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Note

PHASE BEHAVIOUR OF COBALT, NICKEL AND ZINC PHTHALOCYANINES

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We have reported recently on the phase behaviour of copper and zinc phthalocyanines [1]. The various metal-substituted phthalocyanines are of current interest as potential materials for thin-film gas sensors, particularly in view of their thermal stability, high conductivity and sensitivity to a variety of gases [2–8]. A number of studies have been made to examine the importance of the metal atom in the adsorption/absorption processes for various gases, the results indicating that no particular phthalocyanine is superior for the whole range of gases of interest. For example, Jones and Bott [5] have shown that for electrophilic gases the sensitivity (conductivity change) increases progressively as heavier metals from the first transition series are used.

The electrical properties of these materials are strongly dependent upon the specific crystal forms and a requirement of any particular gas-sensing film is that the crystal form utilized should be both well defined in terms of its gas-sensing properties and that the phase should be stable over the temperature range likely to be encountered in the gas-sensing environment. Our previous studies, together with the results of Fustoss-Wegner [9] on metal-free phthalocyanine, indicate that, at least for certain phthalocyanines, the phase change occurs in two stages with a well-defined intermediate state. In the present work we have extended these measurements to cobalt and nickel phthalocyanines to try to determine the generality of this behaviour and we have also given closer consideration to the intermediate state in zinc phthalocyanine. Measurements have been made using differential scanning calorimetry, infrared absorption spectroscopy to characterize the phases and transmission electron microscopy.

EXPERIMENTAL

The cobalt and nickel phthalocyanines were supplied by Fluorochem Ltd. and the zinc phthalocyanine by Thorn-EMI Central Research Laboratories. The as-supplied material was purified by entrainer sublimation in a three-

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zone electrically heated tube furnace in a steady 0.5 l min^{-1} flow of zero-grade argon. Phase changes were studied using a Perkin-Elmer DSC-2 differential scanning calorimeter calibrated with AnalaR tin and high purity indium.

RESULTS AND DISCUSSION

Infrared spectra of cobalt and nickel phthalocyanines

As a precursor to the DSC studies the IR spectra of the α and β phases of CoPc and NiPc were determined. α-NiPc was prepared by dissolving β-NiPc in 98% sulphuric acid using, for comparative purposes, the method of Griswold [10], in which the α form is prepared from the crude β form, and the method of Iwatsu et al. [11], in which the α form is prepared from the sublimed β form.

The α-form spectra for the two preparation methods were identical and both these and the β spectra were identical with those reported by Kobayashi et al. [12]. α-CoPc was prepared by precipitation from a solution of sublimed β form, dissolved in sulphuric acid, by the addition of water [13]. The spectra obtained were in agreement with those reported by Steinbach and Joswig [14] and Metz et al. [15].

DSC studies

Figure 1 shows a typical DSC thermogram of an α-NiPc sample heated at 10 K min^{-1}. It is apparent that there are two endothermic peaks in contrast to CuPc and ZnPc which show two exothermic peaks, and one exothermic and one endothermic change, respectively. However, in agreement with

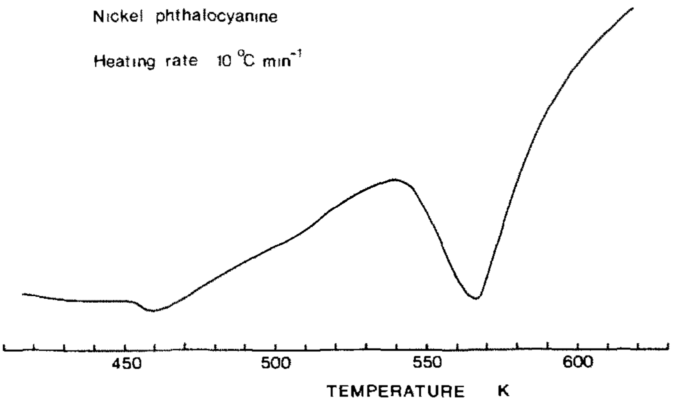

Fig. 1. DSC thermogram of an NiPc sample heated at 10 K min^{-1}.

