Taylor & Francis
Taylor & Francis Group

SHG-Activity of Polar Nano-Structures of LC-RED-PEGM-7 Based Sono-Gel Hybrid Materials

Omar G. Morales-Saavedra
R. Castañeda
M. Villagran-Muniz
Laboratorio de Fotofísica, CCADET-UNAM, Ciudad Universitaria,
Coyoacán, México D.F, México

J. O. Flores-Flores
J. G. Bañuelos
J. M. Saniger
Laboratorio de Materiales y Sensores, CCADET-UNAM, Ciudad
Universitaria, Coyoacán, México D.F, México

E. Rivera
Laboratorio de Polímeros, IIM-UNAM, Ciudad Universitaria,
Coyoacán, México D.F, México

The synthesis of sol-gel materials induced by ultrasonic action (sonolysis) is implemented as an alternative method for the fabrication of highly pure organic-inorganic composites with good monolithic and optical properties. A newly synthesized liquid crystalline mesogen (named here RED-PEGM-7) was introduced as dopant specie within the SiO_2 matrix in order to create an active nonlinear optical hybrid material at room temperature. A comparative characterization of the structural properties between a pure reference sample and several doped composites was performed by X-ray diffraction (XRD) and atomic force microscopy (AFM); where, an optimal dissolution concentration of tetraethoxysilane (TEOS) and the liquid crystalline (LC) mesogen, to obtain good mechanical and nonlinear optical properties in thin film layers has been found.

Keywords: SHG; sol-gel hybrid materials; sonolysis

INTRODUCTION

The sol-gel technique has been used in recent years as a standard method to confine and encapsulate diverse dopants species into a glassy SiO_2 matrix in order to create novel advanced materials with different optical and mechanical properties [1–6]. On the other hand, second order nonlinear optical (NLO)-processes are of particular interest since they offer several potential applications; emphasis has been put on materials suitable for electro-optical systems and integrated optical circuits adopting the guided-wave format, which provides additional routes to the conception and realization of photonic and telecommunication devices. Besides materials, like poled polymers, recently ferroelectric liquid crystals have been intensively investigated regarding their NLO properties too (for example second harmonic generation, SHG) [6–10]. It has been a difficult task however, to combine the synthesis of many of these promising ferroelectric liquid crystalline molecules with the desired optical properties, which are usually expected at room temperature [6,11].

Other important problem to develop efficient devices suitable for optical sciences and photonics is the material malleability and mechanical consistence required in several technological implementations, for instance in waveguiding and quasi-phase-matched (QPM) structures [12–13]. In these cases, deposition of organic spin-coated thin films is required to fill up the guiding optical channels, which have to remain stable for long periods of time. Besides, a systematized poling of the molecular structure has to be achievable too. Polymerization of liquid crystalline mesogens as well as the combination of organic optical chromophores within guest-host polymeric systems have been reported in order to create more stable and solid structures once they have been dissolved and spin-coated into the waveguiding channels created by standard photolithographic techniques [12].

From the sol-gel sciences point of view, easy material processing offered by the colloidal state and recent developments on the deposition of doped sol-gel thin film layers, satisfy in high degree the requirements mentioned before [6]. Since the gelation process takes long time before the doped colloidal mixture reaches a dry-solid and stable state, this process allows an efficient deposition of doped colloidal dispersions (sols) onto the micrometric integrated structures registered in different kind of wafers and substrates. The high malleability of these materials permits them to adopt a very wide variety of shapes required for photonic proposes. In situ poling of the dopant-species is also possible, in order to improve its NLO-performance. Once the drying process is completed, the rigidity of the hybrid

sol-gel material in the desired format is achieved. The constituting organic compounds may contribute to a desired peculiar physical or chemical property, whereas the inorganic part of the hybrid composite, contributes to its mechanical and thermal strength [14–15]. These materials can show, depending on the purity of the sol-gel precursor solvents, a very stable behavior within a wide range of temperatures. Thus, the different optical properties of the dopant species are preserved, without decomposition of the fragile guest molecules.

In this work, the development of novel NLO-sol-gel materials generated by ultrasonic action (sono-gel materials) is reported. These materials exhibit an amorphous SiO_2-matrix with a high purity level and nanometric porous dimensions, which can be easily doped with LC-molecules and other organic compounds. Here, instead of the traditional use of different catalyst agents like acids and bases, introduced to start the gelation process, energetic pulsed ultrasonic waves were applied at the $TEOS/H_2O$ interface in order to produce acoustical cavitation which starts the hydrolysis reaction. The resulting colloidal mixture was then doped with a newly sinthetized rod-like liquid crystalline mesogen (named here RED-PEGM-7). This chromophore has been specially designed for second order NLO-effects, which has been measured at room temperature, for different spin-coated hybrid composites. The experimental results showed in this work, have been carried out as a first step to develop photonic organic-inorganic devices, and as a practical alternative to expensive inorganic crystals, where the use of specially designed NLO-LC-molecules plays an important role.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation

The sol-gel method used to synthesize amorphous SiO_2, based on the hydrolysis of different precursors like TEOS, TMOS, etc., followed by condensation reactions of the hydrolyzed species, has been intensively adopted as a well established way to create glassy doped materials with good optical quality. Both, hydrolysis and condensation reactions occur normally in the presence of acidic or basic catalysts where ethanol or methanol are used commonly as standard solvents for the precursor and water reactants. Fundamental and experimental details for the sol-gel synthesis of SiO_2 can be found extensively in the literature [1]. On the other hand, several scientific papers reporting emulsification action of the reactive mixtures induced by ultrasonic irradiation have been published in recent years, where the use of

solvents is fully evaded [16–19]. In such way, it is possible to obtain sonolyzed-gel materials with an elastic modulus several orders of magnitude higher than those prepared by conventional methods [20]. In this work, a new approach for the preparation of highly pure LC-doped SiO_2 sonogels is exploited (avoiding the use of both, solvents and catalysts at all), where the hydrolyzed species are substituted by molecular radicals generated by ultrasound (more details on the synthesis, chemistry and methodology to produce this new kind of sono-gel materials, could be found in reference [21]).

