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Observation of Anthracene Single Crystals with Delayed Fluorescence Tomography

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Anthracene single crystals are studied with delayed fluorescence tomography. This method allows the observation of the interior of thick 'as grown' crystals. It is shown that the spatial distribution of impurities and inclusions can be observed. Limitations and possible improvements are discussed.

INTRODUCTION

Numerous investigations have revealed that photoelectric as well as luminescent properties of aromatic organic crystals are sensitive to crystal imperfections such as impurities and defects.^{1–4} However, relatively little attention has been paid so far to the spatial distribution of impurities and defects in the crystal. Concerning this point observations with etch pattern,^{5–6} X-ray topography⁷ and electron microscopy^{8,9} are relevant. These methods are appropriate to observe crystal surface or thin crystals. We propose here the use of delayed fluorescence generated by a laser microprobe, for non-destructive characterization of thick 'as grown' crystals.

An anthracene crystal emits strong blue fluorescence when it is excited with ultraviolet light. When irradiated with strong red light it emits weak blue fluorescence, which has the same spectrum as the normal prompt fluorescence, but has a lifetime six orders of magnitude longer than that of the normal fluorescence. This delayed fluorescence (DF) is caused by mutual annihilation of triplet excitons, which are long-lived.¹⁰ The occurrence of DF is not confined to anthracene, but is quite general among aromatic organic crystals.¹¹ It

has been reported that the intensity and lifetime of DF are reduced by deformation of a crystal¹² or by the existence of impurities¹³. Here we report an attempt to get a tomographic image of anthracene crystals by DF detection, which should yield the spatial distribution of impurities and defects.

EXPERIMENTS

Anthracene crystals, typically 10 mm in diameter, were grown by the Bridgman method from materials of various purities. They were cleaved in the (001) plane and cut in other planes with a chemical saw. They were polished on filter papers soaked with benzene and also on polishing cloth with diamond paste and then rinsed with toluene.

The apparatus is shown in Fig. 1. A crystal is irradiated by a He-Ne laser (5 mW) through a red-pass filter (F1) which eliminates blue plasma light from the laser tube. The crystal emits DF along the illuminating beam which passes through the crystal. The intensity distribution of DF along this beam should reflect the distribution of impurities or defects. To get a two-dimensional mapping of DF intensity the focused laser beam is scanned in a horizontal plane through the crystal and the DF image of that plane is photographed

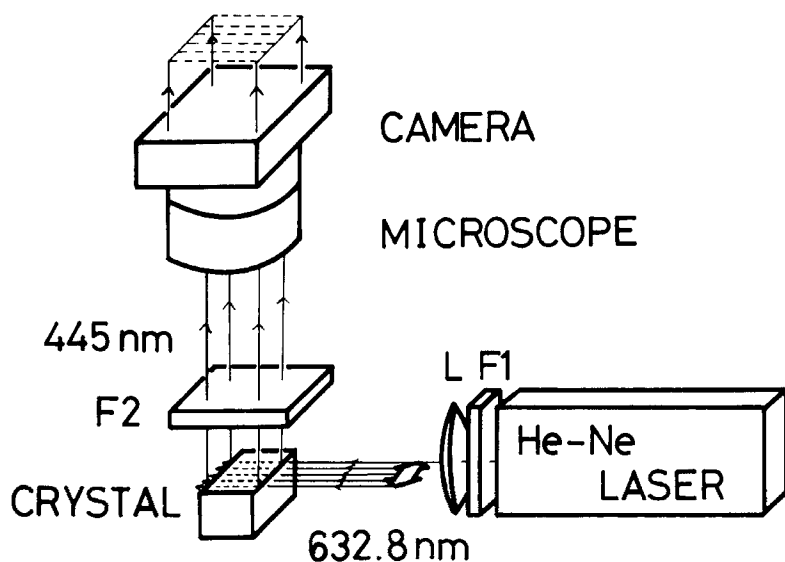


FIGURE 1 Schematic drawing of the apparatus.

with a blue-pass filter (F2), through a microscope and a camera, with the shutter of the camera open. This is a kind of tomography which has been used successfully for observation of quartz crystals.¹⁴ In ref. (14) the crystals were photographed with scattered light, whereas in the present work DF is monitored. When the blue-pass filter (F2) is removed the image by scattered light is obtained. In this case both scattered light and DF contribute to the image, but the image is formed essentially by scattered light, because DF is very weak as compared with scattered light. Comparison of DF-detected tomography and scattered-light-detected tomography helps in interpreting the obtained image.

RESULTS

Inclusions

Fig. 2 shows that the DF tomography in fact reflects the information from the bulk of the crystal and not from the surface. Irradiation with white light from the side of the crystal (Fig. 2b) shows both the image of the surface and of the interior. A surface image photographed with a polarization microscope is shown in Fig. 2a. Both DF and scattering tomography images (Fig. 2c, d) are clearly different from the surface

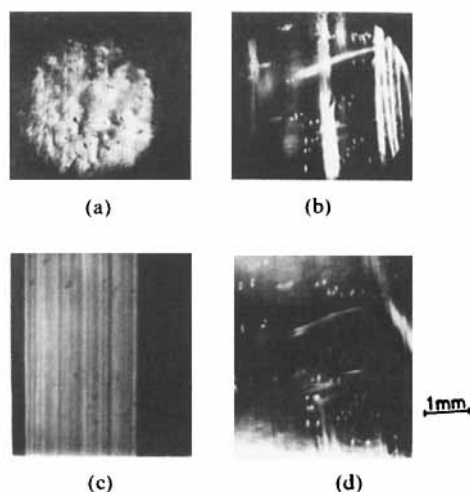


FIGURE 2 Images of the same field of an 'as grown' crystal. (a) Surface image with a polarization microscope. (b) Scattering image by irradiation with white light from the side of the crystal. (c) DF image. (d) Scattering image with laser beam.

image. DF and scattering images correspond well to each other: bright spots in the scattering image appear as dark spots in the DF image, indicating that they are inclusions or bubbles. These spots are seen in pairs in the scattering image but are single in the DF image. This is thought to be due to birefringence, the weaker spots being not observed in the DF image.

