

Structural Characterization of Y-like Titanylphthalocyanine

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Abstract

Y-Titanylphthalocyanine (Y-TiOPc) is widely used as the photoconductor for laser printers. However, little is known about its crystal structure. Therefore, an attempt has been made to grow single crystals from water-containing solution on the assumption that the Y-phase includes water. An autoclave was utilized for the crystal growth so as to suppress the solvent evaporation and thus to increase the solubility of TiOPc. The single crystals have successfully been obtained, but these are found to be phase I according to the structure analysis. However, our single crystal exhibits an intense, Y-phase-like reflection around 790 nm as revealed from polarized reflection measurements on single crystals. The present fact evidently indicates that the Y-like layer of TiOPc is formed on the surface whose thickness amounts to at least 2000 Å and that the core of the single crystal is phase I. The present interpretation is also borne out by X-ray diffraction analysis on powders as well as XPS measurements monitoring O1s and Ti2P signals.

Introduction

Titanylphthalocyanine (TiOPc, Fig. 1) is a blue pigment whose Y-phase is widely used as the photoconductor for laser printers.¹ Figure 2 shows the solution spectrum of TiOPc as well as the solid state spectra in evaporated films for phases, I, II and Y. It is remarkable to note that the molecular spectrum in solution gives a very narrow single absorption band around 700 nm while the solid state spectra for near-IR-active phases II and Y are characterized by extremely broad absorption bands.² Phase Y is crystallographically characterized by a diffraction peak around $2\theta=27^\circ$ (CuK α radiation). However, details of its structure remain unclarified. For this reason, we have attempted to grow the single crystals and analyze the structure in an attempt to improve the photoconductive characteristics of the Y-phase.

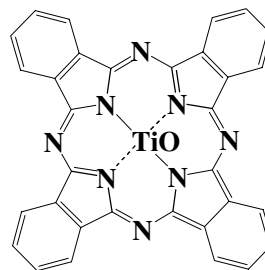


Figure 1. Molecular structure of TiOPc.

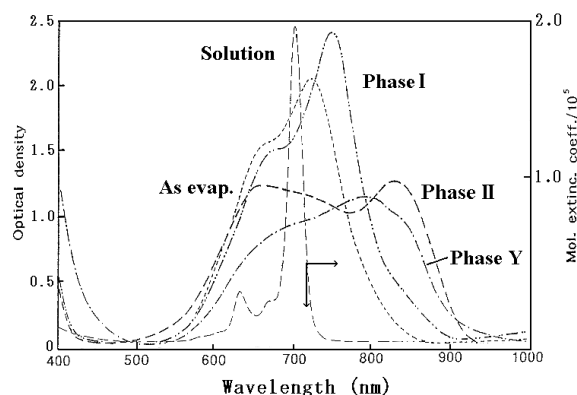


Figure 2. Solution spectrum of TiOPc as well as solid state spectra of evaporated films.

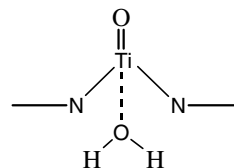


Figure 3. Assumed structure for water inclusion in TiOPc.

On the basis of our previous investigations on solvated magnesiumphthalocyanines (MgPc/(H₂O)₂(N-methylpyrrolidone)₂)³ as well as on the information of water inclusion in

Y-phase,⁴ we firmly believed that the oxygen atom of water might coordinate to the central Ti atom as shown in Fig. 3. For this purpose, a trial was made to grow single crystals from water-containing solution. However, TiOPc was found to be quite insoluble in any organic solvents. Then, an attempt was made to use an autoclave in order to suppress the solvent evaporation and thus to increase the solubility. This technique was quite successful to yield single crystals from water-containing solution. However, the single crystal thus prepared was found to be phase I, but it exhibits an intense near-IR absorption which can be attributed to the Y-phase. Therefore, our phase is called hereafter “Y-like phase”.