For this purpose, a polymetacrylate cylindrical reaction chamber divided in two compartments was implemented (see Fig. 1a). The hole in the middle point of the chamber acts as support for a pyrex glass vessel (80–100 ml), two neoprene o-rings seals the upper and the lower part of the chamber, allowing a perfect isolation of the two compartments. The reactant mixture is then introduced into the vessel, which has the function of reaction container as will be explained in more detail later. The chamber physical separation and the four holes placed on the lid of the chamber permits different applications, as explained below:

1) Hole (A) placed in the upper part of the chamber (top cover) serves as an input for the ultrasonic tip; hole (B) is used to introduce electrodes which control the pH-measurements continuously. Holes (C) and (D) are used as an input and output valves to regulate the gas-flow, which controls the reaction environment of the system. Moreover, a thermocouple (type K) is also introduced trough hole (C), parallel to the feed pipe of the selected gas, in order to control the reaction temperature accurately. For the present application,
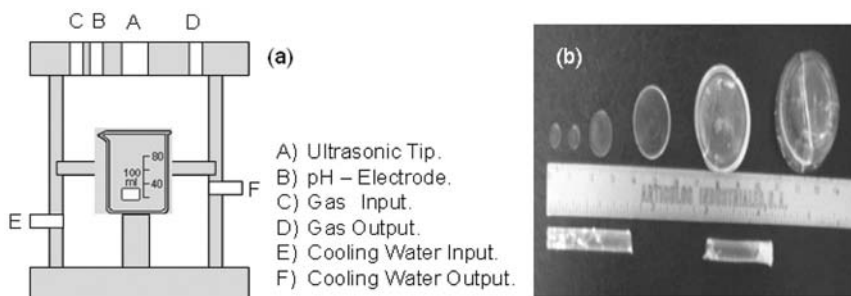

A) Ultrasonic Tip.
B) pH – Electrode.
C) Gas Input.
D) Gas Output.
E) Cooling Water Input.
F) Cooling Water Output.

FIGURE 1 (a) Schematic representation of the reaction chamber used to induce sol-gel process via ultrasonic action and (b) Picture of several pure sonolyzed sol-gel samples.

only an oxygen-environment was used (flow rate of about 300 ml min^{-1}).

2) In the lower part of the chamber, points E and F correspond to the input and output valves of a water cooling system. With this system, it is possible to control the reaction temperature, which most occur at low temperature in order to avoid excessive overheating of the reactant water.

As precursor solution, a mixture of 25 ml of tetraethoxysilane (TEOS-Fluka 99%, cat. Nr. 86578) and 25 ml of three-distilled water were placed into the glass vessel. The three-distilled water was boiled previously in order to eliminate dissolved gases and further cooled to room temperature. The initial pH of water was 6.5. In order to avoid any mixture over-heating under the action of ultrasonic waves, the temperature of the reactants was stabilized at 1°C for 1 hour; variations on this temperature were carefully maintained below 2% for optimal experimental conditions. The tip of the ultrasonic-wave generator which acts as an ultrasonic-homogenizer (Cole-Parmer-CPX, 20 KHz, max. power 600 W) was then placed in hole A. In order to fix the reaction atmosphere, the whole experimental system was sealed and isolated from room conditions, while an oxygen tube (AGA-ONU1072) was coupled to the upper part of the reaction chamber (hole C). Before the ultrasonic irradiation takes place, the selected gas was bubbled for 15minutes through the vessel which contains the reactive TEOS/H_2O-mixture in order to ensure the desired reaction conditions. The metallic ultrasound tip, which has been carefully located at the TEOS/H_2O surface interface, was then started at 60 Hz and 180 W. Oxygen flow is maintained through the whole sonolysis process. After 3 hours of programmed ultrasonic irradiation (on/off-intermittent sequences of 5 sec.), the chemical reaction start its process creating the sol-gel product. A detailed study concerning to the influence of the ultrasound energy and variations of the gas-atmosphere to create good quality sol-gel samples, is detailed discussed elsewhere [21]. An increment on the temperature of the TEOS/H_2O reactant solution of about 5°C has been observed during ultrasonic action. Twenty four hours later, two phases appear within the reaction vessel. Here, the upper product corresponds to an unreacted TEOS phase, whereas the lower condensed product appears as a colloidal suspension containing the induced hydrolyzed reaction. The unreacted TEOS was then extracted and eliminated while the remainder colloidal suspension was dropped and metered at different volumes into teflon-containers. The RED-PEGM-7 dopant molecule in solution was then added to the deposited colloidal suspension in order

to start the gelation process and the insertion of the dopant agent within the nanometric porous media of SiO_2. It should be noted here that the resulting hybrid materials possess higher purity level compared to other traditional synthesized sol-gel materials, since the use of the ultrasonic waves instead of the reactive solvents and catalyst, provides higher optical quality of the samples (see Fig. 1b).