Impurities

DF tomography turns out to be very effective in getting the distribution of impurities. Three pictures taken with different wavelength for observation (Fig. 3) show the same field of an impurity doped anthracene single crystal. The crystal was soaked in a xylene solution of tetracene and then annealed in a glass tube filled with nitrogen at about 165°C for 10 days. It is seen that the DF image does not correspond well to the scattering image (Fig. 3b,c). In Fig. 3a, the doped crystal was irradiated with a mercury lamp, and the emission ($\lambda \sim 530$ nm) from tetracene was recorded through a suitable combination of filters. This impurity fluorescence image corresponds well to the DF image in the sense that the bright part of the impurity emission image appears as the dark part in the DF image (observed at 400 nm). This means that triplet excitons are quenched by tetracene, so that DF could not be observed where the concentration of tetracene is high. The pattern which is seen in both impurity fluorescence and DF images is not observed in the scattering image. This may be caused by strong surface scattering due to surface roughness which prevents the observation of the pattern originating from the interior of the crystal.

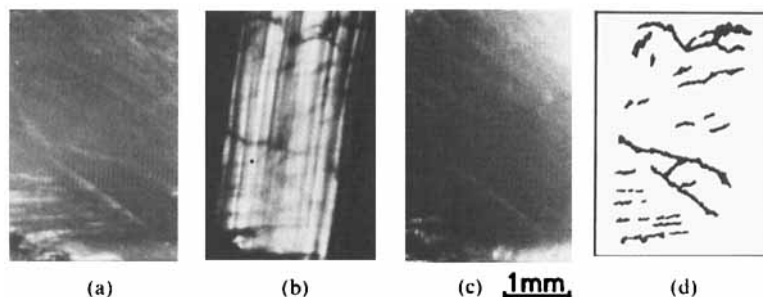


FIGURE 3 Images of the same field of a doped crystal. (a) Impurity emission image. (b) DF image. (c) Scattering image. (d) Schematic of the DF image (b). Dark lines correspond to light lines in (a), and appear to be regions with a high dopant (tetracene) concentration.

Physical defects

Mechanically deformed crystals were studied in order to see the effects of physical defects. We tried two methods of deformation. With the first method, a cleaved crystal plate with surfaces parallel to the (001) plane is deformed by pressing it between two curved metal plates. Almost all the features seen in the DF image are observed in the scattering image. In fact the bending introduces small cracks into the crystal, which scatter strongly and appear dark in the DF image. With the second method, crystals are deformed¹⁵ plastically, whereby the crystal slides along the (001) plane. If defects reduce the intensity of DF, it is expected that the deformed part appears dark and the undeformed part bright in the photograph. So far no clear correspondence has been observed.

DISCUSSION

It is now clear that DF tomography gives information concerning the distribution of impurities and inclusions of about 10^{-2} mm in magnitude. The advantage of the method lies primarily in its high sensitivity to impurities. As for the resolution of the image, the diffusion of triplet excitons sets a limit. The diffusion length of triplet excitons in the (001) plane of anthracene crystal is reported to be $10 \pm 5 \mu\text{m}$.¹⁶ Accordingly DF originates from a columnar region, $10 \mu\text{m}$ in diameter, even when the probe laser beam is focused very tightly. The quality of the image is severely influenced by surface scattering. The roughness of the crystal surface makes it difficult to observe a bulk image, because the surface scattering disturbs the bulk image. An improved surface polishing and the use of an index matched solution may reduce the difficulty. There is another problem which is related to the intrinsic character of DF. The concentration of triplet excitons in the crystal at time t is determined by¹⁰

$$\frac{\partial n}{\partial t} = \alpha I - \beta n - \gamma n^2 + D \nabla^2 n \quad (1)$$

where α is the singlet-triplet absorption coefficient for red excitation light which has the intensity I , β is the rate constant for monomolecular decay, γ is the rate constant for biomolecular decay, D is the

diffusion constant of triplet excitons. The intensity of DF is given by

$$I_{\text{DF}} \propto \frac{1}{2} f \gamma n^2 \quad (2)$$

where f is the fraction of triplet-triplet annihilation which leads to delayed fluorescence. With a low excitation intensity with red light the concentration of triplet excitons is low, so that $\beta \gg \gamma n$. When the excitation is spatially homogeneous, i.e., $\nabla^2 n = 0$,

$$I_{\text{DF}} \propto \frac{1}{2} f \gamma \alpha^2 / \beta^2 I^2 \quad (3)$$

With a high excitation intensity $\gamma n \gg \beta$ and

$$I_{\text{DF}} \propto \frac{1}{2} f \alpha I \quad (4)$$

Eq. (4) does not contain β . This means that with a high excitation intensity, DF does not contain information regarding imperfections in the bulk which affect β . Accordingly a low intensity probe beam has to be used for the measurement to be meaningful. An image intensifier may profitably be used to enhance the quality of the image.

It has been shown here that DF tomography can be a sensitive method to probe the spatial distribution of impurities and inclusions in an organic crystal. This method may be applicable to a wide range of organic crystals.

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