

Optical investigations concerning layered metalphthalocyanine nanostructures affected by NO₂

TADEUSZ PUSTELNY¹, JOLANTA IGNAC-NOWICKA², BOZENA JARZABEK³, ANNA BURIAN³

¹Department of Optoelectronics, Silesian University of Technology, ul. Bolesława Krzywoustego 2, 44-100 Gliwice, Poland; e-mail: pustelny@zeus.polsl.gliwice.pl

²Department of Environment and Safety Management, Silesian University of Technology, ul. Roosevelta 26–28, 41-800 Zabrze, Poland; e-mail: jnowicka@zeus.polsl.gliwice.pl

³Center of Polymers Chemistry of Polish Academy of Science, ul. M. Skłodowskiej-Curie 34, Zabrze, Poland; e-mail: jarzabek@cchp-pan.zabrze.pl

The paper deals with investigations concerning the coefficient of optical transmission of selected metalphthalocyanine layers, *viz.* CuPc, NiPc, PbPc, FePc and CoPc by means of optical spectroscopy. The coefficient of transmission was investigated for phthalocyanine layers in the presence of atmospheric air and after the exposition of these layers to 100 ppm nitrogen dioxide. These investigations concerned wavelengths in the range from about 300 to 1300 nm. Moreover, several phthalocyanine layers were measured in the air and at 100 ppm NO₂ applying the X-ray diffraction method. These investigations have made it possible to determine changes occurring in the structure of phthalocyanine exposed to nitrogen dioxide.

Keywords: phthalocyanines, optical transmission, X-ray diffraction, nanolayers, nitrogen dioxide detection.

1. Introduction

Phthalocyanines (Pc) have been known to be organic dyestuffs for a long time. Their color depends, to some extent, on their crystalline shape and on the kind of the metal atom in the central part of the macroring. The phthalocyanine of lead is yellowish green, whereas the phthalocyanines of nickel, cobalt and copper display a tint of azure [1], [2]. Industrially, phthalocyanines are obtained by heating phthalocyanine anhydride with urea and a metal oxide as a catalyst [1].

At present more than 70 varieties of metalphthalocyanines (MPc) are known, differing from each other by the central metal ion in the molecule and their morphological structure. Phthalocyanines are organic compounds of a cyclic structure. The microring of the admixed metalphthalocyanine contains a metal atom in its

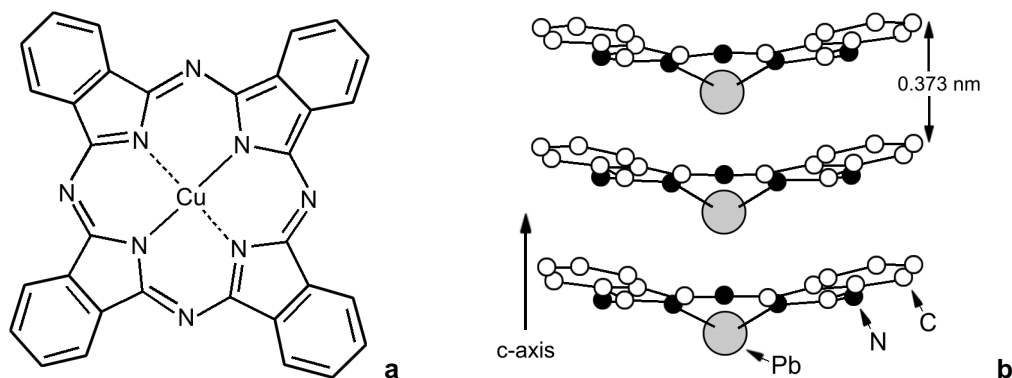


Fig. 1. Molecular structure of: copper phthalocyanines – planar structure (a), lead phthalocyanine – three-dimensional arrangement of the molecules in the cell (b)

centre. They are typical aromatic compounds (which is confirmed by the even character of the bonds in the molecule [3], [4]), with a planar structure, whose diameter amounts to about 1.2 nm [4]. An exception is lead phthalocyanine, in which the ion of lead Pb^{2+} is too big for the macroring of the molecule [5]–[7]. The structures of copper and lead phthalocyanines have been presented in Fig. 1.

