

# $K_{\beta}/K_{\alpha}$ X-Ray Intensity Ratios for Co, Ni, Cu, and Zn in Phthalocyanines Complexes

H. BALTAS<sup>a,\*</sup>, B. ERTUGRAL<sup>b</sup>, C. KANTAR<sup>c</sup>, S. SASMAZ<sup>c</sup>, E. YILMAZ<sup>a</sup>  
AND U. CEVIK<sup>d</sup>

<sup>a</sup>Department of Physics, Rize University, 53100 Rize, Turkey

<sup>b</sup>Department of Physics, Giresun University, 28100 Giresun, Turkey

<sup>c</sup>Department of Chemistry, Rize University, 53100 Rize, Turkey

<sup>d</sup>Department of Physics, Karadeniz Technical University, 61080 Trabzon, Turkey

(Received May 4, 2010; in final form January 25, 2011)

The  $K_{\beta}/K_{\alpha}$  X-ray intensity ratios of Co, Ni, Cu and Zn in metalophthalocyanines complexes have been studied. Co, Ni, Cu and Zn elements have been excited by using 59.5 keV photons emitted by 50 mCi <sup>241</sup>Am radioactive source.  $K$  X-rays emitted by samples have been counted by a Si(Li) detector with resolution 0.16 keV at 5.9 keV. We have found that  $K_{\beta}/K_{\alpha}$  X-ray intensity ratios of Co, Ni, Zn, and Cu complexes have changed depending on chemical structures of Co, Ni, Zn and Cu. The measured values have been compared with the theoretical predictions and experimental values of pure elements.

PACS: 32.30.Rj, 32.80.-t, 31.70.-f

## 1. Introduction

Nowadays metalophthalocyanines form an important group of organic compounds that belongs to the most studied subjects of organic functional materials [1]. The most important industrial application of phthalocyanines is the formation of color complexes with metal cations that are used as highly stable pigments and dyes [2]. In addition, they can find commercial applications as: photovoltaic materials in solar cells [3] systems for fabrication of light emitting diodes (LED) [4], liquid crystalline [5] and non-linear optical materials [6] sensitizers for photodynamic (PDT) cancer therapy [7], photoconductors in xerography [8] dyes at recording layers for CD-R and DVD-R optical storage discs [9] as well as diverse catalytic systems [10].

Accurate and reliable data on X-ray intensity ratios are very important in the fields of atomic, molecular and medical physics. These data also serve as important inputs in the XRF technique which is considered to be one of the most powerful methods for elemental analysis. There have been various investigations on the  $K_{\beta}/K_{\alpha}$  intensity ratios and fluorescence cross-sections.

In the recent years several studies have been carried out to measure the dependence of  $K_{\beta}/K_{\alpha}$  ratios on the chemical state of the elements. Iwatsuki and Fuka-

sawa [11] have measured  $K_{\beta 2}/K_{\beta 1,3}$  X-ray intensity ratios of arsenic, selenium and bromine in various chemical states. Çevik et al. [12] have found chemical effects on the  $K_{\beta}/K_{\alpha}$  X-ray intensity ratios of Mn, Ni and Cu complexes. Similarly,  $K$ -shell X-ray fluorescence cross-sections and intensity ratios for some pure metals have been measured using 59.5 and 123.6 keV  $\gamma$ -rays [13]. In many compounds, transfer of electron from the ligand atom to the  $3d$  state of the metal can also cause change in the  $3d$  electron population of the metal which will cause a change in the  $K_{\beta}/K_{\alpha}$  ratio [14–16].  $K_{\beta}/K_{\alpha}$  X-ray intensity ratios of Fe and Ni in pure metals and in  $\text{Fe}_x\text{Ni}_{1-x}$  alloys have been measured by Raj et al. [17, 18].

In this paper, we report the  $K_{\beta}/K_{\alpha}$  X-ray intensity ratios for Co, Ni, Zn and Cu in  $\text{C}_{112}\text{H}_{96}\text{N}_8\text{O}_{16}\text{Co}$ ,  $\text{C}_{112}\text{H}_{96}\text{N}_8\text{O}_{16}\text{Ni}$ ,  $\text{C}_{112}\text{H}_{96}\text{N}_8\text{O}_{16}\text{Zn}$ ,  $\text{C}_{112}\text{H}_{96}\text{N}_8\text{O}_{16}\text{Cu}$  metalophthalocyanines complexes.

