Annex 3

Self-presentation

1. First name and surname.

Beata Derkowska-Zielińska

2. Diplomas obtained, academic/artistic degrees – including the titles, place and year of issue, and the title of doctoral thesis.

2004r	Doctor of Physics (PhD) Faculty of Physics, Astronomy and Informatics Nicolaus Copernicus University, Torun, Poland *Linear and nonlinear optical properties of ZnMgSe and ZnAgSe mixed crystals*
2001r	Doctor of Physics (PhD) University of Angers, France *Contribution à l'étude des propriétés optiques linéaires et non linéaires des semi-conducteurs* $A^{II}B^{VI}$
1997r	Master of Physics (MSc) Faculty of Physics and Astronomy Nicolaus Copernicus University, Torun, Poland

3. Information concerning employment in scientific/artistic institutions.

2005 – 2013	Assistant Professor (in Polish nomenclature: adiunkt) Department of Semiconductor and Carbon Physics Faculty of Physics, Astronomy and Informatics Nicolaus Copernicus University, Torun, Poland
2005 – 2006	Postdoctoral Fellow Laboratory of Optical Properties of Materials and their Applications (POMA), University of Angers, France
2003 – 2005	Research Assistant Department of Technical and Applied Physics Faculty of Physics, Astronomy and Informatics Nicolaus Copernicus University, Torun, Poland
2002 – 2003	Postdoctoral Fellow Experimental Condensed Matter and Quantum Optics, Department of Physics, University of Toronto, Toronto, ON, Canada
1997 – 2003	Ph.D. studies – co-tutelle system Faculty of Physics, Astronomy and Informatics Nicolaus Copernicus University, Torun, Poland and POMA Laboratory, University of Angers (France)
1997 – 1998	Physics teacher in Secondary School (IV LO) in Torun

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4. Indication of achievements* pursuant to article 16 item 2 of the act of law dated 14 March 2003, concerning scientific degrees and scientific titles, and degrees and titles in the domain of arts (Official Journal No. 65, item 595 with later amendments):

In accordance with the above Act I have chosen a monothematic series of 8 publications on the nonlinear optical properties of organic and inorganic semiconductors materials to indicated academic achievement:

H1.
B. Derkowska, M. Wojdyła, R. Czaplicki, Z. Sofiani, W. Bała, B. Sahraoui
Influence of the central metal atom on the nonlinear optical properties of MPcs solutions and thin films
Optics Communications 274, 206, 2007.
I estimate that my percentage contribution is 75 %.

H2.
B. Derkowska, K. Jaworowicz, O. Krupka, M. Karpierz, M. Wojdyła, W. Bała, J.G. Grote, F. Kajzar, B. Sahraoui
Influence of different peripheral substituents on the nonlinear optical properties of cobalt phthalocyanine core
J. Appl. Phys. 101, 083112, 2007.
I estimate that my percentage contribution is 70 %.

H3.
B. Derkowska, M. Wojdyla, W. Bala, K. Jaworowicz, M. Karpierz, R. Czaplicki, B. Sahraoui
Dependence of the third order nonlinear optical susceptibility on concentration and peripheral substituent of metallophthalocyanines
Molecular Crystals and Liquid Crystals 485, 965, 2008.
I estimate that my percentage contribution is 70 %.

H4.
B. Derkowska
Third order nonlinear optical properties of metallophthalocyanines (MPcs)
Nonlinear Optics Research Progress, Chapter 9, pp. 189 – 222, Editors: James L. Davies and Daniel A. Hall, Nova Science Publishers, Inc. 2008.
I estimate that my percentage contribution is 95 %.

H5.
B. Derkowska, F. Firszt, B. Sahraoui, A. Marasek, M. Kujawa
Study of the third order nonlinear optical properties of $Zn_{1-x}Mg_xSe$ *and* $Cd_{1-x}Mg_xSe$ *crystals*
Opto-Electronics Review 16, 8, 2008.
I estimate that my percentage contribution is 80 %.

H6.
B. Derkowska, B. Sahraoui, Z. Essaïdi, A. Marasek, F. Firszt, M. Kujawa
Nonlinear optical properties of $Zn_{1-x}Mg_xSe$ *and* $Cd_{1-x}Mg_xSe$ *crystals*
Optical Materials 31, 518, 2009.
I estimate that my percentage contribution is 75 %.

Dw.

H7.
B. Derkowska, F. Firszt, B. Sahraoui, A. Marasek
Experimental results of third order nonlinear optical susceptibility of oriented and annealed ZnSe crystals
IEEE 2009, E-ISBN 978-1-4244-5746-5, (ThP.13 – pp. 1-3).
I estimate that my percentage contribution is 85 %.

H8.
B. Derkowska, F. Firszt, A. Marasek, B. Sahraoui
Dependence of nonlinear refractive index of ZnSe on Be and Mg content
Opto-Electronics Review 18, 384, 2010.
I estimate that my percentage contribution is 85 %.

Publications and the statements of co-authors are attached to this report as Annex 4 „Publications constituting the habilitation dissertation” and Annex 5 „Statements of co-authors”.

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4b) Description of scientific/artistic objective of the above work/works and accomplished results, including description of their possible use.

4.1. Preface

I present a monothematic series of publications, which relate to the nonlinear optical properties of organic and inorganic semiconductor materials. The experimental results, which are the backbone of this work, have been published in seven pree-reviewed scientific publications and one chapter of the book. The whole dissertation is divided into two parts on the basis of the type of material studied.

Metallophthalocyanines

H1.
B. Derkowska, M. Wojdyła, R. Czaplicki, Z. Sofiani, W. Bała, B. Sahraoui
Influence of the central metal atom on the nonlinear optical properties of MPcs solutions and thin films
Optics Communications 274, 206, 2007.

H2.
B. Derkowska, K. Jaworowicz, O. Krupka, M. Karpierz, M. Wojdyła, W. Bała, J.G. Grote, F. Kajzar, B. Sahraoui
Influence of different peripheral substituents on the nonlinear optical properties of cobalt phthalocyanine core
J. Appl. Phys. 101, 083112, 2007.

H3.
B. Derkowska, M. Wojdyla, W. Bala, K. Jaworowicz, M. Karpierz, R. Czaplicki, B. Sahraoui
Dependence of the third order nonlinear optical susceptibility on concentration and peripheral substituent of metallophthalocyanines
Molecular Crystals and Liquid Crystals 485, 965, 2008.

H4.
B. Derkowska
Third order nonlinear optical properties of metallophthalocyanines (MPcs)
Nonlinear Optics Research Progress, Chapter 9, 189, Editors: James L. Davies and Daniel A. Hall, Nova Science Publishers, Inc. 2008.

Mixed crystals based on ZnSe and CdSe

H5.
B. Derkowska, F. Firszt, B. Sahraoui, A. Marasek, M. Kujawa
Study of the third order nonlinear optical properties of $Zn_{1-x}Mg_xSe$ *and* $Cd_{1-x}Mg_xSe$ *crystals*
Opto-Electronics Review 16 (1), 8, 2008.

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H6.
B. Derkowska, B. Sahraoui, Z. Essaïdi, A. Marasek, F. Firszt, M. Kujawa
Nonlinear optical properties of $Zn_{1-x}Mg_xSe$ *and* $Cd_{1-x}Mg_xSe$ *crystals*
Optical Materials 31, 518, 2009.

H7.
B. Derkowska, F. Firszt, B. Sahraoui, A. Marasek
Experimental results of third order nonlinear optical susceptibility of oriented and annealed ZnSe crystals
IEEE 2009, E-ISBN 978-1-4244-5746-5, (ThP.13 – pp. 1-3).

H8.
B. Derkowska, F. Firszt, A. Marasek, B. Sahraoui
Dependence of nonlinear refractive index of ZnSe on Be and Mg content
Opto-Electronics Review 18, 384, 2010.

4.2. Discussion of the results of the dissertation

The aim of the study was to learn how substituting different metal atoms into the ring of the phthalocyanines and/or the replacement of peripheral substituents around the metallophthalocyanines cores, as well as the introducing Mg and/or Be dopants into ZnSe and CdSe mixed crystals, correlate with nonlinear optical properties. The methods, which were used to measure nonlinear optical properties, were degenerate four wave mixing (DFWM), nonlinear transmission (TNL), third harmonic generation (THG) and second harmonic generation (SHG).

All experimental results presented in this dissertation were obtained at the Laboratory of Optical Properties of Materials and their Applications University of Angers (France) in the group of Prof. Bouchta Sahraoui.

The dissertation is divided into two parts on the basis of the type of material studied. In the first part of the habilitation dissertation I describe organic semiconductor materials (metallophthalocyanine), research methodologies, experimental results and the obtained results. In the second part I present mixed ternary and quaternary semiconductor crystals based on ZnSe (i.e. $Zn_{1-x}Mg_xSe$, $Zn_{1-x}Be_xSe$ and $Zn_{1-x-y}Be_xMg_ySe$) and CdSe (i.e. $Cd_{1-x}Mg_xSe$) obtained by Bridgman method.

4.2.1. Introduction

The dynamics of civilization development in the twentieth century brought great progress in many fields of science, including optics. Constructing the laser made of possible for physicists to measure new phenomena that occur during the interaction of laser radiation with high power of matter [1-4]. There is a new branch of physics called nonlinear optics, which includes all phenomena that do not meet the principle of superposition of light waves (i.e. for which the optical properties of the medium depends on the intensity of the incident light). Laser radiation reveals optical properties impossible for non-coherent classical light sources. The interaction of such light with materials can modify their properties. As a result from laser light interaction with matter, we can observe new and very interesting effects. The generation of optical harmonics and the processes of frequency mixing of laser light are a new and promising method of measuring the properties of many materials.