In the solid phase phthalocyanines occur in three polymorphous variants: α , β , γ [8], [9]. In the variants of α and β metalphthalocyanines the molecules are distributed parallelly to each other forming vertical piles [8], [9] – Fig. 1. In the α -phase phthalocyanine consists of crystalline grains with a diameter of about 10 nm, whereas the phase β consists of bigger crystalline grains with an optical fibrous structure. This latter phase is composed at a temperature of more than 200°C [8], [9].

Thin phthalocyanine layers for sensor structures may be obtained by means of vacuum evaporation, *e.g.*, on a glass substrate [10], [11]. The morphology of thin metalphthalocyanine layers depends markedly on the conditions of their deposition. Phthalocyanines previously doped by transition metal atoms deposited on a substrate at room temperature form a polymorphous structure α [8]. In the case of depositing CuPc layers in such a way on an amorphous glass substrate, two different types of preferred orientations of CuPc crystalline grains have been observed [10], [11]. Both these orientations are characterized by a fibrous structure, the fibre axis running perpendicularly to the surface of the substrate. The orientation of the molecules towards the surface of the substrate depends on the preferred orientation of the crystalline grains [11]. In the case of the polymorphous structure β literature describes an orientation of the molecules, in which the planes of the molecules are inclined towards the substrate at an angle of about 26° [11].

From literature one knows that phthalocyanines are semiconductors of *p*-type [12], and as such they are characterized by acceptor conductivity. The absorption of electron-acceptor gases generates in the phthalocyanine charges in the shallow acceptor levels. Phthalocyanines display an ability of binding the molecules of

electron-acceptor gases in a coordinated way [12]. To this group of gases belongs also NO_2 . A coordinated bond is a bond intermediate between bonds in the physical and chemical absorption. In the coordinated bond the electron pair is provided by one reagent (NO_2) and the other one (MPc) provides only an electron vacancy.

2. Determination of the value of the transmission index

In order to determine the value of the transmission index in the function of the wavelength the method of optical spectroscopy was applied. These investigations concerned the wavelength of 270–1300 nm for five metalphthalocyanines: copper (CuPc), nickel (NiPc), lead (PbPc), iron (FePc), and cobalt (CoPc). The samples were prepared by vacuum-evaporating phthalocyanines on a sodium glass substrate at room temperature. The temperature of the source of evaporation of Pc amounted to 322°C. The thicknesses of the obtained phthalocyanine layers were about 200 nm. Figure 2 presents the dependence of the quantity of transmission as a function of the wavelength for the five metalphthalocyanines mentioned above. The recorded absorption bands of all the investigated metal phthalocyanines (except PbPc) are contained in the wavelength range of 290–330 nm and 560–690 nm for all phthalocyanine layers occurring in the atmospheric air. In the case of PbPc the recorded minimum values of optical absorption are 345, 430 and 850 nm. The differences in the absorption bands are connected with the structure of the phthalocyanine molecules [5]. Phthalocyanine molecules to which such atoms as Cu, Ni, Fe or Co have been admixed have a planar structure of the microring, whereas the molecules of PbPc display a three-dimensional

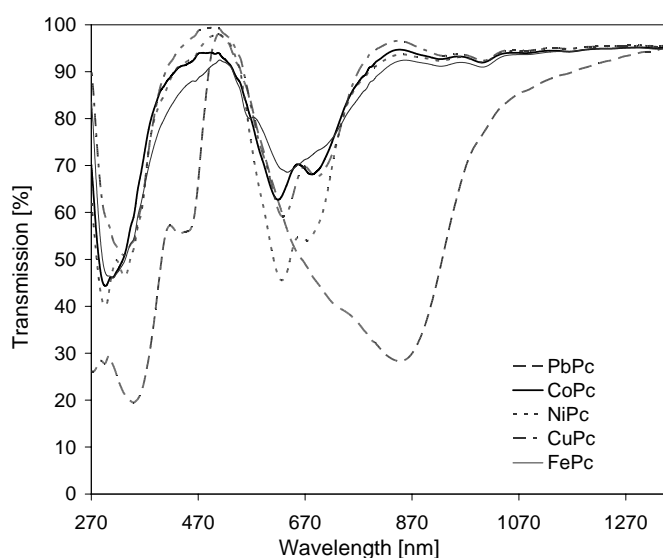


Fig. 2. Magnitude of the transmission as a function of the wavelength in the case of lead, cobalt, nickel, copper and iron phthalocyanines, vapoured at 320°C, deposited on a sodium glass substrate.

structure due to the big size of the central lead atom. As may be seen in these investigations, the structure of the molecules influences considerably their optical properties.

