

# Influence of central metal atom in MPc (M = Cu, Zn, Mg, Co) on Raman, FT-IR, absorbance, reflectance, and photoluminescence spectra

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In this paper we present the comparative study of photoluminescence (PL), absorption (A), FT-IR, Raman scattering (RS) and reflection (R) spectra of metallophthalocyanines (MPc; M = Zn, Co, Mg, Cu) thin layers. Investigated thin films were deposited by the quasi molecular beam evaporation method on the quartz and silicon substrates. The measurements were carried out in the 350-1150 nm spectral region at wide temperature range from 13K to 320K (PL) and 70K to 550K (FT-IR, RS). The thin films of ZnPc and MgPc show PL emission from the violet to near-IR region whereas CoPc and CuPc layers do not show measurable emission. The temperature dependence of MPc photoluminescence spectra measured in such a wide spectral range are presented for the first time. The obtained emission spectra exhibit several transitions but some of them are visible only at certain temperature range. The changes of both, bands intensities and band positions versus temperature have been studied. Similar investigations have been performed for the FT-IR and Raman scattering spectra. Integral intensities and band position of Raman and FT-IR modes in MPc thin layers indicate sharp kinks at 180 K and 380 K. The obtained transmission and reflection spectra of all investigated thin layers have been also compared with mentioned above results.

(Received October 20, 2008; accepted March 19, 2009)

**Keywords:** Thin films, Metallophthalocyanines, Photoluminescence, Absorption, Reflection, FT-IR, Raman scattering spectra

## 1. Introduction

Metallophthalocyanines are p-type semiconductors which possess very interesting optical and electrical properties. Due to their the low cost of production, high thermal and chemical stability, metallophthalocyanines, especially as thin films, can be applicable in many advanced technological devices. Thin layers of metallophthalocyanines as well as their junctions with a number of organic and inorganic semiconductors or metals can be utilized for optoelectronic applications such as light-emitting diodes, photovoltaic cells, and organic field effect transistors. The thin layers of metallophthalocyanines are very useful as a transporting and injection layers in optoelectronics devices. For this reason the knowledge of the optical and electrical properties is very important. Moreover, the nonlinear optical properties of these materials can take full advantage in optical limiting, optical communications, optical computing, harmonic generation and optical switching devices [1-6].

Due to these exceptional properties, metallophthalocyanine thin films have been recently intensively investigated especially by the optical methods such as absorption, ellipsometry and Raman spectroscopy.

It is evident that the emission properties of such structures are very important, thus the PL measurements are indispensable. The photoluminescence and Raman spectroscopy can be useful tools to study of various intra- and intermolecular energy transfer processes. Although, the emission observed from the different phthalocyanine complexes in the solution have been already reported [7-10]. Unfortunately, a little attention has been paid to the photoluminescence spectroscopy and temperature dependences of vibrational modes of MPc's thin layers. Moreover, in the literature there are not data concerning a temperature dependences of photoluminescence spectra of MPcs thin films.

Despite of many years of phthalocyanine research, the electronic structure of these materials at solid state is still not fully understood. In general, the luminescence spectra for the solid state phthalocyanine complexes are very much broader than those corresponding to solution spectra and can be interpreted in terms of the Davydov coupling. The mentioned above effect of broadening and splitting of the main  $\pi-\pi^*$  states is compatible to the number of translationally inequivalent molecules in the unit cell [11]. Besides, thin solid films often possess various defects which can result in carrier traps and efficient recombination. Unfortunately, there is a little known about

a variety of electronic properties, such as intra- and intermolecular energy transfer processes, doping-induced defect formation, density and energy distribution of native and extrinsic defects in polycrystalline MPc films. In order to improve devices technology, the deposition technique must provide film with reproducible electrical and optical response characteristics. Thus, the detailed informations on intrinsic centers or contaminants in metallophthalocyanine thin films, which can produce effective recombination, are required. For these investigation we used the temperature dependences of photoluminescence, absorption, FT-IR and Raman spectra.