Pulsed lasers, which produce a beam of huge light intensity, carry strong electric fields comparable with intensity of internal fields. In such a strong electric field, the properties of

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atoms or molecules, as well as the material environment as a whole, are changed [1-4]. When the electric field strength of the incident wave is of the same order of magnitude the intraatomic (10^8 V/cm), which is responsible for binding of valence electrons, the properties of the material are dependent on the excitation conditions [5]. In the presence of such a strong field the refractive index of the material depends on the electric field strength $\vec{E}(\vec{r},t)$, which leads to a violation of the principle of superposition. The individual waves, which propagate in material, interact with each other and as a result there are a number of nonlinear optical phenomena [6]. The nonlinear effects include changes in polarizability and the refractive index of the material caused by electric $\vec{E}(\vec{r},t)$ and magnetic $\vec{H}(\vec{r},t)$ fields. Other examples of nonlinear optical effects are second and third harmonic generation [1, 7].

4.2.2. Theory

In the case of conventional optics, the electric polarization vector $\vec{P}(\vec{r},t)$ is assumed to be linearly proportional to the electric field $\vec{E}(\vec{r},t)$ of an applied optical wave

$$P_i(\vec{r},t) = \chi_{ij}^{<1>} E_j(\vec{r},t). \tag{1}$$

However, when the intense light field (i.e. a laser light) interacts with an optical medium new effects arise and the electric polarization vector $\vec{P}(\vec{r},t)$ can be replaced by a power series in the field strength $\vec{E}(\vec{r},t)$ as follows [1, 8-12]:

$$P_i(\vec{r},t) = P^{<0>} + \chi_{ij}^{<1>} E_j(\vec{r},t) + \chi_{ijk}^{<2>} E_j(\vec{r},t) E_k(\vec{r},t) + \chi_{ijkl}^{<3>} E_j(\vec{r},t) E_k(\vec{r},t) E_l(\vec{r},t) + \dots, \tag{2}$$

where $\chi_{ij}^{<1>}$ is the linear susceptibility (second-rank tensor),
$\chi_{ijk}^{<2>}$ is the second order nonlinear optical susceptibility (third-rank tensor), and
$\chi_{ijkl}^{<3>}$ is the third order nonlinear optical susceptibility (fourth-rank tensor).

The first term $\vec{P}^{<0>}$ is responsible for existence of polarization without applying an external electric field. This polarization is called spontaneous.

The second term, $\chi_{ij}^{<1>} E_j(\vec{r},t)$, is related to linear optical phenomena, such as transmission, absorption, and reflection.

The third term, $\chi_{ijk}^{<2>} E_j(\vec{r},t) E_k(\vec{r},t)$, is related to second order nonlinear optical effects, such as second harmonic generation (SHG), optical rectification (OR), sum-frequency generation (SFG) and difference-frequency generation (DFG). Second order nonlinear optical interactions can occur only in noncentrosymmetric crystals, that is, in crystals that do not display inversion symmetry ($\chi_{centrosymetric}^{<2>} = 0$).

The fourth term, $\chi_{ijkl}^{<3>} E_j(\vec{r},t) E_k(\vec{r},t) E_l(\vec{r},t)$, is related to third order nonlinear optical effects, such as two photon absorption, degenerate four wave mixing (DFWM), third harmonic generation (THG), etc. Third order nonlinear optical interactions can occur both for centrosymmetric and noncentrosymmetric media.

Therefore, second order nonlinear optical polarization is expressed as follows:

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$$P_i^{<2>}(\vec{r},t) = \chi_{ijk}^{<2>} E_j(\vec{r},t) E_k(\vec{r},t)\,, \tag{3}$$

and third order nonlinear optical polarization is expressed in the following way:

$$P_i^{<3>}(\vec{r},t) = \chi_{ijkl}^{<3>} E_j(\vec{r},t) E_k(\vec{r},t) E_l(\vec{r},t)\,. \tag{4}$$

The second order nonlinear optical susceptibility $\chi_{ijk}^{<2>}$ is the third-rank tensor consisting of 27 components. Assuming the Kleinman symmetry conditions, this tensor is symmetric respect to the pair indices j and k, resulting in a reduction to 18 components. Whereas the total symmetry of the tensor for all indices i, j, k causes reduction to 10 components. The third order nonlinear optical susceptibility $\chi_{ijkl}^{<3>}$ is a fourth-rank tensor, and thus is described in terms of 81 separate elements. These components are nonzero and depend on the symmetry of the material. For materials possessing a higher degree of spatial symmetry, the number of independent elements is very much reduced. Material with a specified crystallographic structure can be described by the point group symmetry, which includes collections of the symmetry transformations. Therefore, in the case of tetragonal materials (D_{4h}), which include metallophthalocyanines, the tensor of third order nonlinear optical susceptibility $\chi_{ijkl}^{<3>}$ is described in terms of 21 non-zero elements, of which 4 are independent, whereas the tensor of second order nonlinear optical susceptibility $\chi_{ijk}^{<2>}$ of this material is equal zero. In the case of regular materials (T_d), which include mixed crystals based on ZnSe and CdSe, the tensor of third order nonlinear optical susceptibility $\chi_{ijkl}^{<3>}$ of this material, is described in terms of 21 nonzero elements, of which only 2 are independent, whereas the tensor of second order nonlinear optical susceptibility $\chi_{ijk}^{<2>}$ of this material is described in terms of 6 nonzero elements, of which only 1 is independent [1-4, 13, 14].

In general, third order nonlinear optical susceptibility is considered to be a complex quantity [13, H4]:

$$\chi^{<3>} = \chi_R^{<3>} + i\chi_I^{<3>}\,, \tag{5}$$

where $\chi_R^{<3>}$ is the real part of third order nonlinear optical susceptibility, related to the nonlinear refractive index changes, which can be extracted from degenerate four wave mixing (DFWM) measurements,

$\chi_I^{<3>}$ is the imaginary part of third order nonlinear optical susceptibility, related to the two-photon absorption coefficient calculated from transmission measurements.

Two-photon absorption consists in the simultaneous absorption of two photons, the result of which is the electron transition from a ground state to an excited state. Therefore, two-photon absorption takes place when the photon energy of the incident beam ($h\nu$) is larger than the half of the energy band gap ($E_g/2$) and lower than the energy gap (E_g) of studied material [15, 16]:

$$E_g > h\nu > E_g/2\,. \tag{6}$$

Knowing the two-photon absorption coefficient β we can calculate the imaginary part of the third order nonlinear optical susceptibility $\chi_I^{<3>}$, by using the following relationship:

$$\chi_I^{<3>} = \frac{n^2 c \lambda}{48\pi^3} \beta , \tag{7}$$

where n is the refractive index,
β is two-photon absorption coefficient,
c is the velocity of light, and
λ is the wavelength.

In general, the refractive index n of a centrosymmetric material can be expressed as follows [1]:

$$n = n_0 + n_2 I , \tag{8}$$

where n_0 is the linear or low-intensity refractive index,
n_2 is nonlinear refractive index that characterizes the strength of the optical nonlinearity, and
I is the intensity of the incident wave.

From equation (8) one can see that the refractive index changes with increasing intensity. On the other hand, the nonlinear refractive index n_2 is related to the real part of the third order nonlinear optical susceptibility in the following way [1]:

$$n_2 = \frac{12\pi^2}{n_0^2 c} \chi_R^{<3>} . \tag{9}$$

In materials subject to an intense light field, the material becomes a source of various processes that can lead to a change in its optical properties. These modifications can thus make an additional contribution to those already existing in the material and have an influence on the size of third order nonlinear optical susceptibility [1, 17]. Therefore, third order nonlinear optical susceptibility can be described as the sum of the individual component effects [17-19]:

$$\chi_{ijkl}^{<3>} = \chi_{ijkl}^{<3>el} + \chi_{ijkl}^{<3>m} + \chi_{ijkl}^{<3>term} + \chi_{ijkl}^{<3>e-s} , \tag{10}$$

where $\chi_{ijkl}^{<3>el}$ is an electronic polarization mechanism related to deformation of the electron cloud,
$\chi_{ijkl}^{<3>m}$ is a molecular orientation mechanism associated with the movement of atoms,
$\chi_{ijkl}^{<3>term}$ is a thermal effects, and
$\chi_{ijkl}^{<3>e-s}$ is an electrostriction mechanism related to a change in the dimensions of the material under electric field.

