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Optical and structural characterization of thin films containing metallophthalocyanine chlorides

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ABSTRACT

The structural and optical investigation of thin films containing aluminum and gallium phthalocyanine chlorides is presented. The films were fabricated by Physical Vapor Deposition technique onto quartz substrates and annealed after fabrication in an ambient atmosphere for 24 h at the temperature equal to 150 °C or 250 °C. The experimental results and theoretical calculation of the Third Harmonic Generation process are reported. The third order nonlinear optical properties are expected and can be more or less accurately predicted due to the assembly of the molecules and theoretical calculations of the frequency-dependent dipole polarizabilities, third hyperpolarizabilities, third order susceptibilities, frontier and second frontier molecular orbitals. These parameters were used to understand the relationship of optical properties with the molecular structures. We found that the annealing process causes formation of nanostructures and the value of the third order optical susceptibility makes these materials interesting for future nonlinear optical applications.

1. Introduction

Phthalocyanine is an organic compound that forms stable complexes with several metals that have long been known as blue or green dyes and pigments. The metallophthalocyanine chlorides (MClPc, M = Al and Ga) are not only blue pigments, but also nontoxic p-type organic semiconductors with good thermal and chemical stability. These materials are extremely attractive for use in optical and electronic devices. The performances of these devices are strongly dependent on the nature of the material and its processing, design, and deposition technique. The factors including film fabrication technique, morphology of the film and the temperature of the annealing process are very important for the efficiency of optical or electronic devices.

Third order nonlinearities are usually described by the third order susceptibility $\chi^{(3)}(-\omega_4;\omega_3,\omega_2,\omega_1)$, where the frequencies fulfill the following equation: $\omega_4 = \omega_3 + \omega_2 + \omega_1$ and are of special interest since they provide a mechanism for all optical switching, *i.e.* control of light by light. In the case where all frequencies have the same value (ω), the third order susceptibility $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$ describes effects that can also be conveniently viewed as light-induced changes in the refractive index of the nonlinear medium. The typically weak Van der Waals interactions in organic systems permit their optical characteristics, to a large extent, to be traceable to the properties of the constituent molecules. It has been well recognized in the field of third order optical nonlinearities that the third order hyperpolarizability γ, the microscopic analogy of $\chi^{(3)}$, attains high values for those molecules that possess extensive π-electron conjugation [1]. Macrocyclic molecules like phthalocyanines provide one example of a π-conjugated system that is virtually two dimensional, and therefore are interesting samples for studying optical nonlinearities. The properties of phthalocyanines are to some extent dependent on the presence and identity of the central metal atom. The role of the central metal atom has been investigated in some experiments [2–6]. A clear enhancement of the cubic hyperpolarizability has been observed for phthalocyanines containing cobalt, and the result has been justified on the basis of its uncompleted *d*-shell character [2,3]. More systematic data on the spectral dependence of the nonlinear response are needed in order to properly take into account the effect of

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frequency dispersion factors. Third Harmonic Generation (THG) experiments of spin-coated thin films of octaalkoxyphthalocyanines [7] and naphthalocyanines [8] also throw some light on the effects of metal substitution.

The main experimental techniques that have been used for third order nonlinear optical (NLO) processes of phthalocyanines are: THG [9], degenerate four-wave mixing (DFWM) [10] and Z-scan [11]. The primary emphasis of this work has been to measure $\chi^{(3)}$ for THG processes in AlPcCl and GaPcCl (Fig. 1). The main aim of this paper has been focused on a determination of the microscopic third order NLO behavior of the title phthalocyanine chlorides by the theoretical approaches and experimental investigation. So, we present here an *ab-initio* study utilizing time-dependent Hartree–Fock (TDHF) procedure on dispersion-free and frequency-dependent dipole polarizabilities, second hyperpolarizabilities as well as THG measurements. The linear optical characterizations and $\chi^{(3)}$ values determined by UV–Vis and THG spectroscopies, respectively, for AlPcCl and GaPcCl have been compared with quantum mechanical calculations. The highest occupied molecular orbitals (HOMOs), the lowest unoccupied molecular orbitals (LUMOs) and the HOMO–LUMO band gaps have been also evaluated by density functional theory DFT calculations.