TABLE 1

Heating parameters for NiPc

Heating rate (K min^{-1})	Sample mass (mg)	Activation energy (kcal mol^{-1})	Heat of transition (cal g^{-1})
10	9.9	79.3	1.25
10	24.9	48.0	0.27
20	16.4	54.7	4.33
20	17.6	60.7	3.86
40	7.9	70.9	–

those materials the peak temperatures were found to be dependent upon the sample heating rate; the higher the heating rate the lower the peak temperatures. Infrared spectra indicated that the β form was not achieved unless the sample had been heated to a temperature above that of the second peak.

Activation energies and heats of transition (enthalpy changes) were calculated for the second peak by the methods used in our previous work [16,17]. These are listed in Table 1. At 40 K min^{-1} the peak was not sufficiently well defined to justify calculation of the enthalpy change. It is clear that both the activation energy and heat of transition are determined by both the mass of the sample and the heating rate. Bearing these variations in mind and also the inevitable spread in results of this type, it can be seen that both the activation energies and enthalpy changes are larger than for either CuPc or ZnPc.

Figure 2 shows a DSC thermogram of a sample of α-CoPc. It can be seen that the plot consists of a large endothermic peak extending over a wide temperature range, followed by a much smaller endothermic peak. Measurements at a variety of heating rates failed to "localize" the first peak to

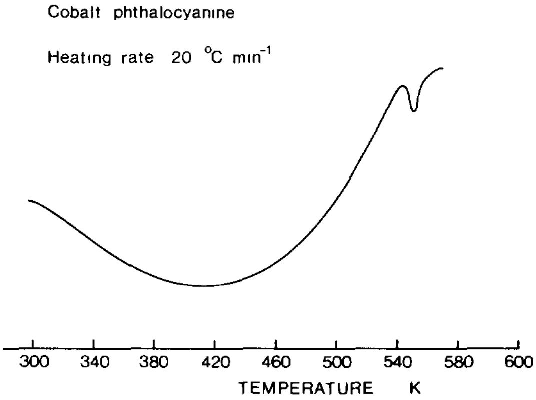

Fig. 2. DSC thermogram of an CoPc sample heated at 20 K min^{-1}.

TABLE 2

Heating parameters for CoPc

Heating rate ($K\ min^{-1}$)	Sample mass (mg)	Activation energy ($kcal\ mol^{-1}$)	Heat of transition ($cal\ g^{-1}$)
10	11.5	183.8	0.135
20	8.3	198.1	0.997
20	13.3	176.3	0.701
20	14.5	–	0.663
40	11.9	–	0.715

within a smaller temperature range, unlike the behaviour of the other Pc's that we have studied where a slower heating rate tends to give a narrower peak. However, whilst the "peak position" is difficult to determine for the very broad first peak, measurements at varying heating rates indicated that for increasing heating rate the first peak moves to lower temperatures whereas the second peak moves to higher temperatures. The activation energies and enthalpy changes associated with the second peak are shown in Table 2. The rather different behaviour of CoPc compared with the other Pc's, as shown in Fig. 2, is reflected in the parameters in Table 2, the activation energies being rather high and the enthalpy changes much lower than for NiPc.