## 2. Experimental details

The thin layers of metallophthalocyanines (MPc: M=Zn,Co,Mg,Cu) were deposited by the quasi molecular beam evaporation on the quartz substrates. The pressure in the vacuum chamber was about  $2 \times 10^{-5}$  Tr. The substrates were precleaned with acetone, isopropanol and deionised water. During the deposition, the substrate was located 10 cm above the MPc source and kept at room temperature. The MPc used in our experiment was purchased from Sigma Aldrich Co. and used without further purification. The MPc powder was evaporated from a quartz crucible source which was heated by a tungsten coil up to 620K.

The photoluminescence (PL) measurements were carried out using 42mW Omnichrome Helium-Cadmium laser ( $\lambda=325\text{nm}$ ) applying the phase-sensitive technique. The laser beam was modulated by the mechanical chopper, which was tuned to the lock-in amplifier (EG&G 7260) reference signal. Sensitive silicon photodiode (Hamamatsu S-8745) with preamplifier was used to detect PL emission. For spectral selection the prism monochromator SPM-2 Carl Zeiss Jena was used. PL spectra were measured in the wide temperature range from 13K to 320K. For this purpose the samples have been placed in a closed cycle He cryostat (HC2 - APD Cryogenics Inc.). The temperature was controlled by a programmable temperature controller (Lake Shore 330) with accuracy  $\pm 0.1\text{K}$ . The absorption and reflection spectra were recorded using the SPM-2 monochromator (Zeiss Jena) coupled with 250W tungsten or 20W deuterium lamp for measurements in VIS-IR and UV region, respectively.

The Raman spectra were recorded using the double grating monochromator GDM 1000 (Zeiss Jena) equipped with the photomultiplier EMI 9658 AM. Excitation was provided by  $\text{Ar}^+$  ion laser (Zeiss Jena) operating at  $\lambda=488\text{ nm}$  at the incident angle of  $36^\circ$  and focused on the sample surface. The spectral resolution was  $4\text{ cm}^{-1}$ .

The Raman scattering spectra of MPc layers were investigated in the spectral range  $1250\text{-}1650\text{ cm}^{-1}$ . This frequency region corresponds to heavy atom-nitrogen (M-nitrogen) in-plane stretching and bending vibrations as well as displacements on C-N-C bridge bond of the phthalocyanine molecule.

The FT-IR spectra of MPc samples palletized with KBr and polyethylene were recorded in the spectral range

from  $400\text{ to }1800\text{ cm}^{-1}$  with resolution of  $4\text{ cm}^{-1}$  using the Perkin-Elmer Spectrum (series 2000).

The analysis of the Raman and FT-IR spectra were performed using a curve-fitting method with Lorentzian components. The intensities of these bands were reduced using Bose-Einstein population factor.

## 3. Results and discussion

Among four investigated materials only ZnPc and MgPc exhibit measurable photoluminescence. CuPc and CoPc do not show fluorescence because of strong spin-orbit interaction. Figures 1 (a,b) present absorption (at room temperature) and PL spectra of ZnPc (at 175K) and MgPc layers (at 225K).