## 2. Experimental details

In this work, the measurements of Co, Ni, Zn and Cu X-ray intensity ratios were performed for  $\text{C}_{112}\text{H}_{96}\text{N}_8\text{O}_{16}\text{Co}$ ,  $\text{C}_{112}\text{H}_{96}\text{N}_8\text{O}_{16}\text{Ni}$ ,  $\text{C}_{112}\text{H}_{96}\text{N}_8\text{O}_{16}\text{Zn}$ ,  $\text{C}_{112}\text{H}_{96}\text{N}_8\text{O}_{16}\text{Cu}$  complexes. The phthalonitrile compound and metalophthalocyanine complexes were prepared according to the published procedure [19]. The studied complexes were illustrated in Fig. 1. The samples were irradiated by 59.5 keV photons emitted by an annular <sup>241</sup>Am radioactive source. A Si(Li) detector (FWHM

\* corresponding author; e-mail: hbaltas@ktu.edu.tr

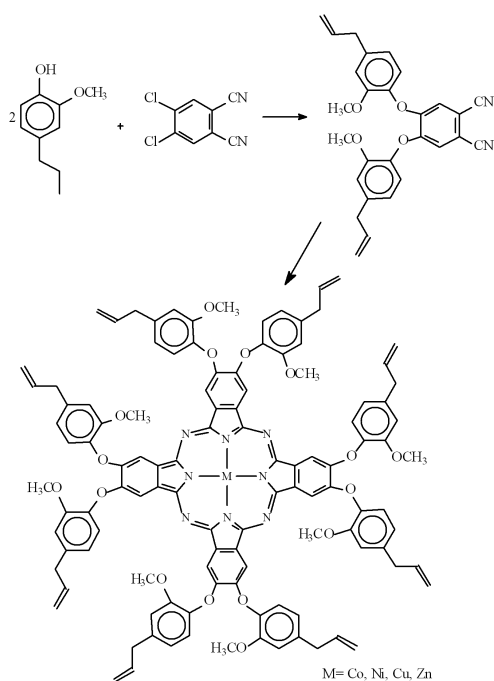


Fig. 1. The structural formula of phthalonitrile compound and phthalocyanines complexes.

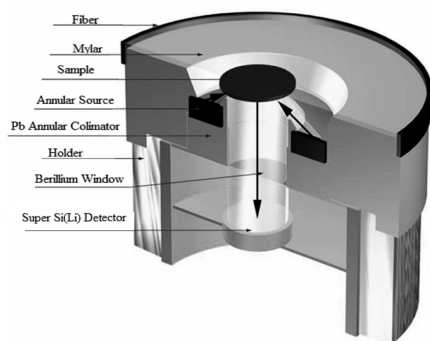


Fig. 2. Geometry of the experimental setup.

0.16 keV at 5.9 keV, active area 13 mm<sup>2</sup>, thickness 3 mm and Be window thickness 30 μm) was used for  $K_{\alpha}$  and  $K_{\beta}$  lines measurement. The experimental setup for the annular source in the direct excitation mode used in this study is shown in Fig. 2. The output from the pre-amplifier, with pulse pile-up rejection capability, was fed to a multi-channel analyzer interfaced with a personal computer provided with suitable software for data acquisition and peak analysis. The lifetime was selected 5000 s for all elements. The samples were placed at 45° angles with respect to the direct beam and fluorescent X-rays emitted 90° to the detector. The peak areas were calculated from the spectrum obtained for each measurement. Figure 3 shows a typical  $K$  X-ray spectrum of Co in  $C_{112}H_{96}N_8O_{16}Co$  complexes.

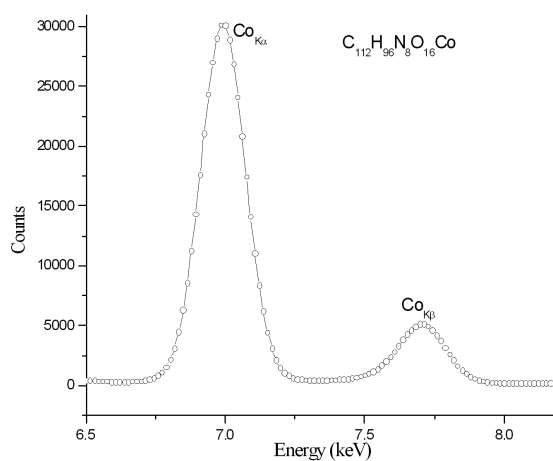


Fig. 3. Typical  $K$  X-ray spectra of Co in  $C_{112}H_{96}N_8O_{16}Co$ .