"Intermediate" phase

These and previous results indicate that H_2Pc, CuPc, ZnPc, NiPc and CoPc all show two peaks in their DSC thermograms. However, the variations in relative peak magnitudes and exothermic/endothermic behaviour suggest that the $\alpha \rightarrow \beta$ transition may not involve identical mechanisms in each case. In an attempt to characterize the materials in the inter-peak ranges we determined the infrared spectra for both ZnPc and CoPc samples which had been heated to temperatures above the first peak but below the second. The spread of the first peak in the case of CoPc meant that some of the spectra obtained were actually from the upper temperature region of the first peak. However, the results obtained were qualitatively the same for both materials. The spectra obtained were identical to the α-phase spectra with the exception of one (CoPc) or two (ZnPc) extra-small peaks in the fine structure. The transition to the β form is clearly associated exclusively with the second peak. As the "intermediate phase" is thus essentially still in the α form it was felt necessary to investigate the phenomenon causing the first thermogram peaks which, with the exception of NiPc, are larger than the second (conversion to β) peaks. Observations of the crystallinity of ZnPc films were therefore made using transmission electron microscopy. ZnPc layers were deposited on single-crystal KCl substrates and then transferred to microgrids and also directly onto carbon layers on microgrids. The results were the same for both types of substrate. The room-temperature deposited films exhibited electron scattering patterns with three diffuse rings and electron micrographs showed that the films consisted of randomly oriented microcrystallites. Heating to progressively higher temperatures through the first thermogram peak resulted in an increase in crystallite size and increased sharpness in the scattering pattern. However, there was no indication of any change in the crystal structure. It is apparent that the first peak is associated solely with the coalescence and growth of α-phase crystals.

Electron microscope studies of phthalocyanines suffer from the tendency of films to degrade within a few seconds of exposure to the electron beam. It is thus necessary to ensure that such observations are not the result of beam-induced effects. The present studies were therefore repeated using a polarizing microscope. Qualitatively identical results were obtained.

SUMMARY

The present results indicate that phthalocyanines heated to progressively higher temperatures undergo not only a fairly well-defined transition to a stable β form but at lower temperatures undergo a gradual exothermic or endothermic change associated with the growth of α-form microcrystallites into larger crystals. Results to be reported elsewhere indicate that the electrical properties, including gas sensitivity, also change during microcrystallite growth. Thus stability requirements suggest that phthalocyanines in which the β phase shows the greater gas sensitivity would appear to be more appropriate to microcircuit-based thin-film gas sensors where elevated temperatures are to be expected.

REFERENCES

1 K.A. Mohammed and R.A. Collins, Thermochim. Acta, 104 (1986) 377.
2 R.L. van Ewyk, A.V. Chadwick and J.D. Wright, J. Chem. Soc., Faraday Trans. 1, 77 (1981) 73.
3 C.L. Honeybourne and R.J. Ewen, J. Phys. Chem. Solids, 44 (1983) 833.
4 C.L. Honeybourne, R.J. Ewen and C.A.S. Hill, J. Chem. Soc., Faraday Trans. 1, 80 (1984) 851.
5 T.A. Jones and B. Bott, Sensors and Actuators, 9 (1986) 27.
6 M.E. Musser and S.C. Dahlberg, Surface Sci., 100 (1980) 605.
7 T.G. Abdel-Malik, Indian J. Phys., 57A (1983) 231.
8 J.D. Wright, A.V. Chadwick, B. Meadows and J.J. Miasik, Mol. Cryst. Liq. Cryst., 93 (1983) 315.
9 M. Fustoss-Wegner, Thermochim. Acta, 23 (1978) 93.

10 F.H. Moser and A.L. Thomas, The Phthalocyanines, Vol. 2, CRC Press, Boca Raton, FL, 1983, p. 9.
11 F. Iwatsu, T. Kobayashi and N. Uyeda, J. Phys. Chem., 84 (1980) 3223.
12 T. Kobayashi, F. Kurokawa and N. Uyeda, Spectrochim. Acta, Part A, 26 (1970) 1305.
13 M. Kalliat and A. Nath, J. Inorg. Nucl. Chem., 43 (1981) 271.
14 F. Steinbach and H.-J. Joswig, J. Chem. Soc., Faraday Trans. 1, 75 (1979) 2594.
15 J. Metz, O. Schneider and M. Hanack, Spectrochim. Acta, Part A, 38 (1982) 1265.
16 J. Chiu, Polymer Characterization by Thermal Methods of Analysis, Dekker, New York, 1974, p. 26.
17 E.M. Barrall and J.F. Johnson, in P.E. Slade and L.T. Jenkins (Eds.), Thermal Characterization Techniques, Dekker, New York, 1970, Chap. 1.