Impact of annealing process on stacking orientations and second order nonlinear optical properties of metallophthalocyanine thin films and nanostructures

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The paper presents the second order nonlinear optical properties of Cu, Co, Mg and Zn metallophthalocyanines thin films. The films were fabricated by physical vapor deposition in high vacuum onto fused silica glass substrates. In order to investigate both optical and structural properties an annealing process in an ambient atmosphere for 12 h at temperatures equal to either 150 °C or 250 °C applied after the fabrication process. Atomic force microscopy images were obtained for an observation of the structural property changes. The thickness of the thin films was in the range from 80 nm to 120 nm. The size and shape of the forming nanostructures were different for different metallophthalocyanines and depended on the phase of the material. As-deposited sample of copper phthalocyanine formed the smallest nanostructures – standing columns with 100 nm of the height and 40 nm of the diameter. Annealed sample formed the largest nanostructures – lying cuboids with dimensions: 10 × 1000 × 40 nm. The second harmonic generation measurements have been carried out in order to investigate the second order nonlinear optical properties and their dependence on the structure of the thin films after the annealing process. Moreover the fits based on the two models have been carried out in order to understand deeper the origin of the experimental findings. It was found that the annealing process can significantly modify both the structural and the second order nonlinear optical properties of the metallophthalocyanine thin films.

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1. Introduction

During the last few years, organic nonlinear optical materials have gained a great deal of research interest, because they offer several advantages such as large nonlinearity, fast response and low losses compared to inorganic materials [1–4]. These properties play a very important role in applications in optoelectronics, photovoltaic and photonic devices including flat-screen TVs, e-book readers, optical storage, optical switching, organic thin film transistors, organic photovoltaic devices, holography, biosensors, optical communications, solid-state lighting, but also in harmonic generation and photosensitizers for photodynamic therapy [5–11].

Second order optical nonlinearities in organic compounds derive from a highly polarizable charge asymmetry of a π-conjugated system restricted to groups of different electron affinities. The polarization is a nonlinear function of the applied field and the efficacy of the molecule to be polarized asymmetrically is represented by its first order hyperpolarizability. The second order nonlinear optical effects can occur only in molecules lacking an inversion center. A bulk material, thin film or nanostructures composed of nonlinear molecules must also lack a center of symmetry to exhibit second order optical properties, which can be defined by the second order optical susceptibility χ (2). Moreover, these materials should exhibit low optical losses and they have to be thermally, physically and photochemically stable for industrial applications [12,13].

Phthalocyanines (Pcs) are very special organic materials because of their variety, architectural flexibility and exceptional environmental stability. Pcs offer great opportunities to adapt their properties over a wide range either by substituting different metal atoms into the ring or by altering peripheral and axial functionalities. This substitution facilitates the tailoring of physical parameters of metallophthalocyanines (MPCs) over a broad range and,
consequently, allows modulating the physical, electrical and optical behavior of the compounds. Phthalocyanines can adopt more than 70 different metallic and non-metallic ions into the ring cavity [14].

Metallophthalocyanines represent a large family of materials with centrosymmetric planar structure of 16 member rings with 18 delocalized π-electrons which leads to their special optical properties and extraordinary stability [15–17]. The metal-free phthalocyanine forms completely planar molecular structure with C4v symmetry. The diameter of the phthalocyanine cavity can also fluctuate. Table 1 illustrates these effects. From these differences in geometries of MPCs, four different states of the phthalocyanine ring are identified: metal ion size smaller than the phthalocyanine cavity size, metal ion size approximately equal to phthalocyanine cavity size, metal ion size greater than phthalocyanine cavity size and metal ion size much larger than phthalocyanine cavity size. These four states exhibit four structural effects of the phthalocyanine ring: ring contraction, equilibrium ring geometry, ring expansion and metal non-planarity.