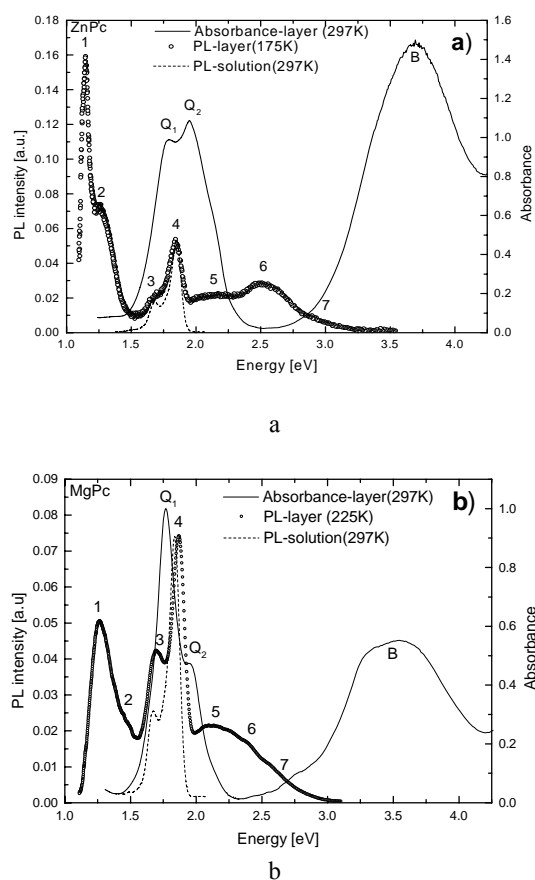


Fig.1. Absorption (A) and photoluminescence (PL) spectra of ZnPc (a) and MgPc (b) layer obtained at RT. Dashed line presents fluorescence spectrum of ZnPc and MgPc dissolved in DMSO, respectively.

For comparison PL spectra of corresponding solutions are also presented in these figures. We chose measurements at 175K for ZnPc and 225K for MgPc because at these temperatures PL spectra are very abundant and all transitions are clearly visible. As it can be

seen from these figures, absorption spectra of ZnPc and MgPc thin films exhibit two main bands which are usually denoted as Q and B bands. The Q band, which exists in the visible region of spectrum, is split into two distinct peaks. The Q band is connected with  $\pi-\pi^*$  ( $a_{1u}$  to  $e_g$ ) transition in the phthalocyanine macrocycle [12,13]. The double structure of Q band can be explained by Davydov splitting effect [11]. In the UV spectral region the electronic transition from  $\pi$  to  $\pi^*$  ( $b_{2u}$  to  $e_g$ ) orbitals give us the intense band called Soret or B band. The PL spectra were determined using  $\lambda=325\text{nm}$  excitation line, so all of the observed emission bands are induced by excitation of Soret band ( $S_2$ ). The emission spectra of ZnPc layer measured at 175K (Fig.1a) and MgPc layer measured at 225 K (Fig.1b) are dominated by several bands. For both spectra we identified seven maxima with similar positions but different intensities (see Figs. 1a and 1b). Particular transitions were denoted by consecutive arabic numerals.

The present knowledge of the emission of metallophthalocyanines is still very limited respect to variety process giving contribution to the observed PL spectra, so their conclusive interpretation remains difficult [14,15]. However, we propose a scheme of radiative transitions which explains the origin of particular transitions (see Fig. 2).

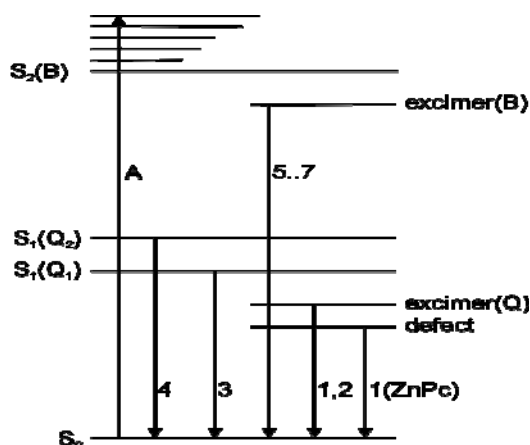


Fig.2. Radiative transitions in MPc layers.

Table 1 The energy peak position, broadening and integral intensity of PL peaks for ZnPc layers at 175K.

