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PHOTOCONDUCTIVITY OF N-ETHYLCARBAZOLE SINGLE CRYSTAL INDUCED BY A Q-SWITCHED RUBY LASER

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The intrinsic photoconductivity of N-ethylcarbazole single crystal induced by a Q-switched ruby laser was investigated. The experimental results show that charge carriers are uniformly generated in the bulk of the crystal by the photoionization of excitons produced by two-photon absorption.

As the results of the extensive studies on the intrinsic photoconductivity of molecular crystals such as anthracene, two basic mechanisms, exciton-exciton collision ionization and exciton photoionization, have been proposed. Which of the former or the latter mechanism is dominant depends on the experimental conditions such as the excitation light intensity (I), the wavelength of the excitation light, and the purity of the crystals.

It is a current aspect that the exciton-exciton collision mechanism is important with strongly absorbed light generating a high density of excitons near the surface of the crystal. Proof of the existence of this kind of singlet exciton - singlet exciton interaction resulting in free-carrier generation was recently offered by Braun[1] and by Johnston and Lyons.[2] However, in the excitation of weakly absorbed light, the situation is different and the exciton photoionization seems to be dominant in so far as the excitation energy is sufficient to generate free-carriers via the exciton photoionization and the density of excitons is too small to change the lifetime of excitons.

In the experiments of the photoconductivity of anthracene crystals with Q-switched ruby lasers, Hasegawa[3] observed a photocurrent proportional to I^4 up to the laser intensity of about 10^{26} photons/cm^2.sec., and he interpreted it in terms of exciton-exciton collision ionization. His result is discrepant from those obtained by Kepler[4] and Courtens[5] that charge carriers are generated by the photoionization of singlet excitons resulting in a observed photocurrent proportional to I^3. This discrepancy can not be considered to be due to the intensities of the laser pulses deciding the density of excitons, because the light intensities are almost equal in these experiments. Thus, this discrepancy remains open to question, although the cubic dependence of the photocurrent is recently predominant.

In spite of these extensive studies of anthracene crystal, there is no report with other molecular crystals except for 9,10-dichloroanthracene.[6] In order to confirm that the above criterions leading to exciton-exciton collision ionization or exciton photoionization are generally applicable to molecular crystals, it would be worth while investigating other molecular crystals than anthracene.

In the present paper we wish to report the intrinsic photoconductivity of N-ethylcarbazole single crystal (EtCz), a good model compound of poly-N-vinylcarbazole (PVCz), induced by a Q-switched ruby laser (up to about 10^{26} photons/cm^2.sec.). Assuming that the band gap of EtCz is almost equal to that of N-isopropylcarbazle (4.7 eV),[7] it is expected that free-carriers can well be generated energetically both by the photoionization of excitons (singlet or triplet) and by the exciton-exciton collision ionization, the excitons being produced by two-photon absorption under the excitation of a Q-switched ruby laser (1.78 eV). The present experimental results show that carriers are generated by the photoionization of excitons produced by two-photon absorption.

EXPERIMENTAL EtCz was synthesized and purified by the previously reported methods.[8] EtCz single crystals were obtained from the melt in a Bridgman furnace. The purity of the crystals was confirmed from the results that the fluorescence lifetimes were constant, about 20 nsec, over the whole spectral region.

Photocurrent was measured by charge-integration method. EtCz crystal approximately 1 mm thick, cut parallel to the direction of growth in the Bridgman furnace (crystallographic a-axis) and polished and etched using distilled methanol, was sandwiched between two transparent blocking electrodes of nesa-coated quartz plates. A Q-switched ruby laser (Nippon Electric Company, SLG-2008) beam (about 25 nsec half-duration and about 10 MW output) was passed through a filter Toshiba VR66 which eliminates the xenon flash lamp radiation, and was led to the crystal. $CuSO_4$ solution and neutral density filters were used to vary the incident light intensity. The laser pulse intensity was determined by monitoring the reflection light intensity from a MgO-coated surface with LSD-39A photodiode. The incident photon flux onto the crystal was calibrated using a power meter (Ballistic thermopile Model-100). The transient photocurrent was preamplified and displayed on an oscilloscope. In carrying out the photoconductivity experiments, it was necessary to illuminate the crystal with the laser beam at least for 3 times with electrodes shorted, in order to neutralize the internal space-charge field caused by the preceding measurements. In the fluorescence lifetime measurements, the light emitted from the crystal was monochromatized and detected with a photomultiplier (HTV R446).