### 3. Theoretical calculations

The  $K_{\beta}/K_{\alpha}$  X-ray intensity ratio values were calculated using the relation,

$$\frac{IK_{\beta}}{IK_{\alpha}} = \frac{N_{K_{\beta}} \beta_{K_{\alpha}} \varepsilon_{K_{\alpha}}}{N_{K_{\alpha}} \beta_{K_{\beta}} \varepsilon_{K_{\beta}}}, \quad (1)$$

where  $N_{K_{\beta}}$  and  $N_{K_{\alpha}}$  are the net counts under the  $K_{\beta}$  and  $K_{\alpha}$  peaks,  $\beta_{K_{\beta}}$  and  $\beta_{K_{\alpha}}$  are the self-absorption correction factors of the target,  $\varepsilon_{K_{\beta}}$  and  $\varepsilon_{K_{\alpha}}$  are the detector efficiencies for  $K_{\beta}$  and  $K_{\alpha}$  X-rays.

The self absorption correction factor  $\beta$  is calculated for both  $K_{\beta}$  and  $K_{\alpha}$  separately by using the following expression:

$$\beta = \frac{1 - \exp(-(\mu_{inc}/\sin\theta + \mu_{emt}/\sin\phi)t)}{(\mu_{inc}/\sin\theta + \mu_{emt}/\sin\phi)t}, \quad (2)$$

where  $\mu_{inc}$  is the mass attenuation coefficient (cm<sup>2</sup>/g) of incident photons and  $\mu_{emt}$  is of emitted characteristic X-rays [20, 21].  $t$  is the thickness of the target in g cm<sup>-2</sup>,  $\theta$  and  $\phi$  are the angles of incident photon and emitted X-rays with respect to the normal at the surface of the sample. The product  $I_0G\varepsilon$ , containing the terms related to the incident photon flux, geometrical factor and absolute efficiency of the X-ray detector, was determined collecting the  $K_{\alpha}$  and  $K_{\beta}$  X-ray spectra of the samples, which are atomic number ranges, were selected  $23 \leq Z \leq 66$  for <sup>241</sup>Am in the same geometry using the equation

$$I_0G\varepsilon_{K_i} = \frac{N_{K_i}}{\sigma_{K_i}\beta_{K_i}m_i}, \quad (3)$$

where  $N_{K_i}$  is the measured intensity (area under the photopeak) corresponding to the  $K_i$  group of X-rays,  $I_0$  is the intensity of the incident radiation,  $G$  is a geometrical factor,  $\varepsilon_{K_i}$  is the detection efficiency for the  $K_i$  group of X-rays and  $\beta_{K_i}$  is the self-absorption correction factor for the target material, which accounts for the absorption in the target of the incident photons and the emitted characteristic X-rays. Theoretical values of  $\sigma_{K_i}$  ( $i = \alpha, \beta$ )

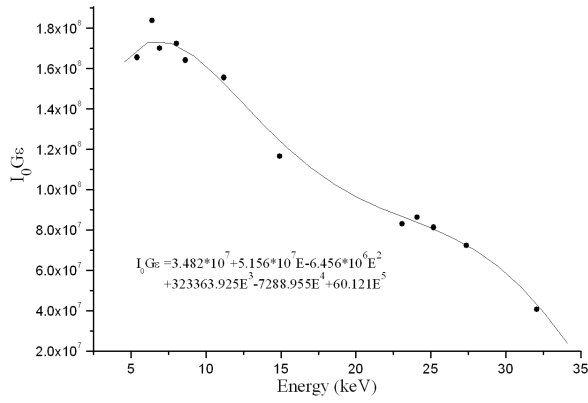


Fig. 4. The variation of the factor  $I_0 G \epsilon$  as a function of the mean  $K$  X-ray energy for  $^{241}\text{Am}$ .

