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ELECTROLUMINESCENCE IN FULLERENE CRYSTALS

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Abstract Broadband electroluminescence emission from fullerene crystals is reported and described. The spectral distribution is comparable to that of the photoluminescence at high excitation densities. The emission intensity is nonlinearly dependent on the current. The response of the crystal to the application of an alternating current is investigated and the frequency dependence of the emission intensity is described. The observed high frequency cut-off behaviour cannot be mimicked by a simple equivalent circuit and so the system is modelled using a rate equation model to describe the state of the system. Fits of the model to the observed behaviour provide rate constants which compare favourably to those reported for excited state decay in fullerenes.

INTRODUCTION

Luminescence studies have shown that a highly nonlinear emission process is affected at high excitation densities[1] and transport studies support the association of this phenomenon with a transition from a localised molecular-like to a banded or extended state behaviour, i.e. an optically driven Mott-like transition[2]. The resultant nonlinear emission process is characterised by a cubic dependence of the output on the input intensity accompanied by a strong red shift of the emission spectrum. The unique nature of this process prompts an investigation of its applications potential, in particular in the form of an electroluminescent device. In this paper, the characteristics of the previously reported[3] electroluminescent output of fullerene crystals are briefly described. Furthermore the dynamic response of

the emission is probed through the application of an ac voltage in an attempt to shed further light on the dynamics of the emission process as well as to assess the potential role of the nonlinear current-intensity characteristics in pulse shaping applications.

EXPERIMENTAL

C_{60} crystals were generated by vacuum sublimation of fullerene powder as described previously[3]. The sample employed was of dimensions ~200x200x200μm^3 and was mounted using silver paste on a substrate with two gold strip lines. The crystal is therefore symmetrically contacted. All processing was performed under inert atmosphere, and the sample was mounted in a cryostat cooled to liquid nitrogen temperatures.

The sample was connected to a Keithley voltage source which provided a dc voltage. The light output was monitored using a photomultiplier. For the frequency dependent measurements, a Kontron function generator was connected in series and the transient response was monitored using a Hewlett-Packard 54111D digitising oscilloscope.

RESULTS AND DISCUSSION

Employing the dc source only, the current, voltage and light output were simultaneously monitored. As is shown in figure 1, the current/voltage characteristics are approximately linear until a voltage of ~10V. Below this region, no light emission is detectable. Increasing the voltage above this point, however, results in the abrupt turn-on of light emission. The light emission increases highly nonlinearly with the current[3] above the threshold and the current-voltage characteristics become somewhat nonlinear. The emission has a broad distribution, as shown in figure 2, which is comparable to the photoluminescence observed from fullerene crystals at high excitation densities[1].

The origin of the nonlinearity of the optical and electronic properties of fullerenes at high excitation densities

have been discussed in terms of an optically induced insulator to metal transition[4] dependent on a critical excited state density. The relationship of the electroluminescence emission to this behaviour has been discussed previously[3]. Of particular interest are the kinetics of the formation of this critical density in the case of electron injection and the dynamic response of the contacted crystal were probed.