Transition No.	1	2	3	4	5	6	7
Energy [eV]	1.14	1.25	1.76	1.84	2.11	2.52	2.96
Broadening [eV]	0.053	0.209	0.287	0.081	0.258	0.392	0.313
Integral intensity [a. u]	0.007	0.019	0.008	0.003	0.005	0.013	0.001

Above 175K the integral intensity increases. However, for excitonic transitions (3, 4) we observe opposite dependence. This behavior can be explained by the energy migration from excimer to exciton. The increasing of the energy transfer can be also caused by the change of the molecular structure in thin film while temperature decreases [16]. At higher temperatures, the

It is clearly visible that PL transitions in infrared region (1, 2) are distinctly separated from first electronic absorption transitions (Q-bands). We suppose that these bands are mainly due to excimer fluorescence. However, in case of ZnPc spectrum, the narrow and strong peak (1) is probably connected with the defect state. In the red region the spectra of solutions and thin layers are comparable that is why the transitions 3 and 4 origin from the Frenkel exciton recombination. Others transitions (5, 6, 7) are associated with excimer emission connected with second electronic excited states (B bands). The photoluminescence spectra for ZnPc and MgPc layers are strongly temperature affected. The typical temperature dependence of the PL spectra of MPc (MgPc) thin layers is presented in Fig. 3.

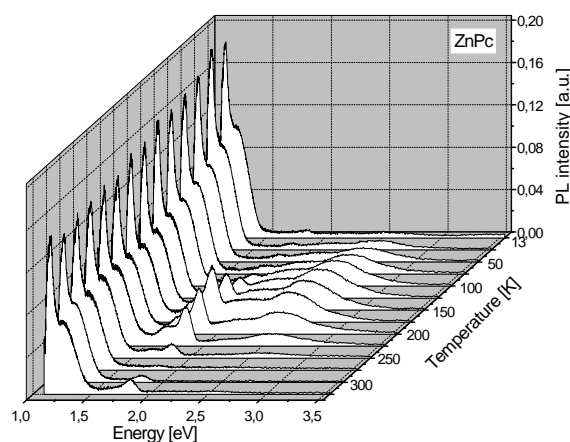


Fig. 3. The temperature dependence of PL spectra of ZnPc layer.

It is clearly visible, that intensity of transition in the near-IR region (peak 2) strongly decreases with increasing temperature up to 175K.

bands in the visible range are strongly attenuated. This effect is usually explained by the exciton-phonon interaction or/and trapping of exciton on the nonradiative defect states [17]. Aside from intensity of particular bands their positions also depend on temperature. In order to estimate the energy peak positions versus temperature we fit the superposition of seven Gaussian functions to the PL

data. The calculated fitting parameters for ZnPc layer at 175K are collected in Table 1. In this case the energy peaks position for transitions 1, 2, 4, 7 stay almost invariable with temperature. The values of these energies are also given in Table 1. The changes of the energy peaks position for transitions 3, 5 and 6 with temperature are shown in Fig. 4.

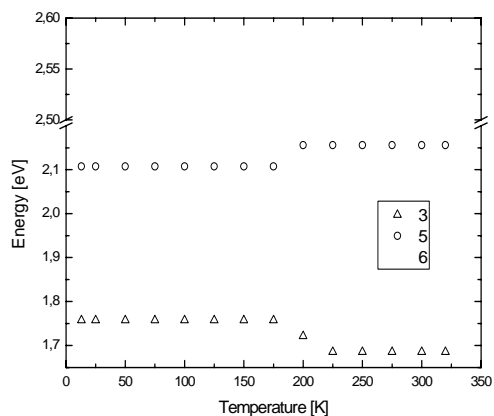


Fig. 4. The energy peak position versus the temperature for ZnPc layer.

As we can see the energy peak position of transition 6 at 13K is equal about 2.55 eV and shifts to the lower energies with temperature increase achieving minimum (2.52 eV) at 175 K. Above this temperature the energy peak position shifts to higher energies up to 2.59 eV at 320K. The energy peak position of transition 5 is constant (2.12 eV) up to 175 K. Above this temperature we observe increase of value up to 2.16 eV. The energy peak position of transition 3 exhibits similar jump at the same temperature. At 175 K and below this temperature the energy is equal 1.76 eV but above 200 K, achieves 1.69 eV. Similar changes in the bands position were observed for MgPc layer. We also observed that the broadening parameters of each transition, which are given in Table 1, have the same value in the whole temperature range measured.

