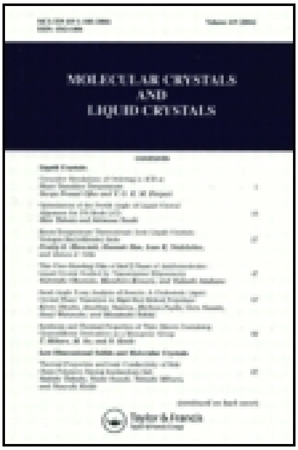

Molecular Crystals and Liquid Crystals

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KINETICS OF PHOTOCURRENT RISE AND DECAY IN MOLECULAR CRYSTALLINE MATERIALS

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Abstract Vapour-grown crystals of tetracyanoquinodimethane showed photocurrents whose rise and decay were first-order processes with lifetimes of 1.1 and 1.2 ms, in good agreement with the value of 1.2 ms deduced from variable-frequency chopped-light measurements. Solution-grown crystals gave longer lifetimes (4.2 ms) and smaller photo- and dark-currents. For lead phthalocyanine single crystals the decay of photocurrent was slower than the rise in vacuum and ammonia but particularly in nitrogen dioxide. Both rise and decay involved at least two first-order processes whose rates increased as the applied field was increased. These observations are discussed in terms of effects of carrier trapping and de-trapping on rise and decay rates respectively. This interpretation is also supported by activation energies which were deduced from temperature dependence of rise and decay rates to be 0.08 eV and 0.22 - 0.28 eV respectively, and by the form and magnitude of transients observed in pulsed-light drift mobility experiments. The importance of these measurements in interpreting the effects of adsorbed gases on electronic processes in molecular crystals is discussed.

INTRODUCTION

Measurements of the rates of rise and decay of photocurrent in molecular crystalline materials are of value not only in assessment of the potential of these materials in applications such as optical sensing and photocopying, where fast response is important, but also as a means of measuring charge-carrier lifetimes. These lifetimes together with the photoconduction quantum yield and the charge-carrier mobility determine the magnitude of photocurrent, and their dependence on temperature, applied field and ambient gas also provide valuable information on the chemical and physical perfection of the material. Carrier lifetimes have been measured as a function of wavelength and temperature in tetracyanoquinodimethane by Eley, Kinnear and Willis[1] using a chopped-light technique developed originally by Ryvkin[2]. Illumination of the sample using equal light and dark periods of varying length (t) produces a signal with oscillations of magnitude $\Delta\sigma_{\sim}$ related to the true steady-state photocurrent $\Delta\sigma_{stat}$ by the equation:

$$\Delta\sigma_{\sim} = \Delta\sigma_{stat} \tanh (t/2\tau) \qquad (1)$$

where τ is the carrier lifetime. This equation may be applied to determined τ from data on $\Delta\sigma_{\sim}$ as a function of t, provided the rise and decay processes both follow first order kinetics with equal rate constants. The applicability of these conditions can be verified by direct measurement of the kinetics of photocurrent rise and decay.

In this paper we report further measurements of rise and decay kinetics and chopped-light photoconductivity which show that in several systems the conditions for equation 1 to be applicable are not satisfied. We also report results of measurements of photocurrent kinetics and pulsed light drift mobility for lead phthalocyanine single crystals in the presence of various gases.

EXPERIMENTAL

Tetracyanoquinodimethane (TCNQ) was purified by entrainer sublimation in a quartz tube previously washed with a solution of TCNQ in acetonitrile, and crystals were grown by a similar method or from solution in acetonitrile. The acetonitrile was neutralised and dried by distillation off TCNQ and molecular sieve under nitrogen and stored over fresh molecular sieve. Lead phthalocyanine was synthesised from phthalonitrile and entrainer sublimed five times under O_2-free nitrogen, with hot and cold zones at 490°C and 410°C respectively. Photocurrent rise and decay kinetics and chopped light data were measured using Keithley 610C and 616 electrometers with a Datalab DL 905 transient recorder. Pulsed light drift mobility experiments used a Chelsea Instruments pulsed Xenon lamp model 3921 with a pulse half width of 2.5 μ sec, illuminating a semitransparent gold electrode on the upper large needle face of the lead phthalocyanine crystal whose thickness was 0.01 cm. The transient pulse was measured using a conventional FET amplifier, type 2N 3819, feeding the transient recorder.

