

Evaluation of electrical conductivity and thermal diffusivity of vanadyl naphthalocyanine

J. THOMAS, V. N. S. PILLAI*, V. P. N. NAMPOORI, C. P. G. VALLABHAN

International School of Photonics and *School of Environment Studies, Cochin University of Science and Technology, Cochin 682 018, India
E-mail: photonix@md2.vsnl.net.in

Metal phthalocyanines have attracted much attention because of their potential application in electronic devices, optical data storage, photoconductors and sensors [1, 2]. They are also very good candidates for high density optical data recording (ODR) media due to their thermal and chemical stability and facility for synthetic modification. An essential requirement for the ODR material is the long wavelength absorption. Metal naphthalocyanines absorb at a longer wavelength than the phthalocyanines because of their additional benzoannulation [3]. For constructing practical ODR devices the thermal properties of the organic dyes are of considerable importance [4–7]. It is also necessary to investigate the electrical properties of metal naphthalocyanines prior to their utilization in optoelectronic devices. Although there are a number of reports on the optical properties of metal naphthalocyanines [8, 9], only very few investigations are found on the electrical properties of these interesting materials.

In the present study, we report the electrical conductivity and thermal diffusivity of pristine and iodine doped vanadyl naphthalocyanine (VONc). VONc was synthesized and purified by the method reported by Yanagi *et al.* [9]. The compound was characterized by elemental analysis, IR and electronic spectra. The data were in good agreement with those reported in the literature [3].

VONc was doped with iodine in the solution phase [10, 11] by stirring 100 mg of powdered sample with a saturated solution of iodine in carbon tetrachloride for 48 h. The doped material was filtered and washed with carbon tetrachloride to remove excess iodine. The iodine doped vanadyl naphthalocyanine (VONcI) was dried at 360 K in vacuo for 2 h.

The pellet samples of 5.0 mm diameter and 0.8 mm thickness were prepared at a pressure of 2000 kg cm^{-2} . The electrical conductivity was measured in a shielded cell under dynamic vacuum in the temperature range 100–450 K using a Keithley model 617 electrometer. The samples studied were heated to 375 K and cooled to ambient temperature before measurement, to avoid the interference of moisture and adsorbed oxygen. A photoacoustic method was used to measure the thermal diffusivity of the pellet samples (see Fig. 1). The light source used was a 488 nm radiation from an Ar^+ laser (Liconix-5000 series) at a power level of 30 mW. The laser beam was chopped by a mechanical chopper (Stanford Research System model SR 540). By varying the chopping rate the characteristic frequency (f_c)

was determined by front surface illumination of the sample.

The Arrhenius plot of the temperature dependence of electrical conductivity (σ) for VONc and VONcI are shown in the Fig. 2. In the pristine sample, the temperature dependence is very weak below 300 K. Above this temperature the behavior is in accordance with an Arrhenius relationship. The increase in conductivity at higher temperature must be due to an enhancement in carrier density with increase in thermal energy. The activation energies at different temperature ranges are given in Table I.

The electrical conductivity of vanadyl naphthalocyanine increases when doped with iodine. The behavior of VONcI indicates that considerable changes have

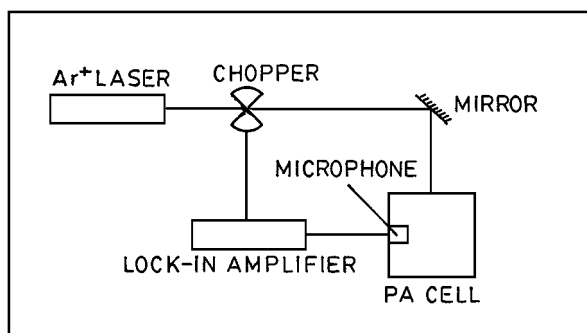


Figure 1 Schematic diagram of the photoacoustic set up used for thermal diffusivity measurement.