The transmission and reflection spectra of MPC; ( $M = \text{Zn, Co, Mg, Cu}$ ) which were measured in the Q band region are presented in Fig. 5.

The splitting of Q band into two distinct components is observed in both, reflection and transmission spectra for all MPC's studied. It is clearly visible that the intensity distribution of main transmission bands depends on the coordinated metal ion. Similar distribution is observed for ZnPc and MgPc as well as for CuPc and CoPc, respectively. This behavior can be explained by the electronic configuration of coordinated ions.  $\text{Zn}^{2+}$  and  $\text{Mg}^{2+}$  ions in MPC molecule are characterized by closed-shell electronic configuration while  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  have partially occupied 3d subshell [11].

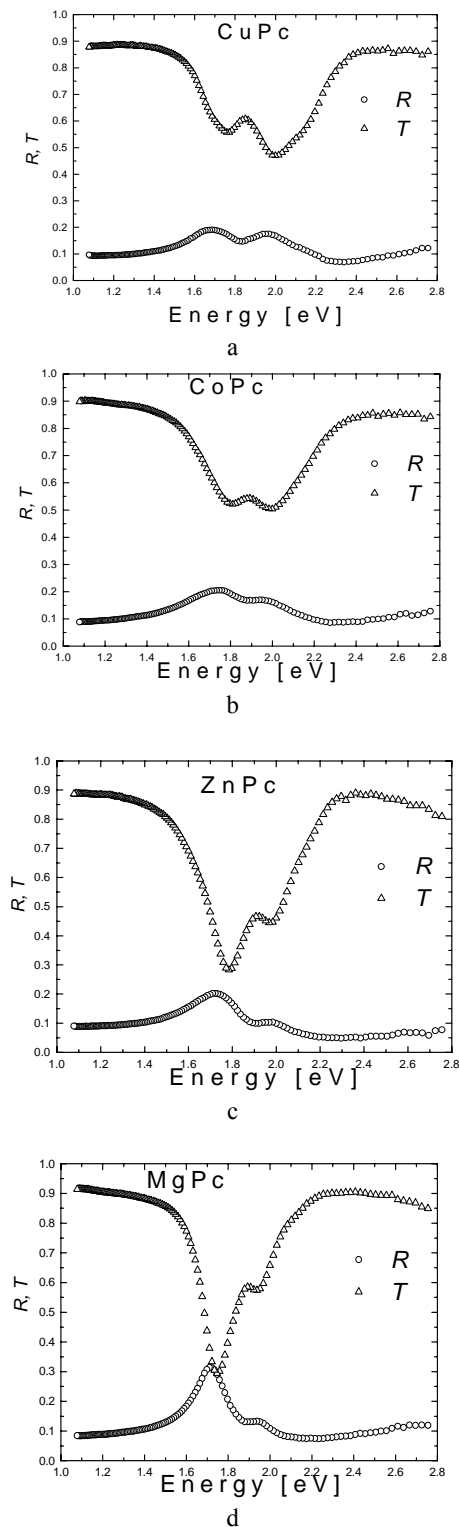


Fig. 5. Reflection and transmission spectra of MPC ( $M = \text{Cu, Co, Zn, Mg}$ ).

The typical nonpolarized Raman spectra of CuPc, ZnPc and MgPc layers grown onto (001) Si substrate recorded at room temperature in the spectral range from 1250 to 1650  $\text{cm}^{-1}$  are presented in Fig. 6.