X-ray production cross sections were calculated by

$$\sigma_{K_i} = \sigma_K(E) \omega_K f_{K_i}, \quad (4)$$

where  $\sigma_K(E)$  is the  $K$ -shell photoionization cross-section of the given element for the excitation energy  $E$  [22],  $\omega_K$  is the  $K$ -shell fluorescence yield [23], and  $f_{K_i}$  is the emission rate of the fractional X-ray for  $K_\alpha$  and  $K_\beta$  X-rays [24].

The factor  $I_0 G \epsilon_{K_i}$  was fitted as a function of energy using the equations for  $^{241}\text{Am}$  [15]:

$$I_0 G \epsilon_{K_i} = A_0 + A_1 E_x + A_2 E_x^2 + A_3 E_x^3 + A_4 E_x^4 + A_5 E_x^5, \quad (5)$$

where  $E_x$  is the  $K_\alpha$  and  $K_\beta$  X-ray energy. The variations of the factors  $I_0 G \epsilon_{K_i}$  as a function of the mean  $K$  X-ray energy are shown in Fig. 4.

#### 4. Result and discussion

The measured values of the  $K_\beta/K_\alpha$  X-ray intensity ratios for Co, Ni, Zn, and Cu in  $\text{C}_{112}\text{H}_{96}\text{N}_8\text{O}_{16}\text{Co}$ ,  $\text{C}_{112}\text{H}_{96}\text{N}_8\text{O}_{16}\text{Ni}$ ,  $\text{C}_{112}\text{H}_{96}\text{N}_8\text{O}_{16}\text{Zn}$  and  $\text{C}_{112}\text{H}_{96}\text{N}_8\text{O}_{16}\text{Cu}$  phthalocyanines complexes are listed in Table I. Experimental  $K_\beta/K_\alpha$  X-ray intensity ratios for these elements have been compared with theoretical estimates [25–27] and other experimental results [13, 28, 29]. Theoretical estimates based on relativistic Hartree–Fock and Hartree–Slater theories were calculated by Scofield [25, 26]. Our experimental values agree to within 0.03–23% Hartree–Fock theory and to within 0.4–20% Hartree–Slater theory, respectively. Also, these values are approximately 8% higher than the theoretical values of Manson and Kennedy [27].

TABLE I

The experimental  $K_\beta/K_\alpha$  intensity ratios of Co, Ni, Cu and Zn in the different phthalocyanines complexes.

Elements and compounds	$I(K_\beta)/I(K_\alpha)$	Theoretical predictions using data from			Result of other experiments		
		Scofield [25]	Scofield [26]	Manson & Kennedy [27]	Cevik et al. [13]	Salem et al. [28]	Ertugral et al. [29]
Co	–	–	0.1218	0.1219	$0.137 \pm 0.008$	–	$0.139 \pm 0.007$
$\text{C}_{112}\text{H}_{96}\text{N}_8\text{O}_{16}\text{Co}$	$0.132 \pm 0.007$	–	–	–	–	–	–
Ni	–	0.1401	0.1227	0.1221	$0.141 \pm 0.012$ [12]	0.135	$0.133 \pm 0.003$
$\text{C}_{112}\text{H}_{96}\text{N}_8\text{O}_{16}\text{Ni}$	$0.127 \pm 0.007$	–	–	–	–	–	–
Cu	–	0.1379	0.1216	0.1208	$0.136 \pm 0.005$	–	$0.135 \pm 0.003$
$\text{C}_{112}\text{H}_{96}\text{N}_8\text{O}_{16}\text{Cu}$	$0.124 \pm 0.007$	–	–	–	–	–	–
Zn	–	0.1410	0.1241	0.1233	$0.136 \pm 0.005$	0.138	$0.137 \pm 0.005$
$\text{C}_{112}\text{H}_{96}\text{N}_8\text{O}_{16}\text{Zn}$	$0.133 \pm 0.007$	–	–	–	–	–	–

The results show that the Co, Ni, Cu and Zn  $K$  X-ray intensity ratio in the complexes is lower than the pure metals. The reason is that the outer electrons of metals in the complexes structure are strongly bound to the ligand atoms, and therefore subsequent transition probabilities of electrons from these outer shells to inner shells ( $O \rightarrow M$  or  $O \rightarrow N$ ) decrease corresponding to transition rules. Therefore,  $M \rightarrow K$  or  $N \rightarrow K$  transition probabilities decrease (Fig. 5). For this reason,  $K_\beta$  transitions

ratios may decrease, resulting in reduced  $K_\beta$  net peak area in the spectrum. At the same time,  $K_\alpha$  transitions ratios are not affected. Therefore, the  $K_\beta/K_\alpha$  X-ray intensity ratio decreases (see Eq. (1)).

