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Optical absorption studies of copper phthalocyanine thin films

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Abstract

The optical absorption of thermally evaporated copper phthalocyanine (CuPc) was studied in the UV-VIS-NIR region. The absorption spectra recorded in the UV-VIS region show two well-defined absorption bands of the phthalocyanine molecules, namely, the Soret (*B*) and the *Q*-band . The *Q*-band shows its characteristic splitting (Davydov splitting) of the main absorption peak in the metal phthalocyanine correlates with the relative tendencies of the metal to out-of-plane bonding. Some of the important spectral characteristics such as the molar extinction coefficient ($\varepsilon_{\text{molar}}$), the oscillator strength (f), the electric dipole strength (q^2) and absorption half-bandwidth ($\Delta\lambda$) of the principle optical transitions were evaluated. The analysis of the spectral behavior of the absorption coefficient α in the absorption region revealed two indirect allowed transitions with corresponding energies 2.95 ± 0.03 and 1.55 ± 0.02 eV.

The spectra of the infrared absorption allow characterization of vibration modes for the powder, as-deposited material and thin films of CuPc annealed at 423 K for two hours. Discussion of the obtained results and their comparison with the previous published data are also given.

Keywords: Optical absorption; CuPc; Thin film

1. Introduction

The metal-substituted phthalocyanines have received increasing attention over the last decade, primarily because of their potential as surface conductivity-based gas sensors [1–3]. These properties which have proved particularly relevant, as their ease of preparation, thermal and chemical stability and high sensitivity [4,5]. In addition to these applications , being very good absorber of light in the UV-VIS region, they are widely used as excellent laser dyes capable of optical amplification in the red region [6]. These properties together with the structural similarity to chlorophyll have resulted in many investigations directed towards their applications in solar energy conversion [7]. Also they have the potential to serve as an active material for molecular electronic devices such as electrochromic displays , chemical sensors [8], optical data storage [9], color filters and organic laser material [10]. The objective of this work is to study the optical absorption spectra of CuPc thin films in the UV-VIS-NIR region and determine the important optical absorption parameters of the principle optical transitions. In addition, the infrared spectrum is studied to provide information about stretching and bending motions of the atoms in this molecule. The influence of heat treatment on these parameters is also considered.

2. Experimental details

The copper phthalocyanine (CuPc) powder used in this study were obtained from Kodak, UK. Thin CuPc films of different thicknesses were prepared by conventional thermal evaporation technique, using a high vacuum coating unit (Edwards type E 306 A, England). The films of CuPc were vacuum deposited onto thick flat quartz substrates from a quartz crucible source heated by a tungsten coil in a vacuum of 10^{-5} Pa during deposition. The substrates were kept at room temperature and the deposition rate was controlled at 3 nm s^{-1} using a quartz crystal thickness monitor (Model FTM4, Edwards, England). The absorbance spectra of CuPc films were measured at normal incidence at room temperature in the

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range of 200–1000 nm by using a double - beam spectrometer (JASCO model V - 570 UV-VIS-NIR). Infrared spectroscopy on CuPc was performed using an ATI Mattson (Infinity series FTIR) infrared spectrophotometer in the infrared spectral range 1800–400 cm^{-1}. For this study 1 mg of CuPc powder was mixed with 50 mg of vacuum dried IR grad KBr. Measurements were also made on thin films of thickness 400 nm deposited onto optically flat single crystal substrate of KBr at room temperature.

3. Results and discussion

3.1. Infrared characterization

In the phthalocyanines, the characteristic infrared vibration frequencies range fall into two categories. The first, comprises the high-frequency band stretching region while the other is the mid- and low-frequency region which contains the “finger prints” of phthalocyanine. The stretching modes for individual bonds, such as N-H and C-H, have frequencies at practically constant values, irrespective of the overall molecular structure and thus assignments are relatively easily made. Absorption bands in the lower-frequency region and in the far-infrared , however , are associated with both stretching and bending fundamentals here the complexity of the spectra makes definite assignments in these regions difficult and correlation tentative.

Fig. 1a–c compares the infrared spectra of powder, as-deposited and annealed thin films of CuPc. The position of the major bands in the spectra of the CuPc is given in Table 1. The similarity of the spectra highlights the thermal stability of CuPc. This indicates that the thermal evaporation technique is considered as a good method for preparation thin films of CuPc.