RESULTS AND DISCUSSION

Tetracyanoquinodimethane

This material was studied in order to compare lifetimes derived from analysis of curves of rise to and decay from steady-state photocurrents with those from the chopped light method. Figure 1 shows the action spectra of the

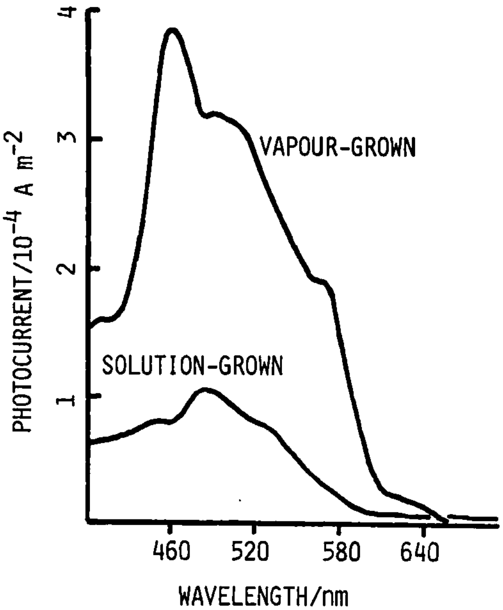

FIGURE 1. Photoconduction action spectra for TCNQ crystals.

steady-state photocurrents for crystals grown by sublimation and from solution. The shapes of the curves are similar for both crystals and from comparison with earlier work from this laboratory[3] they suggest that the crystals are of high purity and perfection since no peaks occur in the region 500 - 600 nm. The magnitude of both photocurrent and dark current is higher for the sublimed crystal than for the solution-grown sample. Figure 2 shows

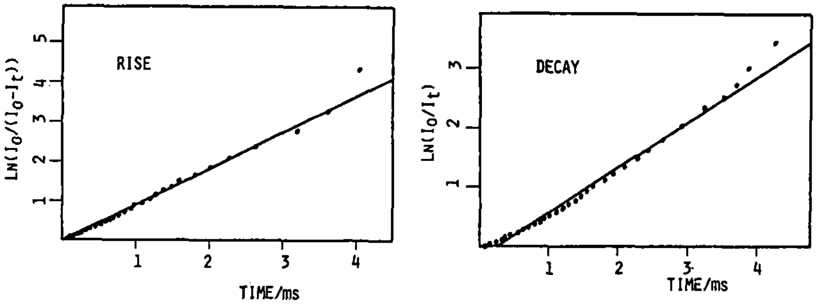

FIGURE 2. First-order plots of photocurrent rise and decay for a vapour-grown TCNQ crystal

the rise and decay of photocurrent using white light for the sublimation-grown crystal fitted to a first-order kinetic equation, yielding lifetimes of 1.1 ± 0.1 and 1.2 ± 0.1 ms respectively. The good fit and close agreement of lifetimes from both rise and decay curves suggest that the processes are both first-order and of very nearly equal rate so that the chopped light method may be applied. Figure 3 shows the chopped light data which give a lifetime of 1.2 ± 0.1 ms for the sublimation-grown crystal, in good agreement with the rise and decay values. The lifetime for the solution grown crystal is significantly longer, 4.2 ± 0.3 ms. These values are slightly shorter than, but not grossly different from the range of 10 - 40 ms reported by Eley, Kinnear and Willis[1]. Since the steady-state photoconductivity, $\Delta\sigma_{stat}$, is related to the carrier generation rate, g, lifetime, τ, and mobility, μ, by the equation:

$$\Delta\sigma_{stat} = g\tau e\mu \qquad (2)$$

the observation of higher (3.6x) photocurrent for the

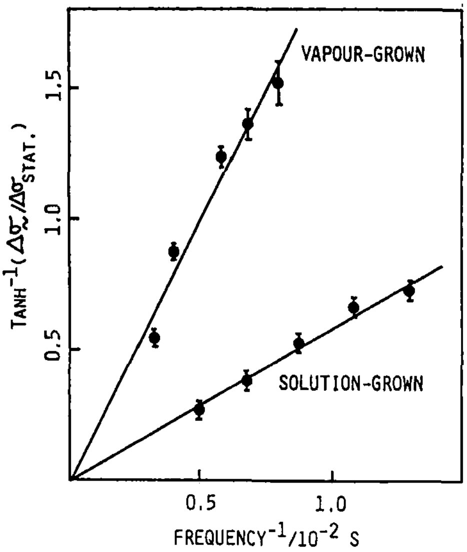

FIGURE 3. Chopped-light data for TCNQ crystals.

