

PHOTOCONDUCTION OF MIXED ORGANIC CRYSTALS OF NAPHTHALENE DOPED WITH ANTHRACENE IMPURITY

MUHAMMAD SALEH and AHMED TAHIR NAVEED

Department of Physics, Bahauddin Zakariya University, Multan, Pakistan

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Mixed organic crystals of naphthalene doped with varying concentrations of anthracene impurity were grown from the melt, following extensive purification efforts in specially designed crystal growing tubes. Such crystals grow with the plane of maximum growth corresponding to the «ab» crystallographic plane, and cleave readily in this plane. A simple technique for determining impurity concentration \sim ppm along the said mixed crystals is described in detail. The spectral response of photoconduction of mixed organic crystals of naphthalene doped with anthracene impurity \sim 1 ppm is divided into two regions. The one at 350 nm is similar to that of anthracene and the photocarrier generation is related with the weak $n-\pi^*$ transition of the anthracene impurity in the said crystals and the polarity for radiations which induce $\pi-\pi^*$ excitations in the wavelength region of 200 nm to 320 nm. In $\pi-\pi^*$ excitation region, the photocurrent with the illuminated electrode positive is much larger than that with the illuminated electrode negative.

1. Introduction

Crystals containing small amounts of certain «impurities» in solid solution, for example anthracene with a few parts per thousand of naphthalene may be grown by the Bridgman method¹⁾. In such crystals the fluorescence is characteristic of the impurity rather than of the host compound as a result of the transfer

of excitation energy²⁾. The starting material for these crystals consists of a mixture of host and impurity weighed out in the required proportions, rather than a single material. It should be noted that the impurity concentration of the finished crystal is not necessarily the same as that of the original materials^{3,4)}. The final concentration may readily be determined, however, by preparing a solution in ethylalcohol of a portion of the finished crystal and comparing the absorption spectrum of this solution with the spectrum of a similar solution made up from known amounts of the materials⁴⁾.

The work reported here is aimed at studying the photoconduction of »home-grown« mixed organic crystals of naphthalene doped with known concentrations ~ 1 ppm of anthracene impurity (Sec. 2.2.5) and to examine a relation of the spectral response between photoconduction and optical absorption (Sec. 3, 4 & 5).

2. Experimental

2.1. »Home-grown« mixed organic crystals

Mixed organic crystals of naphthalene doped with varying concentrations (200 ppm—400 ppm) of anthracene impurity were grown from the melt following extensive purification efforts including adsorption column chromatography, sublimation and zone-refining in specially designed crystal growing tubes⁴⁻⁶⁾. However, the impurity concentration of the finished crystal was not the same as that of the original materials (Sec. 2.2.5). Such crystals grow with the plane of maximum growth corresponding to the »ab« crystallographic plane and cleave readily in this plane⁴⁾.

2.2. Impurity concentration in home-grown mixed organic crystals

2.2.1. Basis of experiment

The procedure adopted for the measurement of impurity concentration along the length of the mixed organic crystals was to measure extinction coefficient ϵ from the calibration graph of absorbance A versus concentration c at λ_{max} (Sec. 2.2.3), and hence to estimate the impurity concentration in the mixed organic crystals using the Beer's law (Sec. 2.2.4). The instrument employed for the above said experimental work was UV-visible spectrophotometer type Lambda 3B, Perkin-Elmer, U. S. A.

2.2.2 Selection of suitable range of wavelengths

Small quantities of pure anthracene and naphthalene (say, a fraction of mg) were separately dissolved in 50 ml ethylalcohol solvent (C_2H_5OH) and then spectra for the said solutions in the range 200 nm to 400 nm were recorded using UV-visible spectrophotometer (Fig. 2.1). Absorbance peaks for naphthalene solution were observed in the range 200—320 nm while for the anthracene solution absorbance peaks in the range 270—380 nm were noticed. The range 320—380 nm free from naphthalene absorbance peak was, therefore, selected to find out λ_{max} for known concentration of anthracene stock solution (Sec. 2.2.3).

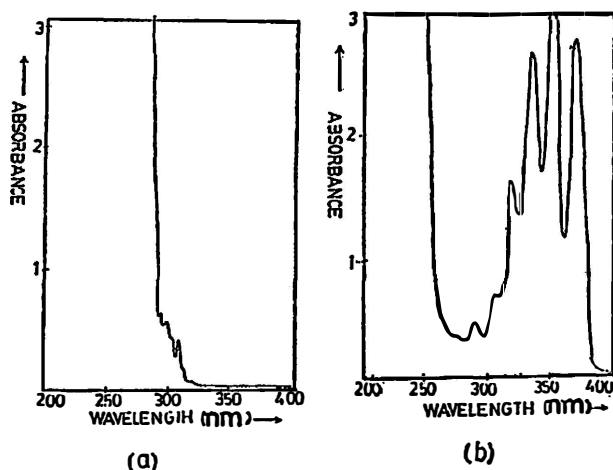


Fig. 2.1. Variation of absorbance with wavelength

(a) For naphthalene

(b) For anthracene.