This article is devoted not only to second order nonlinear optical properties of Physical Vapor Deposition (PVD) deposited MPCs thin films and nanostructures (where M = Co, Cu, Zn and Mg), investigated by Second Harmonic Generation (SHG) technique, but also to the structural properties of the generated nanostructures as a function of the applied temperature during the annealing process and mutual correlations between the structural and nonlinear optical properties. The aims was achieved in this work through theoretical and experimental investigation of the Second Harmonic Generation (SHG) of the systems, which sheds light into the differences in the nonlinear optical spectra of MPCs after the annealing process and Atomic Force Microscopy (AFM) in order to investigate thin film structure before and nanostructures after the annealing. To reach this goal, four different MPCs have been investigated. Three of them: copper phthalocyanine (CuPc), cobalt phthalocyanine (CoPc) and zinc phthalocyanine (ZnPc) contain 3d electron shell of the metal atoms. CuPc and CoPc form flat molecular structure with D₄h symmetry, while ZnPc forms non-planar (zinc metal adopting position out of the plane) molecular structure with C₄ᵥ symmetry. MgPc forms flat molecular structure with D₄h symmetry, but the central metal lacks d electrons. Investigation was focused on metallophthalocyanines (MPCs) because the substitution of different metal atoms into the ring should lead to changes in the structural and linear/nonlinear optical properties of the thin films.

The long-range aim of this study is to learn how the substitution of the different metal atoms into the ring of the MPCs correlate with the nonlinear optical properties and also to enhance those properties via control of the nanostructures forming inside thin film's during annealing process.

2. Experimental methods

2.1. Deposition of thin films and nanostructures

The all investigated MPCs thin films and nanostructures were fabricated by PVD technique using typical vacuum evaporation equipment [18–22]. The thin films have been deposited on a fused silica glass substrate. The process of the deposition has been carried out under pressure of approximately 2·10⁻⁵ Torr. Powders of the source material (CoPc, ZnPc, CuPc and MgPc, 97% Sigma–Aldrich Co.) were loaded onto a quartz effusion cell with a nozzle diameter equal to 10 mm. The materials were thermally evaporated from a quartz crucible heated by tungsten resistance coil. The temperature of evaporation source has been manually controlled (using K-type thermocouple and autotransformer). Temperatures of source for metallophthalocyanines materials are presented in Table 2.

Table 1
The variation in phthalocyanine cavity size and the non-planarity of large metal ions in simple metallophthalocyanines.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cavity diameter [10⁻⁵ m]</th>
<th>Distance of M from N₈ plane [10⁻⁸ m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂Pc</td>
<td>393</td>
<td>0</td>
</tr>
<tr>
<td>MgPc</td>
<td>374</td>
<td>0</td>
</tr>
<tr>
<td>MnPc</td>
<td>387</td>
<td>0</td>
</tr>
<tr>
<td>FePc</td>
<td>385</td>
<td>0</td>
</tr>
<tr>
<td>CoPc</td>
<td>382</td>
<td>0</td>
</tr>
<tr>
<td>NiPc</td>
<td>386</td>
<td>0</td>
</tr>
<tr>
<td>CuPc</td>
<td>386</td>
<td>0</td>
</tr>
<tr>
<td>ZnPc</td>
<td>396</td>
<td>7.5</td>
</tr>
<tr>
<td>SnPc</td>
<td>393</td>
<td>118</td>
</tr>
<tr>
<td>PtPc</td>
<td>396</td>
<td>121</td>
</tr>
<tr>
<td>PbPc</td>
<td>395</td>
<td>125</td>
</tr>
</tbody>
</table>

Table 2
Parameters of PVD process for MPCs thin films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature of deposition [°C]</th>
<th>Time of deposition [min]</th>
<th>Thickness [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuPc</td>
<td>350</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>MgPc</td>
<td>340</td>
<td>20</td>
<td>120</td>
</tr>
<tr>
<td>ZnPc</td>
<td>360</td>
<td>15</td>
<td>90</td>
</tr>
<tr>
<td>CoPc</td>
<td>360</td>
<td>15</td>
<td>80</td>
</tr>
</tbody>
</table>
532 nm ± 1 nm) and rejected the fundamental laser beam before the photomultiplier. The second harmonic signals were measured by an appropriate photomultiplier (HAMAMATSU R1828-01) and integrated box-car average system and next processed by a computer. A portion of the input beam was measured by a fast photodiode Ph2 to control the input energy. For each sample, the measurements of the second harmonic signal intensity as a function of the angle of incidence was performed on a total of 50 laser impulses for each angular position. Finally, the so-called Maker [23–25] fringes were generated by rotating the sample through the range of ±70° to the normal and recorded.