The basic mechanism responsible for the nonlinear optical effects is a deformation of the electron clouds around the atoms in the electric field of the light wave (electronic nonlinearity). Electronic nonlinearity is directly related to the non-resonant interaction of an electromagnetic wave with the atoms (molecules) of a material. Electronic nonlinearity leads to relatively small changes in the refractive index. The arrangement of the asymmetrical molecules in the electric field of the light wave is a source of orientation nonlinearity (molecular orientation). The change of refractive index is associated with the rotation of the molecule. Therefore the relaxation time corresponding to this process is much longer than in the case of electronic nonlinearity. Electrostriction is the result of the tendency to reduce the internal energy of the induced dipole by the applied electric field (also from the light beam) and results from the translational motion of molecules. Electrostriction causes an increase of material density in the high-field resulting in an increase of refractive index. Absorption nonlinearity occurs for light frequencies close to the frequency of the absorption bands. If the absorption coefficient depends on the light intensity, for example due to the saturation of the absorption, then there is also a dependence of the real part of the dielectric permittivity on the light intensity. The absorption process is much slower than the electronic nonlinearity. The thermal expansion is also the mechanism, which leads to changes of the refractive index and decreases the density of the medium under the influence of a temperature increase, thereby reducing the refractive index (thermal nonlinearity). In a semiconductor, the influence of temperature changes of the crystal lattice on the refractive index follows mainly from the dependence of the energy gap on temperature.
As we cut down the duration of the light pulse to picosecond value, many of these effects are reduced or do not occur. When one uses a laser delivering impulses of 30ps duration, one can neglect thermal and electrostrictive effects because they are very slow. Two essential local effects contribute to the nonlinearities in materials submitted to such laser pulses: electronic cloud deformations ($\chi_{ijkl}^{<3>el}$) and nucleus reorientation (translations, rotations and vibrations) ($\chi_{ijkl}^{<3>m}$). In consequence, one can consider $\chi_{ijkl}^{<3>}$ as being composed of two contributions corresponding to these mechanisms

$$\chi_{ijkl}^{<3>} = \chi_{ijkl}^{<3>el} + \chi_{ijkl}^{<3>m}, \tag{11}$$

whereas the electrostriction mechanism ($\chi_{ijkl}^{<3>e-s}$) and the thermal effects ($\chi_{ijkl}^{<3>term}$) may be neglected in the picosecond regime because they are slower [20].

From the comparison of the various nonlinear mechanisms in the material it follows that the materials of high value nonlinear refractive index n_2, as well as third order nonlinear optical susceptibility $\chi^{<3>}$, are generally characterized by a very slow rise times of nonlinearity, and a short relaxation times τ usually accompanied by weak nonlinearity. As a consequence, although the value of n_2 can vary by several orders of magnitude, the ratio n_2/τ differs only by a few orders [19]. It should also be remembered that in the material different nonlinear mechanisms might appear at the same time.
A separate comparison of the parameters related with nonlinearity cannot be the basis for selecting the optimal medium. Besides the value of the nonlinear refractive index n_2 as well as the third order nonlinear optical susceptibility $\chi^{<3>}$ or the relaxation time τ there are also other important parameters such as: the value of linear absorption coefficient α and diffusion coefficient, as well as the applied wavelength λ and the value of the linear refractive index n_0. The role of the individual parameters depends on the application of the nonlinear element.

In order to facilitate comparison of nonlinear media we introduced the so-called figure of merit (*F*) [H4]:

$$F = \frac{\chi^{<3>}}{\alpha}. \tag{12}$$

At the molecular level, a similar equation to equation (2) can be written for the light-induced molecular dipole moment. The microscopic parameter, which characterizes the third order nonlinear optical susceptibility of the molecule, is hyperpolarizability (γ) [21]:

$$p_i = \alpha^*_{ij}\, E_j + \beta^*_{ijk}\, E_j E_k + \gamma^*_{ijkl}\, E_j E_k E_l + \dots, \tag{13}$$

where E_j, E_k, E_l are components of the local electric field $\vec{E}_{loc}$,

α^*_{ij} is the linear polarizability,

β^*_{ijk} is the first order hyperpolarizability (second order effect), and

γ^*_{ijkl} is the second order hyperpolarizability (third order effect).

To determine the relationship between the parameters describing the third order nonlinear optical effects on the macroscopic and microscopic level, we should consider the local field at the point of molecule location. Determination of the local electric field $\vec{E}_{loc}$ requires a particular model that would allow one to obtain the relationship between the local electric field $\vec{E}_{loc}$ and the external applied field $\vec{E}$ to the material. Only for gases, one can assume that the local field is identical to the applied external field. In a condensed medium, we need to take into account the influence of the environment on particles material. Using the Lorentz model [22-24] with our expression for polarization $\vec{P}$, we can obtain a general form of second order hyperpolarizability in the following form:

$$\gamma^* = \frac{\chi^{<3>}}{F^4 N}, \tag{14}$$

where N is the number of molecules per unit volume,

F is the local field correction factor approximated by the Lorentz expression:

$$F = \frac{n^2 + 2}{3}, \tag{15}$$

where: n is the refractive index of material.

In the case of solutions, assuming that the solvent does not interact with the dissolved molecules, one can obtain the following relationship between the third order nonlinear optical susceptibility of the solution $\chi^{<3>}$ and second order hyperpolarizability γ^* of the solute molecules [25]:

$$\chi^{<3>}_{solution} = F^4 N \gamma^* + \chi^{<3>}_{solvent}. \tag{16}$$

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In the case when the $\chi^{<3>}_{solvent}$ of the solvent is very weak compared to the $\chi^{<3>}_{solution}$ of the solution, the second order hyperpolarizability (γ^*) characterizing molecular optical nonlinearities can be estimated through the following equation:

$$\gamma^* = \frac{\chi^{<3>}_{solution} M}{F^4 N_A C}, \tag{17}$$

where N_A is the Avogadro's number,
M is the molar mass, and
C is the concentration of the solute.

The intensity of third harmonic is given by [1, 2, H1, H4, H6]:

$$I_{3\omega} = \frac{576\pi^6}{n_{3\omega} n_\omega^3 \lambda_\omega^2 c^2} \left|\chi^{(3)}\right|^2 I_\omega^3 L^2 \frac{\sin^2(\Delta kL/2)}{(\Delta kL/2)^2}, \tag{18}$$

where $I_{3\omega}$ is the intensity of third harmonic,
I_ω is the intensity of fundamental beam at frequency ω,
$n_{3\omega}$ and n_ω are the refractive indices at frequency 3ω and ω, respectively,
L is the path length,
Δk is the wave vector mismatch between the incident fundamental and the generated TH beams defined as:

$$|\Delta k| = \left|\vec{k}_3 - 3\vec{k}\right| = \frac{3\omega}{c}\left(n_{3\omega} - n_\omega\right) = \frac{6\pi}{\lambda_\omega}\left(n_{3\omega} - n_\omega\right), \tag{19}$$

where $\vec{k}$, $\vec{k}_3$ are the wave vectors at frequency ω and 3ω, respectively.

The optical path length is given by:

$$L = \frac{d}{\cos\theta_t} \quad \text{and} \quad \theta_t = \arcsin\left(\frac{\sin\theta_i}{n_\omega}\right),$$

where d is the thickness of the crystal,
θ_i is the incident angle.

From the theoretical expression (18) we can determine the third order nonlinear optical susceptibility $\chi^{<3>}$ by analyzing the experimental results based on the technique of interference Maker.

The value of second order nonlinear optical susceptibility can be determined from the following formula [2, H1, H4, H6]:

$$I_{2\omega} = \frac{128\pi^5}{n_{2\omega} n_\omega^2 \lambda_\omega^2 c} \left|\chi^{(2)}\right|^2 I_\omega^2 L^2 \frac{\sin^2(\Delta kL/2)}{(\Delta kL/2)^2}, \tag{20}$$

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where $I_{2\omega}$ is the intensity of second harmonic,
I_ω is the intensity of fundamental beam at frequency ω,
$n_{2\omega}$ and n_ω are the refractive indices at frequency 2ω and ω, respectively,
Δk is the wave vector mismatch defined as:

$$|\Delta k| = \left|\vec{k}_2 - 2\vec{k}\right| = \frac{4\pi}{\lambda_\omega}\left(n_{2\omega} - n_\omega\right), \tag{21}$$

where $\vec{k}$, $\vec{k}_2$ are the wave vectors at frequency ω and 2ω, respectively.

4.2.3. Experiment

Various experimental techniques can be used for estimating the third order nonlinearity of given materials, even though each technique addresses only a particular facet of the nonlinearity due to the frequency dispersion of $\chi^{<3>}$. The most common methods used to measuring third order nonlinear optical susceptibility are: nonlinear transmission, degenerate four wave mixing (DFWM) and third harmonic generation (THG). However, second harmonic generation (SHG) can be use to measure second order nonlinear optical susceptibility.

The transmission of an incident beam I_l as a function of intensity is referred to nonlinear transmission. From a nonlinear transmission technique one can extract the values of two-photon absorption (TPA) coefficient (β), which can be related directly to the imaginary parts of the third order nonlinear optical susceptibility ($\chi^{<3>}$). From degenerate four wave mixing (DFWM) one can determine the modulus of the third order nonlinear optical susceptibility $\left|\chi^{<3>}\right|$, so we get information about the imaginary and the real part of third order nonlinear optical susceptibility. This technique allows one to study physical phenomena, which give a contribution to the third order optical nonlinearity such as: electronic nonlinearity, molecular orientation, electrostriction, thermal nonlinearity as well as absorption nonlinearity. If one uses a laser delivering impulses of 30ps duration in DFWM experiments, we can neglect thermal and electrostrictive effects because they are very slow. Two essential local effects contribute to the nonlinearities in materials submitted to such laser pulses: electronic cloud deformations and nucleus reorientation (translations, rotations and vibrations) [20].

Another technique used to determine the third order nonlinear optical susceptibility is third harmonic generation (THG). This method allows for the determination of the purely electronic contribution (the effects associated with the deformation of the electron cloud) to third order nonlinear optical susceptibility (because no other mechanism is fast enough to produce a nonlinear polarization oscillating at the third-harmonic frequency of the incident beam). Therefore, the other contributions like thermal, photochromic orientation or other motional contributions, being much slower, are automatically discriminated.