Having measured the value of the coefficient of transmission, the layers of the investigated phthalocyanines were exposed for 45 minutes to the effect of nitrogen dioxide NO_2 with a concentration of 100 ppm in synthetic air. The samples of nickel and copper phthalocyanines did not change their blue color after gassing them with nitrogen dioxide. The spectral characteristics of the transmission of nickel phthalocyanine are to be seen in Fig. 3, and those of copper phthalocyanine in Fig. 4. The minimum values of transmission denoted therein indicate the presence of absorption bands of light by phthalocyanine. As may be seen in Figs. 3 and 4, the characteristics of transmission have only slightly changed their positions after the tested

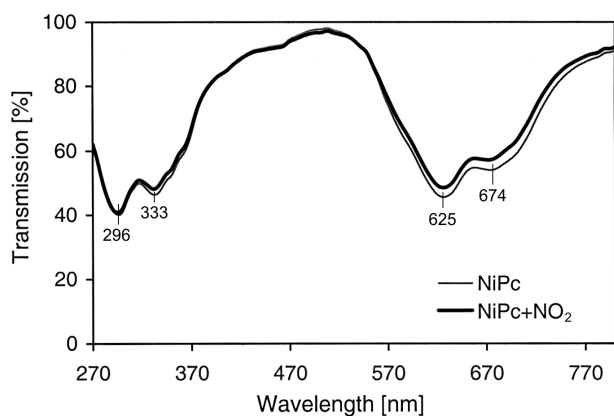


Fig. 3. Magnitude of the optical transmission as a function of the wavelength in the case of NiPc in the presence of synthetic air and after its exposition to 100 ppm NO_2 for 45 minutes.

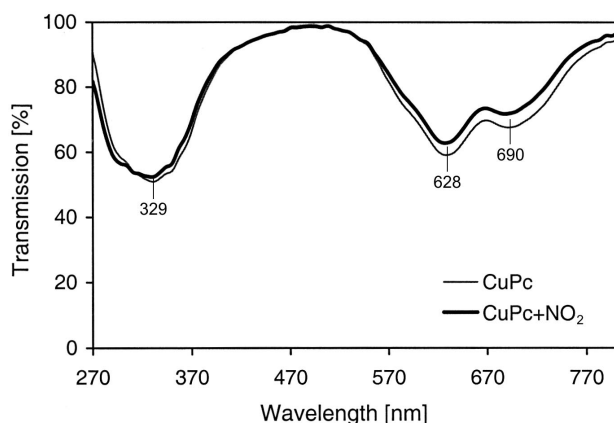


Fig. 4. Magnitude of the optical transmission as a function of the wavelength in the case of CuPu in the presence of synthetic air and after its exposition to 100 ppm NO_2 for 45 minutes.

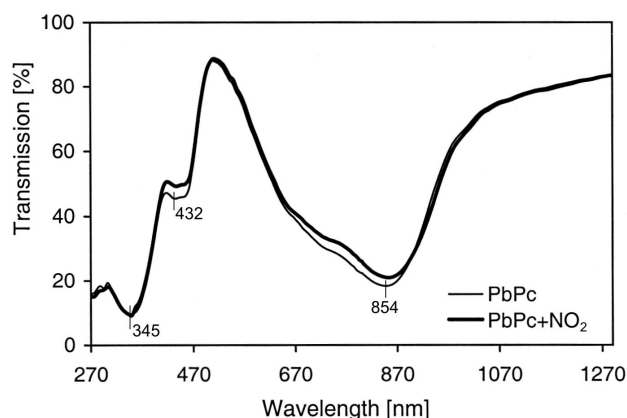


Fig. 5. Magnitude of the optical transmission as a function of the wavelength in the case of PbPu in the presence of synthetic air and after its exposition to 100 ppm NO_2 for 45 minutes.

metalphthalocyanine layers had been affected by NO_2 . This complies with the fact that in the case of these samples no changes of the color could be observed, even after the phthalocyanine layers had been gassed for a long time at a temperature of about 100°C . It ought to be stressed that in the case of investigations carried out by means of the plasma resonance method the absorption of NO_2 in those layers is quite visible [13]–[15].