AFM imaging was performed with an Agilent 5500 instrument equipped with a MSNL-D Bruker cantilever in contact mode.

### 3. Theoretical models of SHG

Second Harmonic Generation is a nonlinear optical process during which the fundamental beam at the frequency \(\omega\) interacts with a nonlinear medium and causes a generation of an additional spectral component at frequency \(2\omega\). The SHG process is strongly dependent on the crystalline structure of the materials. Generally, this method has been especially developed in order to determine the value of second order nonlinear susceptibility of a non-centrosymmetric material by measuring the change in intensity of second harmonic signal versus the incidence angle. Fig. 2 shows an example of second harmonic signal as function of the incidence angle \(\theta\) for the reference material. The SH signal has been recorded while rotating the sample with respect to the fundamental beam. The registered patterns show the typical shape, i.e. the Maker fringes. The fringes become tighter with the increase of incidence angle \(\theta\) because the length of interaction \(L\) in sample increases nonlinearly with the angle. When the thickness of the material \(d\) is higher than the coherence length \(L_c\), the wave’s constraint and free interfere to each other, and the intensity of second harmonic signal can pass through a series of maxima and minima.

A few theoretical models, using various approximations, have been described in order to determine the value of \(\chi^{(2)\text{eff}}\) from the Maker fringes patterns [26–28] obtained by the SHG technique.

#### 3.1. Comparative model

This model (also known as the Lee model [29]) compares directly the maximum amplitude of the light intensity for the second harmonic of the nonlinear medium with that of a reference material, used for the calibration of the experimental setup. In the case of the present study, we obtain the nonlinear optical properties of the MPc sample by comparing to that of 0.5 mm thick Y-cut quartz.

The comparative model gives the order of magnitude of the second order nonlinear susceptibility \(\chi^{(2)\text{eff}}\). Taking into account the thickness of the thin film, \(d\), and coherence length of quartz \(L_CQ\) the \(\chi^{(2)\text{eff}}\) value of the investigated material is calculated using the Equation (1):

\[
\chi^{(2)\text{eff}} = \chi^{(2)Q}(2/\pi) \cdot (L_CQ/d) \cdot \left(\frac{I_{2\omega}/I_{2\omega Q}}{I_{2\omega}/I_{2\omega Q}}\right)^{1/2}
\]

with:

\[
L_CQ = \lambda_o/\left[4\left(n_{Q(2\omega)} - n_{Q(\omega)}\right)\right]
\]

where \(\chi^{(2)\text{eff}}\) and \(\chi^{(2)Q}\) are, respectively, second order nonlinear susceptibilities of the studied material and quartz. \(I_{2\omega}\) and \(I_{2\omega Q}\) denote the second harmonic intensities of studied material and quartz, respectively, \(\lambda_o\) — the wavelength of fundamental beam (1064 nm), \(n_{Q(\omega)}\) and \(n_{Q(2\omega)}\) the refractive indices of quartz at the wavelength of the fundamental and the second harmonic beam, respectively \((n_{Q(2\omega)} = 1.534 \text{ at 1064 nm and } n_{Q(2\omega)} = 1.547 \text{ at 532 nm})\) [26]. The value of \(\chi^{(2)Q}\) for quartz is equal \(1.0 \times 10^{-12} \text{ m/V}^2\) (at \(\lambda_o = 1064 \text{ nm}\) [30–32].