Degenerate four wave mixing is the third order nonlinear optical process, in which three laser beams (two pump beams and a probe beam) interact within material to generate a fourth beam (phase-conjugated beam) [1, 13, H4, 26-29]. This is a process, in which a phenomenon called phase-conjugation is observed. We have three laser beams of the same frequency (ω) and the fourth beam is generated when its frequency ω_4 and the wave vector $\vec{k}_4$ satisfy the energy conservation law and phase-matching:

$$\omega_4 = \omega - \omega + \omega, \qquad \vec{k}_1 = -\vec{k}_2, \qquad \vec{k}_4 = -\vec{k}_3.$$

The formation of a fourth beam can also be explained by a diffraction grating model (dynamic holography): two of the beams interfere inside the sample to form the diffraction grating of nonlinear refractive index and/or the diffraction grating of absorption. The third beam diffracts on this grating to form a phase-conjugate signal that retraces the probe path [28].
Third harmonic generation (THG) describes the process in which a fundamental laser field of frequency ω generates, through nonlinear polarization in the material, a coherent optical field at frequency 3ω. This process is described as follows $\chi^{<3>}(-3\omega;\omega,\omega,\omega)$.
The value of third order nonlinear optical susceptibility depends on the frequency of the interacting waves. Thus, for example, measuring the third order nonlinear optical susceptibility using third harmonic generation $\chi^{<3>}(-3\omega;\omega,\omega,\omega)$ and degenerate four wave mixing $\chi^{<3>}(-\omega;\omega,-\omega,\omega)$ two different values of the third order nonlinear optical susceptibility $\chi^{<3>}$ were obtained.
Second harmonic generation (SHG) technique is used to determine the second order nonlinear optical susceptibility. Second harmonic generation describes the process in which a fundamental laser field of frequency ω generates, through nonlinear polarization in the material, a coherent optical field at frequency 2ω.

In the present work degenerate four wave mixing and nonlinear transmission measurements were performed using a Nd:YAG laser (Quantel Model YG472) working at 532nm with 30ps pulses duration and a 1Hz repetition rate. Third harmonic generation experiment was carried out using a Q-switched Nd:YAG laser (model Leopard D-10 manufactured by Continuum Lasers) working at 1064nm with 16ps pulse duration and 10Hz repetition rate.

4.2.4. Results

4.2.4.1. Metallophthalocyanines

In recent years there has been a significant increase in interest of organic compounds, which due to their interesting physicochemical properties, simplicity and low-cost production technology provide serious competition for traditional semiconductor materials currently used in micro- and optoelectronics. Organic materials can be used in gas sensors, solar cells, for the construction of light-emitting diodes and photodiodes as well as in transistors matrix used for the construction of modern electronic displays. The thin film structures are used for constructing diode and laser. In these kinds of structures it is very important to know the linear and nonlinear optical coefficients. Determination and preparation of materials with strong optical nonlinearity contributes to the construction of new optical systems.

Due to the fact that the use of organic compounds in a micro- or optoelectronics is relatively new, many phenomena in these materials still remains unknown. Therefore, these materials require extensive research. Understanding the essence of the basic mechanisms operating in organic structures will enable the improvement of their operational parameters and the elimination of certain defects. From this point of view, it is essential to the continued expansion of research on this class of materials. Secondly, the devices based on organic compounds, despite the many advantages, have also disadvantages (stability, efficiency), which could exclude them from the possibility of mass production at this stage. Therefore, the research on improving their property is necessary and can bring huge benefits.

Phthalocyanines represent a large family of π-conjugated materials, which are of interest in optical devices such as optical communication, optical storage, optical computing, harmonic generation, optical switching, optical limiting, optical rectifying devices, optical recording, displays, printers, dynamic holography, liquid crystals, frequency mixing, optical switching, organic light emitting diodes (OLEDs), organic field effect transistors (OFET), photovoltaic cells (PV), gas sensors and nonlinear optics. Phthalocyanines and other metallomacrocycle molecules are also very interesting in respect of their possible application in the field of molecular electronics [30]. Phthalocyanine-based molecular electronic devices may play significant role in generation and processing of information. Phthalocyanines (Pcs) have emerged as an important class of materials for third order nonlinear optics because of their versatility, exceptionally high thermal stability, architectural flexibility, ease of processing and fabrication. Phthalocyanines are found to exhibit a variety of efficient third order nonlinear optical effects [30]. In addition, their chemical versatility allows the manipulation of the electronic distribution of the macrocyclic core and, therefore the fine-tuning of the nonlinear optical response. Phthalocyanines (Pcs) are very special organic systems in a way that they offer tremendous opportunities in tailoring their physical and chemical properties over a wide range either by substituting different metal atoms into the ring or by altering peripheral and axial functionalities. Phthalocyanines are capable of including more than 70 different metallic and non-metallic ions into the ring cavity. It is possible to incorporate a variety of peripheral substituents around the phthalocyanine core as well as replace some of the isoindole units by other heterocyclic moieties, giving rise to different phthalocyanine analogues.

Phthalocyanines and their derivatives are organic compounds, which belong to the group of coordination compounds often called as complexes - a central atom or ion is bonded to the coordination with ligands. The chemical structure of phthalocyanine is similar to well-known naturally occurring porphyrins. Ligand phthalocyanine (Pc = $C_{32}H_{16}N_8^{-2}$) consists of four isoindole rings (pyrrole ring + benzene) connected by azomethane bridge. Ligand phthalocyanine is able to bind in its center a metal cation thereby forming metallophthalocyanines. Coordination bonds formed between the central atom and the nitrogen atoms of isoindole rings. One of the characteristics of the coordination compound is the number of ligand atoms linked directly to the central atom so-called coordination number. In the case of MPc, the central metal-formed coordination bonds with four nitrogen atoms, so the coordination number is 4. Determining the number of electrons associated with the metal in the complex (both from metal and from the ligand) we obtain usually the number of 18. In metallophthalocyanines complexes, which are characterized by high symmetry, the system of 18 electrons surrounding metal is highly delocalized forming so-called two-dimensional coupled system of 18π. The metallophthalocyanines compounds are called the macrocyclic compounds (ring structure) and are characterized by an unusual chemical and thermal stability [H4]. Phthalocyanines (Pcs) are poryphyrin derivatives, which characterize with high symmetry and extensively delocalized two-dimensional 18π-electron systems, exhibiting a large number of unique properties. This large nonlinearity originates from their extensively delocalized two-dimensional π-electron distribution [31, 32].

Metallophthalocyanines (MPcs) are currently intensively investigated since they offer a wide range of potential applications in micro- and optoelectronics organic devices. In many cases, organic semiconductor devices can replace the classical inorganic components. Phthalocyanines and their derivatives demonstrate a lot of unique optical and electrical properties, which are of interest for use in modern micro- and optoelectronics organic devices. Semiconductive properties of phthalocyanine crystals were first observed in 1948 [33]. The ability of metallophthalocyanines to transport of charge (holes and electrons) due to a significant overlap of the π-type orbitals of the neighboring molecules, which determines their semiconducting properties. Self-organizing molecules in crystals enhances the overlapping of orbitals, which is a key aspect of improving the mobility of carriers. Metallophthalocyanines, like most organic semiconductor materials, are *p*-type semiconductors, which are capable of transport holes than electrons [34]. Modern multi-layer

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OLED structures consist of several layers. One of them is a hole injection layer. Metallophthalocyanine (MPc) are often used material for this layer.

For studies we selected phthalocyanines complexes coordinated with transition metal ions such as copper (Cu^{2+}), cobalt (Co^{2+}) and zinc (Zn^{2+}) as well as with metal of the main group i.e. magnesium ion (Mg^{2+}). These compounds differ in the degree fill of *3d* subshell, the magnesium phthalocyanine (MgPc) is devoid of *3d* electrons, zinc phthalocyanine (ZnPc) has completely filled *d*-shell, while cobalt phthalocyanine (CoPc) and copper phthalocyanine (CuPc) have the unfilled *3d* orbital. Therefore, we can say that MgPc and ZnPc have a closed shell structures, while CoPc and CuPc have an open shell structure.

Whereas, DNA-CTMA and liquid crystal (LC) are used as the functional groups. Deoxyribonucleic acid (DNA), by the unique properties resulting from the structure in the form of a double helix, is a very promising material for use in modern photonics. DNA has excellent optical and photophysical properties (i.e. low optical loss, strong fluorescence amplification, etc.), suggesting the potential use of these materials for electro-optical systems or optical memory [35]. The material, which I used for research came from Chitose Institute of Technology (CIST) in Japan.

Pure DNA is soluble only in water. Therefore, it was necessary to carry out the procedures of substitution of sodium ions contained in the DNA chain with surfactant hexadecyltrimetylammonium chloride (CTMA). The obtained in this way DNA-CTMA complex is insoluble in water, but soluble in a number of organic solvents like chloroform, benzene and a large number of alcohols including isopropanol, methanol, ethanol and butanol. These solvents are more convenient in device fabrication than water.

The obtained DNA-CTMA complex was functionalized with metallophthalocyanine by solubilizing them directly in DMF (dimethylformamide).

Liquid crystals are substances, which made up of highly anisotropic molecules forming an intermediate phase between the liquid and the crystalline state of aggregation, often called the fourth state of matter. Characterized them both the flow ability (liquid characteristic) and long-distance order forming molecules (crystals characteristic). In the liquid crystal phase, the molecules have a relative freedom of movement and at the same time the partially ordering their center of gravity, and thus they possess the properties of liquid and solid.