The changes of the  $K_\beta/K_\alpha$  X-ray intensity ratios for Co, Ni, Cu and Zn in the metalophthalocyanine complexes can be interpreted due to changes in the electron population of the valence bands ( $3d$  and  $4s$ ). Changes in the number of  $3d$  electrons are the only important con-

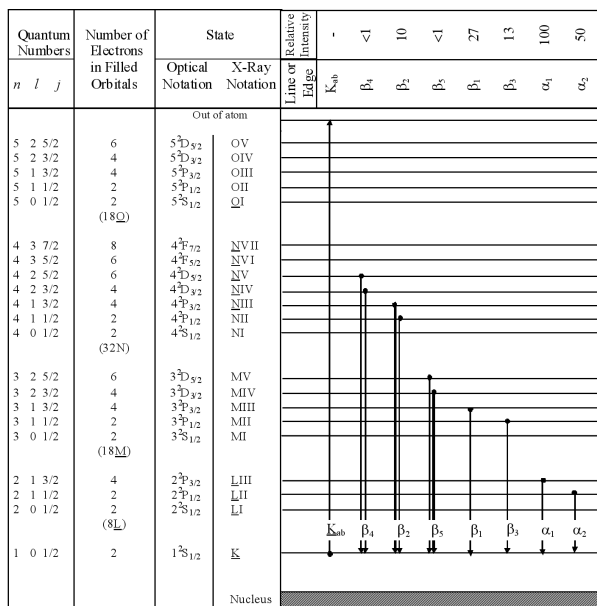


Fig. 5. The  $K_{\alpha}$  and  $K_{\beta}$  X-ray transitions from L, M and N shells.

tributions for the change in the  $K_{\beta}/K_{\alpha}$  intensity ratio and the effect of changing 4s and 4p electrons can be neglected. In fact, the change in the number of 3d electrons modifies 3p orbital much more strongly than 2p orbital, which must be followed by substantial modification of  $K_{\beta}$  transitions and almost no modification of  $K_{\alpha}$  transitions.

The electronegativity values differences (Table II) between the metals, which constitute the ligands, particularly have a greater effect on the structure of the 3d and 4s orbitals. The  $K_{\beta}/K_{\alpha}$  intensity ratio can be affected by the changing electronegativities around the central emitting atoms. A change in the electronegativity around the central atom can affect the binding energies of the outermost shell electrons because the outermost electron cloud of the central atom is pulled by the ligands due to the increase of the electronegativity values. Therefore, this factor may cause some variations [30]. Also, as seen in Table II, the change in 3d electron population for Co, Ni, Cu and Zn in the complexes has been evaluated by comparing the predictions of multiconfiguration Dirac-Fock (MCDF) calculations with the measured  $K_{\beta}/K_{\alpha}$  intensity ratios for these 3d transition metals in their compounds [31]. The greatest values of the  $K_{\beta}/K_{\alpha}$  intensity ratios are for  $3d^m-24s^2$  configuration type of the Co, Ni and Zn atoms.

Complexing bond lengths for four-coordinate metalophthalocyanines namely, CoPc [32], NiPc [33], CuPc [34] and ZnPc [35], are listed in Table III. It can be seen from Table III that the NiPc has the shortest bond length in the complexes (ZnPc>CuPc>CoPc>NiPc). Therefore, bond electrons between metal and ligand in NiPc are attracted slightly by metal atoms. Change in the attraction forces of bond electrons can be attributed

TABLE II

Electron configuration, electronegativity, for Co, Ni, Cu and Zn atoms.

Element	Z	Electron configuration	Electronegativity
Co	27	[Ar] $3d^74s^2$	1.8
Ni	28	[Ar] $3d^84s^2$	1.9
Cu	29	[Ar] $3d^{10}4s^1$	1.9
Zn	30	[Ar] $3d^{10}4s^2$	1.6

to hybridization of metal atoms in the complexes. The hybridization of these metals in the complexes has substantial effect because of the change of the local electron population in the 3d states. Strong hybridization of these metals leads to the greater overlapping between metal and ligand atoms, and leads to the approaching metal and ligand atoms to each other. In that case, the symmetry of metal atoms in the complex changes and this causes an increase in the volume of bonding orbital and this increases the interaction area of photons [36].