The synthesis and characterization of the rod-like RED-PEGM-7 molecule and homologues series, N-methyl-N-{4-[(E)-(4-nitrophenyl)-diazenyl]phenyl}-N-(3,6,9,12,15,18,21-heptaoxadodeicos-1-yl)amine, which have been specifically designed for SHG was previously reported in the literature [22]. At room temperature, this LC-compound forms nematic phases and could form smectic phases, under visible laser irradiation, as a consequence of the induced laser photo-alignment. RED-PEGM-7 consists basically on an amphiphilic amino-nitro substituted azobenzene bearing a poly(ethylene-glycol) methyl ether side chain (PEGM). The nitro group and the disubstituted amino group act as electron-acceptor and electron-donor systems respectively. The molecular structure of this dye and absorption spectra of several RED-PEGM-7 sol-gel doped samples, are shown in Figure 2a and 2b respectively. This LC-mesogen can be dissolved in tetrahydrofuran (THF), methanol and chloroform. For the present application, a dissolution containing 15 ml of THF and 10 mg of
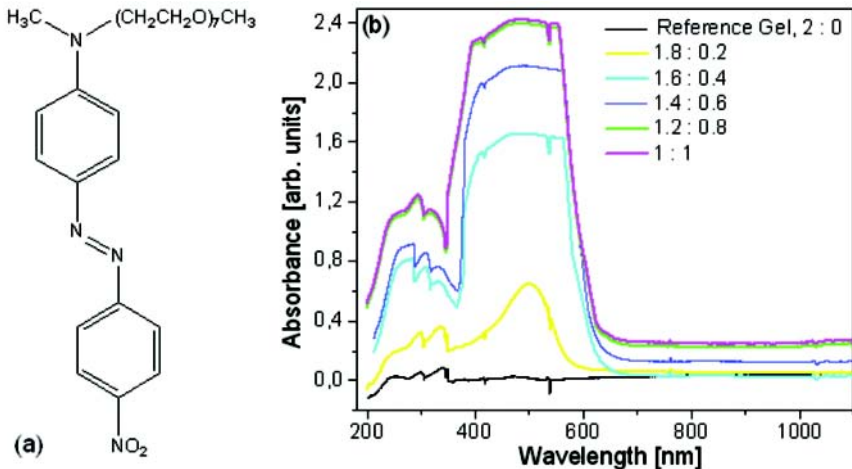

FIGURE 2 (a) Chemical structure of RED-PEGM-7, (b) Comparative absorption spectra of a pure reference sonolyzed sol-gel material and different RED-PEGM-7 doped composites.

RED-PEGM-7 was prepared. The doses of the hydrolyzed-TEOS (H-TEOS) versus dopant-dissolution (H-TEOS:D-D) were prepared with a precise volumetric pipe and deposited into teflon-containers in order to create different doped optical glasses. The hybrid materials were prepared with a total volume of 2 ml, varying the concentrations as follows (units in ml): 1:1, 1.2:0.8, 1.4:0.6, 1.6:0.4, 1.8:0.2. A pure sol-gel sample (2:0) was also prepared for reference and calibration purposes. The samples were then isolated with a plastic cover to avoid atmosphere and temperature variations, and conserved for three weeks at room temperature in a dry-dark environment in order to complete its drying process. Afterwards, monolithic cylindrical samples of about 5–8 mm of diameter and 0.6–1.5 mm thickness were obtained in most cases, as will be explained in sections 3.2–3.4 (see Fig. 1b). RED-PEGM-7, which is a polar compound, shows an intense red colour within the sol-gel-phase obtained by sonolysis. Figure 2b shows the linear absorption spectra of several doped composites compared with the reference sample. A wide absorption band centered at 499 nm is observed, whereas the red and IR-windows present a considerable minor absorption. Another enhancement of the absorption band at 300 nm is observed in the UV region for samples heavily doped. The pure sol-gel reference sample is practically transparent through the UV-VIS-IR spectra.

