BRIEF COMMUNICATIONS

Environmental Effect on Surface Conductivity and the $\alpha \to \beta$ Phase Transition of Zinc Phthalocyanine

M. SAKAGUCHI AND M. OHTA

*Department of Applied Chemistry, Faculty of Engineering,
Niigata University, Niigata, Japan*

A study was carried out on the temperature dependence of the surface electrical conductivity (σ) of α-zinc phthalocyanine (ZnPc) crystals in various heating atmospheres. The σ of α-ZnPc crystals in NH_3 decreased abruptly due to the formation of the NH_3–ZnPc complex at 25°C. The effect of the heating atmosphere on σ of α-ZnPc crystals appeared remarkably during the $\alpha \to \beta$ phase transition. This phenomenon should be caused by (1) the change in the hole concentration due to an electron transfer between the ZnPc crystals and the ambient gas and (2) the lowering in the mobility of carrier due to the thermal diffusion of constituent atoms. © 1986 Academic Press, Inc.

The important influence of ambient gases on the solid phase reaction has been reported on the investigation of the phase transition reaction in various polymorphic crystalline materials (*1–3*). For example, the cubic → hexagonal phase transition of ZnS crystals was promoted by HCl and inhibited by H_2S (*1*). Also, the $\alpha \to \beta$ phase transition point of metal phthalocyanine (MePc) crystals was controlled by the interface reaction between the crystal and ambient gas (*3*).

It is known that the electrical conductivity of MePc crystals increases in proportion to the amount of O_2 sorbed on the crystal (*4, 5*) and decreases abruptly around the phase transition point (*6–8*). However, the effect of ambient gases on the electrical conductivity of MePc crystals has not been fully investigated. In particular, it should be very difficult to study how the electrical conductivity during the phase transition reaction is controlled by the ambient gas.

In this paper, the surface electrical conductivity (σ) of α-zinc phthalocyanine (ZnPc) crystals in various ambient gases was investigated in connection with the interface reaction between the crystal and the ambient gas, especially during the $\alpha \to \beta$ phase transition reaction.

Experimental

Materials. Crude and pure α-ZnPc crystals were prepared as follows. (1) The crude α-ZnPc crystal was prepared by recrystallization from concentrated sulfuric acid solution using a commercial β-ZnPc crystal (Eastman–Kodak Co.). (2) The pure α-ZnPc crystal was prepared by purifying the

130

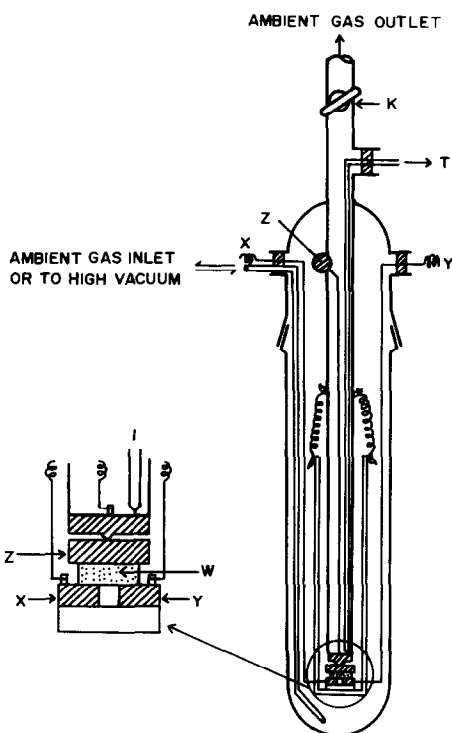AMBIENT GAS OUTLET

AMBIENT GAS INLET
OR TO HIGH VACUUM

FIG. 1. Apparatus for measurement of the surface electrical conductivity. I, thermocouple for sample; K, cock; T, thermometer for sample; W, sample; X, anode; Y, cathode; Z, guard electrode.

commercial β-ZnPc crystal by consecutive Soxhlet extractions with dimethylformamide and methyl alcohol, and sublimation *in vacuo* (100 mPa at 480°C) as in a similar method described previously (3) followed by the transforming to the α crystal. The sample (diameter: 9.5 mm, thickness: 1.0 mm) used for a σ measurement was prepared by compressing crude or pure α-ZnPc crystal powder (200 mesh through) under the pressure of 200 kg/cm^2 for 5 min.