crystal with shortest τ implies that this crystal must have a higher carrier generation rate and/or mobility. The higher dark conductivity of this sublimed crystal is consistent with a higher mobility, and the shorter lifetime may also be associated with higher carrier velocity v, since $\tau = 1/vSN_r$, where S is the capture cross section of recombination sites whose density is N_r. However, the differences between these crystals are not large for this class of materials, and as such do not warrant more detailed interpretation.

Lead phthalocyanine

Figure 4 shows the 500 nm photocurrent rise and decay curves for a single crystal of lead phthalocyanine at room temperature in vacuum and at a pressure of 5 x 10^4 Pa NO_2.

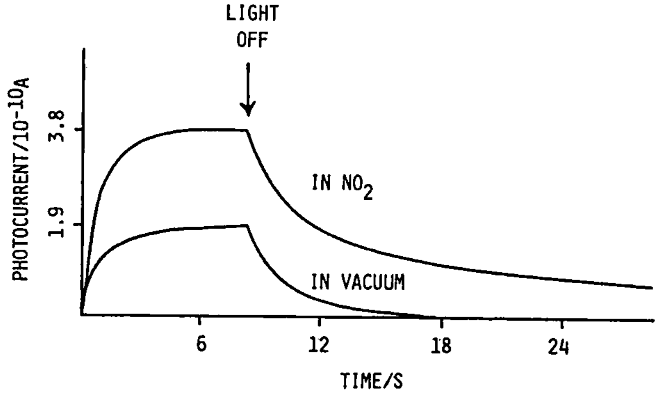

FIGURE 4. Rise and decay of photocurrent for a lead phthalocyanine crystal in vacuum and in NO_2.

In both cases, but especially in NO_2, the decay is clearly slower than the rise, so the Ryvkin equation cannot be applied to interpret chopped light data. We have also found this to be the case for other systems (e.g. perylene/TCNQ, perylene), and this emphasises the importance of verifying equal first-order rise and decay rates before using the chopped light method.

Figure 5 shows attempted first-order plots for typical rise and decay curves for a crystal in 5 x 10^4 Pa NO_2. In this case, the rise kinetics are well represented by a single first-order process while the decay, in addition to being substantially slower than the rise, follows more complex kinetics involving at least two distinct first-order processes with different rates. The same crystal in ammonia (5 x 10^4 Pa) or on evacuation to 10^{-2} Pa following exposure to ammonia showed these more complex kinetics for the rise as well as the decay of photocurrent. Table 1 summarises the dependence on ambient gas and applied field of the characteristic lifetimes for these rise and decay processes.

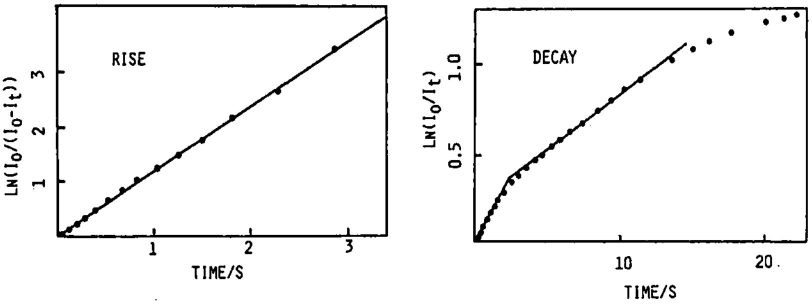

FIGURE 5. First-order plots of photocurrent rise and decay for a lead phthalocyanine crystal in NO_2.