2.2. SHG Measurements

Prepared sol-gel hybrid spin-coated layers (0.5–3 μm thickness) have been studied as active media for SHG. The SHG-technique is illustrated in Figure 3. A commercial diode pumped passive Q-switched Cr:Nd:YAG Laser, operating at $\lambda_\omega = 1064$ nm, with a repetition rate of 25 KHz and a pulse duration of $\tau = 5$ ns (Smart Laser Systems, SMS-Berlin) was implemented to provide the fundamental wave. Typical pulse power of 80 μJ were integrated through the windows of an optical chopper (50 Hz) in order to irradiate the doped optical glasses, the intensity at the sample can be varied between 50–80 MW/cm^2. To avoid any possible damage of the samples caused by high intensities of strong focused beams, different neutral density filters were also used. It was possible to select the polarization of the fundamental laser beam by means of an IR-coated Glan-Taylor polarizer and a $\lambda/2$-quarz-retarder. A second polarizer was used as analyzer allowing the characterization of the SHG-light. The second harmonic wave ($\lambda_{2\omega} = 532$ nm) was detected by a sensitive photomultiplier (HAMA-MATSU: R-928) behind interferencial optical filters centered at 532 ± 10 nm. The SHG-device was calibrated by means of a y-cut
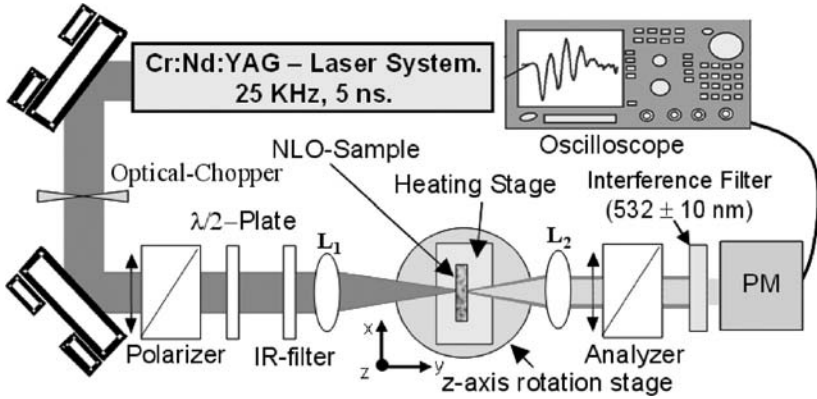
FIGURE 3 Experimental setup for SHG.

α-quartz crystal, wedged in the d_{11}-direction ($d_{11} = 0.54 \, \text{pmV}^{-1}$), which is used as a standard NLO-reference via the *Maker-Fringes* method [23].

2.3. XRD and AFM Measurements

Standard characterization methodologies like XRD, AFM and the BET-technique (*Brunauer, Emmett, Teller*) [24], have been applied to the pure and doped sol-gel samples in order to determine the surface area of the porous network, the porous dimensions, its crystallinity and purity level and the grain size and texture of these composites. Standard differential scanning calorimetry (DSC)-measurements and the pulsed photoacoustic technique have been also implemented in order to determine different thermodynamic phase transition of RED-PEGM-7 within the SiO_2 network.

3. RESULTS AND DISCUSSIONS

3.1. Photoacoustic and DSC Measurements

According to DSC and laser photoacoustic measurements, RED-PEGM-7 shows an amorphous/vitreous phase at room temperature and a liquid crystalline mesophase within the synthesized SiO_2 matrix. The observed phase transition diagram shows the following sequence (see Fig. 4): Amorphous/Vitreous: (-30 to 45)°C → LC: (45 to 105)°C → ISO: (105 to 210)°C. The single pulsed laser photoacoustic technique revealed a higher experimental resolution in order to determine the response of different phase transitions accurately
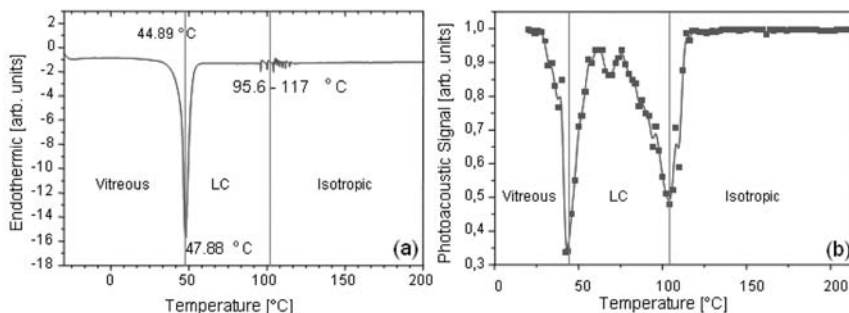
FIGURE 4 Temperature phase transition of hybrid materials: (a) resolved by DSC (heating process, $\Delta T = 5°C$ min^{-1}) and (b) resolved by the pulsed photo-acoustic technique ($\Delta T = 2°C$ min^{-1}).

[25]. Beyond 210°C, the doped sample starts its degradation process induced by combustion of the LC-mesogen. A shelter created by the SiO_2 matrix protects the dopant agent, since this molecule shows itself thermal stability only up to 185°C [22].

3.2. XRD and BET Measurements

In order to estimate the surface area generated within the porous media of the sonolyzed SiO_2 matrix; 25 mg of the pure sol-gel reference sample were studied by the BET-method, from 25 to 1000°C (RIG-100 equipment). The BET-studies indicated large surface areas varying from 500 to 650 $m^2 g^{-1}$, compared to those obtained by traditional sol-gel methods. Other recent methodologies implemented to create amorphous SiO_2, for instance by the aerogel-route, have reported surface areas of up to 2000 $m^2 g^{-1}$. Last kind of composites are however, very difficult to synthesize [26–27]. A wide temperature range varying from 20 to 600°C, where the sample presents stability of its surface area has been observed. After 600°C, the sample shows a drastic structural collapse and the average surface area drops from 550 to only 2 $m^2 g^{-1}$ as the temperature arises to 1000°C [21]. High resolution AFM measurements on the sonolyzed SiO_2 matrix of a pure reference sample showed porous dimensions varying between 10–35 nm.