Neither did the layer of lead phthalocyanine display larger changes in the transmission characteristics due to the effect of NO_2 , and its color did not change visibly. The spectral characteristics of the transmission of the PbPc layer in the presence of air and 100 ppm NO_2 have been gathered in Fig. 5.

Figure 6 presents the transmission characteristics as a function of the wavelength of CoPc and FePc within the visible range of the spectrum. According to these characteristics the changes in the transmission after the exposition of the CoPc and FePc layers to NO_2 are much greater than in the case of CuPc, NiPc and PbPc. The color of the CoPc and FePc changed distinctly from blue to violet, when affected by nitrogen dioxide. As far as cobalt phthalocyanine is concerned, its layer (in the presence of air) is characterized by only one optical absorption band for short waves (290 nm) and two absorption bands in the red range (620 and 680 nm). After the action of the mixture of synthetic air-nitrogen dioxide with a concentration of 100 ppm by the CoPc layer, however, two absorption bands were recorded for short wave (290 and 350 nm) and only one in the red range at 680 nm. In the case of a phthalocyanine layer with an admixture of iron some different but equally distinct changes in the extent of the emission have been observed, caused by the interaction of the layer with NO_2 . In the case of the FePc layer in air it has been found that there is only one absorption band for the short wave of 310 nm, as well as for 570 nm and for 640 nm in the visible range. After the absorption of NO_2 the first band was split into two bands for 300 and 310 nm, whereas the next two bands were markedly shifted towards the wavelengths

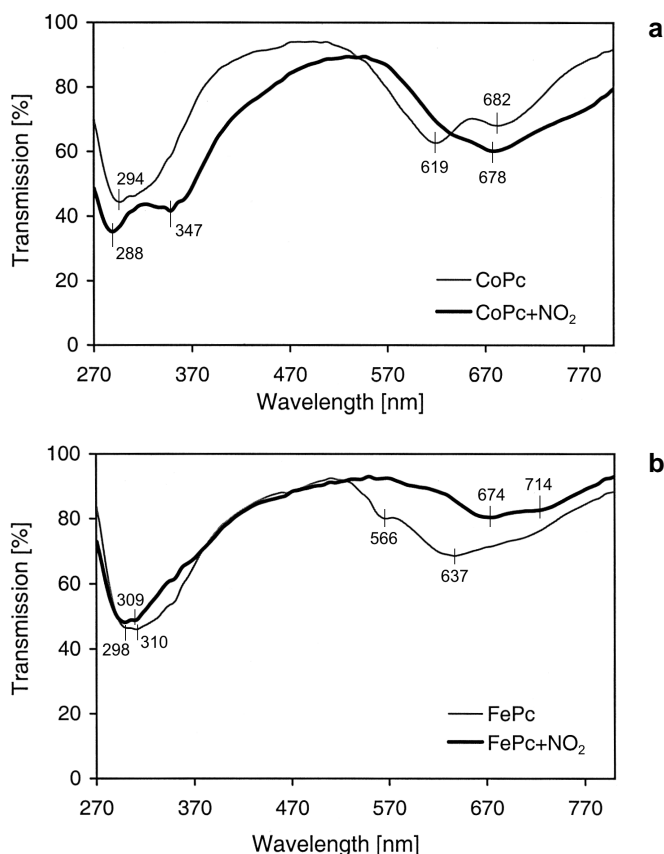


Fig. 6. Magnitude of the optical transmission as a function of the wavelength in the case of CoPc (a) and FePc in the presence of air and after their exposition to 100 ppm NO₂ for 45 minutes (b).