Procedure. The σ measurement in various ambient gases (vacuum, He, O$_2$, and NH$_3$) at 25 ~ 350°C was carried out by using the apparatus shown in Figs. 1 and 2. Prior to the σ measurement, the sample painted with carbon paste was held with two springs between main electrodes (X and Y) and guard electrode (Z), which are gold-evaporated.

O$_2$ was obtained by evaporation of pure liquid O$_2$. NH$_3$ was obtained by drying cylinder NH$_3$ of high purity through a soda lime tube (S) at 25°C. Helium was obtained by purifying cylinder He through a glass tube containing the molecular sieve 5 Å (N) at −196°C. The flow rate of these ambient
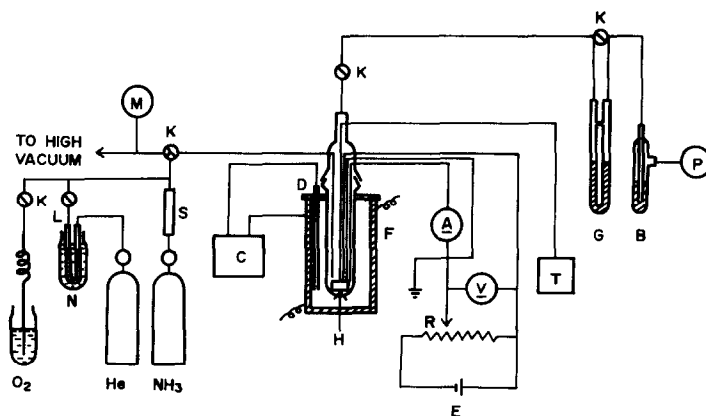

FIG. 2. Apparatus for measurement of the surface electrical conductivity. A, pico ammeter; B, bubbler; C, temperature control system; D, thermocouple; E, regulated dc power supply; F, electric furnace; G, flow meter; H, electrode system (see Fig. 1); K, cock; L, molecular sieve tube; M, McLeod gauge; N, liquid N$_2$ bath; P, air pump; R, slide rheostat; S, soda lime tube; T, thermometer for sample; V, digital multimeter.
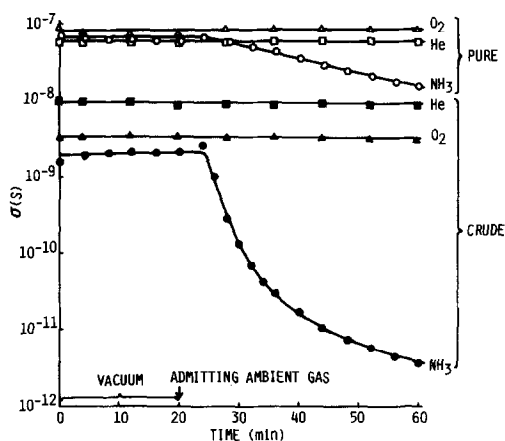
FIG. 3. Effect of vacuum, He, O_2, or NH_3 ambient gas on the surface electrical conductivity of crude and pure α-ZnPc samples at 25°C.

gases was maintained constant (100 cm³/min). The applied direct current voltage was selected at 6 V to obtain ohmic contact. A heating or cooling rate of the sample on the σ measurement was 2.5°C/min.

Both the $\alpha \rightarrow \beta$ phase transition reaction of ZnPc crystals and the interface reaction between the crystal and the ambient gas were investigated by using an apparatus which enabled simultaneous measurement of high-temperature X-ray powder diffraction and differential thermal analysis (DTA).