The absorption at $1605 \pm 4\,cm^{-1}$ can be assigned to a general skeletal vibration of porphyrin ring system. The medium intensity absorption peaks that appear in the region 1600–1300 cm^{-1} most likely arise from the skeletal vibrations of the tetrapyrrolic macrocycle. The bands at 1495 ± 5, 1424 ± 5, $1350 \pm 1\,cm^{-1}$ are assigned to the $C=C$ and $C=N$ skeletal vibrations of the porphyrin ring [11]. The other bands involve a number of CH deformation, C–C stretching and bending modes in the pyrrole ring [3]. The spectrum of CuPc in the fingerprint region is complex, and only tentative assignments of the absorption bands can be made. The peak at $1280 \pm 1\,cm^{-1}$ has been previously assigned to a C–H bending and CN stretch of porphyrin in CuPc [12]. Other absorption band most likely associated with the tetrapyrrole ring system are bending modes found at 1224 ± 4 and $820 \pm 1\,cm^{-1}$ [13]. The band at $726 \pm 2\,cm^{-1}$ in the IR spectra has been previously assigned to the C–H out-of-plane deformations and has been said to be a good indicator for phthalocyanine crystalline phases ordering [14–16]. Thus the similarity between the CuPc in powder and as-deposited annealed thin films is quite likely to be associated with the highly textured phthalocyanine structure of the films [17].

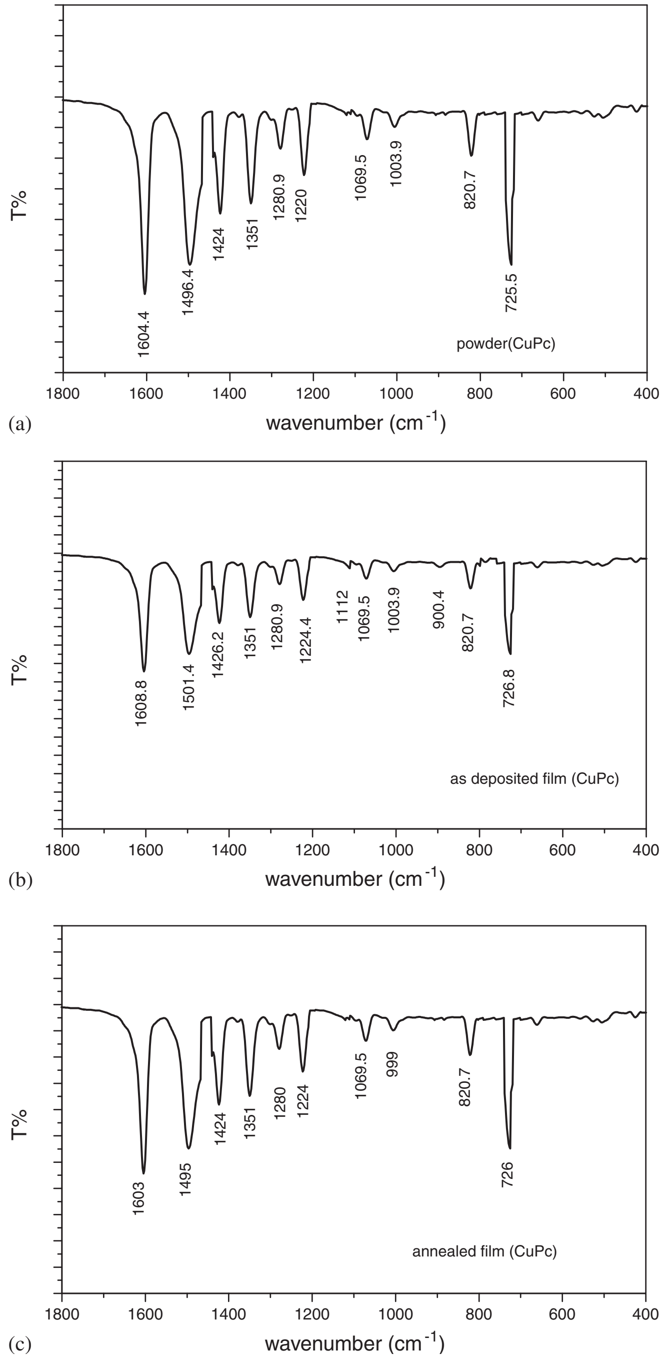

Fig. 1. (a) Infrared absorption spectra for the powder CuPc, (b) infrared absorption spectra for the as-deposited CuPc film, and (c) infrared absorption spectra for the annealed CuPc film.

3.2. UV-VIS Absorption characterization

The UV-VIS spectrum observed for phthalocyanines originates from molecular orbitals within the aromatic 18 π electron system and from overlapping orbitals on the central metal atom [18]. A close examination of the