675 and 715 nm. The largest changes in the transmission spectrum after the exposition of the investigated phthalocyanines to NO₂ were recorded in the case of iron phthalocyanine, Fig. 6b. These phthalocyanines were investigated employing the method of surface plasma resonance [13] and displayed an imperceptible ability to desorb NO₂ from the phthalocyanine surface. Most probably considerable changes in the transmission spectrum indicate an inclination of the Pc layer to a more intensive and deeper absorption of nitrogen dioxide, thus impeding the desorption. In the case of nickel and copper phthalocyanines (Figs. 3 and 4, respectively) the spectra display only insignificant changes. These layers, investigated by means of the method of surface plasma resonance, demonstrated a better ability to regenerate after the absorption of NO₂. The desorption of nitrogen dioxide from CuPc and NiPc proceeded easier than that of CoPc and FePc layers.

Thus, we may conclude that small changes in the transmission spectrum after the exposition of the Pc layer to NO₂ indicate an only weak binding of the gas molecule (NO₂) with the molecule of phthalocyanine, which facilitates its desorption.

3. Investigations on phthalocyanine layers by means of X-ray diffraction

The layers of copper, nickel, cobalt, iron and lead phthalocyanines obtained by vacuum evaporation on sodium glass substrates were subjected to investigations, making use of the X-ray diffraction method, both as clean layers and after their exposition to the effect of nitrogen dioxide (wide angle X-ray diffraction measurements were performed in the TUR M6-2 diffractometer with CuK α lamp, while 34 kV voltage and 20 mA current were used).

The results of X-ray diffraction of the structure of CuPc deposited on glass and of the glass substrate itself have been presented in Fig. 7. Glass is an amorphous material, so that no diffraction peaks can be observed, whereas the phthalocyanine layer displays a systematic layered structure, visible due to the diffraction peak occurring at an angle

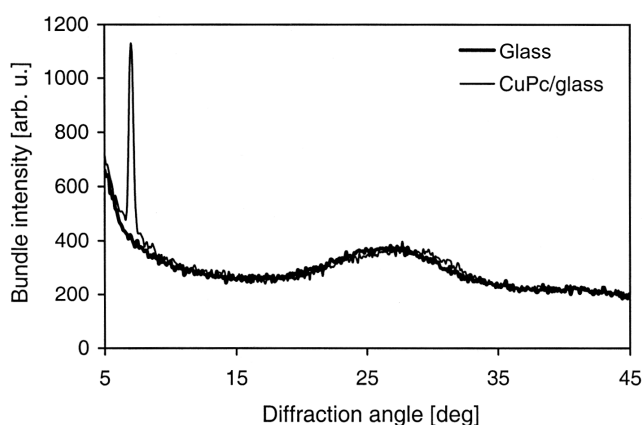


Fig. 7. Diffraction of X-ray for the sodium glass and for the CuPc structure on glass.

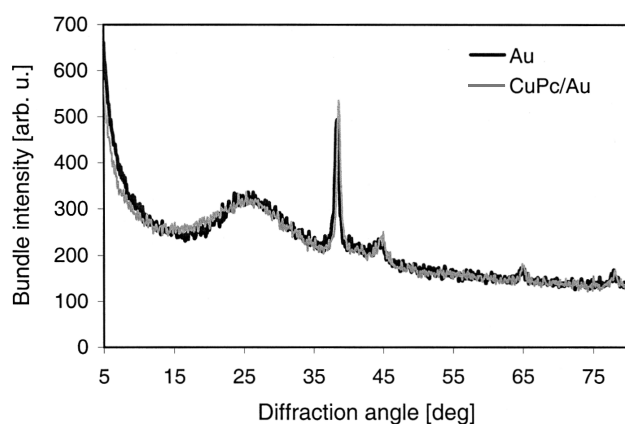


Fig. 8. Diffraction of X-ray for the gold layer and for CuPc/gold structure on glass.

of 7° . The investigations concerned a structure in a form of a layer of copper phthalocyanine deposited on the layer of gold and on a glass substrate, as well as a structure containing only a layer of gold on glass. The results of measurements of these structures by means of the X-ray diffraction method have been gathered in Fig. 8. There one can see peaks which are characteristic for gold, whereas no peak characteristic for phthalocyanine appeared in Fig. 7.