The present paper deals with the crystal growth of the Y-like phase and discusses its electronic characterization.

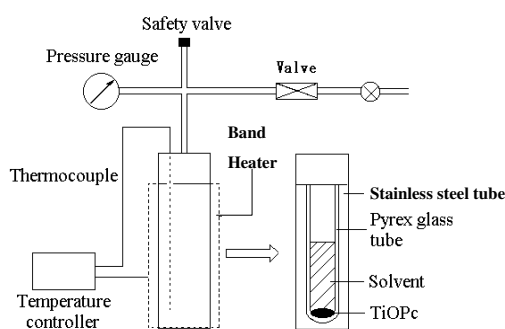


Figure 4. Autoclave apparatus for the crystal growth.

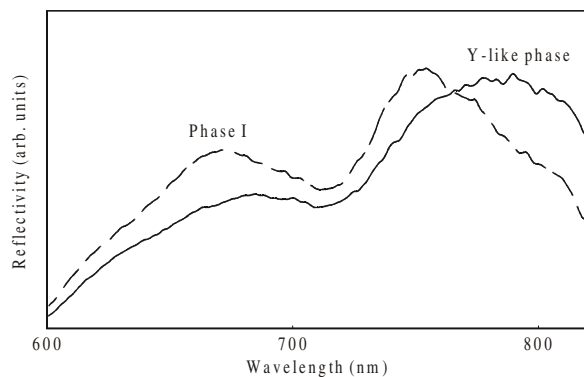


Figure 5. Reflection spectra of the Y-like phase as well as phase I.

Experimental Section

Crystal Growth Using an Autoclave

TiOPc was purchased from Dainichiseika Color and Chemicals MFG. Co. and purified twice by sublimation using a two-zone furnace.⁵ Fig. 4 shows the schematic drawing of the autoclave (Taiatsu Co. Ltd.; model TPR-2) employed for the crystal growth. Special attention was paid to a variety of factors which can affect the process of the crystal growth: for example, solvent choice, ratio of water to solvent, temperature setting for dissolving TiOPc and cooling rate for the re-crystallization. Among these, the cooling rate was found to be the key factor in the crystal growth. Furthermore, some solvents such as dimethylsulfoxide and dimethylacetamide are apt to decompose at high temperatures, therefore, all solvents were degassed by argon in order to suppress the decomposition of solvents as well as of TiOPc.

The single crystals of phase I used as the reference were grown from the vapor phase using a two zone furnace.⁵

Results and Discussion

1. Characterization of the Single Crystals

Table 1 details the solvents employed in the experiment and the conditions for the crystal growth. The best result was obtained when pyridine or 1-chloronaphthalene was used together with 5% of water under the conditions that the setting temperature was 250 °C and the cooling of 2 °C per hour. The single crystals obtained were, however, identified as phase I according to the structure analysis. The present phase I is called hereafter “Y-like phase”, because it turned out later that there is a skin layer of Y-phase on the surface of the single crystal.

When 2-methyl-2,4-pentanediol was used as the solvent in the presence of water, the central Ti atom of TiOPc was eliminated to give rise to the single crystals of metal-free phthalocyanine (H₂Pc). This might have happened presumably due to chelating reactions of the solvent molecule to the Ti atom. Furthermore, when water was used as solvent in the absence of any organic solvent, TiOPc was totally decomposed.

2. Reflection Spectra Measured on Single Crystals

Fig. 5 shows the reflection spectra of the Y-like phase as well as phase I measured on single crystals by means of a microscope-spectrophotometer (Carl Zeiss; UMSP80).

Table 1. Solvents and Crystal Modifications.