2.2.3 Selection of λ_{max}

Spectrum in the selected range (324—380 nm) for anthracene stock solution concentration ~ 0.25 mg/ml was observed with the help of UV-visible spectrophotometer (Fig. 2.2) and wavelength 3549 nm corresponding to the maximum absorbance, that is, 3.2 was designated as λ_{max} (Table 1).

TABLE 1.

Absorbance A	Wavelength λ' (nm)
3.14	3737
3.20	3549
3.08	3357
2.81	3215
1.76	3075
1.16	2917

Variation of anthracene absorbance against different values of wavelengths.

2.2.4 Determination of extinction coefficient

Anthracene stock solution concentration ~ 0.25 mg/ml (Sec. 2.2.3) was further diluted using the solvent ethylalcohol and five different grades of solution having concentrations varying from 0.005 mg/ml to 0.025 mg/ml were prepared. The absorbance for each grade of solution corresponding to the selected wavelength,

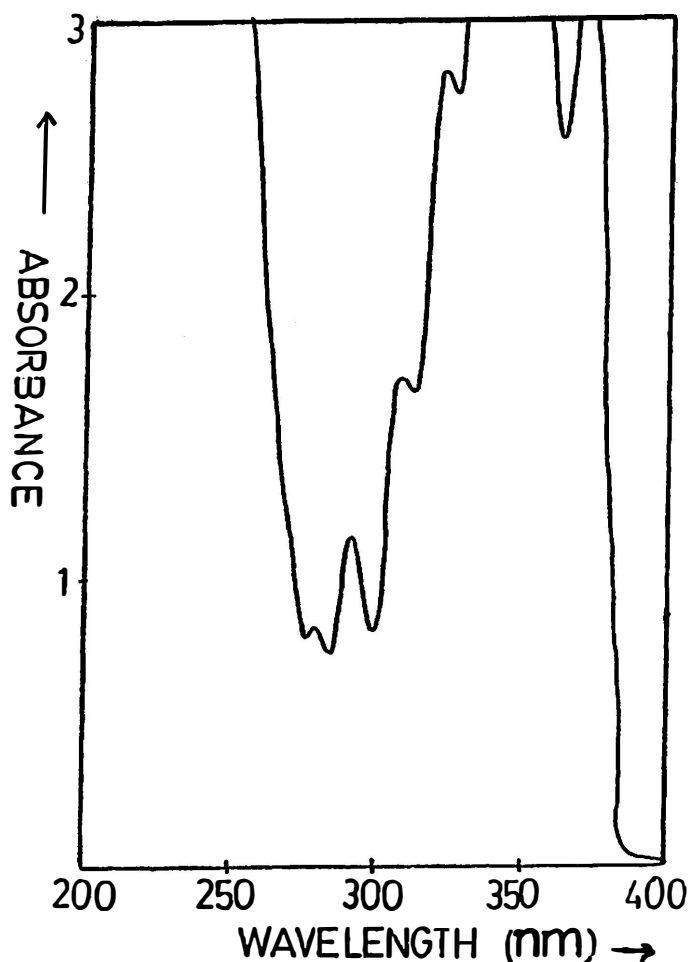


Fig. 2.2. Plot of absorbance versus wavelength for anthracene stock solution.

i. e., λ_{max} was observed (Table 2). The value of the extinction coefficient ϵ was then calculated from the slope of the calibration graph (Fig. 2.3) of absorbance versus concentration and was found to be 39.56 ml/mg.

2.2.5 Estimation of impurity concentration in «home-grown» mixed organic crystals

Specimens from extreme and middle portions of «home-grown» mixed organic crystals were taken, weighed and dissolved in 50 ml of ethylalcohol to prepare solutions with concentration 0.1 mg/ml. The absorbance at λ_{max} for each solution was then recorded with the help of UV-visible spectrophotometer (Table 3) to find out anthracene impurity concentration at different portions of the mixed organic crystal using the Beer's law and from the known value of the extinction coefficient ϵ (Sec. 2.2.4).

