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Electroluminescence in Pentacene Doped Anthracene Crystals

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The recombination radiation spectrum and its transient behavior were measured on a pentacene doped anthracene crystal. The recombination radiation spectrum was more sensitive to chemical or physical impurities than optically sensitized fluorescence spectrum. The intensity of both anthracene and pentacene emission was approximately proportional to the current. Anthracene or pentacene emission was found to consist of three components differing by their decay times; component 1 (decay time $<10^{-5}$ s), components 2,3 (decay times in the millisecond region, $\tau_2<\tau_3$). The component 1 was due to singlet excitons generated directly by carrier recombination. The component 2, the decay time of which was 2—3 ms, was due to triplet exciton annihilation, for its decay time was not affected by a reverse bias voltage and was equal to one half of the observed phosphorescence lifetime. The component 3, which was removed by a reverse bias voltage, was due to detrapped-trapped carrier recombination. Pentacene chemical impurity works as carrier traps or tirplet exciton traps. Anthracene lattice defects work as carrier traps. The SCLC measurement showed the existence of an electron discrete trap introduced by pentacene and electron and hole exponential traps. The present experimental results showed het importance of traps in the recombination process in a mixed crystal.

For several years electrochemical electrodes have been used to produce electroluminescence in anthracene crystals from the recombination of the injected electrons and holes.[1,2] For pure crystals the electroluminescence

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1) W. Helfrich and W. G. Schneider, *Phys. Rev. Lett.*, **14**, 229 (1965).

2) W. Helfrich and W. G. Schneider, *J. Chem. Phys.*, **44**, 2902 (1966).

spectra and fluorescence spectra are the same if it is recognized that reabsorption may be more prominent in electroluminescence, since this is produced in the bulk of the crystal. However, electroluminescence can easily be modified in intensity and energy distribution by doping the crystal with any materials which will act as a carrier trap.[3,4] It has been seen that the bulk properties of a molecular crystal are easily perturbed by included molecules. The traps caused by the guest are more evident in the spectral distribution of electroluminescence than in that of optically sensitized fluorescence. As electron-hole recombination events finally produce singlet and triplet excitons, it is expected that electroluminescence will show a time behavior relating to the lifetime of these excitons, 10^{-8} and 10^{-3} s respectively.[2] It should be, however, born in mind that the transient behavior of the singlet exciton is not usually detected because of the slower rate-determining steps (carrier recombination) involved. The traps will change the temporal dependence of electroluminescence, particularly that due to the long lived triplet exciton. We have studied the electroluminescence of a pentacene doped anthracene crystal to see the influence of the traps on the recombination radiation of a mixed crystal. We measured the temperature dependence of Space-Charge-Limited-Currents (SCLC) to get insight into the distribution of the traps in the crystal and steady state electroluminescence. The temporal dependence of anthracene and pentacene emission was measured to study the growth reaction of electroluminescence.

Experimental

The crystal ingot was melt grown in a Bridgeman type furnace[5] under helium gas from highly purified anthracene containing 10^{-4} M pentacene (Princeton Organics). Single crystals, 1 mm thick, were cleaved parallel to ab plane from the bottom portion of the ingot where pentacene concentration was thought to be 10^{-6} M considering the segregation coefficient. Neither the sensitized fluorescence nor the absorption of pentacene was observed in the conventional way with the crystal used in the work. Electron and holes were injected along the c′-direction, *i.e.*, perpendicular to the cleavage plane. The electrode contact area was $0.44\ \mathrm{cm}^2$. Solution of anthracene ions were used as injecting contacts.[1,2] (*i.e.*, Na-anthracene ion salt in tetrahydrofuran as an electron injecting electrode and anthracene-$AlCl_3$ in CH_2Cl_2 as a hole injecting electrode). The crystal temperature was varied by blowing cold nitrogen gas over the crystal held in a quartz Dewar system. Steady state measurements of the current-voltage (J-V) dependence, electroluminescence intensity-current (I-J) dependence and electroluminescence spectral distribution-current dependence were made over the temperature range from 200 to 300 K. Using a pulsed voltage supply the transient behavior of anthracene and pentacene electroluminescence was observed. The experimental apparatus for the pulsed voltage measurement is shown in Fig. 1. Each wavelength region was selected by combining appropriate band pass filters Optics Technology 550R, 600R and Corning glass 2-63, for pentacene and O-T 500B plus Corning glass 5-57, 5-64 and 5-61 for anthracene. The pulsed voltage supply used was capable of producing a square voltage pulse of 4000 V for up to 120 ms duration with rise and decay times of $<10^{-5}$ s/kV. A cooled EMI 9558 photomultiplier used as a detector was coupled with a time averaging computer to increase signal/noise ratio when required. As the number of the traps depends on the concentration of pentacene, experimental data were produced all at the same crystal platelet.