RESULTS AND DISCUSSION

Two-photon absorption of EtCz crystal When EtCz was irradiated by ruby laser, the blue emission of about 50 nsec could be observed, the spectrum of which is shown in Fig.1. It agrees well with that of EtCz crystal excited by UV-irradiation. This indicates that the emission caused by ruby laser excitation is the fluorescence from the lowest excited singlet state of EtCz. In Fig.2., the intensity of the fluorescence is plotted against that of the exciting laser pulse. The intensity of the fluorescence was pro-potional to square of that of the laser pulse, indicating that the fluorescence by ruby laser excitation is caused by two-photon process. The following two processes can be considered for the fluorescence; (1) excitation to the lowest excited singlet state by the simultaneous two-photon absorption, (2) a S-T absorption followed by delayed fluorescence caused by the triplet-triplet annihilation. However, the possibility (2) is eliminated because the triplet state of EtCz is located at 3.02 eV above the ground state judging from its phosphorescence spectrum[9] and therefore a photon energy of ruby laser (1.78 eV) is energetically insufficient for S-T absorption. Thus, the fluorescence caused by the excitation of ruby laser is due to the lowest excited singlet state produced by two-photon absorption. It should be noted that the lowest excited singlet excitons are uniformly produced in the bulk of the crystal in the present case, which is a definite contrast to the case of one-photon excitation in the UV-region.

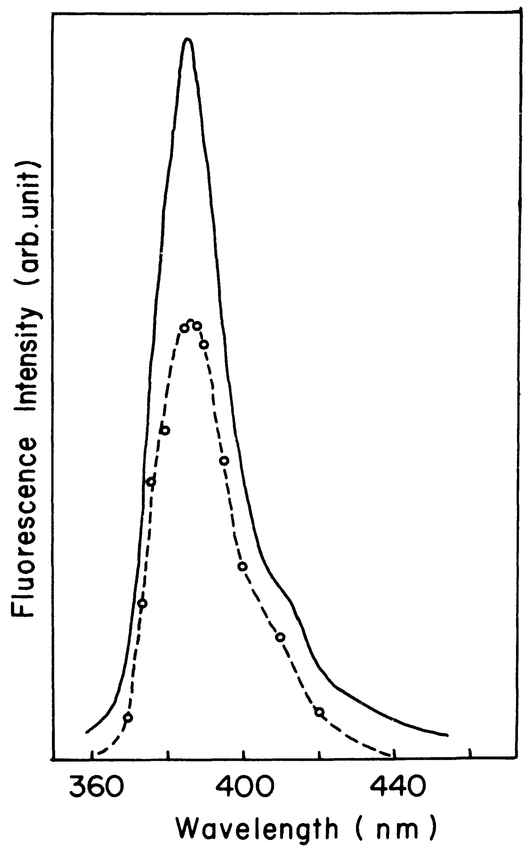

Fig.1 The fluorescence spectra of EtCz excited by ruby laser (– – –) and excited at 330 nm (——) at room temperature.

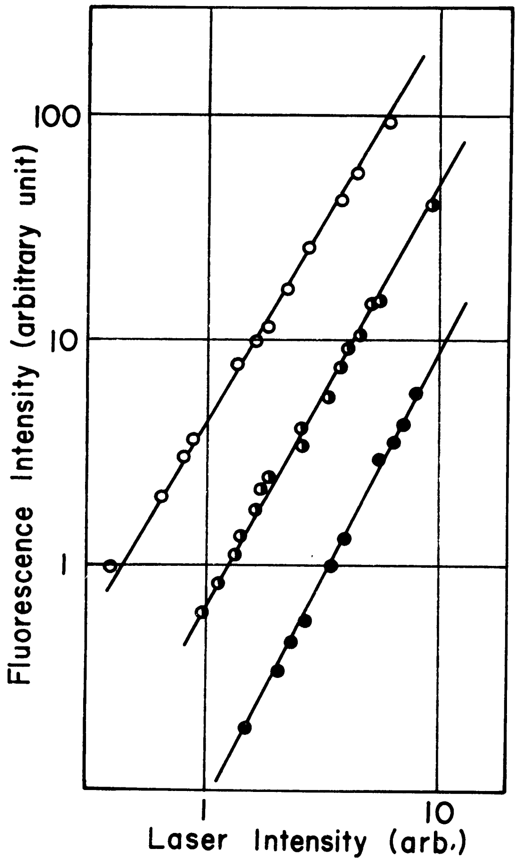

Fig.2 Log-log plot of fluorescence intensity versus laser pulse intensity. ● ; at 365 nm, ○ ;at 390 nm, ◑ ; at 410 nm.