TABLE 2.

c (mg/ml)	A
0.005	0.144
0.010	0.442
0.015	0.605
0.020	0.790
0.025	0.981

Variation of anthracene absorbance against different values of concentrations of anthracene impurity in ethylalcohol at $\lambda_{max} = 354.9$ nm.

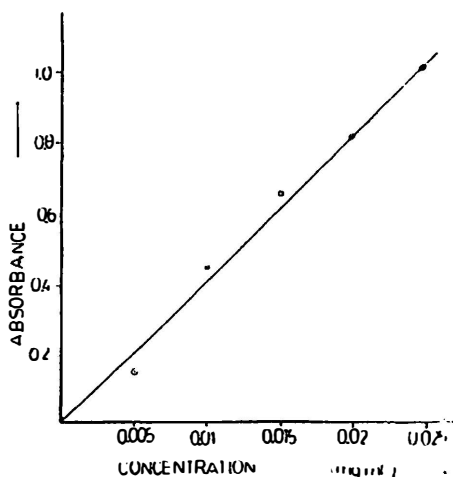


Fig. 2.3. Calibration graph between absorbance and impurity concentration at $\lambda_{max} = 354.9$ nm

TABLE 3.

Position of ingot from the lower end	A	c (ppm)
Lower (0—0.02 m)	0.040	1.011—0.9
Middle (2—0.04 m)	0.035	0.885—0.95
Upper (4—0.06 m)	0.042	0.95 —1.062

Variation of anthracene impurity distribution along the length of the »home-grown« mixed organic crystal ingot.

The graph between impurity concentration versus distance in the ingot (Fig. 2.4) clearly shows that the extreme portions of such mixed organic crystals have the maximum anthracene impurity concentration whereas the middle portion has the minimum anthracene impurity concentration.

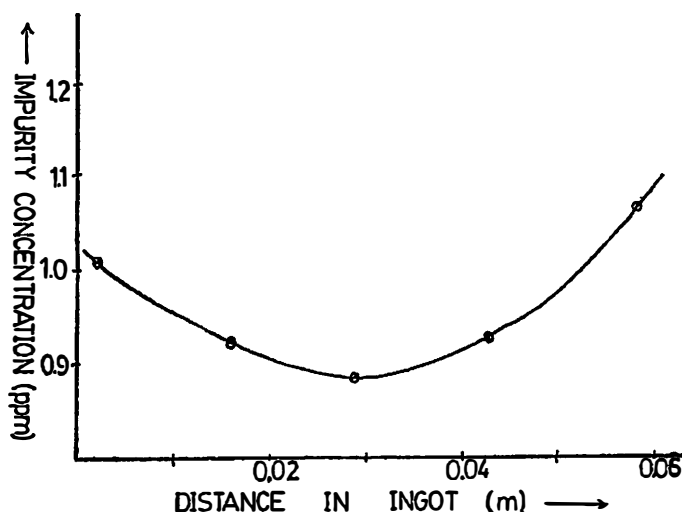


Fig. 2.4. Distribution of impurity concentration in «home-grown» mixed organic crystals.

2.3 Preparation of specimens and photoconduction

The growth vessel was cut open to tip out the ingot and the plates cleaved from the crystal boule had surfaces of about 5 mm × 5 mm, which were «ab» planes and thickness varying between 0.5 and 0.95 mm. Such crystals have anthracene impurity concentration ~ 1 ppm (Sec. 2.2.5). The crystal specimens were equipped with semi-transparent silver coated electrodes on two opposite faces and were also provided with a ring of «aquadag» paint to provide more durable contacts. Such layers were estimated to be about 15 nm thick. The specimen was mounted behind an aperture of 1–2 mm in diameter in the copper lid of the specimen chamber⁷⁾ and irradiated with monochromated light from a UV-visible spectrophotometer, type Lambda 3B, Perkin-Elmer, U. S. A. at various wavelengths, lying in the spectral range 200 nm to 400 nm. Different voltages were applied between the two electrodes, using a stabilized power supply. Photoconduction current at room temperature was measured with a measuring amplifier type 53201 from Leybold-Heraeus Company, Germany. The detailed measurement for the anisotropy of the photoconductivity has not been performed.

3. Results

Photoconduction current for specimen No. 11.05 (representative of a group of specimens), having anthracene impurity concentration ~ 7 ppm was measured

for applied bias fields from 1.6 kVcm^{-1} to 2.9 kVcm^{-1} between silver electrodes, at wavelengths lying in the spectral range 200 nm to 400 nm. The photoconduction current was normalized, i. e., photoconduction current per unit radiant flux incident on the specimen at a particular wavelength was calculated. The normalized current was plotted against photon energy (see comparison with wavelength) and the results are presented in Fig. 3.1. The peaks of photocurrent are located at about 350 nm in the photoconduction current distribution curves and with the illuminated electrode at a negative potential with respect to the collecting electrode (electrons collected at the back electrode) the photo-current is smaller (Fig. 3.1) than that of illuminated electrode positive with respect to the collecting electrode (holes collected at the back electrode). This is the same characteristic compared with that of anthracene.