Solvent	Water content (%)	Setting temp. for dissolving TiOPc (°C)	Cooling rate (°C / h)	Crystal phase
acetone	10	250	5	Y-like phase & phase I
pyridine	5	140	2	Y-like phase & phase I
1-chloronaphthalene	5	200	2	Y-like phase & phase I
2-methyl-2,4-pentanediol	5	220	2	H ₂ Pc
dimethylsulfoxide	5	160	–	decomposition (solvent)
dimethylacetamide	5	170	–	decomposition (solvent)
water	100	250	–	decomposition (TiOPc)

The Y-like phase exhibits an intense near-IR reflection band peaking at 790 nm. The present spectrum is in good agreement with that of the Y-phase reported in Ref. 6. On the other hand, in phase I, a prominent band appears at about 750 nm together with a small band around 670 nm.

Since the reflection measurements give information about the surface (*ca.* 2000 Å in depth) while the X-ray yields bulk information, the present result can be interpreted in the following way. On the surface of the single crystal, there is a skin layer of Y-phase while the core is still phase I, as shown in Fig. 6. The thickness of the skin layer is estimated to be at least 2000 Å according to the penetration depth of the electromagnetic radiation at a wavelength of about 800 nm.

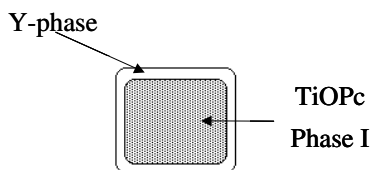


Figure 6. Cross-sectional view for the assumed structure of Y-like particles.

The above interpretation is also borne out by X-ray diffraction analysis as well as XPS measurements as described below.

3. X-Ray Diffraction Diagrams Measured on Powders

Figs. 7 (a) and 7 (b) show the X-ray diffraction diagrams for the Y-like phase and phase I. All diffraction peaks of phase I in the whole 2θ range are in complete agreement with the previous report.⁷ The diffraction peaks of phase I in the range of 8-14° are characterized by symmetrical band shapes while those of the Y-like phase are asymmetrical, indicating that some high-angle components are superimposed on the signal of phase I. In the 2θ range of 25.5-27.5°, the diffractions at 26.2 and 27.3° in the Y-like phase are typically characteristic of the Y-phase. These results clearly support the existence of the skin layer of the Y-phase on the surface of phase I as shown in Fig. 6.

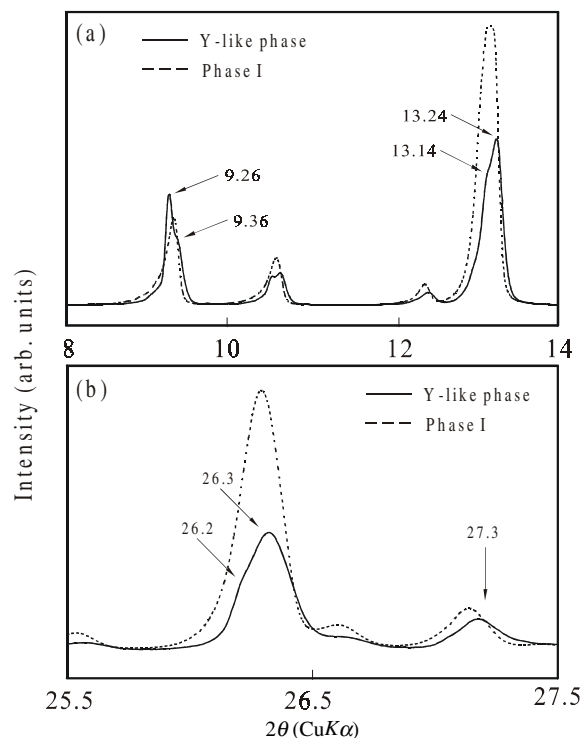


Figure 7. X-ray diffraction diagrams for the Y-like phase and phase I: (a) $2\theta = 8 - 14^\circ$ and (b) $2\theta = 25.5 - 27.5^\circ$.