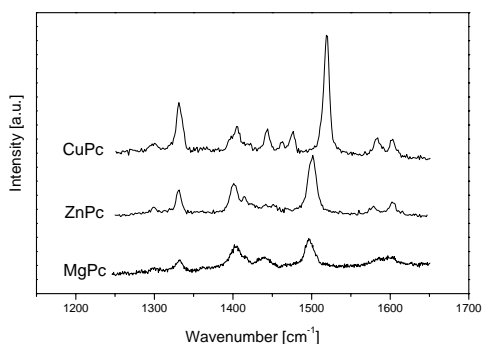


Fig. 6. The Raman spectra of CuPc, ZnPc and MgPc layers.

The low temperature dependences of the integral intensities of selected  $B_{1g}$  modes, which correspond to metal – nitrogen stretching mode ( $1331 \text{ cm}^{-1}$ ) and displacement of C-N-C bridge bond ( $1501 \text{ cm}^{-1}$ ) for ZnPc molecules, are presented in Fig. 7 a, b. The FT-IR study performed for ZnPc thin layers also indicates similar behavior (Fig. 8 a and b). As it can be seen from Fig. 8 (a and b) the temperature dependence of integral intensity of  $1599 \text{ cm}^{-1}$  mode indicates the change at about 200 K and very strong discontinuity at higher temperature.

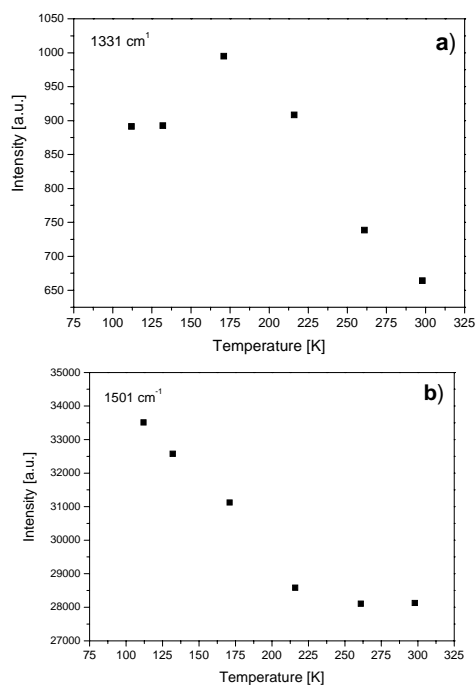


Fig. 7. The temperature dependences of the integral intensities of  $1331 \text{ cm}^{-1}$  – a) and  $1501 \text{ cm}^{-1}$  – b) modes for ZnPc layer obtained from Raman spectra.

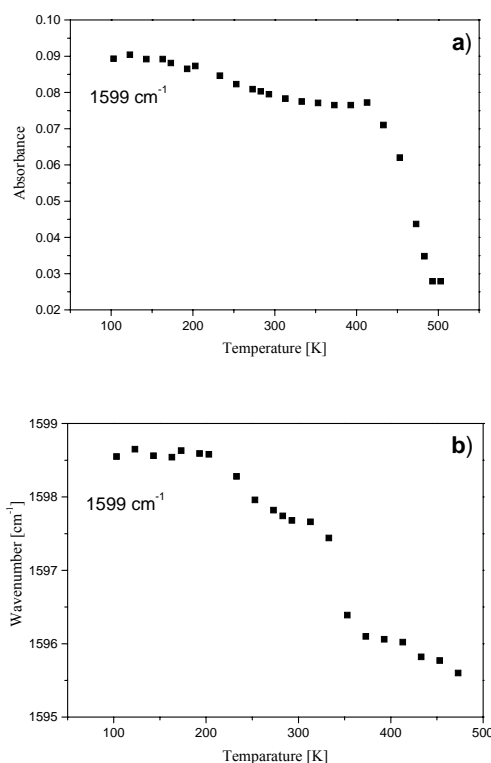


Fig. 8. The temperature dependences of infrared absorbance and band position of  $1599 \text{ cm}^{-1}$  mode for ZnPc layer obtained from FT-IR spectra.