The first physicist who has studied liquid crystals was O. Lehman. Watching the liquid crystals under the polarizing microscope he found that they exhibit optical anisotropy. Since then, the liquid crystals attracted a lot of attention, which led in time to better understanding of their properties.

The material studied was nematic liquid crystal called 6CHBT (1-(4-hexyl-cyclohexyl)-4-isothiocyanato-benzene). In the nematic liquid crystals, the long axes (long axes are generally identified with one of the axis of symmetry and the axis of the smallest moment of inertia) are almost parallel to the highlighted direction. Nematic molecules are freedom of translational (no long-range translational ordering).

The aim of work was study of the nonlinear optical properties of metallophthalocyanines (in the form of solutions and thin films) depending on:

- substitution different metal atoms into the ring – i.e. cobalt (Co^{2+}), copper (Cu^{2+}), zinc (Zn^{2+}) or magnesium (Mg^{2+}) [H1, H3, H4, 36],
- host-guest system with:
    - liquid crystal (6CHBT: 1-(4-hexyl-cyclohexyl)-4-isothiocyanato-benzene) [H2-H4],
    - complex DNA-CTMA [H2, 37, 38].

The study of nonlinear optical properties were done using the methods of:

- nonlinear transmission (TNL) [H1-H4, 38],
- degenerate four wave mixing (DFWM) [H1-H4, 38],
- third harmonic generation (THG) [H1, H4, 36-38].

In the frame of study was determined:

- the linear absorption coefficient (α) (dla $\lambda_{ex.} = 532$ nm),
- two-photon absorption coefficient (β) (dla $\lambda_{ex.} = 532$ nm),
- the imaginary part of third order nonlinear optical susceptibility ($\chi_I^{<3>}$) (for $\lambda_{ex.} = 532$ nm),
- the third order nonlinear optical susceptibility ($\chi^{<3>}$) (for $\lambda_{ex.} = 532$ nm and $\lambda_{ex.} = 1064$ nm),
- the second order hyperpolarizability (γ),
- figure of merit (F).

From the study, we obtained:

- the value of the linear absorption coefficient (α) for ZnPc and MgPc is smaller than for CoPc and CuPc in both case of solutions and thin films,
- the value of two photon absorption (β) and calculated the imaginary part of third order nonlinear optical susceptibility ($\chi_I^{<3>}$) is the highest for ZnPc and the smallest for CoPc,
- the values of third order nonlinear optical susceptibility ($\chi^{<3>}$) for ZnPc and MgPc are the same and they are about two-three times larger than for CuPc and CoPc,
- the value of second order hyperpolarizability (γ) is the smallest for CoPc and increases about two times as follows: CuPc, MgPc and ZnPc,
- the value of figure of merit (F) is the highest for ZnPc and MgPc, and the smallest for CuPc and CoPc,
- the value of α, β, $\chi^{<3>}$ and γ increases with increasing concentration of MPc,
- the $\chi^{<3>}(-3\omega;\omega,\omega,\omega)$ value of MPc at $\lambda_{ex.} = 1064$ nm is less than $\chi^{<3>}(-\omega;\omega,-\omega,\omega)$ value of MPc at $\lambda_{ex.} = 532$ nm, however, the relationship remains the same, that is, the values of third order nonlinear optical susceptibility for ZnPc and MgPc are comparable and they are about 2-3 times higher than for CuPc and CoPc,
- the $\chi^{<3>}$ value of DNA-CTMA and LC is very small,
- the $\chi^{<3>}$ value of MPcs-LC and CoPc-DNA-CTMA systems increases compared with the values of third order nonlinear optical susceptibility pure MPcs (CoPc),
- the value of third order nonlinear optical susceptibility ($\chi^{<3>}$) for ZnPc-LC and MgPc-LC systems is the same and higher for CoPc-LC and CuPc-LC.

Conclusions:

It can be noted that the increase of nonlinear optical properties in all cases is the following: CoPc < CuPc < MgPc < ZnPc. It can be concluded that the differences in the values may be due to the different degree of interaction of the metal ion with π-electron system of the macrocycle. The degree of influence depends on the number of electrons on the outer shell *3d*

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of the central cation ($Mg^{2+} \rightarrow 1s^2...2p^6$, $Co^{2+} \rightarrow 1s^2...3d^7$, $Cu^{2+} \rightarrow 1s^2...3d^9$, $Zn^{2+} \rightarrow 1s^2...3d^{10}$). Therefore, magnesium phthalocyanine (MgPc) is devoid of *3d* electrons, cobalt phthalocyanine (CoPc) and copper phthalocyanine (CuPc) have the unfilled *3d* orbital, and zinc phthalocyanine (ZnPc) has completely filled *d*-shell.

The absorption spectra of thin films [H1, H4] and solutions [H2-H4] of metallophthalocyanines studied (MPcs) are very similar, although some changes are observed in the energy structure in the dependence of the substituted metal. We can notice that there are at least five absorption bands centered on the phthalocyanine ligand in the case of thin films (conventionally labelled as Q, B, N, L and C bands) and two major absorption regions in the case of solutions (Q and B bands). The absorption spectra of MPc solutions present a narrow Q-band in the visible region and a relatively wide B-band in the near ultraviolet. These bands arise due to $\pi \rightarrow \pi^*$ transitions on the phthalocyanine macrocycle. Much wider B-band (also called as Soret band) is associated with shorter molecules lifetime in this state and the contribution of several overlapping resonances lines. Splitting of Q-band into two components takes place due to the Davydova effect. One can see the vibrational structure of $Q_{vib.}$-bands. All transitions are $\pi \rightarrow \pi^*$ type. Phthalocyanines are characterized with high symmetry and extensively delocalized two-dimensional 18π-electron systems. Comparing the absorption spectra of various metallophthalocyanines, one can see that the metal plays a crucial role in determining the shape and position of each band, as well as values of nonlinear optical properties. However, the shape of the spectra and the position of the absorption bands for ZnPc and MgPc are very similar. The similarity of the spectra follows from the fact that the outer shell cation L (n = 2) for MgPc and M (n = 3) for ZnPc are completely filled, and participation of the electron associated with the cation in absorption is negligible. In addition, the *3d* subshell of the metal lies deep below the HOMO level of these molecules and will not affect the mixing of orbitals. Therefore, we see mainly the transition centered on the phthalocyanine ligand. The differences related to the position and intensity of the absorption bands studied MPcs are due to varying degrees of interaction a metal ion with π-electron system of the macrocycle.

The enhancements of $\chi^{<3>}$ of MPcs we can also explain from the electronic structures of the upper occupied and lower vacant molecular orbitals for the ground states of MPcs [C]. The lowest energy molecular orbitals of CuPc are different from those of CoPc, ZnPc and MgPc. This suggests that the different electronic transport behaviour observed in the different MPcs can be directly related to the properties of molecular orbitals. In the case of ZnPc with completely filled *d*-shell, we can suppose that the probability for change transfer mechanism is very less. The 3*d* subshell of ZnPc is filled and deep enough to form rather pure molecular orbitals. The valence electronic structures of ZnPc and MgPc are very similar. ZnPc and MgPc exhibit a large gap between the HOMO and LUMO. Therefore in the energy structure of metallophthalocyanines with the central metal ion, which is devoid of *d* electrons (MgPc) or is in configuration of d^{10} (ZnPc) mutual mixing of metal and ligand orbitals is neglected. As a result, all the observed transitions occur between centring orbitals on the ligand phthalocyanine (Pc). Whereas, the intramolecular transitions with charge transfer as well as transitions *d-d* type do not complicate the absorption spectra of these compounds. Phthalocyanines containing certain transition metals (such as CuPc, CoPc) have a more complex energy structure because *3d* metal orbital lies between HOMO (π) and LUMO (π^*) levels of Pc ring. As a result, the spectra of these compounds may have additional structures originating from intramolecular transitions with charge transfer (CT) [H4, 39].

Electron excitation energy of Q and B bands depends on the amount of electrons held in the *3d* subshell coordinated cation. With an increase the number of *3d* electrons the excitation energy of Q and B bands decreases. Differences in the absorption spectra of MPcs studied can be explained also by different electronegativity of the central metal, which affects the charge

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distribution in the molecule. Comparable structure of spectra possess Pc complexes with metals of similar electronegativity i.e., ZnPc and MgPc as well as CoPc and CuPc.

The values of third order nonlinear optical susceptibility of MgPc and ZnPc are comparable and they are about 2-3 times higher than for CuPc and CoPc. Thus, this relationship is opposite to the electronegativity of the central metal, which depends on the density distribution of electron charge in the molecules, that is the charge distribution between the metal and the ligand phthalocyanine. According to Pauling scale, the electronegativity of coordinated metal are equal 1.2 and 1.6 for the Mg, Zn, respectively and 1.8 and 1.9 for the Co and Cu, respectively.

Differences in the nonlinear optical properties of various MPc can also be related to the size of the phthalocyanine cavity ring and its deflection as well as the symmetry of the molecule. Co^{2+} and Cu^{2+} ions have a similar size to the size of the phthalocyanine cavity ring (approx. 3.82Å – 3.86Å) and at room temperature they represent the macrocycle in the equilibrium geometry. As a result, their structures are planar and have D_{4h} symmetry. Contrary to this, the Zn^{2+} ion is larger than the equilibrium cavity ring but not so large that it cannot be placed in it. This results in tension of the ring and as a consequence the cavity dimensions of ZnPc is the greatest (approx. 3.96Å). However, this results in only a slight deviation ZnPc molecule from the ideal D_{4h} symmetry. The MgPc molecule in the crystal is non-planar and forms a pyramidal structure with C_{4v} symmetry.