XRD-studies performed in both, the pure reference material and hybrid composites are shown in Figure 5. As expected at room temperature, the pure sol-gel reference sample shows a XRD-pattern characteristical of an amorphous silicon oxyde phase, which is certified by a broad peak centered at 21.985°. The XRD-pattern of the doped composite at room temperature (sample 1.4:0.6) shows a similar
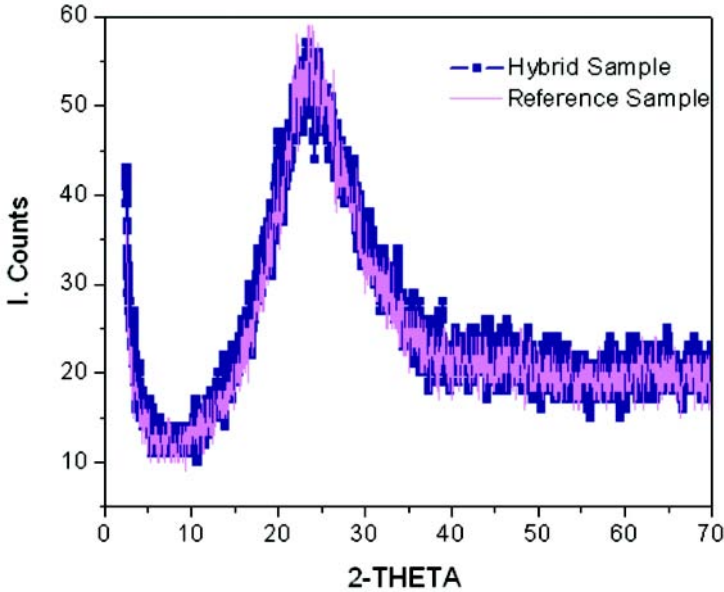
FIGURE 5 XRD-patterns: comparison between a doped composite (1.4:0.6) and the pure reference sample (at room temperature), showing same crystallographic structure.

amorphous structure to that observed for the reference sample, so that the hybrid optical composite remains as an amorphous/glassy phase. Surprisingly, SHG-signals arising from the spin coated hybrid composites were detected only in the vitreous-phase (vide infra).

3.3. SHG Measurements

According to other theoretical and experimental studies on the synthesis of organic-inorganic sol-gel hybrid materials for NLO-applications [7,28–30], an optimal TEOS:Chromophore-concentration can be found in order to obtain the highest possible 2nd-order NLO-response in such systems for each NLO-chromophore, which allows at the same time an increment on the molecular concentration and an enhancement of the temporal stability of the second order NLO-response, but it also increases the aggregation problems. Last fact represents a limitation for the non-linear response of these materials due to intermolecular interactions introduced by molecular aggregation problems. In such studies, it has been proved that the competition between the chromophore electric-field and

the chromophore-chromophore electrostatic interactions leads to a maximum value of the NLO-response versus chromophore number density. On the other hand, it has been also stated that H-TEOS, which forms SiO_2 after drying, among other cross-linking agents, acts as screener unit for the electrostatic interactions between non-linear chromophores, which eliminates in some degree the aggregation problems for high chromophores concentrations. In fact, this could be the case considering the high saturation level observed in the absorption spectra of our heavily doped samples (see Fig. 2b). According to these studies, the thin film samples prepared with the selected H-TEOS:LC-Dopant concentrations were studied as active media for SHG. A relation in agreement with these reports have been found between the SHG-signal and the H-TEOS:Push-pull-chromophore concentrations. Moreover, a dependence on the mechanical stability of the samples with the selected dissolution concentrations has been also found. The calibrated SHG signals to obtain the d_{eff}-values for different unpoled doped thin film glasses are shown in Figure 6 (S-P configuration).

The d_{eff}-values measured at room temperature reveals an optimal concentration between the H-TEOS and RED-PEGM-7 doped solution
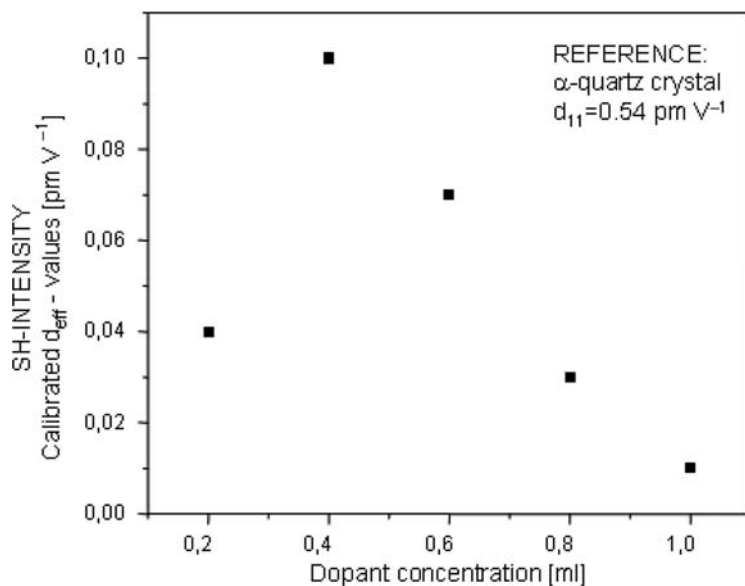

FIGURE 6 d_{eff}-values of different doped RED-PEGM-7 sonogel materials, taken at room temperature ($3\,\mu m$ layers).

in order to obtain the best possible SHG signal among the studied thin film composites. The moderate 1.6:04 doped material shows the highest d_{eff}-coefficient valued to $0.10\,\text{pm V}^{-1}$, which is about 20% of the reference value. This fact represents an experimental evidence of the screener action induced by SiO_2, which avoids electrostatic interactions between non-linear chromophores and eliminates aggregation problems, at least for this TEOS:RED-PEGM-7 concentration, compared to the deeply-doped samples. As expected, no SHG-signal arises from the pure reference sample, and within other phases detected by DSC and photoacoustic.