To compare the influence of central metal atom of MPC molecules similar investigations have been performed for MgPc thin layer. The obtained results for Raman and FT-IR temperature dependences are presented in Fig. 9 and Fig. 10, respectively. As it can be seen from Fig. 9 and Fig. 10 the influence of metal atom is evident.

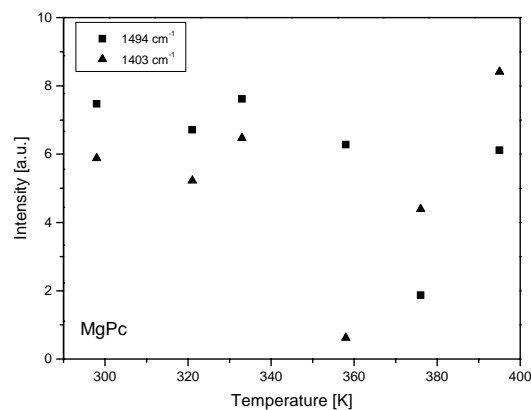


Fig. 9. The temperature dependences of the integral intensities of  $1403 \text{ cm}^{-1}$  – a) and  $1494 \text{ cm}^{-1}$  – b) modes for MgPc layer obtained from Raman spectra.

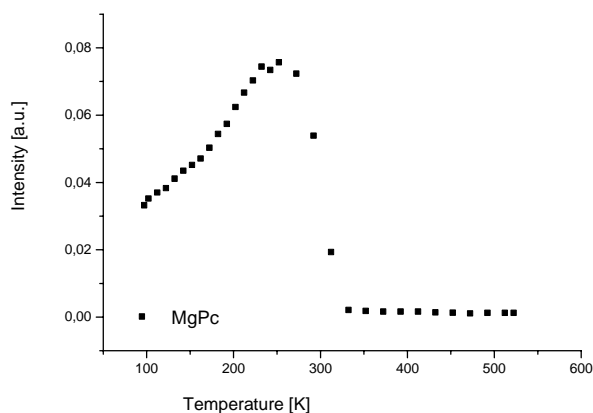


Fig. 10. The temperature dependence of the integral intensity of  $2920\text{ cm}^{-1}$  mode for MgPc layer obtained from FT-IR spectra.

These behaviors obtained for MPc thin layer can be correlated with change of molecular symmetry due to metal ion position in molecule ring and its distortion of planarity versus temperature. The most probably structure of MPc at room temperature is  $D_{4h}$  planar symmetry. At low temperatures the metal atom adopts a position out of the plane of the ring, giving  $C_{4v}$  symmetry. These changes in molecular symmetry can change both, the energy and probability of particular transitions. These results are consistent with the results obtained from X-ray measurement for MgPc by Janczak et al. [16].

#### 4. Conclusions

In this paper we report the low temperature PL emission study of metallophthalocyanines (MPc: M = Zn, Mg,) thin layers in the wide spectral range from violet to near-IR. The IR-VIS PL measurements of MPc's thin films were carried out for the first time. To ascribe the observed emission bands with particular excited states the PL and absorption spectra have been compared. Moreover, the influence of temperature on the PL spectra of MPc layers was investigated. The obtained temperature dependence revealed the mechanism of energy transfer between excimer and exciton states. Some differences between particular transmission and reflection spectra observed for investigated materials, were explained by various electronic configurations of coordinated metals.

The result obtained from Raman and FT-IR study give also the proof of the influence of central metal atom on planarity of MPc thin layer.

The observed unusual behavior of Raman, FT-IR and PL spectra is probably connected with central atom ion position in molecular ring of MPc and its distortion of planarity.

#### Acknowledgements

This work was supported in part by the Polish Ministry of Science and Higher Education under grant No. N 204 16 31/2635 (UMK-746-Ch) and Research Project of Poznan University of Technology DS 64-001/08.

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