The $\chi^{<3>}(-3\omega;\omega,\omega,\omega)$ value of MPcs studied for $\lambda_{ex.}$ = 1064 nm is smaller than the $\chi^{<3>}(-\omega;\omega,-\omega,\omega)$ value of the same materials for $\lambda_{ex.}$ = 532 nm. Such difference in the values of studied materials is not surprising and originates from the different measurement techniques (DFWM and THG) and the operative nonlinear optical processes associated with them. Degenerate four wave mixing (DFWM) technique (in the ps regime) may be used to measure different contributions, including electronic, orientation and thermal effects. While, third harmonic generation (THG) method allows determining only the purely electronic contribution to third order nonlinear optical susceptibility.

We also know that the value of the third order nonlinear optical susceptibility depends on the frequency of the interacting waves. Thus, measuring the third order nonlinear optical susceptibility using third harmonic generation $\chi^{<3>}(-3\omega;\omega,\omega,\omega)$ and degenerate four wave mixing $\chi^{<3>}(-\omega;\omega,-\omega,\omega)$ there is obtained two different values of the third order nonlinear optical susceptibility $\chi^{<3>}$. It should be noted that the excitation wavelength of our DFWM measurements (532 nm) is near the Q and B bands in the absorption spectra. Therefore, in DFWM measurements, the one-photon resonance in the Q band and two-photon resonance in the B band give rise to a remarkably high $\chi^{<3>}$ value. THG experiment conducted at 1064 nm gives a third harmonic at 355 nm. The 355 nm (3ω) lies at the Soret band in the absorption spectra of MPc, which has very high absorption. Therefore, the large $\chi^{<3>}(-3\omega;\omega,\omega,\omega)$ value in MPcs arises from the three-photon resonant contributions at the Soret band. As a consequence of the three-photon resonance, the $\chi^{<3>}(-3\omega;\omega,\omega,\omega)$ value of MPcs is larger than normally.

The nonlinear optical properties of cobalt phthalocyanine (CoPc) with the liquid crystal (LC) and cobalt phthalocyanine (CoPc) with DNA-CTMA surfactant complex were studied with the original intention of exploring the possible influence of the molecule aggregation on the nonlinear optical properties of the systems. The formation of ordered aggregate in CoPc, which exerts specific effect on the electronic structure of the system, is expected to affect the nonlinear absorption properties. The value of the third order nonlinear optical susceptibilities ($\chi^{<3>}$) of host-guest system CoPc-LC and CoPc-DNA-CTMA increase in comparison with

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the value of the third-order nonlinear optical susceptibilities of CoPc. We suppose that this is caused by increase of the charge-transfer effects and of the dipole moments of the molecule with the increase of the chain length. Effectively, we can observe in the host-guest system of CoPc-LC and CoPc-DNA-CTMA very high diffraction efficiency in the four wave mixing experiment. In this connection we can see how the substituting different peripheral substituents around the cobalt phthalocyanine core correlate with nonlinear optical properties. The obtained results consisted of a systematic image of nonlinear optical properties of metallophthalocyanines. In addition, the performed studies may also bring a lot of valuable information about the materials studied in other terms of their applications such as organic light emitting diodes (OLEDs), organic field effect transistors (OFET), photovoltaic cells (PV) and gas sensors.

4.2.4.2. Mixed ternary and quaternary semiconductor crystals based on ZnSe and CdSe

The interest in semiconductors from the II-VI group as good materials for the construction of light-emitting diodes (LEDs) and semiconductor lasers emitting in the blue-green was developed in the nineties. The first laser diode based on II-VI compounds emitting blue-green was developed in 1991. In 1994, a green LED (ZnSe/ZnTeSe) emitting light at a wavelength of 512nm and ZnSe/ZnCdSe LED emitting blue light at a wavelength of 489nm were presented.

The production of light-emitting diodes that emit a narrow band in the blue, green and red enables flat and large brightness TV screens. Moreover, these materials can be used in displays, which possess large area, and as economic sources of light. Lasers emitting green, blue and violet can be used in medicine, laser printers of high definition, television projection, underwater communication and devices to record information. The II-VI compounds are also used in the construction of holographic storage, optical fibers, scanners, projectors, UV detectors and can be used in devices that emit white light.

To realize these kinds of devices we need to use semiconductor materials with high-energy band gap. Potential candidates for their implementation from II-VI group are semiconductors made on the basis of ZnSe and CdSe. Moreover, adding dopant such as magnesium (Mg) and beryllium (Be) to these materials will increase their energy band gap. Larger material energy band gap can provide better confinement of carriers, as well as device design emitting radiation of a shorter wavelength. The preparation of such structures allows one to obtain the fundamental parameters (such as: energy band gap, lattice constant, linear and nonlinear absorption coefficients, linear and nonlinear refractive indices and high order nonlinear optical susceptibility) depending on introduce the content of dopants. Determining the influence of the above parameters on the material composition will allow for the production of structures that can be used in photonics, opto- and microelectronics as well as nonlinear optical devices. For this type of application, we require the control of energy band gap depending on the content of each component in the mixed semiconductor compounds. Therefore, the possibility of obtaining the new materials with useful new physical properties is one of the reasons why it is worthy investigating mixed crystals, such as $Zn_{1-x}Mg_xSe$, $Zn_{1-x}Be_xSe$ and $Zn_{1-x-y}Be_xMg_ySe$, as well as $Cd_{1-x}Mg_xSe$. Changing the concentration relation of the components allows one to obtain compounds with a wide range of physical properties. In addition, dopants and natural defects present in the new materials can dramatically change the electrical and optical properties of semiconductor crystals.

The interest in $Zn_{1-x}Mg_xSe$ is related to the possibility of using this compound in structures that emit light in the wavelength rang from 400nm to 550nm. The combination of magnesium halide (MgSe) with broadband II-VI compounds (ZnSe) has been used in lasers as a limiting layer. The application of a limiting layer ($Zn_{1-x}Mg_xSe$) for an active layer improves

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the reliability of the laser structure by removing the mechanical stress and dislocation network, as well as providing a reduction of the threshold current density and hence a longer life for the laser. Replacement of the zinc atoms by beryllium atoms ($Zn_{1-x}Be_xSe$) in II-VI compounds (ZnSe) increases covalent bonds, which significantly increases the hardness of the material and thus reduces the probability defects being generated and their migration within the crystal. Such properties should increase the stability of devices built using these materials. Short bonds between atoms and small values of ionic ensure high rigidity of the crystal lattice $Zn_{1-x}Be_xSe$. However, $Cd_{1-x}Mg_xSe$ crystals exhibit *n*-type conductivity and their resistivity strongly depends on the magnesium content.

The aim of the work was study of the nonlinear optical properties of mixed ternary and quaternary semiconductor crystals obtained by Bridgman method depending on:

- the content of Mg impurities introduced into ZnSe [H5, H6, H8],
- the content of Be impurities introduced into ZnSe [H8],
- the content of Mg and Be impurities introduced into ZnSe [H8],
- the content of Mg impurities introduced into CdSe [H5, H6],
- the orientation of ZnSe crystal and its annealing in zinc air [H7].

The study of nonlinear optical properties were done using the methods of:

- nonlinear transmission (TNL) [H5-H8],
- degenerate four wave mixing (DFWM) [H5-H8],
- third harmonic generation (THG) [H6],
- second harmonic generation (SHG) [H6].

In the frame of study the following parameters were determined:

- the linear absorption coefficient (α) (for $\lambda_{ex.} = 532$ nm),
- two-photon absorption coefficient (β) (for $\lambda_{ex.} = 532$ nm),
- the imaginary part of third order nonlinear optical susceptibility ($\chi_I^{<3>}$) (for $\lambda_{ex.} = 532$ nm),
- the third order nonlinear optical susceptibility ($\chi^{<3>}$) (for $\lambda_{ex.} = 532$ nm and $\lambda_{ex.} = 1064$ nm),
- the second order nonlinear optical susceptibility ($\chi^{<2>}$) (for $\lambda_{ex.} = 1064$ nm),
- nonlinear refractive index (n_2),
- figure of merit (F).

From the study, we found:

- the value of the linear absorption coefficient (α) for $Zn_{1-x}Be_xSe$ increases with increasing Be content,
- the value of the linear absorption coefficient (α) for $Zn_{1-x}Mg_xSe$ increases with increasing Mg content,
- the value of two photon absorption (β) and calculated the imaginary part of third order nonlinear optical susceptibility ($\chi_I^{<3>}$) increases with increasing Be or Mg content respectively for $Zn_{1-x}Be_xSe$ and $Zn_{1-x}Mg_xSe$,

- the value of two photon absorption (β), and calculated the imaginary part of third order nonlinear optical susceptibility ($\chi_I^{<3>}$) is the highest for $Zn_{1-x-y}Be_xMg_ySe$ mixed quaternary crystal,
- the values of third order nonlinear optical susceptibility ($\chi^{<3>}$) and nonlinear refractive index (n_2) decrease with increasing Be or Mg content for $Zn_{1-x}Be_xSe$ and $Zn_{1-x}Mg_xSe$, respectively,
- the value of the figure of merit (F) decreases with increasing Be or Mg content for $Zn_{1-x}Be_xSe$ and $Zn_{1-x}Mg_xSe$, respectively,
- the values of third order nonlinear optical susceptibility ($\chi^{<3>}$) and second order nonlinear optical susceptibility ($\chi^{<2>}$) for $Cd_{0.70}Mg_{0.30}Se$ are higher than for $Zn_{0.67}Mg_{0.33}Se$ with a similar Mg content in crystal,
- the value of energy band gap (E_g) increases with increasing Be or Mg content for $Zn_{1-x}Be_xSe$ i $Zn_{1-x}Mg_xSe$, respectively.