2. Experimental methods

2.1. The film preparation

The AlClPc and GaClPc thin films were fabricated by a Physical Vapor Deposition (PVD) technique using typical home-made equipment [12–16]. The thin films were successfully deposited on a quartz substrate. The process of fabrication was carried out under pressure about $3*10^{-3}$ Pa. The powders of AlClPc and GaClPc (97% Sigma–Aldrich Co.) were loaded into a quartz effusion cell with a nozzle diameter of 10 mm. The source material was thermally evaporated from quartz crucible surrounded and heated by tungsten resistance coil. The temperature of the evaporation source was manually controlled (K-type thermocouple). The temperatures of the source for metallophthalocyanine chlorides were kept at 270 °C during whole evaporation process. The deposition rate was in the range 0.1–0.2 nm/s and depended on the source material, its temperature and distance between the source material and the substrate. The quartz plates were located on the holder about 10 cm above the evaporation source. The thickness of fabricated AlClPc and GaClPc thin films was about 100 nm. Substrates were held at room temperature during the deposition process. Selected samples were immediately subjected to an annealing process to assure different orientation of the molecules on the substrate, different nanostructures assembling on the surface and related linear (transmittance) and third order nonlinear optical properties.

2.2. Characterization of nanostructural thin films

Third Harmonic Generation (THG) measurements were carried out using the rotational Maker fringe technique [17] in the transmission scheme [3,18]. A fused silica glass plate was used as a reference material for THG measurements. A Q-switched mode-locked Nd:YAG laser working at 1064 nm with 16 ps pulse duration, 1.6 mJ power per pulse and the repetition frequency of 10 Hz was used as a fundamental laser beam. The fundamental beam was focused on the sample using a lens, whose focal distance was about 250 mm. A diameter of the beam was equal to 0.4 mm at the film, which allowed achieving the power density equal to 5 GW/cm^2. The intensity at the entrance to the sample was described by Gaussian distribution in space and time. A rotation stage with the mounted sample allowed the variation of the incidence angle, with a resolution of 0.5°. After passing the sample, the transmitting filter was used to cut the pump laser beam before the photomultiplier. Detector saturation was prevented using linear neutral density filters, whose transmittance value was taken into account during data fitting. The third harmonic signals were detected by the photomultiplier (HAMAMATSU R1828-01), integrated by a box-car average system and processed by a computer. A fast photodiode (Ph2A) was used to monitor the input energy. Finally, the so-called Maker fringes were generated by rotating the sample through the range of ±70° to the fundamental laser beam and recorded.

The linear optical properties – the transmission spectra were measured at normal incidence in the spectral range 190–1100 nm using a double – beam spectrophotometer (Perkin Elmer Lambda 2 UV/VIS/NIR). In order to determine structural properties of the films, X-Ray Diffraction (XRD) and Atomic Force Microscopy measurements were taken. The AFM imaging was performed in the contact mode, with an Agilent 5500 instrument equipped with an MSNL–D Bruker cantilever. The process of formation of the crystalline phase and the type of the self-assembling nanonstructures

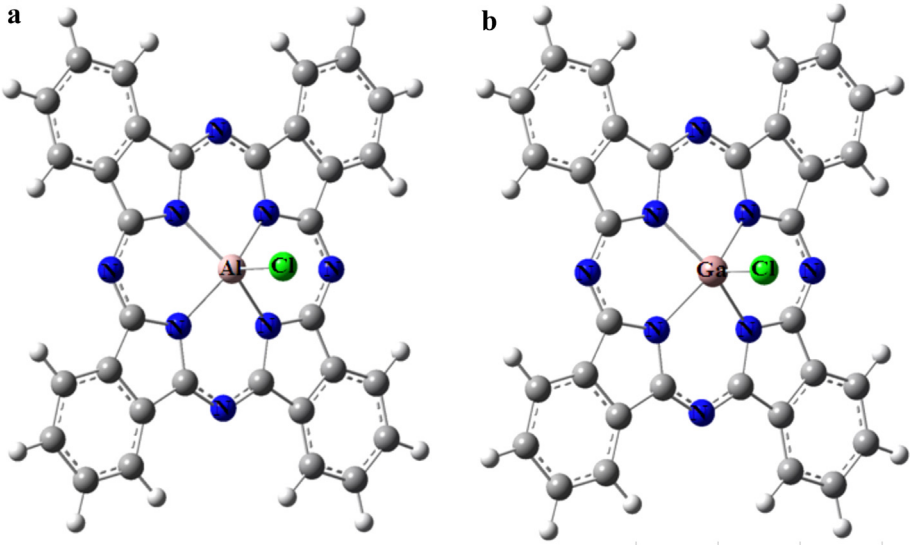

Fig. 1. Chemical structures of AlClPc (a) and GaClPc (b).