#### 3.2. Theoretical model of Herman and Hayden

The theoretical model of Herman and Hayden was developed in 1995 [33]. In this model, the wave equation is resolved in a homogenous and nonmagnetic nonlinear material, which explains the Maker fringes. For an absorbing nonlinear material the \(\chi^{(2)\text{eff}}\) value is calculated using the Equation (3):

\[
I_{2\omega}(\theta) = \left[\frac{128\pi^3}{\lambda_o^2 \cdot \left(n_{2\omega}^2 \cdot \cos^2(\theta_{2\omega}) - n_{\omega}^2 \cdot \cos^2(\theta_{\omega})\right)}\right] \cdot \left(\chi^{(2)\text{eff}}\right)^2 \cdot (I_{\omega}/d)^2 \cdot \sin^2\Phi \cdot \Theta^2
\]

and the phase angle \(\Phi\) may be expressed by relation:

\[
\Phi = 2\pi d/\lambda_o \cdot \left[n_\omega \cdot \cos(\theta_{\omega}) - n_{2\omega} \cdot \cos(\theta_{2\omega})\right],
\]

where: the refractions are neglected, \(I_{2\omega}\) and \(\lambda_o\) denote the light intensity and the wavelength of the fundamental beam, \(\chi^{(2)\text{eff}}\) — effective second order nonlinear susceptibility, \(d\) — the film thickness, \(\theta_{\omega}\) and \(\theta_{2\omega}\) — the angles between the fundamental and the second harmonic beams, respectively, \(n_\omega\) and \(n_{2\omega}\) — the refraction indices for the fundamental and of second harmonic wavelength, respectively.
4. Results and discussion

Metallophthalocyanines can form several polymorphic phases connected with polycrystalline structure when evaporated under vacuum \((10^{-5} - 10^{-6} \text{ Torr})\) onto substrates maintained at room temperature. The two most formed phases are: stable \(\beta\) form and metastable \(\alpha\) form. Crystallization to the \(\alpha\)-phase can also occur at substrate temperature between the range 50 and 150 \(\degree C\). Further increase of the temperature of the substrate – above 200 \(\degree C\) (different for different metal atoms) irreversibly transforms the material into the \(\beta\) form. The main difference between both of these forms is the tilt angle of the molecule within the columns, the tilt angle relative to the substrate and arrangement of the common columns in the crystalline structure. The majority of MPcs molecules have a planar coordination around the central metal ion, which means that the metal and ligand atoms are in the same plane. However, there are also cases where the large metal ions adopt a position outside the plane of the ring. From these differences in geometries of MPcs molecules, four different states of the phthalocyanine ring are identified: metal ion size is approximately equal to phthalocyanine cavity size (CoPc, CuPc, both central metals contains d electrons), metal ion size is smaller than the phthalocyanine cavity size (MgPc and the central metal lacks d electrons), metal ion size is greater than phthalocyanine cavity size (ZnPc) and metal ion size is much larger than phthalocyanine cavity size (PbPc). These four states exhibit four structural effects on the phthalocyanine ring: ring contraction, equilibrium ring geometry, ring expansion and metal non-planarity (ZnPc, central metal contains d electrons). All these parameters play a significant role for the physical properties and the mutual position of molecules inside neighboring layers. Thus, the obtained thin films possessing different phases and different crystalline structure, that lead to different linear and nonlinear optical properties.

The metastable and stable phases of MPcs thin films can be obtained by using different substrate temperature and different deposition methods. In this study, it will be shown that changing of the structure and the morphology can also be obtained by applying the appropriate temperature during the annealing process after the deposition of thin film. The annealing process appears highly significant, because it leads to great changes concerning the arrangement of the structure and polymorphic forms.

The AFM images of the as deposited and annealed MPc (Zn and Cu) thin films have confirmed the different polymorphic crystalline structure of the MPc thin film before and after the annealing process. The AFM images of the same CuPc, ZnPc and MgPc thin films before and after the annealing process are shown in Fig. 3.