The structure of CuPc phthalocyanine augmenting on the layer of gold did not display any systematic arrangement of molecules in the form of respective monolayers, and the diffraction pattern of the X-ray in the radiograph did not show any intensification in the shape of the peak, as the case of CuPc phthalocyanine deposited on a glass substrate – Fig. 7. It may be concluded that CuPc phthalocyanine retains its arranged structure, growing on the glass substrate, but in an absolutely disordered way on the gold substrate. Identical results, deprived of a diffraction peak caused by phthalocyanine were obtained in the case of the structure containing lead phthalocyanine on gold and glass. It proves that the kind of the substrate, on which the layer of metalphthalocyanine grows is of crucial importance for its morphological structure [10].

3.1. Investigations concerning the effect of NO_2 on the structure of phthalocyanine

Further characteristics are presented by the results of X-ray diffraction of the layers of metalphthalocyanines neglecting the share of the glass substrate. Figure 9 presents the results of investigations concerning copper and nickel phthalocyanines as well as the same layers after exposition to 100 ppm nitrogen dioxide. The compared layers (gassed with NO_2 and not being gassed) were obtained during the same process of depositing them on the substrate. In the case of both these phthalocyanines, CuPc and NiPc, the diffraction peaks from the layers situated in air and those which had been gassed with NO_2 have been recorded. Figure 10 presents the results of similar

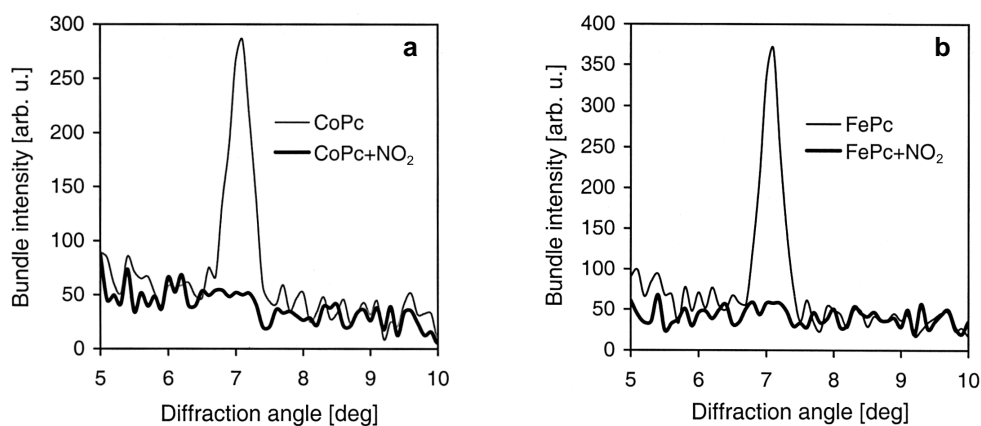


Fig. 9. Diffraction of X-ray on the structures: CoPc and CoPc+ NO_2 (a), FePc and FePc+ NO_2 (b).

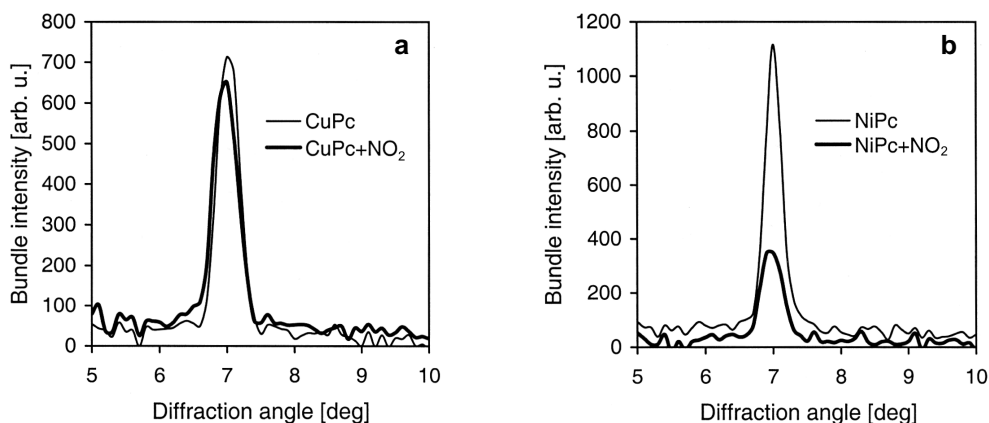


Fig. 10. Diffraction of X-ray on the structures: CuPc and CuPc+NO₂ (a), NiPc and NiPc+NO₂ (b).

investigations concerning CoPc and FePc phthalocyanines. In the case of cobalt and iron phthalocyanines exposed to NO₂ the diffraction peak was reduced to the level of measurement noise. Due to the interaction of phthalocyanines with nitrogen dioxide both these latter layers behaved like an amorphous structure.