TABLE 1

KINETIC DATA FOR LEAD PHTHALOCYANINE SINGLE CRYSTAL

Conditions	Field ($v.cm^{-1}$)	τ_{rise}/s		τ_{decay}/s	
		1	2	1	2
Vac.(10^{-2} Pa)	300	1.2(1)	2.9(2)	1.6(1)	2.9(1)
	900	0.6(1)	1.0(1)	1.2(1)	2.0(1)
NH_3 ($5x10^4$ Pa)	300	1.0(1)	2.0(1)	1.6(1)	2.3(2)
	900	0.40(5)	0.9(1)	0.7(1)	1.2(1)
NO_2 ($5x10^4$ Pa)	300	0.80(2)	-	6.0(1)	16(2)
	900	0.70(2)	-	3.5(6)	7.8(4)

These data show two consistent reproducible features. The decay rates are slower than the rise rates in all cases, and substantially so in the presence of NO_2, and the rates all become faster when the applied field increases. Both these features may be interpreted in terms of limitation of rise and decay rates by trapping processes. Since equilibrium trap populations increase as the carrier density becomes higher, the dominant process involving traps during photocurrent rise is additional carrier trapping, whereas during photocurrent decay detrapping occurs to attain the final lower trap population. The activation energy associated with trapping is low, whereas for de-trapping it is high. Thus the decay is slower than the rise of photocurrent due to slow release of trapped carriers. Strong coulombic interactions between phthalocyanine and NO_2 at the most active adsorption sites on the crystal surface lead to more pronounced trapping phenomena, and correspondingly slower decay in the presence of NO_2. We have previously invoked these interactions to explain the enhanced magnitude of steady-state photocurrents in phthalocyanine crystals in NO_2[4]. Exciton dissociation involving energy transfer to strongly-bound phthalocyanine$^+$ NO_2^- ion pairs provides an effective surface charge-carrier generation mechanism, hence increasing the photocurrent. The present results suggest that this increased photocurrent is partly the result of slower carrier decay rates in addition to the faster generation rate. The effect of increasing the applied field can also be interpreted in terms of field-assisted ionisation of trapped charge carriers via lowering of the coulombic barrier of the trap in the down-field direction (the Poole-Frenkel effect)[5]. This lowering of the barrier not only leads to increased current but also to a more rapid equilibration of traps with carriers and hence a more rapid response of photocurrent at high fields.

The role of adsorbed NO_2 in carrier trapping is also reflected in data we have obtained on the temperature dependence of photocurrent rise and decay rates and on the shapes of charge carrier transients produced by pulsed light excitation in drift-mobility experiments. Figure 6 shows the temperature dependence of rise and decay rates in

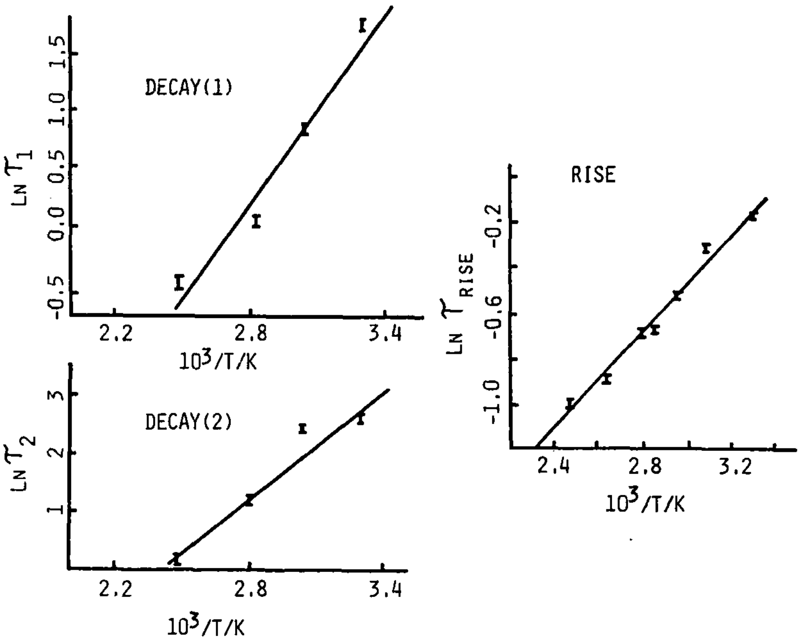

FIGURE 6. Temperature dependence of characteristic lifetimes from rise and decay of photocurrent for a lead phthalocyanine crystal in NO_2.