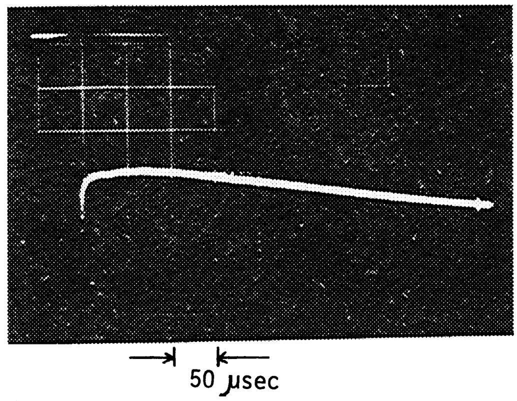

Fig.3 Typical voltage pulse in EtCz single crystal excited by ruby laser. 400 Volts were applied across 0.0060 cm. The voltage pulse has two maxima at about 20 μsec and 75 μsec due to the drift of carriers (holes and electrons). The time of the second maximum changes in proportion to the inverse applied voltages, and the voltage pulse decays with longer time constant of the integrator circuit.

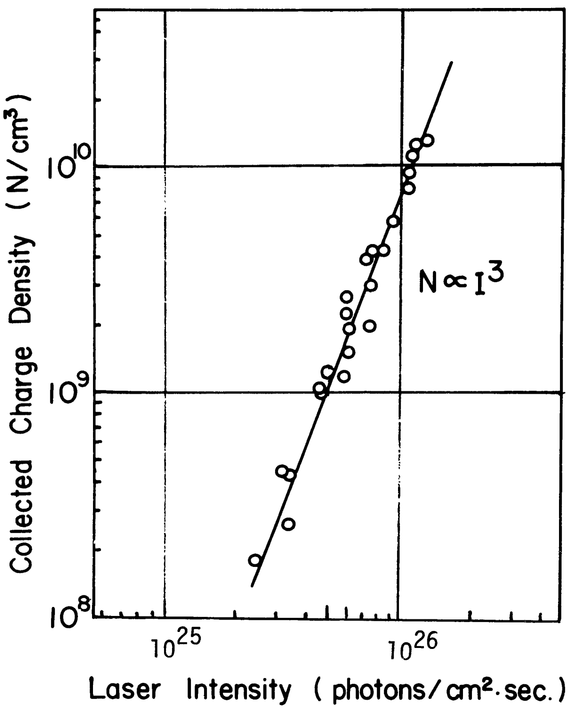

Fig.4 Log-log plot of collected charge density versus incident laser intensity (at room temperature). Applied voltage: 500 V; crystal thickness: 0.14 cm.

Photoconductivity of EtCz crystal induced by a ruby laser

Figure 3 shows the observed typical pulse shape representing the integrated charge displacement as the carriers drift across the crystal, which resembles well to the integrated pulse of the typical triangular current pulse which is to be observed when the carriers are uniformly generated in the bulk of the crystal by the excitation of weakly absorbed light.[10] This indicates that carriers are generated in the bulk of the crystal. The total number of collected charges can be estimated from the peak of the voltage pulse. Although the collected charges depend on the applied field, the generated charges can be collected at the surface of the crystal under the higher applied field. Figure 4 shows the dependence of the collected charge carriers (N) on the intensities of the incident laser light (I). N varies in proportion to I^3, indicating that charge carrier generation in EtCz involves a three-photon process.

The third power dependency of the collected charge on the laser intensity will suggest the following three possible mechanisms for photocarrier generation; (1) photoionization from the lowest singlet exciton state produced by two-photon absorption, (2) photoionization from the lowest triplet exciton state produced by the intersystem crossing from the singlet state, (3) direct three-photon ionization. However, the mechanism (3) can be ruled out from the following considerations. Our preliminary results that the collected charges depend on the temperature and that the apparent activation energies vary with the applied fields can not be explained by the mechanism (3), because the direct three-photon ionization requires almost no activation energy. In addition, in view of the small three-photon transition probability and the observation of the fluorescence caused by two-photon absorption, the mechanism (3) may be also neglected. Therefore, carriers are generated by the photoionization of singlet and/or triplet exciton states. It is a very important problem to determine which of the singlet and triplet exciton states plays an important role to the carrier generation. For the consideration of the carrier generation mechanism, the information of the energy level of the conduction band is a key point. Assuming that the band gap of EtCz is almost equal to that of N-isopropylcarbazole (4.7 eV) reported by Sharp,[7] both mechanisms are energetically possible. The discussion reported by Schott and Berrehar[11] that triplet photoionization is negligible by the excitation of a single pulse with a short duration (less than about 200 μsec) in anthracene crystal would not be easily applied to EtCz, because the triplet state of EtCz locates close to the singlet state. Thus, it must be necessary to take the photoionization of triplet excitons into consideration. This problem is under investigation in detail. From the above results, we believe that the exciton photoionization seems to be dominant in EtCz under the condition that the intensity of the incident laser light is up to 10^{27} photons/cm^2.sec.

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