

Fluoroaluminium 2,3-Naphthalocyanine, Preparation and Electric Conductivity

Yukio Shimura and Makoto Hoshi

Department of Chemistry and Chemical Engineering, Kantogakuin University, 4834 Mitsuura, Kanazawa-ku, Yokohama 236, Japan

Michiko Shimura

Department of Industrial Chemistry, Tokyo Metropolitan University, 2-1-1 Fukazawa, Setagaya-ku, Tokyo 158, Japan

Phthalocyanine compounds are drawing attention as functional pigments in various fields and many interesting research results are reported. Naphthalocyanines having naphthalene rings instead of benzene, on the contrary, have been studied less in spite of the preponderance due to the wide spread π -electrons as electro-conductive materials (1). Here, we have synthesized fluoroaluminium 2,3-naphthalocyanine and measured some of its electrical properties.

PREPARATION OF FLUOROALUMINIUM 2,3-NAPHTHALOCYANINE (AlNcF)

2,3-Naphthalonitrile 17 mmol and AlCl_3 7.5 mmol were mixed and heated for 1 hr at 300°C . The product was pulverized and washed repeatedly with water and acetone to give crude chloroaluminium 2,3-naphthalocyanine (AlNcCl) (2). Yield 80%. It was purified either from pyridine or DMF. AlNcCl 1 g was heated with ammonia 50 ml and pyridine 25 ml for 7 hr at 116°C to obtain AlNcOH , 1 g of which was then heated with 18 ml of 48% HF until dryness. The obtained AlNcF was washed well with water and methanol and purified from pyridine solution.

PROPERTIES OF AlNcF

AlNcF was sublimed slightly on a quartz plate at 3×10^{-5} torr and measured for UV-Vis spectra (Fig. 1). Absorption corresponding to Q band was shown at 717 nm and the one for Soret band was at 324 nm. The band gap at room temperature was estimated ca. 1.72 eV. Absorption maxima of the AlNcF in pyridine appeared at 715 nm and 328 nm.

The specific resistivity for the disk sample of AlNcF prepared by pressing AlNcF powders at $400 \text{ Kg}\cdot\text{cm}^{-2}$ was $3.5 \times 10^2 \Omega\cdot\text{cm}$, an extraordinarily small value as an organic material, at room temperature. The surface resistances

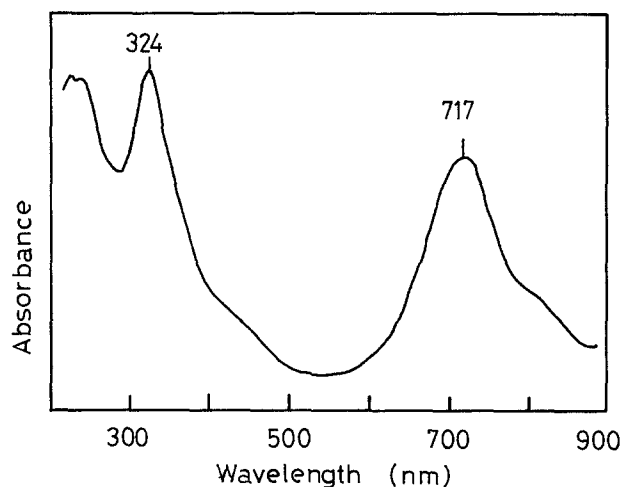


Fig. 1 UV-Vis spectrum for sublimed AlNcF .

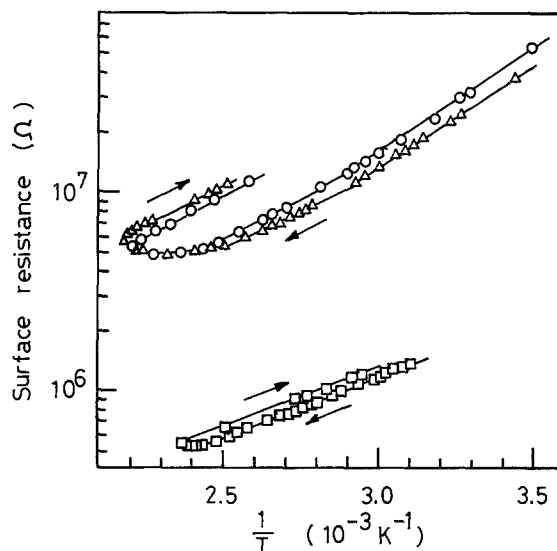


Fig. 2 Surface electric resistance for AlNcF .