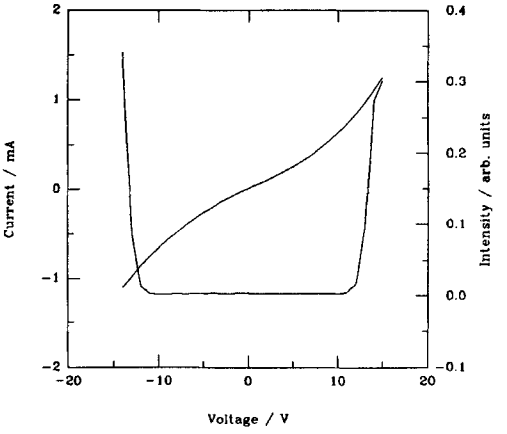

Fig 1 Current/Intensity vs Voltage

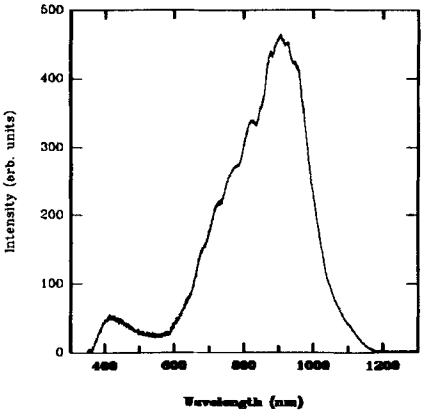

Fig 2 Emission Spectrum

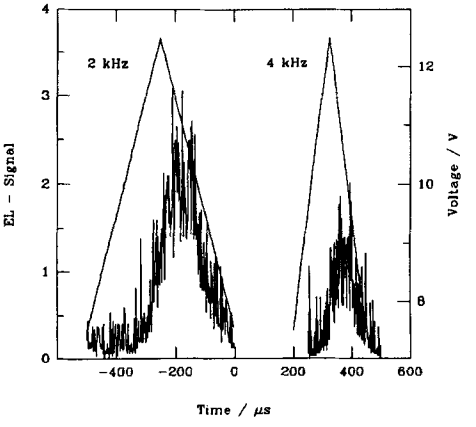

Fig 3 Temporal response at (a) 2kHz and (b) 4kHz

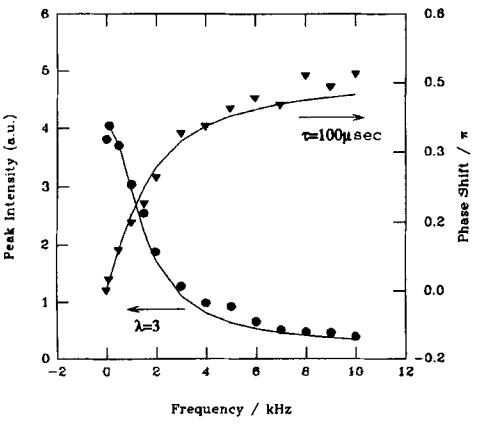

Fig 4 Frequency dependence of peak intensity and phase shift

The crystal was maintained just below the emission threshold by the application of 10V dc. The system was then driven periodically above threshold by the application of a triangular waveform of peak to peak voltage 5V. The net ap-

plied voltage was therefore driven between 7.5 and 12.5V. The driving frequency was varied in the range of 100Hz to 10kHz. At low frequencies, the time evolution of the light emission follows that of the driving waveform closely. However, with increasing frequencies, the rise of the emission ceases to follow that of the voltage, resulting in a phase shift as well as a reduction in the maximum of the light intensity. Figure 3 shows the temporal evolution of the luminescence compared to the driving voltage waveform at (a) 2kHz and (b) 4kHz. At frequencies >10kHz, negligible light emission is detectable. Figure 4 shows the frequency dependence of both the phase shift and the light emission. The phase shift, which is positive, asymptotically approaches $\pi/2$.

In considering an equivalent circuit for the system, a series RC combination is discarded on the basis of the requirement of a dc current. A parallel combination, can provide a similar frequency response with the exception that a frequency dependent phase shift is negative. It appears, therefore, that the origin of the bandwidth limitations have origins in the nature of the emitting state rather than the external circuitry.

The dynamics of light emission as a result of the application of a variable electrical current has been extensively explored for the case of laser diodes. The light output depends mainly on the density of excited states and the output intensity responds to an increase in current with a time constant determined by the recombination time τ. So, to analyse the effect of a change in the current it is necessary to consider a rate equation for the excited state density n. This is given by

$$\frac{dn}{dt} = J - \frac{n}{\tau} \qquad (1)$$

where J is defined as a particle current per unit volume and determines the injected carrier concentration. In a rough approximation, J is assumed to be a sum of the dc current

i_{dc} and a sinusoidal contribution rather than the triangular waveform

$$J = \frac{1}{eV} (i_{dc} + i_0 \sin \omega t) \quad (2)$$

where V is the active volume of the crystal. Under these conditions the temporal dependence of n is given by

$$n = \frac{i_{dc}\tau}{eV} + n_0 \sin(\omega t - \varphi) \quad (3)$$

and the phase shift φ fulfils the equation

$$\varphi = \arctan (\omega\tau) \quad (4)$$

which is in excellent agreement with the experimentally observed dependence as shown by the solid line in figure 4. The fit yields a value for the recombination lifetime of 100μs. This value is not inconsistent with the reported values of excited state lifetimes in fullerenes[5-7].

The peak population density is given by the equation,

$$n_o = \frac{i_o/eV}{\sqrt{\omega^2 + 1/\tau^2}} \quad (5)$$

The frequency dependence of the light output I, is limited by that of the population density, n. The nonlinear dependence of the photoluminescence on input intensity as well as the electroluminescence on the injection current indicate that the relationship between I and n is not linear and is best fitted with a relationship of the form,

$$I = K(n - n_{th})^{\lambda} \quad (6)$$

The data can be fitted well with a value of λ between 2 and 4. The solid line in figure 4 is of a power law of order 3.

On the basis of the fits, application of such a rate equation model to the dynamic response of the electroluminescent emission from fullerene crystals appears justified. In particular, the time constant involved is within the range of those reported for fullerenes. The model is how-

ever, primitive. It assumes a conductivity of the crystal which is largely independent of excitation density, an assumption which seems inappropriate in the light of the nonlinear photoconductivity reported in ref. 2. Furthermore, it assumes that the time constant is density independent which has been shown not to be the case[7]. Further elucidation of the physics of the process may be afforded by short pulse injection, an examination of which is currently underway.

CONCLUSIONS

The electroluminescent emission from fullerene crystals is broadband with a strongly nonlinear dependence of light output on current. These characteristics strongly associate it with the nonlinear luminescence and photoconductive response of fullerenes above a critical excitation density. Examination of the dynamic response indicates that it is determined and limited by the material response time which is of order 100μs.

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