The origin of the observed SHG of the unpoled RED-PEGM-7 chromophore within the amorphous thin film SiO_2 network at room temperature is until now, not completely understood. Probably, the molecular interactions between the SiO_2 matrix and the randomly oriented domains of the nematic phase at room temperature could play an important role while the drying process of the samples takes place, in order to achieve a non-vanishing average orientation. Furthermore, the polar nature of this compound which apparently behaves like a ferroelectric state at this temperature range, since no external poling electric field to produce weakly SHG is needed, could also help to create the average non-centrosymmetric structure required for the second order NLO-response within the amorphous bulk material, because this polar condition is equivalent to a non-centrosymmetric arrangement of the molecules [31–33]. Finally, due to the enhancement of the absorption spectra to the UV region (Fig. 2b), which suggest H-type aggregates, it could be possible that oriented face to face H-aggregates rule the molecular domain orientation of the mesogens within the sol-gel phase in one favored direction, imposed by geometrical factors which may force this preferential molecular arrangement during a very slow drying process. Present experiments are currently under investigations in order to elucidate last observations, where the quadrupole-moment mechanism will be also considered as the cause for SHG of centrosymmetric structures [34].

According to Figure 2b, the absorption spectra of the 1.6:0.4 and 1.4:06 doped samples illustrate an unsaturated transmission curve compared with those of heavily doped samples. This fact suggests high molecular concentration and aggregation problems for the last kind of composites, which are not supported by the screener action of a low mass of SiO_2. Last observation represents a limitation for the non-linear optical response of these hybrid-materials due to the intermolecular interactions caused by molecular aggregation. The poorly 1.8:0.2 doped sample shows also very low SHG-activity and a weak absorption spectra, which may indicate insufficient chromophore loading and

excessive SiO_2 concentration to achieve the possible average non-centrosymmetry induced by the polar NLO-chromophores. Furthermore, a mechanical stability limit for the chromophore loading, which corresponds in high degree to the optimal NLO-response of the samples, was also observed. This relationship has been monitored by AFM measurements as explained in next section.

For comparison proposes, a similar NLO-response for other LC-mesogens within an amorphous phase, either in a pure state or within a sol-gel phase has been previously reported. For instance, the amorphous glass-like blue phases of ferroelectric bent shaped compounds exhibit SHG-activity at room temperature without the action of any external poling field. For the vitrified blue phases and Sm-CP phases, d_{eff}-values of about 0.06-1 pm V^{-1} and 1.10 pm V^{-1} have been reported respectively [11,33–34]. The highest d_{eff}-coefficient of the glassy samples studied in this work lay in the same order of magnitude of some of these mesogens [35–38]. On the other hand, an unpoled SiO_2-methylnitroaniline (MNA) doped matrix, showed SHG at room temperature, the d_{eff}-coefficient was however, not evaluated [6]. In a phase matched geometry with one of the most widely studied ferroelectric LC-materials (DOBAMBC), a d_{eff}-value of 0.0008 pmV^{-1} was determined [39]. This suggests huge potential for poled spin-coated RED-PEGM-7 hybrid thin films which will be considered for future applications.

3.4. AFM Measurements

Figure 7 shows AFM micrographs (obtained by contact-mode) of the topology of three different samples: the pure reference glass, a slightly doped (1.6:0.4) sol-gel hybrid sample and a heavy doped hybrid
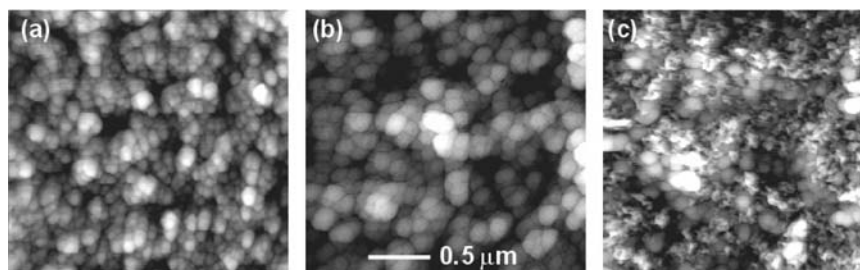

FIGURE 7 AFM-scanned micrographs of different sono-gel materials (same length-scale): (a) reference sample, (b) moderate doped 1.6:0.4-sample and (c) deeply doped 1.2:0.8 sample.

composite (1.2:0.8). The pure reference sample (Fig. 7a) shows a stable and uniform texture with a grain size of around 0.08 microns, whereas the light doped sample (Fig. 7b) shows an enlargement of this structure with a grain size of around 0.15 microns, the texture of this sample remains uniform in size and homogeneous without irregularities. Finally, the heavy doped sample (Fig. 7c) shows a decrement of the grain size varying from 0.05 to 0.1 microns; the resulting irregular texture of this sample exhibits a highly disordered structure, which may be the product of molecular segregation of the dopant chromophore dissolution and the SiO_2 gel. All this leads to phase segregation within the SiO_2 matrix and to the rupture of the monolithic structure, as has been confirmed repetitively after the drying process of several samples.