Results and Discussion

Figure 3 shows the effect of measuring ambient gases (vacuum, He, O_2, NH_3) at 25°C on the σ of crude and pure α-ZnPc samples. Under vacuum, the σ of the pure sample was larger than that of the crude sample. This fact must be caused by the increase of the hole concentration in the crystal resulting from the removal of such impurities (3) included in the crude crystal as amido, imido, etc. The σ of both samples in He or O_2 did not vary from that under vacuum and maintained the constant value,

but the σ on admitting NH_3 decreased abruptly for the crude sample.

The detailed experiment on the interface reaction between the crystal and NH_3 was carried out by using a simultaneous measurement method of high-temperature X-ray powder diffraction and DTA (Fig. 4). The NH_3–ZnPc complex formed on the surface layer of the crystal as soon as the crude crystal sorbed NH_3 at 25°C, then an exothermic peak appeared on the DTA curve, and the peak height in the crude crystal was much higher than that in the pure crystal reported previously (3) (as shown in Fig. 4 for reference). This fact suggests that the formation reaction of the NH_3–ZnPc complex is promoted by the impurity contained. By reference to the results in Fig. 3, it can be understood that the σ decreases in proportion to the rate of formation of the complex.
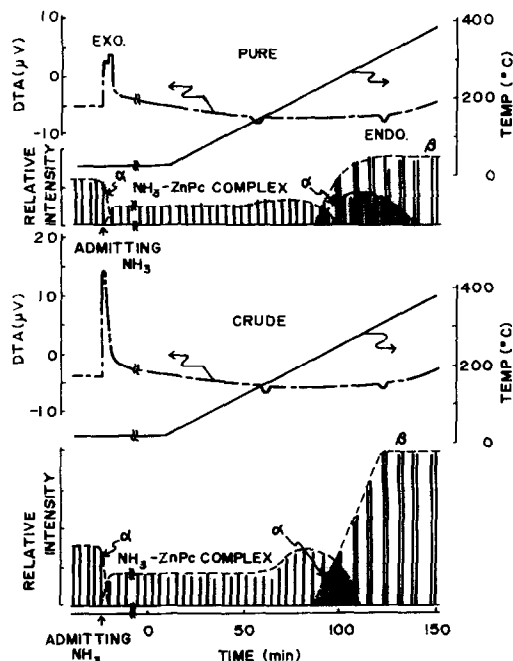

FIG. 4. $\alpha \rightarrow \beta$ phase transition of crude and pure ZnPc crystals by high-temperature X-ray powder diffractometry–differential thermal analysis in NH_3 (flow rate: 100 cm³/min) at 2θ region of 23.0 ~ 27.0°, and at a heating rate of 2.5°C/min.
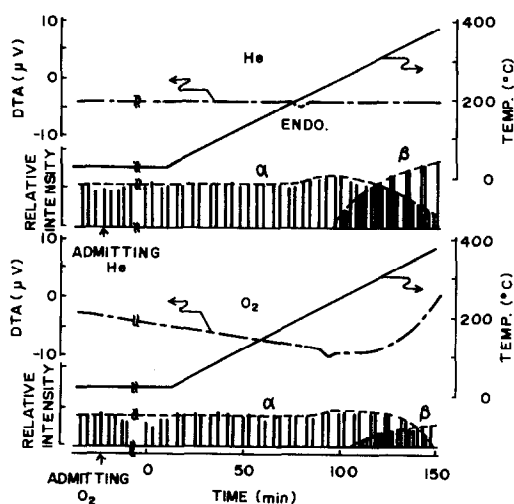
FIG. 5. $\alpha \rightarrow \beta$ phase transition of pure ZnPc crystals by high-temperature X-ray powder diffractometry-differential thermal analysis in He or O_2 (the reaction condition is the same as Fig. 4).