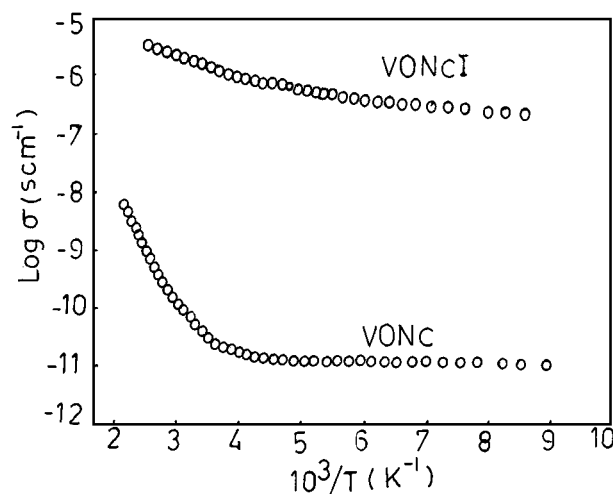
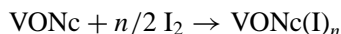


Figure 2 $\text{Log } \sigma$ vs. $10^3/T$ plot of pristine and iodine doped VONc.

TABLE I Electrical conductivity and thermal diffusivity of pristine and iodine doped vanadyl phthalocyanine

| Sample | Activation energy E_a (eV) | | Thermal diffusivity at 300 K ($\text{cm}^2 \text{s}^{-1}$) |
|--------|------------------------------|-----------|--------------------------------------------------------------|
| | 100–270 K | 270–450 K | |
| VONc | 0.01 | 0.05 | 0.26 |
| VONcI | 0.35 | 0.10 | 0.29 |

occurred in the electronic environment of the molecule as a result of doping.



When doped with iodine, the stacked naphthalocyanine molecule must be in fractional oxidation state with disordered parallel chains of I_3^- counterions. The partial oxidation enhances charge mobility in the molecular stack.

The Arrhenius plot of VONcI shows two distinct regions with activation energies of 0.05 and 0.10 eV. The influence of any adsorbed iodine was ruled out since extreme care was exercised in removing it by washing with carbon tetrachloride and annealing it to 375 K before the measurement. A comparison of the activation energies of pristine and iodine doped samples confirm the incomplete charge transfer in the latter case.

According to Rosenwaig *et al.* [12] when the front surface of an optically thick sample is irradiated with a chopped laser beam, the thermal diffusivity is related to the characteristic frequency (f_c) by the relationship $\alpha_s = f_c l_s^2$ where l_s is the thickness of the sample. The characteristic frequency was obtained by plotting $\log A$ against $\log f$ where A is the amplitude of the PA signal and f is the chopping frequency. The chopping frequency corresponding to the point at which a change in slope occurs in the above plot is the characteristic frequency of the sample. $\log A$ vs. $\log f$ plot of pristine and iodine doped samples are given in Fig. 3. The calculated thermal diffusivity values (Table I) show that iodine doping enhances the thermal diffusivity of vanadyl naphthalocyanine. The increase in thermal diffusivity of the iodine doped sample may be due to the disorder of iodine atoms occupying the channels in one dimensional lattices [10, 13].

The thermal diffusivity of vanadyl naphthalocyanine and its iodine doped form has been reported for the first time. The results are useful in the context of optical writing in VONc based media.

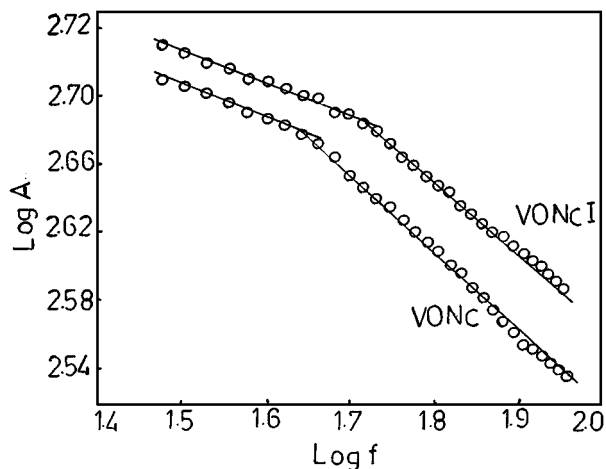


Figure 3 $\log A$ vs. $\log f$ plot of pristine and iodine doped VONc.

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