In fact, the undoped reference samples always showed good mechanical quality and monolithic consistence, whereas the resulting heavily doped materials featured a fractured structure after the drying time, forming several tiny and breakable pieces. The slightly and moderated doped samples were always mechanically stable and showed, in most cases, monolithic consistence. All this could be interpreted qualitatively as follows: there may be a most favorable porous size within the SiO_2 matrix achieved after the drying time, which contains an optimal chromophore concentration to produce measurable NLO-response and mechanical stability. As the chromophore is slightly added to the SiO_2 host matrix, a moderate enlargement of the constituting hybrid particles is observed. If an excessive overloading of the chromophore dissolution is presented, then the solubility limit of the chromophore within the gel-phase is overcome, a phase segregation take place and the dopant molecules are dispersed among SiO_2 particles. As consequence, a chaotic collapse of the sample occurs while drying and the sample becomes highly unstable, the mechanical consistence disappears to create a fragile network. AFM-studies revealed also a good agreement between the optimal NLO-response of the samples, achieved by a convenient SiO_2:Chromophore concentrations and the mechanical stability of the hybrids. Here, best mechanical and NLO-properties for the studied molecule, corresponds to the 1.6:0.4 and 1.4:0.6 moderate doped composites.

Last results on the synthesis and characterization of hybrid sonolized sol-gel composites, has been carried out as mentioned before, as a first step for the development of photonic organic-inorganic devices. Current studies in order to improve finely the SiO_2 Gel:Chromophore concentrations and to create poled spin-coated thin films and planar waveguiding structures with these sono-gel materials and other RED-PEGM homologues, are at present time under investigation, where an important improvement on the SHG signals is expected.

4. CONCLUSIONS

The highly pure SiO_2 sol-gel materials created by ultrasonic action behave as an appropriate host for LC-compounds. Large surface areas of up to $650\,m^2g^{-1}$ at room temperature and stable mechanical behavior up to $1000^{\circ}C$ of the obtained gels, create an excellent environment for the confinement of dopant species. A newly synthesized RED-PEGM-7 liquid crystalline mesogen has been successfully introduced within the amorphous SiO_2 network. The resulting hybrid composites exhibit good mechanical properties and SHG in thin film layers for an optimal Sono-Gel:Dopant concentration. As has been shown in this work, best monolithic consistence and NLO-response were found for the moderated doped samples at rates of: 1.4:0.6 and 1.6:0.4. The reference sample and the less doped composites presented always monolithic integrity, but a negligible SH-signal in last case. The photoacoustic technique has enabled us to determine accurately different phase transitions of the hybrid materials, in order to identify interesting thermodynamic states, to be studied optically. Measurable d_{eff}-values for unpoled hybrid thin films were evaluated implementing the *Maker-Fringes* method. A maximal d_{eff}-coefficient of about $0.10\,pm\,V^{-1}$ was evaluated at room temperature. Finally, a comprehensive AFM and XRD study confirmed an amorphous composition of the pure and hybrid materials. These composites however, exhibit a remaining non-centrosymmetric structure of the polar RED-PEGM-7 domain configuration within the amorphous sol-gel phase, which is suitable for SHG. Further studies in order to determine if these domains could present an improved oriented arrangement and symmetry properties, are currently under investigation.

REFERENCES

[1] Brinker, C. J. & Scherer, G. (1990). *Sol-Gel science, the physics and chemistry of Sol-Gel processing*, Academic Press: San Diego, California.
[2] Fardad, M. A., Mishechkin, O. V., & Fallahi, M. (2001). *Journal of Lightwave Technology*, *19*, 84.
[3] Zhanjia, H., Liying, L., Lei, X., Zhiling, X., Haibo, L., Wencheng, W., Fuming, L., & Mingxin, Y. (2001). *Acta Optica Sinica*, *21*, 111.
[4] Clark, A., Terpugov, V., Medrano, F., Cervantes, M., & Soto, D. (1999). *Optical Materials*, *13*, 355.
[5] Sun, X. D., Wang, X-J., Shan, W., Song, J. J., Fan, M., & Knobbe, E. T. (1997). *Journal of Sol-Gel Science and Technology*, *9*, 169.
[6] Sanchez, C. & Leveau, B. (1996). *Pure. Appl. Opt.*, *5*, 689.
[7] Reyes-Esqueda, J., Darracq, B., Garcia-Macedo, J., Canva, M., Blanchard-Desce, M., Chaput, F., Lahlil, K., Boilot, J. P., Brun, A., & Levy, Y. (2001). *Optics Communications*, *198*, 207.
[8] Choi, D. H., Lim, S. J., Jahng, W. S., & Kim, N. (1996). *Thin Solid Films*, *287*, 220.

 [9] Hosoya, Y., Ohsugi, S., Muto, S., & Kurokawa, Y. (1996). *Thin Solid Films*, *283*, 221.

[10] Liying, L., Lei, X., Zhanjia, H., Zhiling, X., Jie, C., Wencheng, W., & Fuming, L. (1999). *Physics Letters A*, *262*, 206.

[11] Rauch, S., Selbmann, Ch., Bault, P., Sawade, H., Heppke, G., Morales-Saavedra, O., Huang, M. Y. M., & Jákli, A. (2004). *Phys. Rev. E*, *69*, 021707.