NO_2. The activation energies associated with the decay (0.22 and 0.28 ± 0.05 eV for the two characteristic decay processes) are significantly higher than that for the rise (0.08 ± .01 eV) reflecting the higher activation energy for de-trapping. Figure 7 shows the photocurrent transients for the single crystal of lead phthalocyanine in a vacuum

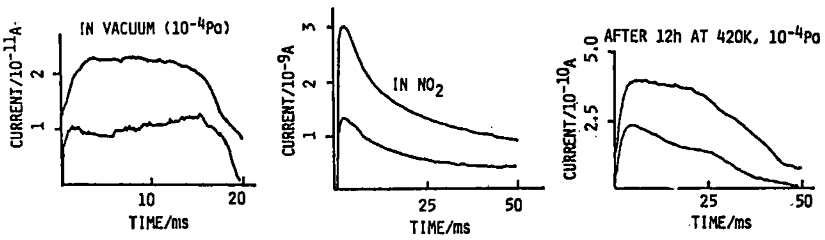

FIGURE 7. Drift mobility transients for a lead phthalocyanine crystal in vacuum, in NO_2 and after removal of NO_2 and heating to 420K for 12h. at 10^{-4} Pa. (Applied fields 1000 and 2000 v.cm^{-1}.)

of 10^{-4} Pa, exposed to NO_2 and finally after baking at 420 K in 10^{-4} Pa for 12 hours. The weak but well-defined hole transients in vacuum become much larger in NO_2 and trapping is so severe that no clear transit time can be identified. After removal of most of the NO_2 by baking in vacuum, the transients recover some of their original character, with some gradual decline in magnitude due to trapping as the charge sheet moves through the crystal[6] but nevertheless a clearly observable transit time. The final pulse magnitude (still approximately 20 x higher than the original value), together with the observation of trapping from the form of the transient curves, confirms that baking under these conditions does not remove all the NO_2 species from the surface. This was also deduced earlier from observations of the magnitude and action spectrum of the steady-state photocurrent[4]. From the observed transit times and the known sample thickness and applied field the hole drift mobility can be calculated to be 6×10^{-4} cm^2/v.s. for the sample in vacuum and 4×10^{-4} cm^2/v.s. after exposure to NO_2 and then baking in vacuum. Repeating the measurements with reversed polarity showed very similar values for electron transients. These values are much smaller than those reported by Cox and Knight[7] for metal-free phthalocyanine, although they also reported that the mobilities of holes and electrons were nearly equal (1.1 and 1.2 cm^2 v^{-1} s^{-1} respectively). The origin of the low mobility in lead phthalocyanine is not clear. Westgate and Warfield[8] reported transients on lead phthalocyanine crystals severely limited by trapping, in contrast to our data. Our measurements are on crystals of the triclinic modification of lead phthalocyanine[9] and one possible interpretation of the apparent low mobility is that it reflects poor overlap between the non-planar lead phthalocyanine molecules in this triclinic lattice. Further experiments measuring temperature dependence are planned, to provide more information on this unusually low mobility.

The natures of the processes leading to the two different rate constants in both the rise and decay data in Table 1 are also not yet clear. Although the lead phthalocyanine crystal was of high quality and prepared from material five times entrainer sublimed in oxygen-free nitrogen, previous studies of the temperature dependence of semiconduction[10] revealed magnitudes of conduction and its activation energy which are inconsistent with intrinsic processes. Since we know of no means to purify the material further, it is concluded that the rise and decay kinetics are subject to the influence of the unknown remaining impurities. Although there may be more than two separate processes for both the rise and the decay of photocurrent, the absence of information on the nature and distribution of impurities in the crystal prevents detailed theoretical modelling and renders more complex deconvolution of the kinetic data not worthwhile.

CONCLUSIONS

This work shows that study of the kinetics of photocurrent rise and decay can provide valuable information on crystal quality and on the effects of adsorbed gases on electronic processes in molecular crystals. These kinetics are frequently complex so that simple chopped-light experiments for carrier lifetime determination are not possible. Although inherent impurities in lead phthalocyanine prevent detailed interpretation of these kinetics, the observed dependence of the rates and drift mobility data on ambient gas and applied field have provided useful information on the interactions beteen lead phthalocyanine and gases. In view of the promise of this and related materials in gas detection and the very limited information available from other techniques on the nature of these interactions, these experiments could usefully be extended to other related materials.

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