The image of CuPc before annealing (Fig. 3a) shows very homogeneous morphology of the thin film – metastable \(\alpha\) form. MPcs particles tend to form columns with the diameter of about twenty nanometers and length of about seventy nanometers. After annealing, the CuPc thin film presented almost completely homogeneous morphology with well-defined flat structures (Fig. 3b). CuPcs particles tend to form structures with many valleys and hills with a height of one hundred nanometers. The thin film indicates
stable β phase. Copper phthalocyanine is an example, where the central metal atom adopts position inside the Pc ring plane. In this case, the 3d-like orbitals of CuPc is half occupied and positioned in the gap between the Pc HOMO and LUMO. The unfilled d valence orbital can be split into several levels due to the interaction between the π-conjugation electrons of Pc ring and metal d electrons. This phenomenon will decrease the transition energy in low-lying d orbital-ligand or d−d transition. The unfilled d valence shell of Cu atoms will couple with the conjugated electrons of Pc ring leading to the extension of the conjugated systems. As a result, the CuPc with larger conjugated electron system will show larger optical nonlinearity.

The results of this experiment show that the second order nonlinear optical response of the metallophthalocyanines are strongly associated with the occurrence of the metal d subshell and the electronic structures of the upper occupied and lower vacant molecular orbitals for the ground states of MPcs for as-deposited samples (z-phase). The Mg atom is a main group element without the d valence orbital, does not exhibit the second order nonlinear optical properties and obtained experimental values of \( \chi^{(2)}_{\text{en}} \) are negligibly small. Furthermore, an enhancement of \( \chi^{(2)}_{\text{en}} \) mainly comes from the d valence orbital contribution of central metal atoms (Zn, Cu and Co) of the metallophthalocyanine compound for as-deposited samples. It is observed that the values \( \chi^{(2)}_{\text{en}} \) of the copper substituted phthalocyanine are larger than those of the zinc substituted phthalocyanine. In the case of ZnPc with completely filled d shell, we can suppose that the probability for the charge transfer mechanism is very less. The 3d subshell of ZnPc is filled and deep enough to form rather pure molecular orbitals. The ZnPc exhibits a large gap between the HOMO and LUMO. As a result, the CuPc with larger conjugated systems show larger optical nonlinearities than the ZnPc.

CoPc have more complex electronic structure, where metal 3d levels are located between the Pc HOMO and LUMO. For such systems, there are extra linear absorption features that may arise from charge transfer transitions. In the case of CoPc, several 3d orbitals are located near the ground states, such that the HOMO is of metal – 3dn type. The probability of the charge transfer mechanisms for this type of the electronic structures: from ligand (Pc) to metal (M) and from metal (M) to ligand (Pc) are significant. These large intramolecular charge-transfers which can enhance the delocalized movements of the large metal d electrons and π-conjugation electrons of Pc ring in the molecules reduce the second-order optical nonlinear response of the material. Presented experimental results show that the value of the nonlinear optical susceptibilities for CoPc is smaller than values for CuPc or ZnPc.

The image of ZnPc before annealing (Fig. 3c) shows a much mixed morphology without a homogeneous region. After annealing, the film presented more homogenous morphology with well-defined structures (Fig. 3d), which may be evidence that most of the molecules are in standing or flat-on orientation. The particles tend to form neighboring domains with dimension of several hundred nanometers, regardless of the orientation. Zinc phthalocyanine is an example of a molecule, where the metal ion is larger than the equilibrium cavity size of the ring but not so large and giving the largest cavity diameters of the phthalocyanines. The molecule’s structure shows non-planarity with the lowest energy state structure having the zinc atom 0.075 Å out of the plane of the ring. The as-deposited and annealed MgPc thin films present mixed morphology without homogeneous region of the thin film metastable γ form. After annealing, particles tend to form a little more homogenous morphology, but the structure is rather unpredictable and well-defined regions does not exist. The thin film does not change the phase and still form the metastable γ form. Cobalt phthalocyanine is an example, where the central metal atom adopts position inside the Pc ring’s plane, but the morphology of thin film is similar to ZnPc films. The as-deposited films show mixed morphology without homogeneous region and annealing process causes the change of the morphology. After annealing process, the film presents homogenous morphology.