Conclusions:

We can see that the value of the third order nonlinear optical susceptibility decreases with increasing Be or Mg for $Zn_{1-x}Be_xSe$ and $Zn_{1-x}Mg_xSe$, respectively. The origin of this behaviour comes from the dependence of the third order nonlinear optical susceptibilities on the energy band gap E_g of the crystals studied. As a general rule, the processes of the third order nonlinear optical susceptibilities scale with E_g^{-4} [H5, H8, 16, 40]. For this reason, when the energy band gap of the material studied increases, the value of the third order nonlinear optical susceptibility decreases.

In the case of $Cd_{1-x}Mg_xSe$ with a low content of Mg, no nonlinear response was observed for the studied wavelength. We have also found that the value of third order nonlinear optical susceptibility for $Cd_{0.70}Mg_{0.30}Se$ is higher than for $Zn_{0.67}Mg_{0.33}Se$ with a similar content of Mg in the material. The energy band gap for $Zn_{0.67}Mg_{0.33}Se$ is higher than for $Cd_{0.70}Mg_{0.30}Se$. This behaviour is not surprising and can be understood if one take into consideration that the free carrier concentration in $Cd_{1-x}Mg_xSe$ samples is about four orders of magnitude higher than that in $Zn_{1-x}Mg_xSe$ ones with comparable Mg content respectively. It is commonly known that when the electric conductivity increases, the values of nonlinear optical properties increase too [41]. From the measurements performed, one can conclude that the incorporation of Mg as constituent into ZnSe and CdSe crystals plays a crucial role in the observation of the nonlinear optical response.

These results consisted of the systematic study of the nonlinear optical properties of mixed crystals and provided information on the mechanisms responsible for them, which enabled a fuller understanding of nonlinear optical processes occurring in the material and this is directly related to new practical applications. The experimental obtained results may be used for the possible design of other materials in this class with desired properties. The dependence of nonlinear optical properties on the energy gap will enable appropriate designed material parameters to obtain high values of nonlinearity. This predictive capability is extremely important from the standpoint of searching for materials with large nonlinearities. It should be noted that to our knowledge, these kinds of measurements are made for the first time on compositions such as $Zn_{1-x}Mg_xSe$, $Zn_{1-x}Be_xSe$ and $Zn_{1-x-y}Be_xMg_ySe$ with different Mg and/or Be content. Therefore, this work is useful in extending the knowledge of the nonlinear optical properties of ternary and quaternary semiconductor crystals depending on the content of Mg and Be impurities introduced into ZnSe and CdSe obtained by the Bridgman method.

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4.2.5. Summary

Presented a monothematic series of publications is dedicated to the determination of nonlinear optical properties of organic and inorganic semiconductor materials. In these articles we presented the selected experimental techniques, such as nonlinear transmission, degenerate four wave mixing, second and third harmonic generation. These methods are used to determine the value of nonlinear absorption, nonlinear refractive index, as well as second ($\chi^{<2>}$) and third ($\chi^{<3>}$) order nonlinear optical susceptibility.

In my opinion, the most important results obtained and presented in this habilitation dissertation are:

- presentation a mechanism for nonlinear optical processes occur in the selected metallophthalocyanines depending on the change of the central atom and mixed crystals depending on the content of dopants Mg and/or Be introduced into ZnSe and CdSe,
- description new nonlinear materials based on host-guest system such as metallophthalocyanines-liquid crystal (MPc-LC) and cobalt phthalocyanine-deoxyribonucleic acid (CoPc-DNA-CTMA), in which depending on the type of material it is possible to change the nonlinear refractive index, and thus third order nonlinear optical susceptibilities.

Additionally it should be noted that the studies of nonlinear optical properties of MPC-LC, CoPc-DNA-CTMA, as well as $Zn_{1-x}Mg_xSe$, $Zn_{1-x}Be_xSe$ and $Zn_{1-x-y}Be_xMg_ySe$ containing different contents of Mg and/or Be were carried out for the first time in the world. The implementation of these studies enabled the understanding of the physicochemical processes occurring in these materials and provided additional information on the physical mechanisms responsible for them, and thus contributed to better understanding of the optical processes occurring in the materials. Understanding the basic nature of the mechanisms operating in the organic and inorganic structures will allow the improvement of their operating parameters and the elimination of certain disadvantages. Therefore, organic and inorganic semiconductor materials require further intensive research. Presented results, in this dissertation based on eight articles published in scientific journals, are beginning of work on solve to the problem of production of material, which will posses important characteristics from nonlinear optical point of view such as large optical nonlinearity, low absorption, low optical losses, and ultrafast response time.

Currently my research is carried out in two directions. The first of them concerns to continue the search and the study of new optimal materials for the nonlinear optics and photonics, in which there is a possibility of full control of nonlinear refractive index changes and nonlinear absorption. The second direction of research is related to make and the study the nonlinear optical properties of organic-inorganic thin films such as MPc/ZnSe (metallophthalocyanine/ZnSe), Alq_3/ZnSe (tris-(8-hydroxyquinolate)-aluminium/ZnSe) and other similar structures. From the obtained studies we can see that both metallophthalocyanines (MPcs) and mixed crystals based on ZnSe and CdSe are materials that can be used in nonlinear optics because they have relatively high value of nonlinear refractive index. Therefore, we expect that the organic-inorganic structure such, as MPc/ZnSe will accentuate not only the individual advantages of each component, but also the properties of the system and the interfacial properties between materials. Thus, we expect to increase in the value of nonlinear optical properties in such systems as compared to the values obtained for particular materials. Organic-inorganic complex structures are expected to open new areas of research in optoelectronics materials. It is expected that the organic-inorganic composites can be used in nonlinear optics, photonics, information storage, gas sensors, thin-film field-effect transistors, and photovoltaic cells, since they combine the high nonlinear optical properties of organic molecules and the high carrier mobility of inorganic materials in one system.

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B. Derkowska-Zielińska

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4c) Statements of co-authors

Below there are articles, which constitute the habilitation thesis together with a detailed description of the co-authors' contribution. Statements of co-authors on their contribution can be found in Annex 5.

H1. **B. Derkowska**, M. Wojdyła, R. Czaplicki, Z. Sofiani, W. Bała, B. Sahraoui, *Influence of the central metal atom on the nonlinear optical properties of MPcs solutions and thin films*, Optics Communications 274, 206, 2007.

> Prof. Bouchta Sahraoui and Prof. Wacław Bała participated in discussions about the results and reviewing the final text of the manuscript. PhD student Michał Wojdyła measured the absorption spectra of the metallophthalocyanines (MPcs). PhD student Robert Czaplicki accompanied Beata Derkowska in carrying out measurements. PhD student Zouhair Sofiani accompanied Beata Derkowska in carrying out measurements.

H2. **B. Derkowska**, K. Jaworowicz, O. Krupka, M. Karpierz, M. Wojdyła, W. Bała, J.G. Grote, F. Kajzar, B. Sahraoui, *Influence of different peripheral substituents on the nonlinear optical properties of cobalt phthalocyanine core*, J. Appl. Phys. 101, 083112, 2007.

> Prof. Bouchta Sahraoui, Prof. Wacław Bała, Prof. Mirosław Karpierz and Prof. François Kajzar participated in discussions about the results and reviewing the final text of the manuscript. Prof. Mirosław Karpierz was also a scientific supervisor of the PhD student Katarzyna Jaworowicz. Prof. James G. Grote made DNA materials available for measurments and participated in discussions about the results. Dr Oksana Krupka helped in the preparation of DNA-CTMA and CoPc-DNA-CTMA samples. PhD student Katarzyna Jaworowicz helped in the preparation of MPcs-LC samples and accompanied Beata Derkowska in carrying out the measurements. PhD student Michał Wojdyła measured the absorption spectra of the metallophthalocyanines (MPcs). PhD student Robert Czaplicki accompanied Beata Derkowska in carrying out measurements.

H3. **B. Derkowska**, M. Wojdyla, W. Bala, K. Jaworowicz, M. Karpierz, R. Czaplicki, B. Sahraoui, *Dependence of the third order nonlinear optical susceptibility on concentration and peripheral substituent of metallophthalocyanines*, Molecular Crystals and Liquid Crystals 485, 965, 2008.

> Prof. Bouchta Sahraoui, Prof. Wacław Bała and Prof. Mirosław Karpierz participated in discussions about the results and reviewing the final text of the manuscript. Prof. Mirosław Karpierz was also a scientific supervisor of PhD student Katarzyna Jaworowicz. PhD student Katarzyna Jaworowicz helped in the preparation of MPcs-LC samples and assisted Beata Derkowska in carrying out the measurements. PhD student Michał Wojdyła measured the absorption spectra of the metallophthalocyanines (MPcs). PhD student Robert Czaplicki accompanied Beata Derkowska in carrying out the measurements.

H4. **B. Derkowska**, *Third order nonlinear optical properties of metallophthalocyanines (MPcs)*, Nonlinear Optics Research Progress, Chapter 9, pp. 189 – 222, Editors: James L. Davies and Daniel A. Hall, Nova Science Publishers, Inc. 2008.