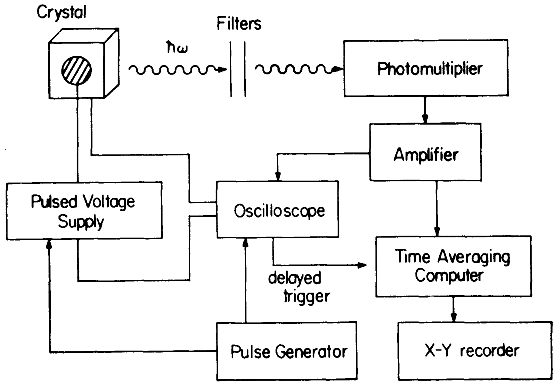

Fig. 1. Experimental apparatus for pulsed voltage measurement.

Results and Discussion

(a) The Temperature Dependence of Space Charge Limited Current (SCLC). As expected, steady state space charge limited hole and electron current-voltage-temperature curves all showed the presence of considerable trapping. At room temperature currents were 10^4—10^6 times smaller than predicted trap free currents.[6] The

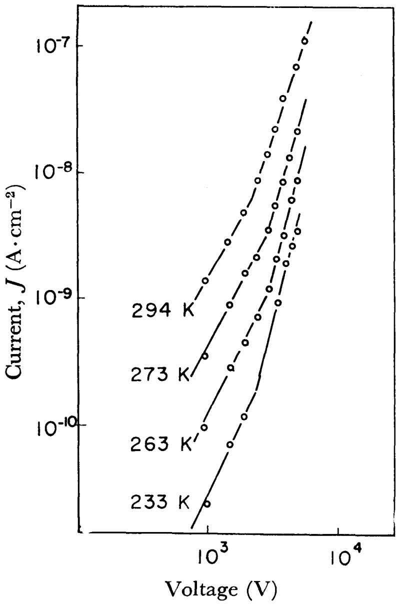

Fig. 2. Dependence of space-charge-limited currents with temperature and applied voltage for a 1 mm thick pentacene doped anthracene crystal. The electrode contact area was $0.44\ \mathrm{cm}^2$.

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3) H. P. Schwob, J. Funfschilling, and I. Zschokke-Granacher, *Mol. Cryst. Liq. Cryst.*, **10**, 39 (1970).

4) H. P. Schwob and I. Zchokke-Granacher, *ibid.*, **13**, 115(1971).

5) Y. Lupien, J. O. Williams, and D. F. Williams, *ibid.*, **18**, 129 (1972).