In principle, these planar centrosymmetric molecules should not present second order nonlinear activity and have been extensively studied for third order applications [15]. Nevertheless, it is possible to stimulate the different symmetry of the thin film and the associated second order nonlinear response by induction of the structural asymmetry during the thin film formation or directly after the process due to e.g. chemical reactions or a changing temperature of the process. In order to induce asymmetry, two main strategies can be followed: peripheral substitution of the macrocycle with donor or acceptor groups and structural modifications of the MPc itself to reduce the symmetry. The resulting noncentrosymmetric structures present variable degrees of polarity in the nonlinear response. Therefore, the structure and surface morphological orientation of MPc thin films as well as possession of d-electrons by the central metal atom are closely connected with the second order nonlinear optical properties.

It is well known that molecules of metallophthalocyanine may exist mainly in two forms: monomer and dimer. In the dimer form, the close proximity of two rings can lead to coupling between the transition of two identical molecules. In the absence of chemical bond the coupling is either due to dipole–dipole interactions between the molecules or by the overlap of the molecular orbitals. These interaction give rise to two new levels of energy and the separation between them is referred to the exciton splitting energy. Most organic molecular crystals contain differently oriented molecules in the unit cell. The presence of more than one (interacting) equivalent molecular entity in the unit cell causes the splitting of bands in the electronic or vibrational spectra – so called Davydov splitting [17]. Various studies on metal–organic compounds have shown that the energy splitting and the transition dipole moments depend on the dimer structure and dipole–dipole interaction. These phenomena define both: linear (e.g.: absorption spectra, luminescence’s intensity and their energy shift) and nonlinear (the values of the second- and third-order susceptibilities) properties. Dipole–dipole interactions and their significance for nonlinear properties have been also reported for the other organometallic chromophores [34]. These interactions between π-systems are known to play an important role in nature. They control the base–base interactions in the helical structure of DNA, the tertiary structure of proteins, complexation in many host-guest systems and porphyrin aggregation. Dipolar interactions and charge transfer interactions are used to construct mesogens or to stabilize a particular phase in nature.

In order to obtain information about the nonlinear effects four MPcs (M = Cu, Co, Zn and Mg) have been investigated. Thin films of MPcs deposited on a 1 mm thick fused silica glass substrate have been measured. Fig. 4a–h show the Maker fringes patterns of MPcs samples for both S – vertical and P – horizontal polarization of laser radiation. All SHG signals on Fig. 4a–f present symmetric angle dependence of the signal intensity which reflects a substantial optical nonlinearity for all investigated MPcs compounds regardless the annealing process. It can be seen that the intensity of the signals are strongly dependent on the annealing process temperature and the laser polarization for all MPcs compounds for which the central metal atom has d electrons inside valence shell. ZnPc, CoPc and CuPc. Good symmetry of SHG signal for both as deposited and annealed MPcs samples has been found and proved the smooth surface and good quality of the films. However in the case of MgPc (Fig. 4g–h) completely different results have been obtained. The central metal lacks d electrons and the metal ion size
Fig. 4. SHG signal dependence as a function of the incident angle of the fundamental beam and temperature of annealing process: CuPc – S laser polarization (a), CuPc – P laser polarization (b), CoPc – S laser polarization (c), CoPc – P laser polarization (d), ZnPc – S laser polarization (e), ZnPc – P laser polarization (f), MgPc – S laser polarization (g) and MgPc – P laser polarization (h).
is smaller than the phthalocyanine cavity size. The MgPc molecules have completely flat and centrosymmetric orientation. These facts affect the arrangement of molecules during the formation of the thin film. The structure of the thin film shows a mixed morphology without a homogeneous region and this MPCs compound does not exhibit SHG signal. This means that the annealing process does not introduce disturbances in the centrosymmetric structure of the material, which would be necessary to induce second order nonlinear effects.