The radiogram presented in Fig. 11 shows the diffraction peaks obtained for the layer of lead phthalocyanine PbPc present in air and after a 45-minute exposition to 100 ppm NO₂. As one may see in Fig. 11, the layer of PbPc deposited on a glass substrate at room temperature has two diffraction peaks with diffraction angles of: $2\theta = 7.0^\circ$ and $2\theta = 7.6^\circ$, due to the different structures of the molecule of lead phthalocyanine (all the other metalphthalocyanines are planar structures). The observed changes in the radiogram of nickel phthalocyanine after its exposition to nitrogen dioxide, however, are similar to those obtained in the case of copper phthalocyanine.

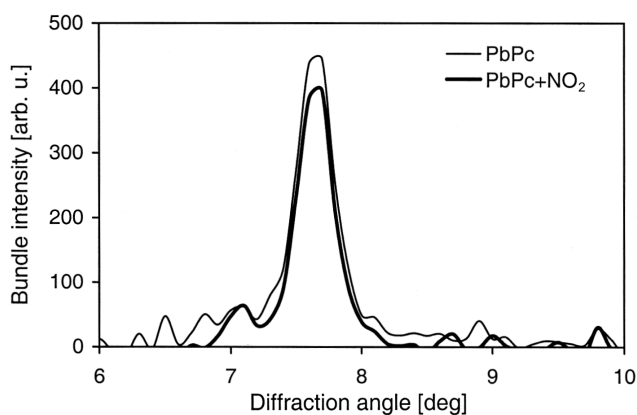


Fig. 11. Diffraction of X-ray on the structures PbPc and PbPc+NO₂.

All the investigations carried out by means of the X-ray diffraction method revealed differences in the structure of metal phthalocyanines deposited on a glass substrate and on glass covered with a layer of gold. These investigations indicate an amorphous character of the layers growing on the layer of gold and their crystallization of the metalphthalocyanines accumulating on the glass substrate in the α -form [11], [12]. Applying the X-ray diffraction method and optical spectroscopy it has been also shown that there are differences in the interaction of various metal phthalocyanines with nitrogen dioxide in synthetic air and with air. Such metalphthalocyanines as CuPc, NiPc and PbPc demonstrated slight changes affected by nitrogen dioxide in the transmission characteristics. The results of investigations are in compliance with the X-ray diffraction method concerning the same metalphthalocyanines affected by NO₂ and did not indicate any essential changes in the radiogram, either.

Such metal phthalocyanines, however, as CoPc and FePc revealed in investigations applying optical spectroscopy changes in the position of the absorption bands in the transmission characteristics. In investigations carried out according to the X-ray diffraction method such changes occur in the case of CoPc and FePc phthalocyanines as a complete reduction of the diffraction peak after their exposition to 100 ppm NO₂. These investigations indicate that both methods, dealt with in this paper permit to record the effect of NO₂ on their optical properties in the case of all the investigated metalphthalocyanines [13]–[15].

4. Conclusions

The results of investigations presented in this paper determine the influence of nitrogen dioxide on the values of the optical parameters of thin-layered structures of metalphthalocyanines. The values of the transmission of Pc layers as a function of the wavelength were determined both while the layers were present in the air and in an NO₂ concentration of 100 ppm. The structure of metalphthalocyanine nanolayers was also investigated applying the X-ray diffraction method. In result of these investigations radiograms were obtained displaying diffraction peaks for diffraction angles of about 7.0°, characterizing such metalphthalocyanines as CuPc, NiPc, CoPc and FePc, as well as for diffraction angles of 7.0° and 7.6° in the case of PbPc. Investigations by means of the X-ray diffraction method were carried out for phthalocyanine layers both in the presence of air (synthetic air) and in the presence of a mixture of synthetic air and 100 ppm NO₂.