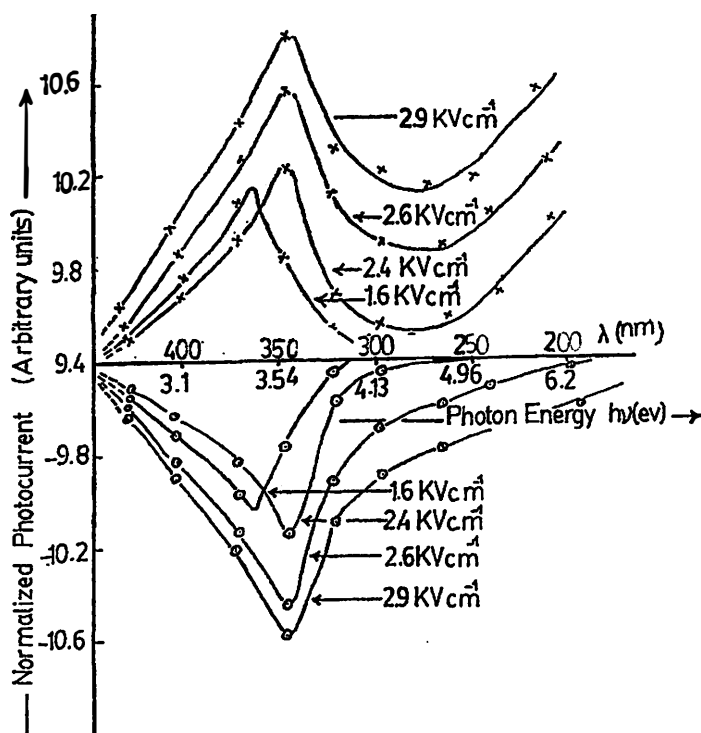


Fig. 3.1. Spectral response curves, i. e., normalized photocurrent in arbitrary units versus photon energy for specimen No. 11.05, thickness $950 \mu\text{m}$, and impurity concentration $\sim 1 \text{ ppm}$.

The variation of absorbance in the wavelength region 200 nm—400 nm for naphthalene solution in ethylalcohol and for anthracene solution in ethylalcohol is given in Fig. 2.1. The peaks observed in the case of naphthalene and anthracene in the wavelength region over 200 nm—320 nm (Fig. 2.1a) correspond to π - π^* excitation with splitting owing to molecular vibrations⁸⁾. Moreover, the peaks are observed in the wavelength region 350 nm—400 nm for anthracene alone which correspond to n - π^* transition (Fig. 2.1b). The spectral response of the photocurrent

is not sharp (Fig. 3.1) as to distinguish the each corresponding peak in optical absorption. It can be roughly classified to those corresponding to π - π^* transition and n - π^* transition.

For the excitation corresponding to the n - π^* transition, the polarity of the applied voltage does not have any influence. In this case owing to the weak optical absorption, the excitations reach as far as the deep interior of the crystal. Therefore, the carrier injection at the surface does not disturb the photo-carrier generation as in the case of the π - π^* transition for which the optical absorption is very strong.

4. Discussions

It may be instructive to compare the photoresponse of «home-grown» mixed organic crystals (naphthalene ($C_{10}H_8$) doped with anthracene ($C_{14}H_{10}$) impurity) with that of anthracene crystals, because both crystals are composed of similar molecules belonging to the monoclinic crystal system with two molecules in a unit cell. Therefore, it is supposed naturally that the photo-response of both crystals may also be similar. If there exist some differences in the response, they must be intimately related with the difference of the molecular structures⁴⁾. To examine how the different bonding atoms contribute to the difference in the photo-response is the main purpose of this study. In the case of anthracene crystals, most of the charge carriers are generated by the excitation to $^1B_{2u}$ and $^1B_{3u}$ states from the ground state of 1A_g . However, the correlation between the optical excitation and the charge carrier generation has not been completely explained yet. This is a most concerned problem in anthracene crystals.