We reported previously (3) that the $\alpha \rightarrow \beta$ phase transition point of the pure crystal was higher in the order $NH_3 <$ He $< O_2$ (as
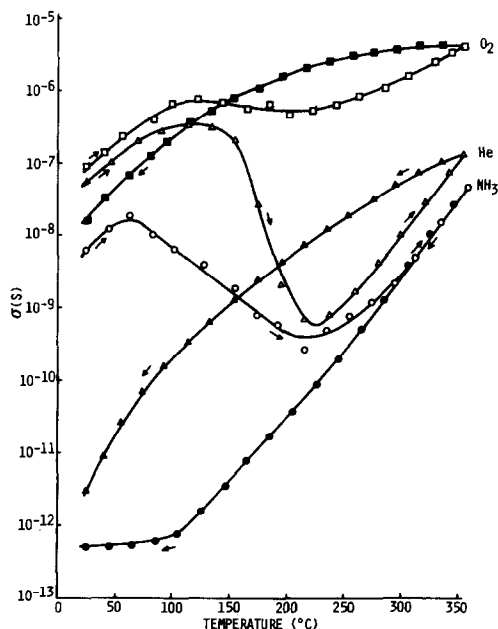

FIG. 6. Temperature dependence of the surface electrical conductivity of pure α-ZnPc sample in various ambient gases.

shown in Figs. 4 and 5). This fact suggests that the intermolecular force of ZnPc crystals is weakened by the sorption of NH_3 and strengthened by the sorption of O_2.

The behavior of the ambient gas as mentioned above was investigated in connection with the temperature dependence of σ of the pure sample (Fig. 6). In Fig. 6, the σ in the initial stage of the $\alpha \rightarrow \beta$ phase transition increased in the order $NH_3 <$ He $< O_2$ similar to that of the effect of the ambient gas on the phase transition point. On heating process, the σ increased with temperature but decreased abruptly near the phase transition point. The degree in the decrease of σ was remarkably affected by the ambient gas. Then, the σ increased again with temperature after the phase transition finished. On cooling process, the temperature dependence of σ indicated the character of the β-ZnPc crystal[1] itself without the reverse $(\beta \rightarrow \alpha)$ phase transition and was individually controlled by the function of the ambient gas.

These results suggest that the σ depended on the concentration of hole in the crystal. The decrease in the σ during the phase transition should be caused by inhibiting to transfer the carrier to the electrode due to the temporarily thermal diffusion of constituent atoms. The decrease in the σ was considerably less in O_2 than that in He, because it was compensated by both the increase in the hole concentration and the increase in the density of π electrons resulted from a strengthening of the intermolecular force of ZnPc crystals due to the sorption of O_2 (acceptor). In NH_3, the σ of the cooling process was much lower than that of the heating process, because the decrease in the hole concentration was due to the sorption of NH_3 (donor).

[1] The temperature dependence of σ of this sample cooled to room temperature did not change when the heating–cooling process repeated.

Acknowledgments

References

1. M. SAKAGUCHI, M. OHTA, M. SATOH, AND T. HIRABAYASHI, J. Electrochem. Soc. 124, 550 (1977).

2. M. SATO AND M. SAKAGUCHI, Denki Kagaku 47, 554 (1979).

3. M. SAKAGUCHI, M. OHTA, T. NOZAWA, AND M. TAKADA, J. Electrochem. Soc. 127, 1832 (1980).

4. J. M. ASSOUR AND S. E. HARRISON, J. Phys. Chem. Solids 26, 670 (1963).

5. S. E. HARRISON AND K. H. LUDEWIG, J. Chem. Phys. 45, 343 (1966).

6. K. WIHKSNE AND A. E. NEWKIRK, J. Chem. Phys. 34, 2184 (1961).

7. C. HAMANN AND I. STORBECK, Naturwissenschaften 50, 327 (1963).

8. C. HAMANN AND M. STARKE, Phys. Status Solidi 4, 509 (1964).