All the presented results indicate a distinct influence of NO₂ on the optical and structural properties of thin metalphthalocyanine layers. The phthalocyanines CuPc, NiPc and PbPc which did not undergo any essential changes in the transmission spectrum affected by NO₂, underwent changes in the presence of 100 ppm NO₂ the position of the peak during the X-ray diffraction and indicate additionally the ability to regenerate their previous properties at a temperature of about 100°C. The phthalocyanines FePc and CoPc were subjected to considerable changes of the spectrum characteristics if affected by nitrogen dioxide. They changed their absorption

bands and ceased to be able to regenerate their former properties after they had been exposed to NO₂. Investigations concerning the structure of metalphthalocyanine layers carried out by means of the X-ray diffraction method have shown that the applied substrate for the deposition of such phthalocyanines as CuPc and PbPc affects essentially their layer structure as well as the values of their transmission index. Moreover, it has been found that the layers of CuPc and PbPc grow on a glass substrate as α -structures with a preferential crystalline orientation in the plane (100). Deposited, however, on the glass plane with a thin layer of gold, they grow as amorphous forms [8], [11]. The influence of nitrogen dioxide on the substrate of the layers was insignificant in the case of CuPc, NiPc and PbPc, and in the case of FePc and CoPc layers no diffraction peaks were detected after their exposition to NO₂. The layers of the phthalocyanines FePc and CoPc behaved after their exposition to NO₂ similarly as amorphous structures. Basing on these investigations it may be stated that some metalphthalocyanines display very interesting optical properties, changing as a result of the effect of NO₂. They may be applied in optical gas sensors, also for the detection of industrial toxic gases.

Acknowledgments – The work was sponsored by the Polish State Committee for Scientific Research (KBN) within the Grant 3 T11B 071 26.

References

- [1] CRAM D.J., HAMMOND G.S., *Organic Chemistry*, WNT, Warszawa 1963 (in Polish).
- [2] ROBERTS J.D., MARJORIE C.C., *Organic Chemistry*, PWN, Warszawa 1969 (in Polish).
- [3] FIESER L.F., FIESER M., *Organic Chemistry*, PWN, Warszawa 1962 (in Polish).
- [4] MŁOCHOWSKI J., *Compound Heterocyclic Chemistry*, PWN, Warszawa 1994.
- [5] SMITH K.M., *Porphyrins, corrins and phthalocyanines*, [In] *Comprehensive Heterocyclic Chemistry*, [Eds.] A.R. Katritzky, C.W. Rees, Vol. 3, Pergamon Press, Oxford 1984, p. 377.
- [6] MASHIKO T., DOLPHIN D., *Porphyrins, hydroporphyrins, corrins and related macrocycles*, [In] *Comprehensive Coordination Chemistry*, [Eds.] G. Wilkinson, R.D. J.A. Mc Clererty, Vol. 2, Pergamon Press, Oxford 1987, p. 813.
- [7] MOSER F.H., THOMAS A.L., *The Phthalocyanines, Vol. 1 – Properties*, CRC Press, 1982.
- [8] COLLINS R.A., BELGHACHI A., *Mat. Lett.* **8** (1989), 349.
- [9] OTTAVIANO L., LOZZI L., PHANI A.R., CIATTONI A., SANTUICCI S., DI NARDO S., *Appl. Surf. Sci.* **136** (1998), 81.
- [10] MIYAMOTO A., NICHGI K., TAOMOTO A., NAMBU T., MURAKAMI M., *Thin Solid Films* **256** (1995), 64.
- [11] RESEL R., OTTMAR M., HANACK M., KECKES J., LEISING G., *J. Mater. Res.* **15** (2000), 934.
- [12] NARAYANAN UNNI K.N., MENON C.S., *Mater. Lett.* **45** (2000), 326.
- [13] PUSTELNY T., IGNAC-NOWICKA J., MACIAK E., OPILSKI Z., *Molecular and Qantum Acoustics* **23** (2002), 253.
- [14] IGNAC-NOWICKA J., PUSTELNY T., OPILSKI Z., MACIAK E., JAKUBIK W., URBAŃCZYK M., *Opt. Eng.* **42** (2003), 2978.
- [15] PUSTELNY T., IGNAC-NOWICKA J., OPILSKI Z., *Opt. Appl.* **34** (2004), 249.

*Received August 18, 2004
in revised form November 15, 2004*