6) M. A. Lampert, *Rept. Progr. Phys.*, **27**, 329 (1964).

results for injected electron currents are shown in Fig. 2. In the low voltage region the electron currents were proportional to the square of the voltage, while at higher voltage they increased with fourth power of the voltage. These results indicate the presence of an exponential energy distribution of electron traps plus a discrete trap. From the temperature dependence of the currents in the low voltage quadratic region, we obtained the depth of an electron discrete trap, 0.44 eV. Here the temperature dependence of the carrier mobility was neglected since it has only minor effects. This depth agrees with the electron trap depth estimated from the difference in electron affinities of anthracene and pentacene, $1.341-0.653=0.7$ eV.[7] Similarly an estimation of a hole trap at 0.6 eV[8] can be made from the respective ionization energies, however the experimental results of hole currents-voltage-temperature dependence only showed the presence of exponential traps. The electron and hole exponential traps are considered to be due to structural defects caused by the inclusion of pentacene molecules.[9]

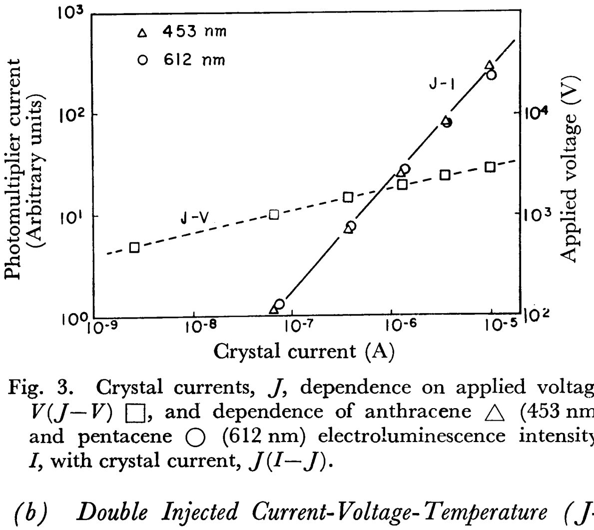

Fig. 3. Crystal currents, J, dependence on applied voltage $V(J-V)$ □, and dependence of anthracene △ (453 nm) and pentacene ○ (612 nm) electroluminescence intensity, I, with crystal current, $J(I-J)$.

(b) Double Injected Current-Voltage-Temperature (J-V-T) Dependence. The relation between the currents and applied voltage (J-V) at room temperature is shown in Fig. 3. $J\propto V^{4.4}$ was found in the crystal. The double injected current was always greater than that observed for single carrier injection, but was still in the order of 10^2—10^4 times smaller than predicted by Child's law (trap free). The current decreased exponentially with respect to T^{-1} over the temperature range 200—300 K, as observed in pure anthracene crystal.[10]

(c) Crystal Current-Electroluminescence Intensity and Spectral Distribution Dependence. The electroluminescence spectra at various temperatures are shown in Fig. 4. The optically excited (anthracene singlet) fluorescence spectrum of the same crystal comes from anthracene only. The 0-0, 0-1 bands of anthracene fluorescence were reabsorbed in both the electroluminescence and the fluorescence spectra. In the electroluminescence spectra, components due to anthracene 453 and 480 nm and those due to pentacene, 612 and 668 nm are easily recognized. The emission peak at 612 nm is the 0-0 level of the first excited singlet state of pentacene, in agreement with an analysis obtained from high resolution fluorescence spectra of pentacene.[11,12] As the crystal currents decreased or the temperature was lowered to 213 K, little change in relative intensity of the pentacene peaks occurred, and no additional peaks appeared in the pentacene fluorescence regions. As the temperature was lowered, the 0-1 band of anthracene singlet emission became visible, together with a broad background emission, maximum 480 nm. The appearance of the background emission indicates that the anthracene lattice has been considerably perturbed, as observed in SCLC measurement and structural defects work as carrier traps at low temperature. If this background emission is substracted, the ratio of anthracene emission: pentacene one decreased as the temperature was lowered. This suggests that pentacene trap becomes prominent at lower tem perature. The fact that chemical impurity, pentacene is more evident in electroluminescence than in the optically sensitized fluoresceyce shows that pentacene electroluminescence is not due to the energy transfer from anthracene singlet. At room temperature both anthracene (453 nm) and pentacene (612 nm) electroluminescence intensity increased approximately linearly with the crystal current as shown in Fig. 3. These results are different from anthracene-tetracene system.[3,4]