[12] Kajzar, F. & Swalen, J. D. (1996). *Organic thin films for waveguiding nonlinear optics*, Gordon and Breach Publishers: Bellingham, Washington, USA.

[13] (a) Selvarajan, A. (2001). *IEEE Journal of Quantum Electronics*, *37*, 1117.
     (b) Priebe, G., Kunze, K., Kentischer, F., Schulz, H., Morales, O., Macdonald, R., & Eichler, H. J. (2000). *Proceedings of SPIE*, *128*, 3143.

[14] Wilkes, G. L., Orler, B., & Huang, H. H. (1985). *Polymer Prep.*, *26*, 300.

[15] Morikawa, A., Iyoku, Y., Kakimoto, M., & Imai, Y. (1992). *J. Mater. Chem.*, *26*, 79.

[16] Suslick, K. S. (1986). *Adv. Organomet. Chem.*, *25*, 73.

[17] de la Rosa-Fox, N., Esquivias, L., Zarzycki, J. (1987). *Diffusion and Defect Data*, *53*, 363.

[18] Suslick, K. S. (1990). *Science*, *247*, 1373.

[19] Noltingk, B. E. & Neppiras, E. A. (1950). *Proc. Phys. Soc. B*, *63*, 674.

[20] Esquivias, L. & de la Rosa-Fox, N. (2003). *Journal of Sol-Gel Science and Technology*, *26*, 651.

[21] Flores-Flores, J. O. & Saniger, J. M. (2005). *Journal of Sol-Gel Science and Technology*, Submitted.

[22] Rivera, E., Belletéte, M., Natansohn, A., & Durocher, G. (2003). *Can. J. Chem.*, *81*, 1076.

[23] Prasad, P. N. & Williams, D. J. (1991). *Introduction to nonlinear optical effects in molecules and polymers*, Wiley InterSciences: New York, Chapter 6, 117.

[24] Greggand, S. J. & Sing, K. S. W. (1982). *Adsorption, Surface Area and Porosity*, Academic Press: London.

[25] (a) Pineda-Flores, J. L., Castañeda-Guzmán, R., Villagrán Muniz, M., & Huanosta, T. A. (2001). *Apply. Phys. Lett.*, *79*, 1166.
     (b) Marchi, M. C., Castañeda-Guzmán, R., Pérez-Pacheco, A., Bilmes, S. A., & Villagrán-Muñiz, M. (2004). *International Journal of Thermophysics*, *25*, 491.

[26] Smirnova, I. (2002). *Synthesis of silica aerogels and their application as a drug delivery system*, Dissertation: TU-Berlin, Germany.

[27] Saraidarov, T., Reisfeld, R., & Pietraszkiewicz, M. (2000). *Chem. Phys. Lett*, *330*, 515.

[28] Harper, A. W., Sun, S., Dalton, L. R., Garner, S. M., Chen, A., Kalluri, S., Steier, W. H., & Robinson, B. H. (1998). *J. Opt. Soc. Am. B*, *15*, 329.

[29] Amano, M., Kaino, T., Yamamoto, F., & Takeuchi, T. (1990). *Mol. Cryst. Liq. Cryst.*, *182 A*, 81.

[30] Andrews, M. P. & Najafi, S. I. (1997). *Sol-Gel polymer photonic devices, CR68*, SPIE-Optical Engineering Press.

[31] Olenik, I. D., Torre, R., & Copic, M. (1994). *Phys. Rev. E*, *50*, 3766.

[32] Barnik, I., Blinov, L. M., Dorozhkin, A. M., & Shtykov, N. M. (1983). *Mol. Cryst. Liq. Cryst.*, *98*, 1.

[33] (a) Walba, D. M. (1991). *Ferroelectrics*, *121*, 247.
     (b) Gall, G. J. (1994). *Sol-Gel Optics III, Proceedings of SPIE*, 2288.

[34] (a) Zhong-Can, O. Y. & Yu-Zhang, X. (1985). *Phys. Rev. A*, *32*, 189.
     (b) Arakelyan, S. M. (1981). *Mol. Cryst. Liq. Cryst.*, *71*, 137.
     (c) Shtykov, N. M., Blinov, L. M., Dorozhkin, A. M., & Barnik, M. I. (1982). *Pis'ma Zh. Eksp. Teor. Fiz.*, *35*, 142.

[35] Morales-Saavedra, O., Bulat, M., Rauch, S., & Heppke, G. (2004). *Mol. Cryst. Liq. Cryst.*, *418*, 607.

[36] Ortega, J., Pereda, N., Folcia, C. L., Extebarria, J., & Ros, M. B. (2000). *Phys. Rev. E*, *63*, 011702.

[37] Morales Saavedra, Omar G. (2003). *Spatially Resolved Second Harmonic Microscopy in Novel Bent Shaped Liquid Crystalline Mesogens and Applications to Organic QPM-Waveguiding Structures*, Dissertation, W&T Verlag: TU-Berlin, Germany.

[38] Macdonald, R., Kentischer, F., Warnick, P., & Heppke, G. (1998). *Phys. Rev. Lett.*, *81*, 4408.

[39] Shtykov, N. M., Barnik, M. I., Beresnev, L. A., & Blinov, L. M. (1985). *Mol. Cryst. Liq. Cryst.*, *124*, 379.