4. X-ray Photoelectron Spectroscopy (XPS)

XPS is generally known to provide surface and bulk information up to the depth of about 50 Å. Figs. 8 (a) and 8 (b) show the XPS spectra for O1s and Ti2p measured on powders of phase I and the Y-like phase, respectively. The O1s band of phase I is distinctly composed of three peaks; whereas the one for the Y-like phase is broad and is displaced toward higher binding energies by about 0.2 eV. The three O1s peaks suggest the existence of three different oxygen states such as oxygen atom bonded to the central Ti atom in TiOPc, oxygen molecules absorbed in the bulk or adsorbed on the surface. However, the details are not known yet. In the Ti2p spectra, a clear difference is recognized at the shoulder around 459.4 eV ($J=3/2$)

between phase I and the Y-like phase. The present XPS results are fairly consistent with our model shown in Fig. 6.

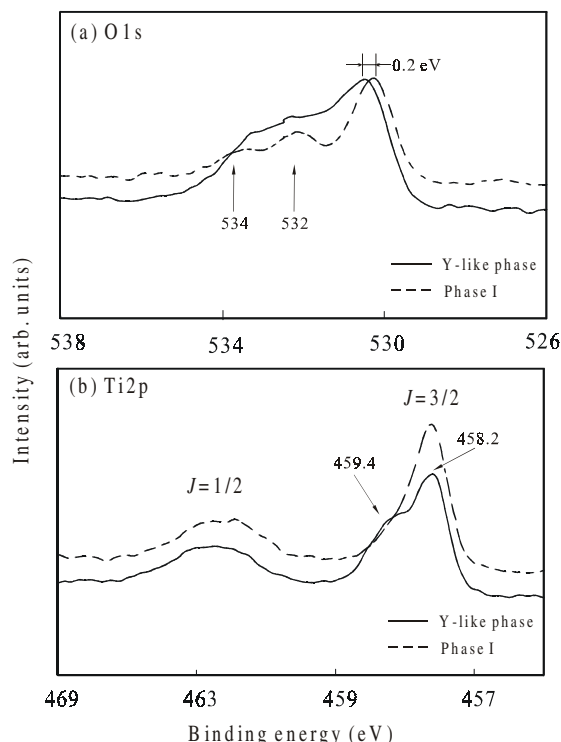


Figure 8. XPS spectra for the Y-like phase and phase I: (a) O1s and (b) Ti2p.

5. Electrophotographic Characteristics

Table 2 shows the electrophotographic sensitivities of the photoreceptors for GaAsAl laser printers using Y-like phase, Y-phase and phase II as the charge generation materials. The photosensitivity as expressed by “half-decay exposure energy” is the highest in Y-phase and decreases in the order of the Y-like phase and phase II. It is of interest to note that our Y-like powders prepared by an autoclave exhibits relatively a good result. We believe that the photosensitivity will greatly be improved if we can maximize the photo-active surface area by grinding powders as small as possible.

Table 2. Electrophotographic characteristics for GaAsAl laser printers.

CGM	half-decay exposure energy ($\mu\text{J}/\text{cm}^2$)
Y-like phase	0.433
TiOPc Y	0.131
TiOPc II	0.592

Conclusions

We have tried to grow single crystals of Y-TiOPc from water-containing solvents using an autoclave. The conclusions can be summarized as follows.

1. The single crystals obtained are characterized by a skin layer of Y-phase on the surface and the core is phase I.
2. A relatively high electrophotographic gain is achieved with the present Y-like phase. For further improvement, fine powders should be prepared so as to maximize the surface area, since the near-IR-active phase is only formed on the surface.
3. Utilization of an autoclave is found to be very effective for the crystal growth of insoluble pigments and can also be applied to the preparation of powders which include water or solvent molecules.

References

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Biography

Hideki Yamakami obtained his Bachelor of Education from Yokohama National University in 2001. He is currently in the graduate course for materials science at Yokohama National University. His research interest includes electronic characterization of organic pigments together with their electronic applications.