These measurements and calculations based on the aforementioned Herman and Hayden model allows estimation of the value of the \( \chi^{(2)} \) effective second order nonlinear susceptibility. In the case of the present studies, the results obtained with the two models (Comparative and Herman—Hayden) give similar values of the effective second order nonlinear optical susceptibility \( \chi^{(2)}_{\text{eff}} \) for the as deposited samples of metallophthalocyanine compounds except in the case of magnesium phthalocyanines (Fig. 5a–b). In the case of the three metallophthalocyanine compounds: CoPc, CuPc and ZnPc, the value of the effective second order nonlinear optical susceptibility is almost the same for both S – and P – fundamental laser polarization. An increase of the annealing process temperature causes an appearance of the polarization effects (especially for CuPc and ZnPc). The susceptibility difference for both polarizations grows with the increase of the annealing process temperature. The value of \( \chi^{(2)}_{\text{eff}} \) of CuPc sample annealed at 250 °C is significantly higher for P – polarization than for S – polarization of fundamental beam. The case of ZnPc is completely different. The value of \( \chi^{(2)}_{\text{eff}} \)

![Fig. 5. Comparison of the obtained second-order nonlinear optical susceptibilities using two models on the studied MPc compounds: S laser polarization (a) and P laser polarization (b).](image-url)

is slightly higher for S – polarization of the beam although the shape of the SH spectrum is significantly different.

Temperature dependence of the effective second order nonlinear optical susceptibility's value does not exhibit a simple relation. It seems that an explanation of this phenomenon is much more strongly connected with the phase change of the thin films structures. Metallophthalocyanines can form many different poly-crystalline structures connected with many polymorphic phases when evaporated under vacuum (10\(^{-5}\)–10\(^{-6}\) Torr) onto a substrate maintained at room temperature which are statistically distributed in the thin films. The most popular phases are: stable \( \beta \) form and metastable \( \alpha \) form. The main difference between both these forms is the tilt angle of the molecule within the columns, the tilt angle relative to the substrate and arrangement of the common columns in the crystalline structure. Although the packing arrangement depends upon the temperature of the deposition process and the temperature of the annealing process. The crystallinity increased with increasing annealing process temperature, while interplanar distance corresponded to the spacing between the stacking axes of the MPC (only for M = Zn, Co and Cu) molecule increased [15] or didn't change for MgPc. The increasing value suggested that the tilt angle between the stacking axis and the normal of the Pc ring became smaller with increasing annealing process temperature. This result indicated that the phase transformation from the metastable \( \alpha \)-phase to the stable \( \beta \)-phase (only for M = Zn, Co and Cu), was purely caused by the temperature of the applied annealing process. The lowest energy molecular orbitals of CuPc are different from those of CoPc, ZnPc and MgPc. This suggests different electronic transport behavior. Therefore, the film structure is ordered regardless of whether the process of annealing is applied or not. Comparison of thin films structure and SH signals intensity clearly indicates an increase of the second order optical susceptibility's value towards columns or hills formed during annealing process of the film. These values are much smaller in the perpendicular direction. This fact indicates that the annealing process introduces varying degrees of polarity for the second order nonlinear response.

The highest values of \( \chi^{(2)}_{\text{eff}} \) are obtained for the samples of zinc metallophthalocyanine. ZnPc molecule is not flat and the zinc metal adopts a position outside the plane of the ligand. The molecule has \( C_{4v} \) symmetry and the central metal atom possesses d electrons inside the valence shell. The structural asymmetry of this compound seems to be the largest, while it expands with the increase of the annealing process temperature and reaches a maximum at temperature equal 250 °C (see Fig. 5).

All investigated metallophthalocyanines demonstrate good agreement between the experimental results and the fittings based on the two models. The highest values of \( \chi^{(2)}_{\text{eff}} \) were obtained for compounds form a well-defined, flat arranged column structure of the thin film. The films with mixed (flat-on and standing domains) structure gave the smaller value of \( \chi^{(2)}_{\text{eff}} \). No value of \( \chi^{(2)}_{\text{eff}} \) was obtained for the MgPc thin films with a mixed morphology without homogeneous region and disordered structure. In this case the central metal atom lacks d electrons inside valence shell and this fact is also strongly related to second order nonlinear optical effects.