□ : 900 nm
△ : 1st run, 50 nm
○ : 2nd run, 50 nm

for the sublimed AlNcF films (ca. 900 nm and 50 nm thick) are shown in Fig. 2. Several runs of heatings and coolings were carried out at 10^{-2} torr on the same samples preheated to 200°C at that reduced pressure for 10 min.

Key words; Electric conductivity, naphthalocyanine

Resistance vs. reciprocal temperature relationship changed with the repetition of the measurement. In case of 900 nm-thick film, activation energy of carrier formation was calculated as 0.28 eV from the lines. In 50 nm-thick film, repetition of heatings and coolings gave hystereses of the curves, of which the slopes were different at higher and lower temperature regions. For these temperatures, activation energies were respectively 0.28 eV and 0.39 eV. In all cases, the smaller activation energies than the band gap 1.72 eV suggest that the conductivity of the AlNcF is arisen from the ionization at impurity levels. From the observation of Seebeck effect, it was proved that AlNcF was a p-type semiconductor.

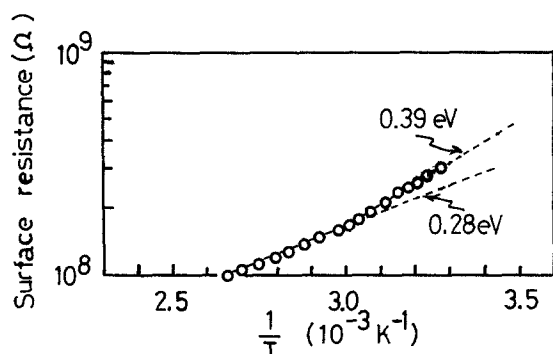


Fig. 3. Surface electric resistance at reduced O_2 concentration.

Fig. 3 shows the surface resistance of AlNcF sublimed film which was measured at 3×10^{-5} torr without the exposure to air. The same two values of activation energies (0.28 eV and 0.39 eV) were obtained as in Fig. 2. In situ reduction by the addition of hydrazine before the sublimation of AlNcF was tried on the sample for resistance measurement. The surface resistance was increased less with the decrease of temperature. It is considered that remaining oxygen in the vessel adsorbs on AlNcF with the decrease of temperature and makes impurity levels in the band gap.

Fig. 4 shows ESR spectra of sublimed AlNcF on quartz measured at ambient temperature along with the ones for metal-free phthalocyanine (H_2Pc) and fluoroaluminium phthalocyanine (AlPcF). The strong ESR signal for AlNcF is almost the same as that for AlPcF in g value (2.003), ΔH_S (1.1 G), and microwave output dependencies. ESR spectrum of H_2Pc ($g=2.003$) is known to arise from $O_2^{\cdot-}$ (3). In reference to DPPH (1,1-diphenyl-2-picryl-hydrazyl) which was adsorbed on KBr powder, the radical densities were estimated as follows: 5×10^{22} , 2×10^{22} , and 2×10^{20} , for AlNcF, AlPcF, and H_2Pc , respectively.

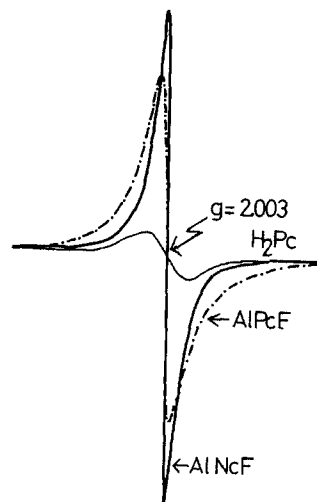


Fig. 4. ESR for sublimed AlNcF.

To conclude, AlNcF is a highly electro-conductive material and the conductivity is brought about by oxygen molecules densely and stably adsorbed on it as well as by horizontally expanded π -electron system of the naphthalocyanine.

REFERENCES

1. L. A. Schechtman and M. E. Kenney, Proc. Electrochem. Soc. **83-3**, 340 (1983)
2. S. W. Beavan, Eur. Pat. Appl. EP 54,992; C. A. **97**, 129504z (1982)
3. J. R. Harbour and R. O. Loutfy, J. Phys. Chem. Solids **43**, 513 (1982)
Y. C. Cheng and R. O. Loutfy, J. Chem. Phys. **73**, 2911 (1980)

Manuscript submitted Aug. 12, 1985;
revised manuscript received Nov. 11, 1985.