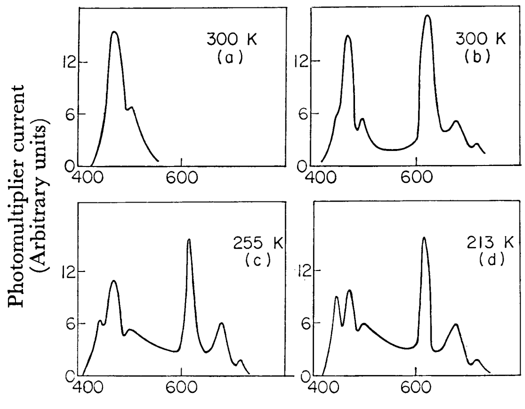

Fig. 4. Comparison of optically sensitized fluorescence spectrum at room temperature (a) and electroluminescence spectra at 300, 255, 213 K (b), (c), (d). The current density was 2.5×10^{-7} A·cm^{-2}.

(d) Transient Behavior of Electroluminescence. The transient behavior of both the crystal current and pentacene emission under 2000 V pulsed voltage is shown in Fig. 5. General behavior of the transient current was similar to that obtained for pure anthracene crystals.[2] The anthracene emission behaves similarly

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7) M. J. S. Dewar, J. A. Hashmall, and N. Trinajstic, *J. Amer. Chem. Soc.*, **92**, 5555 (1970).

8) F. Gutmann and L. E. Lyons, "Organic Semiconductors," Wiley, New York (1967).

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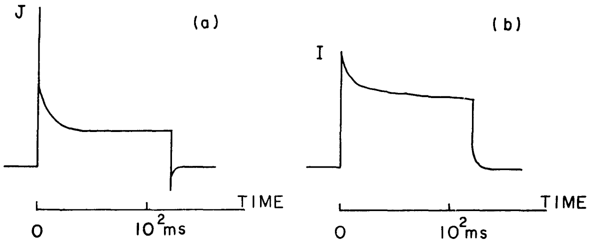

Fig. 5. Transient behavior of crystal current (a) and pentacene electroluminescence (b) under 2000 V.

to that of pentacene. The pulsed voltage was varied from 1000 to 3000 V. Though the voltage pulse decay was less than 10^{-5} s/kV, a considerable tail was observed in both anthracene and pentacene electroluminescence, with a decay time in the millisecond region. Both the anthracene and pentacene emission consist of the prompt decay component (component 1, the decay time $<10^{-5}$ s) and the delayed ones (component 2 and 3, their decay times in the millisecond region). The prompt electroluminescence emanating from both the guest and host is thought due to the singlet exciton produced by the carrier recombination like the pure anthracene crystals.[1,2] The prompt pentacene emission is thought due to the recombination in a pentacene trap, considering the SCLC experimental result. The ratio of the delayed: prompt electroluminescence intensity increased as the voltage was lowered and the current decreased, as shown in Table 1. The transient behavior of the delayed pentacene eimssion is shown in Fig. 6. Two components with different decay times (component 2; 2—3 ms, component 3; 10 ms) are found. Anthracene delayed electroluminescence shows the similar behavior (component 2; 2—3 ms, component 3; 5—6 ms). The component 3 of both anthracene and pentacene emission was removed by applying a reverse bias voltage (500—1500 V), and was considered due to detrapped-trapped carrier recombination. The contribution from component 3 to the total delayed emission increased as the voltage was lowered. Under 3000 V, the component 3 was not observed. The existence of component 3 in anthracene emission indicates that anthracene structural defects work as carrier traps, as observed in SCLC measurement and electroluminescence spectra. The decay time of component 2 was obtained by substracting component 3 or applying a reverse bias voltage. The component 2 is thought to be produced by triplet-triplet annihilation because it was not affected by a reverse bias voltage. The lifetime of anthracene triplet excitons was measured to check the above conclusion. Optical excitation of anthracene triplet by a He-Ne laser (50 mW, 6328 Å) gave red delayed luminescence, the decay time of which was 5.2 ms. In the above measurement a photomultiplier was coupled with a time averaging computer because the emission intensity was very weak. No blue delayed emission was observed in the crystal in a similar experimental condition. The red delayed emission is either phosphorescence of anthracene or delayed fluorescence of pentacene. As the emission intensity was linear with the excitation light intensity, we can regard it as anthracene phosphorescence. The measured anthracene triplet lifetime, 5.2 ms, is comparable with that obtained from the delayed fluorescence excited by a giant ruby laser in an anthracene crystal which contains 2 ppm pentacene.[13] Calculated decay time of anthracene triplet-triplet annihilation, which is a half of anthracene triplet lifetime, agrees with the observed decay time 2—3 ms of the component 2 in anthracene electroluminescence. If we consider the energy levels in a pentacene doped anthracene crystal, the component 2 of pentacene emission is thought due to pentacene triplet-anthracene triplet heterofusions. Impurity delayed fluorescence which comes from trapped triplet-