PhD student Michał Wojdyła measured the absorption spectra of the metallophthalocyanines (MPcs).

H5. **B. Derkowska**, F. Firszt, B. Sahraoui, A. Marasek, M. Kujawa, *Study of the third order nonlinear optical properties of $Zn_{1-x}Mg_xSe$ and $Cd_{1-x}Mg_xSe$ crystals*, Opto-Electronics Review 16, 8, 2008.

Prof. Bouchta Sahraoui participated in discussions about the results and reviewing the final text of the manuscript. Mgr Agnieszka Marasek made samples. Prof. Franciszek Firszt took part with Mgr Agnieszka Marasek in the preparation of crystals as well as the determination of the chemical composition and the energy band gap of the studied samples from photoluminescence and transmission measurements. Student Magdalena Kujawa accompanied Beata Derkowska in carrying out the some measurements. PhD student Zacaria Essaïdi assisted Beata Derkowska in carrying out the measurements.

H6. **B. Derkowska**, B. Sahraoui, Z. Essaïdi, A. Marasek, F. Firszt, M. Kujawa, *Nonlinear optical properties of $Zn_{1-x}Mg_xSe$ and $Cd_{1-x}Mg_xSe$ crystals*, Optical Materials 31, 518, 2009.

Prof. Bouchta Sahraoui participated in discussions about the results and reviewing the final text of the manuscript. Mgr Agnieszka Marasek made samples. Prof. Franciszek Firszt took part with Mgr Agnieszka Marasek in the preparation of crystals as well as the determination of the chemical composition and the energy band gap of the studied samples from photoluminescence and transmission measurements. Student Magdalena Kujawa accompanied Beata Derkowska in carrying out the some measurements. PhD student Zacaria Essaïdi assisted Beata Derkowska in carrying out the measurements.

H7. **B. Derkowska**, F. Firszt, B. Sahraoui, A. Marasek, *Experimental results of third order nonlinear optical susceptibility of oriented and annealed ZnSe crystals*, IEEE 2009, E-ISBN 978-1-4244-5746-5, (ThP.13 – pp. 1-3).

Prof. Bouchta Sahraoui and Prof. Franciszek Firszt participated in discussions about the results and reviewing the final text of the manuscript. Mgr Agnieszka Marasek made samples. Prof. Franciszek Firszt took part with Mgr Agnieszka Marasek in annealing of ZnSe crystals in an atmosphere of zinc.

H8. **B. Derkowska**, F. Firszt, A. Marasek, B. Sahraoui, *Dependence of nonlinear refractive index of ZnSe on Be and Mg content*, Opto-Electronics Review 18, 384, 2010.

Prof. Bouchta Sahraoui participated in discussions about the results and reviewing the final text of the manuscript. Mgr Agnieszka Marasek made samples. Prof. Franciszek Firszt took part with Mgr Agnieszka Marasek in the preparation of crystals, as well as the determination of the chemical composition and the energy band gap of the studied samples from photoluminescence and transmission measurements.

Der.

5a. Description of research activities before Ph.D. degree:

I started the research work and master thesis during the fourth year of studies at the Department of Atomic, Molecular and Optical Physics Faculty of Physics and Astronomy Nicolaus Copernicus University in Torun, under supervision of Prof. Stanislaw Chwirot. The subject of my work was to use digital technology to record and analyze images to detect and analyze the fluorescence fingerprints. I completed my master's degree in 1997.

After completing my master's degree, I started a Ph.D. study at the Department of Physical Fundamentals of Microelectronics Faculty of Physics and Astronomy Nicolaus Copernicus University in Torun, under the supervision of Dr hab. Waclaw Bala. And in 1998, I started a Ph.D. study at the Laboratory of Optical Properties of Materials and their Applications (POMA - Laboratoire des Propriétés Optiques et des Matériaux Application) University of Angers (France), under supervision of Dr Bouchty Sahraoui. It was the Ph.D. study in the system of co-tutelle. The subject of my work involved the study of linear and nonlinear optical properties of ZnMgSe thin films and ZnSe:Ag crystals.

During my Ph.D. studies I spent two periods studying at the Laboratory of Optoelectronics and Nonlinear Optics Department of Electronic Engineering Terza University of Rome (Italy), under the direction of Prof. Gaetano Assanto on the subject: "Optical signal switching" and at CEA-LETI (Technologies Avancées) DEIN/SPE CE Saclay (France), under the direction of Prof. François Kajzar on the subject: "Third order optical nonlinearities in crystals using THG method".

In June 2001, I finished my Ph.D. study in France and I obtained a doctor's degree in physics at the University of Angers (France). After that, I returned to Poland and I continued my Ph.D. studies at the Faculty of Physics and Astronomy Nicolaus Copernicus University in Torun. At the same time, from November 2002 to November 2003, I was a Postdoctoral Fellow at the Experimental Condensed Matter and Quantum Optics Group Department of Physics University of Toronto (Canada), under the direction of Prof. Henry van Driel on the subject: "Ultrafast phenomena in semiconductors: optically injected spin current, coherent control of an optically injected spin-polarized current". After that, I returned to Poland and in 2004 I obtained doctor's degree in physics from the Faculty of Physics, Astronomy and Informatics Nicolaus Copernicus University, Torun.

My scientific achievements before my Ph.D. degree consists of eight articles in reviewed journals and seven articles after conferences (totally: 15 articles). In addition, the results of my research work were presented at about 19 international conferences.

5b. Description of research activities after Ph.D. degree:

After the end of my Ph.D. study and obtaining my doctor's degree (7.01.2004r), I was employed as a research assistant for a period of 1.5 years in the Department of Technical and Applied Physics Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Torun, under the direction of Dr hab. Waclaw Bala. Then in 2005, I was employed as an assistant professor in the Department of Semiconductor and Carbon Physics Faculty of Physics, Astronomy and Informatics Nicolaus Copernicus University in Torun, under the direction of Prof. Franciszek Firszt. At the same time, from November 2005 to September 2006, I was a Postdoctoral Fellow in the Laboratory of Optical Properties of Materials and their Applications, University of Angers (France), under the direction of Prof. Bouchta Sahraoui on the subject: "Contribution to study and diagnostic the nonlinear optical properties of phthalocyanine using for optoelectronics application". The subject of my work was mainly associated with the study of nonlinear optical properties of metallophthalocyanines. The aim of this study was to determine the nonlinear optical properties of metallophthalocyanines by changing the central atom, or by attaching different functional groups in the periphery of the macrocycle. After returning to Poland in September 2006, the subject of my research was still associated with the exploration and research of new materials in terms of nonlinear optics. However, the subject of the work was greatly expanded from the study of linear and nonlinear optical properties of metallophthalocyanines, to those of new organic and metallo-organic materials as well as semiconductor crystals of II-VI group, especially the mixed ternary and quaternary crystals based on ZnSe and CdSe obtained by the Bridgman method, which were measured using degenerate four wave mixing (DFWM), third harmonic generation (THG), second harmonic generation (SHG) and Z-scan techniques.

In 2008, I spent two short-term periods in the Advanced Materials Research Group School of Mechanical Materials and Manufacturing Engineering Faculty of Engineering, Nottingham University (UK) under the direction of Prof. Angela B. Seddon and Prof. Trevor Benson, as well as the School of Engineering and Physical Sciences Physics Department Heriot Watt University (Edinburgh, UK) under the direction of Prof. Ajoy Kar.

My academic achievements after obtaining my Ph.D. degree consists of 28 articles in reviewed journals, 11 articles in conference proceedings (totally: 39 articles) and 2 chapters in books (Annex 7 – List of publications). In addition, the results of my research were presented at 27 international conferences. I was also a principal on four university grants. The Rector of Nicolaus Copernicus University has awarded my research activity in 2006, 2007 and 2010 (2 Team Award and 1 Individual Award).

I have supervised 21 theses (4 licentiate's theses, 3 engineer's theses, 14 master's theses), of which one person has already a doctor's degree at the Faculty of Physics, Astronomy and Informatics Nicolaus Copernicus University in Torun, and two people are currently pursuing doctoral studies (one at the Faculty of Physics, Astronomy and Informatics Nicolaus Copernicus University in Torun, and the other one at the Department of Physics Tampere University of Technology (Tampere, Finland)). At the moment, I take care of two theses (1 licentiate's thesis, 1 engineer's thesis).

In the meantime, I participated in two projects. In the first project, my task was conducting extracurricular classes for children of secondary and high schools from the Kuyavia and Pomerania Province within the framework of Regional Physical, Mathematical, and Computer Circles. In the second one, I conducted classes and popular-scientific lectures with experiments for children of Kuyavia and Pomerania Province secondary schools within the project „Development through Competence".

At the moment, I am a faculty plenipotentiary for the action „Girls to science" and coordinator of the XIII Torun Festival of Science and Arts at the Faculty of Physics, Astronomy and Informatics Nicolaus Copernicus University in Torun. To the present day I conducted several popular science lectures with experience for kindergarten and junior high school students of the Kuyavia and Pomerania Province.

Since 2007 I am Editor of the Central European Journal of Physics. I have reviewed 28 publications in international and national journals. I am a member of the Polish Physical Society (PTF), treasurer of Torun Branch of the Polish Physical Society (TO PTF) and the Polish Society for Crystal Growth (PTWK).

The listing of my published scientific papers and/or creative professional works with information concerning educational achievements, scientific cooperation and promotion of science is presented in Annex 9.

B. Derkowska - Zielińska

Beata Derkowska-Zielińska