TABLE III

Complexing bond lengths for four-coordinate metalophthalocyanines.

Parameter	CoPc [32]	NiPc [33]	CuPc [34]	ZnPc [35]
M-N distance [Å]	1.907	1.830	1.930	1.980

The overall error in the present measurements is estimated to be less than 3–4%. This error is attributed to the uncertainties in different parameters used to deduce  $K_{\beta}/K_{\alpha}$  values; namely, the statistical and other possible errors in the area evaluation under the  $K_{\alpha}$  and  $K_{\beta}$  X-ray peak ( $\leq 2-3\%$ ), in the absorption correction factor ratio ( $\leq 2\%$ ), the product  $I_0G\epsilon$  (2–3%). In this work, in order to reduce the absorption, thin samples were used as the target; furthermore, an absorption correction was also performed for each sample. In order to reduce the statistical error, the spectra were recorded and about  $10^3-10^6$  (or more) counts were collected under the  $K_{\alpha}$  and  $K_{\beta}$  peaks. The  $K_{\alpha}$  and  $K_{\beta}$  photopeak areas were separated by fitting the measured spectra with multi-Gaussian functions plus polynomial backgrounds using software program.

## 5. Summary and conclusions

Phthalocyanines have recently received much attention, especially because of their synthetic [37] and structural aspects [38], spectral properties [39], electrochromic behaviour [40] and electrical conductivity [41]. Also, their use as efficient photosensitizers in obtaining singlet oxygen is becoming especially important in the photodynamic therapy of tumors [42]. In this paper we have presented the experimental result for the

$K_{\beta}/K_{\alpha}$  X-ray intensity ratios of Co, Ni, Zn, and Cu in  $C_{112}H_{96}N_8O_{16}Co$ ,  $C_{112}H_{96}N_8O_{16}Ni$ ,  $C_{112}H_{96}N_8O_{16}Zn$  and  $C_{112}H_{96}N_8O_{16}Cu$  phthalocyanines complexes, respectively. Either transfer from 3d state of metal atom electron to the ligand atom or transfer of electron from the ligand atom to the 3d state of the metal can also cause a change in the 3d electron population of the metal. This will effect the  $K_{\beta}/K_{\alpha}$  ratio. The results indicate that  $K_{\beta}/K_{\alpha}$  X-ray intensity ratios for given complexes, in general, are lower than those with pure form. This result shows that there is electron transfer from 3d transition metal to ligand atoms. These results also indicate that K X-ray spectroscopy for the 3d element is very useful for studying the electronic structure of chemical complexes.

