(3)}$ values obtained for our xerogel samples are in rough agreement with the predictions of a model for non-interacting phthalocyanine molecules. As an example, for the sample with the highest doping level (10^{-4} mol/l in the sol), i.e., a molecular concentration of 4×10^{17} cm^{-3}, the susceptibility should reach $\chi^{(3)} = 2\times10^{-14}$ e.s.u., using a hyperpolarizability $\gamma = 3.9\times10^{-32}$ e.s.u., measured by EFISH at the same wavelength [9]. This value is of the same order of magnitude as that experimentally found.

On the other hand, for spin-coated samples of CuPc incorporated into PMMA with a molecular concentration of about 5×10^{19} cm^{-3} we have measured $\chi^{(3)}$ values about a factor five larger than for our xerogel samples. Moreover, previous studies on evaporated CuPc [11] give $\chi^{(3)} = 1.6\times10^{-12}$ e.s.u. This value is only between one and two orders of magnitude higher than those found in this work, whereas the molecular concentration is nearly 10^3 times larger. Therefore, it appears that such high concentrations either in the spin-coated or evaporated films reduce the nonlinear response associated with each molecule.

The enhancement in the $\chi^{(3)}$ susceptibility at $\lambda = 1.064$ µm after thermal treatment (even for a reduced absorption of phthalocyanine) may be attributed to changes in the molecular arrangement or to local field effects [19].

Though this is only a preliminary work, we have shown enhancement of $\chi^{(3)}$ due to the incorporation of CuPc into a xerogel host. A more thorough study of the role of concentration and aggregation of CuPc in the pores is now under way.

Acknowledgements

Financial support from Grants MAT95-1254-CE and MAT95-0040-C02-02, and Contract CI1 * -CT94-0039, is greatly acknowledged. R.L. acknowledges a scholarship from the Ministerio de Educación y Ciencia, Spain.

References

[1] C.J. Brinker and G.W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Academic Press, San Diego, 1989.
[2] B. Dunn and J.I. Zisik, *J. Mater. Chem.*, *1* (1991) 903.
[3] D. Avnir, D. Levy and R. Reisfeld, *J. Phys. Chem.*, *88* (1984) 5956.
[4] J.C. Pouxviel, B. Dunn and J.I. Zink, *J. Phys. Chem.*, *93* (1989) 2134.
[5] P.N. Prasad and B.A. Reinhort, *Chem. Mater.*, *2* (1990) 660.
[6] E. Toussaere, J. Zyss, R. Griesmar and C. Sanchez, *Nonlinear Opt.*, *1* (1991) 349.
[7] C.C. Leznoff and A.B.P. Lever, *Phthalocyanines. Properties and Applications*, Vols. 1–3, VCH Publishers, New York, 1989/1993.
[8] J.S. Shirk, J.R. Cindle, F.J. Bartoli, Z.H. Kafafi, A.W. Snow and M.E. Boyle, *Int. J. Opt. Phys.*, *1* (1992) 699.
[9] M.A. Diaz-Garcia, I. Ledoux, J.A. Duro, T. Torres, F. Agullo-Lopez and J. Zyss, *J. Phys. Chem.*, *98* (1994) 8761.

[10] H.S. Nalwa, *Adv. Mater., 5* (1993) 341.

[11] M.A. Diaz-Garcia, F. Agullo-Lopez, W.E. Torruellas and G.I. Stegeman, *Chem. Phys. Lett., 235* (1995) 535.

[12] H. Tajalli, J.P. Jiang, J.T. Murray, N.R. Armstrong, A. Schmidt, M. Chandross, S. Mazumdar and N. Peyghambarian, *Appl. Phys. Lett., 67* (1995) 1639.

[13] G.J. Gall, T.A. King, S.N. Oliver, C.A. Capozzi, A.B. Seddor, C.A.S. Hill and A.E. Underhill, *Proc. SPIE, 2288* (1994) 372.

[14] P.D. Fuqua, K. Marsour, D. Alvarez, Jr., S.R. Marder, J.W. Perry and B. Dunn, *Proc. SPIE, 1758* (1992) 499.

[15] E. Blanco, R. Litran, M. Ramirez-del-Solar, N. de la Rosa-Fox and L. Esquivias, *J. Mater. Res., 9* (1994) 11.

[16] F. Kajzar and J. Messier, in D.S. Chemla and J. Zyss (eds.), *Nonlinear Optical Properties of Organic Molecules and Crystals*, Vol. 2, Academic Press, New York, 1987, p. 51.

[17] F. Kajzar, J. Messier and R. Rosilio, *J. Appl. Phys., 60* (1986) 3040.

[18] M.J. Cook, in R.J.H. Clark and R.E. Hester (eds.), *Spectroscopy of New Materials*, Wiley, New York, 1993, pp.109–111.

[19] R.W. Boyd and J.J. Sipe, in S. Miyota (ed.), *Nonlinear Optics: Fundamentals, Materials and Devices*, Elsevier, Amsterdam, 1992, pp. 63–76.