These facts allow concluding that the second order nonlinear optical properties are not only closely related to the phase (stable \( \beta \) and metastable \( \alpha \)) of the molecular material but also to the morphology of \( \beta \) stable phase and its relationship with possession of d electrons by the central metal. Moreover, all investigated thin films and nanostructures have a great stability and exhibited no traces of the laser interaction for \( \beta \) phase (annealed samples) and slight traces for \( \alpha \) phase (as-deposited samples). The effective second order nonlinear optical susceptibility values for each studied
compounds take into account the obtained values of the absorption coefficients \([22]\). Values of the measured and calculated second order nonlinear optical susceptibilities for all metallophthalocyanine compounds are two orders of magnitude higher than the well-known value for quartz (reference material) (Table 3). These values are comparable with second order nonlinear optical susceptibilities for \(\beta\)-barium borate (BBO) or potassium dihydrogen phosphate (KDP) crystals — materials mostly using for the frequency doubling.

5. Conclusions

In this paper, the value of the effective second order susceptibility for thin films of four MPCs (\(M = \text{Cu, Co, Zn and Mg}\)) compounds were experimentally investigated and theoretically calculated. The MPCs thin films and nanostructures were grown by conventional physical vapor deposition technique in high vacuum. The \(\chi^{(2)}\) values have been measured using the SHG technique at 1064 nm. The experimental results of these organometallic complexes have been fitted using two different models. The obtained results showed that the value of \(\chi^{(2)}\) depends on the preparation conditions of the thin films such as the temperature of the annealing process, as well as the type of the central metal atom inside the metallophthalocyanine molecular ring and the direction of the fundamental beam’s polarization relative to the structure obtained after the annealing process. It has been revealed that the polymorphic phase, the temperature stability, the symmetry of molecules and the preferred arrangement of the MPC thin films can greatly influence their second order nonlinear optical properties, through modification of the molecular symmetry.

It has been also shown that the annealing process affects the structural organization and morphology of the MPCs thin films causing the appearance of various forms of nanostructures. This last fact indicates that annealing process can noticeably change the electric dipole moments. The changes in optical properties of the nanostructures are most likely to be due to the dipole–dipole and charge transfer interaction among the different molecular assemblies.

An interesting dependence of the effective second order susceptibility on the metallophthalocyanine’s phases and created nanostructures has been demonstrated. It has been noticed that the size and shape of the nanostructures as well as the \(\chi^{(2)}\) values are affected by the nature of the central metal atom. It has been shown, that the second order nonlinear optical response of the metallophthalocyanines are strongly associated with the occurrence of the metal d subshell and the electronic structures of the HOMO and LUMO molecular orbitals for as-deposited samples (\(x\)-phase).

The experimental results and the fittings based on the two models show that these compounds have a \(\chi^{(2)}\) value approximately larger by two orders of magnitude than the reference material (quartz) and comparable with second order nonlinear optical susceptibilities corresponding to BBO or KPD crystal.

### Table 3

Results obtained for MPCs complexes from calculation based on Comparative and Herman—Hayden models.

| Sample | Polarization | Annealing process temperature [°C] | \(\chi^{(2)}\)  
<table>
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<tr>
<td></td>
<td></td>
<td></td>
<td>(10^{-9} \text{ esu})</td>
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<tr>
<td>CoPc</td>
<td>P</td>
<td>As deposited</td>
<td>28.6 ± 0.9</td>
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<td>S</td>
<td>As deposited</td>
<td>29.5 ± 2.3</td>
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<tr>
<td></td>
<td>P</td>
<td>150</td>
<td>31.5 ± 0.8</td>
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<tr>
<td></td>
<td>S</td>
<td>150</td>
<td>34.8 ± 3.1</td>
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<tr>
<td></td>
<td>P</td>
<td>250</td>
<td>39.4 ± 1.0</td>
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<td>S</td>
<td>250</td>
<td>28.7 ± 2.4</td>
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<td>P</td>
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<td>26.7 ± 2.7</td>
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<td>CuPc</td>
<td>P</td>
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<td>63.5 ± 1.8</td>
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<td>S</td>
<td>As deposited</td>
<td>65.4 ± 5.0</td>
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<tr>
<td></td>
<td>P</td>
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<td>65.3 ± 1.9</td>
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<td>53.6 ± 5.1</td>
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<td>S</td>
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<td>48.3 ± 2.4</td>
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\(^{a}\) Calculated by comparative model.

\(^{b}\) Calculated by model of Herman—Hayden.

### References