### References

- [1] N.B. Mc Keown, *Phthalocyanine Materials: Synthesis, Structure, and Function*, Cambridge University Press, Cambridge 1998.
- [2] C.C. Leznoff, A.B. Lever, *Phthalocyanines. Properties and Applications*, VCH, New York 1996.
- [3] T.D. Anthopoulos, T.S. Shafai, *Appl. Phys. Lett.* **82**, 1628 (2003).
- [4] M. Ishii, Y. Taga, *Appl. Phys. Lett.* **80**, 3430 (2002).
- [5] J. Sluven, Ch. Gorller-Walrand, K. Binnemans, *Mater. Sci. Eng. C* **18**, 229 (2001).
- [6] G. de la Torre, P. Vazquez, F. Agullo-Lopez, T. Torres, *J. Chem. Mater.* **8**, 1671 (1998).
- [7] I. Rosenthal, *Photochem. Photobiol.* **53**, 859 (1991).
- [8] K.Y. Law, *Chem. Rev.* **93**, 449 (1993).
- [9] D. Birkett, *J. Chem. Educ.* **79**, 1081 (2002).
- [10] R. Raja, P. Ratnasamy, *J. Catal.* **170**, 53 (1997).
- [11] M. Iwatsuki, T. Fukasawa, *X-ray Spectrom.* **16**, 79 (1987).
- [12] U. Çevik, I. Degirmencioğlu, B. Ertuğral, G. Apaydın, H. Baltas, *Eur. Phys. J. D.* **36**, 29 (2005).
- [13] U. Çevik, S. Kaya, B. Ertuğral, H. Baltas, S.M. Karabıdak, *Nucl. Instrum. Methods Phys. Res. B* **262**, 165 (2007).
- [14] S. Raj, B.B. Dhal, H.C. Padhi, M. Polasik, *Phys. Rev. B* **58**, 9025 (1998).
- [15] S. Raj, H.C. Padhi, M. Polasik, D.K. Basa, *Solid State Commun.* **110**, 275 (1999).
- [16] S. Raj, H.C. Padhi, D.K. Basa, M. Polasik, F. Pawłowski, *Nucl. Instrum. Methods Phys. Res. B* **152**, 417 (1999).
- [17] S. Raj, H.C. Padhi, M. Polasik, F. Pawłowski, D.K. Basa, *Phys. Rev. B* **63**, 073109 (2001).
- [18] S. Raj, H.C. Padhi, M. Polasik, F. Pawłowski, D.K. Basa, *Solid State Commun.* **116**, 563 (2000).
- [19] S. Şaşmaz, E. Açar, A. Açar, *Dyes Pigment.* **42**, 117 (1999).
- [20] M.J. Berger, J.H. Hubbell, XCOM: Photon cross-sections on a personnel computer (version 1.2), NBSIR85-3597, National Bureau of Standards, Gaithersburg, MD, USA, for version 3.1, 1999, see <http://physics.nist.gov/> (1987).
- [21] E. Storm, I. Israel, *Nucl. Data Tables A* **7**, 565 (1970).
- [22] J.H. Scofield, *Lawrence Livermore Laboratory (UCRL)*, Vol. 51326, 1973.
- [23] M.O. Krause, *J. Phys. Chem. Ref. Data* **8**, 307 (1979).
- [24] N. Broll, *X-ray Spectrom.* **15**, 271 (1986).
- [25] J.H. Scofield, *Phys. Rev. A* **9**, 1041 (1974).
- [26] J.H. Scofield, *At. Data Nucl. Data Tables* **14**, 121 (1974).
- [27] S.T. Manson, D.J. Kennedy, *At. Data Nucl. Data Tables* **14**, 111 (1974).
- [28] S.I. Salem, S.L. Panossian, R.A. Krause, *At. Data Nucl. Data Tables* **14**, 91 (1974).
- [29] B. Ertuğral, G. Apaydın, U. Çevik, M. Ertuğrul, A.İ. Kobya, *Radiat. Phys. Chem.* **76**, 15 (2007).
- [30] E. Cengiz, V. Aylıkçı, N. Kaya, G. Apaydın, E. Traşoğlu, *J. Rad. Nucl. Chem.* **278**, 89 (2008).
- [31] S. Raj, H.C. Padhi, M. Polasik, *Nucl. Instrum. Methods Phys. Res. B* **145**, 485 (1998).
- [32] R. Mason, G.A. Williams, P.E. Fielding, *J. Chem. Soc.*, 676 (1979).
- [33] R.P. Linstead, J.M. Robertson, *J. Chem. Soc.* 1736 (1936).
- [34] C.J. Brown, *J. Chem. Soc. A*, 2488 (1968).
- [35] W.R. Scheidt, W. Dow, *J. Am. Chem. Soc.* **99**, 1101 (1977).
- [36] H. Baltas, U. Çevik, *Solid State Commun.* **149**, 231 (2009).
- [37] *Phthalocyanines, Properties and Applications*, Eds. C.C. Leznoff, A.B.P. Lever, Vol. 2, VCH, New York 1993.
- [38] F.H. Moser, A.L. Thomas, *The Phthalocyanines*, Vols. 1 and 2, CRC Press, Boca Raton (FL) 1983.
- [39] M.J. Stillmann, T. Nyokong, in: *Phthalocyanines, Properties and Applications*, Eds. C.C. Leznoff, A.B.P. Lever, VCH, New York 1989, Ch. 3.
- [40] N. Toshima, S. Kawamura, T. Tominaga, *Chem. Lett.* **22**, 1299 (1993).
- [41] H. Schultz, H. Lehman, M. Reinand, M. Hanack, *Struct. Bonding (Berlin)* **74**, 43 (1991).
- [42] I. Rosenthal, *Photochem. Photobiol.* **53**, 859 (1991).