TABLE 1. THE RESULTS COMPARING THE RELATIVE INTENSITY OF THE DELAYED ANTHRACENE AND PENTACENE ELECTROLUMINESCENCE COMPARED TO THE TOTAL ANTHRACENE AND PENTACENE ELECTROLUMINESCENCE

Applied voltage	Crystal currents	Totalel electroluminescence intensity (relative units)	Ratio $\frac{\text{Intensity delayed}}{\text{Intensity total}}$
Anthracene emission			
3000 V	1×10^{-5} A	294	0.062
2000	1.3×10^{-6}	26	0.17
1000	7×10^{-8}	1.1	0.28
Pentacene emission			
3000 V	1×10^{-5} A	240	0.12
2000	1.3×10^{-6}	28	0.18
1000	7×10^{-8}	1.4	0.37

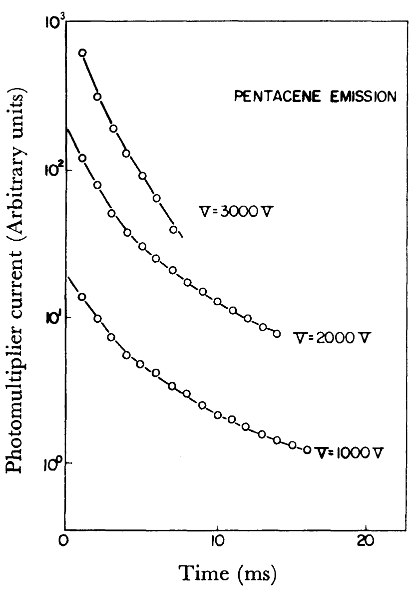

Fig. 6. Transient behavior of the delayed pentacene electroluminescence after the decay of the pulsed voltage 1000, 2000, 3000 V.

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[13] H. Baessler, G. Vaubel, and H. Kallmann, *J. Chem. Phys.*, **53**, 370 (1970).

free triplet exciton annihilation was reported.[14,15] The ratio of the delayed: the total anthracene emission intensity, 0.06 under 3000 V, when the component 3 did not exist is less than the value, 0.39, obtained in a pure anthracene crystal.[2] This is because anthracene triplet exciton is consumed by both annihilation with an anthracene triplet and a pentacene triplet, or the triplet energy is localized or trapped in a mixed crystal.[16]

The electroluminescence of a pentacene doped anthracene crystal is influenced by traps, either pentacene impurity traps or anthracene structural defect traps. Pentacene emission is more evident in the electroluminescence spectra than the optically sensitized fluorescence. Both anthracene and pentacene emission was found to consist of a prompt and two kinds of delayed emission. Pentacene impurity is concluded to work as carrier or triplet exciton traps in the growth reaction of every component of pentacene electroluminescence. The existence of the component 3 and the background defect electroluminescence in anthracene emission indicates that anthracene structural defects work as traps, too.

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