In «home-grown» mixed organic crystals, the carriers are generated under the illumination belonging to two wavelength regions, at 350 nm and a region extending towards the shorter wavelength than about 350 nm. The carrier generation in the latter wavelength region corresponds to those observed in anthracene and naphthalene in the range from 200 nm to 320 nm ($^1B_{3u}$). For mixed organic crystals it is a region of very strong optical absorption with absorption coefficient from several thousands to several ten thousands per cm, and produced by the π - π^* excitation transition of the molecules. In this wavelength region, most of the exciting radiation is absorbed at first near the surface of the crystal. Free carriers are then produced and sent into the crystal. Therefore, the charge carrier generation would be much susceptible to influences from the conditions of the interface both for the carrier injection and space charge barrier formation. As is seen from Fig. 3.1 the large discrepancy of the photocurrent to the same bias field appears depending upon the polarity of the voltage applied on the electrode on which the exciting radiation falls.

For anthracene, the photocurrent in which the illuminated electrode is positively polarized is generally larger than the reverse case⁹⁾. This is explained to be that the hole injection is the more dominant process of the carrier generation than the electron injection at the metal-semiconductor interface under illumination¹⁰⁾. In the case of the mixed organic crystals, the hole injection was also found to be more dominant than the electron injection under illumination and makes an important contribution for photo-generation of the free carriers (Fig. 3.1).

The photocurrent observed in the wavelength region extending towards the longer wavelength than about 350 nm is shown in Fig. 3.1 and is clearly correlated with the $n-\pi^*$ excitation (1B_u) of the anthracene molecule. The optical absorption in this wavelength region is weak with the coefficient of about several tens per cm. Therefore, most of the exciting radiation is absorbed in the interior of the crystal and charge carriers are generated without any surface effect. It is clearly shown in Fig. 3.1 where nearly the same amount of photocurrent is observed for both polarity of the electrode. From this it is known at once that the free carriers are generated by $n-\pi^*$ excitation in the crystal. However, this does not tell us that the energy gap between the electron conduction band and hole conduction band is 3.0 eV, as there exists possibility that the multi-exciton process may be operating for free carrier generation. As we have not made detailed measurement for this excitation region, we cannot discuss so far as the multi-exciton process now. However, the detailed study of the contribution of this excitation to carrier generation may lead to an important information for the study of the mechanism of charge carrier generation in mixed organic materials as it belongs to the weak absorption and we can confine the discussion to the bulk generation only.

5. Conclusions

Mixed organic crystals of naphthalene doped with anthracene impurity have been successfully grown from the melt following extensive purification efforts including adsorption column chromatography, sublimation, and zone-refining in specially designed crystal growing tubes. Such crystals grow with the plane of maximum growth corresponding to the ab crystallographic plane, and cleave readily in this plane. It was experimentally found that the impurity concentration at the extreme portions of the crystal boule was much higher than in the middle portion of the ingot. This could be the result of difference in the segregation coefficients of the host material and the impurity as well as the difference in the size and shape of the molecules of the mixed organic crystals.

The spectral response of photoconduction of mixed organic crystals of naphthalene doped with anthracene impurity ~ 1 ppm is divided into two regions. The one is similar to that of anthracene and naphthalene. The photo-carrier generation is related with the strong $\pi-\pi^*$ transition of both naphthalene and anthracene molecules. In this case, the photocurrent with the illuminated electrode positive is much larger than that with the illuminated electrode negative and, therefore, the excess hole injection makes an important contribution for photo-generation of the free carriers. However, the photo-carrier generation in the other region is related with the weak $n-\pi^*$ transition of anthracene alone and the carrier injection at the surface does not disturb the photo-carrier generation for both polarity of the electrode. Further study of this second region may bring a clue to the elucidation of the carrier generation mechanism in mixed organic crystals.

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FOTOVODLJIVOST MIJEŠANIH ORGANSKIH KRISTALA NAFTALENA DOPIRANIH PRIMJESAMA ANTRACENA

MUHAMMAD SALEH i AHMED TAHIR NAVEED

Department of Physics, Bahauddin Zakariya University, Multan, Pakistan

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Miješani organski kristali naftalena dopirani antracenom u različitim koncentracijama, dobiveni su rastom iz taljevine u specijalno konstruiranim cijevima za rast kristala. Određivanje koncentracije primjese izvršeno je jednostavnom metodom u granicama ppm, koja je detaljno opisana. Spektralni odziv fotovodljivosti miješanih organskih kristala podijeljen je u dvije regije. Prva spektralna regija na 350 nm izaziva generaciju fotonosioca u slabom $n-\pi^*$ prijelazu primjese antracena. Druga spektralna regija u intervalu od 200 nm do 320 nm izaziva generaciju fotonosioca u induciranim $\pi-\pi^*$ prijelazima.