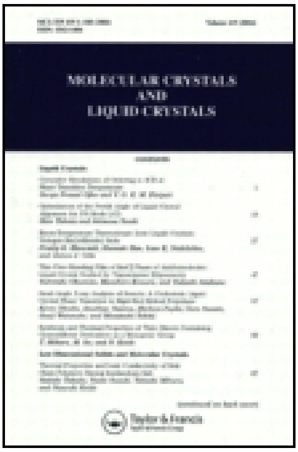

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Solvent Free High Purity Solid C_{60}: Optical Properties

N. J. Halas [a], V. Papanyan [a] [b], R. D. Averitt [a], P. Pippenger [a] & R. A. Cheville [a]

[a] Department of Electrical and Computer Engineering, The Rice Quantum Institute Rice Unaversity, P. O. Box 1892, Houston, TX, 77251 Phone: (713) 527-4020

[b] Institute for Physical Research of Armenian Academy of Sciences, Ashturak 2, 375410, Armenian Republic

Version of record first published: 04 Oct 2006.

To cite this article: N. J. Halas, V. Papanyan, R. D. Averitt, P. Pippenger & R. A. Cheville (1994): Solvent Free High Purity Solid C_{60}: Optical Properties, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 256:1, 225-232

To link to this article: http://dx.doi.org/10.1080/10587259408039251

Mol. Cryst. Liq. Cryst. 1994, Vol. 256, pp. 225–232
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N. J. Halas, V. Papanyan,* R. D. Averitt, P. Pippenger, and R. A. Cheville
Department of Electrical and Computer
Engineering and the Rice Quantum Institute
Rice University, P. O. Box 1892
Houston, TX 77251
(713) 527-4020

We describe a method for obtaining solvent free high purity C_{60}. Purities of as great as 99.97 % have been obtained. Films grown from this high purity source material have been studied using photoluminescence spectroscopy. In addition, films have been grown with intentional addition of solvent impurities. Spectral broadening due to impurity-induced site disorder is observed in the photoluminescence spectra of these films.

I. Introduction

Since the initial appearance of solid C_{60} and the proliferation of experiments investigating the properties of the fullerene solids, numerous references to the role of sample purity and its impact on experimental investigations have been made.[1] The most common impurities in solid C_{60} are other fullerenes, most typically C_{70}, C_{60} oxide, and residual solvent molecules remaining from the wet chemical stages of fullerene purification. The presence of these impurities in fullerene solids in uncharacterized quantities have quite possibly had an effect on the observed electronic properties, the electrical (transport) properties, the molecular-dynamical properties, the chemical reactivity of the solid, and the optical properties that have thus far been reported.

It is potentially possible, however, to obtain highly crystalline fullerene solids with purity levels equivalent to typical inorganic semiconductors. This is because fullerene molecules sublime easily and can be grown into films in the vapor phase under ultrahigh vacuum, MBE-like conditions. Indeed, growth of fullerene films as macroscopic single crystals with long-range order and a mosaic spread of 0.5 degrees, of the range of a typical research-grade single crystal metal, has been reported.[2] Precise control of the impurity levels, however, has not been reported.

We have developed a solvent-free method of producing C_{60} source material of extremely high purity. This method utilizes the difference in vapor pressures between C_{60} and other impurities to produce a mass-selected fullerene source material with purity as high as 99.97%. This solvent-free ultrahigh purity source material was then grown into fullerene films under UHV conditions. In order to isolate the contribution of various impurities to the optical properties of fullerene solids, films were also grown with ultrahigh purity source material to which solvent impurities have been added. Photoluminescence spectroscopy has been used to study the role of solvent impurities in modifying the optical properties of solid C_{60}. The optical experiments are consistent with a model of self-trapped exciton (polaron) formation, and reveal the effects of site disorder due to the presence of impurities on the optical properties of solid C_{60}.

II. High Purity Vapor Phase Separation of C_{60}

The first gas phase separation experiments to demonstrate that fullerenes of varying mass could be partially purified by utilizing differences in their vapor pressure were performed by Cox et.al.[3] A later experiment by Yeretzian et.al. showed the applicability of gas phase methods to partially separate the insoluble fullerenes C_{74} and La@C_{74}.[4] However, both of these experiments were limited in their separation ability because the geometry of the apparatus allowed the fullerenes to effuse with mean free paths that were considerably greater than the length of the temperature gradient. A much higher efficiency is obtained when the mean free path is restricted to a small fraction of the temperature gradient. This restriction can be accomplished either geometrically with baffles or by use of an inert buffer gas.

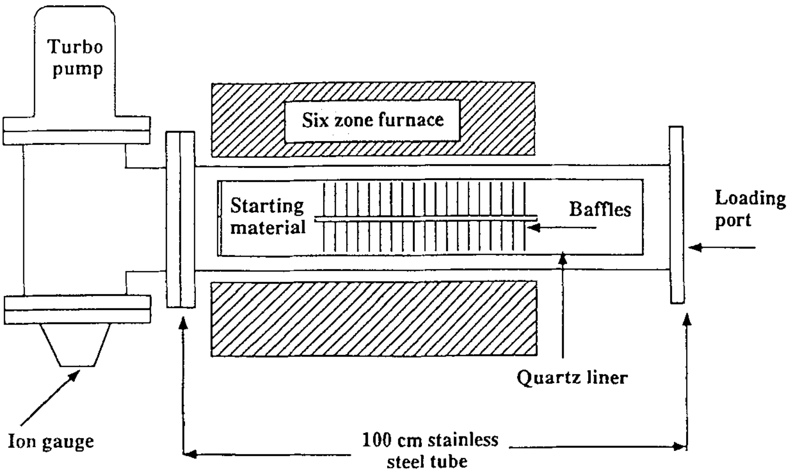

Figure 1. Molecular distillation apparatus described in text.

We have developed a method, based on fractional molecular distillation, which utilizes the difference in vapor pressure between C_{60} and higher fullerenes to produce ultrahigh purity C_{60}. Raw fullerene soot or fullerene extract is introduced into one end of a 100 cm distillation column lined with a series of evenly spaced baffles with circular perforations. This apparatus is shown in Figure 1. The fullerene starting material is heated under high vacuum to 970 K, while a linear temperature gradient of 10 degrees/cm is simultaneously established along the length of the column. As the mixed fullerene vapor traverses to the cooler region of the column by effusion through the perforated baffles, it becomes enriched in the more volatile species. In addition, because of the repeated evaporations and condensations necessary for molecular transport down the column, virtually all volatile impurities are removed and pumped away.

Because the perforations in the baffles are small compared to the mean free path of the fullerenes, effusion is the dominant mass transport mechanism in the column. The theoretical rate of effusion through an aperature for each component in the fullerene mixture (in gm/sec) is:

$$\frac{dW_n}{dt} = kp_nA\sqrt{\frac{M_n}{2\pi RT}} \tag{2.1}$$

where p_n is the partial vapor pressure of the nth component, M_n is the molecular weight of the nth component, A is the effective aperture, k is a geometrical factor which accounts for the thickness of the baffle, R is the gas constant, and T is the temperature. It is important to note that the difference in vapor pressure between components of the initial fullerene mixture dominates the separation process.

Parameter	Trial 1	Trial 2	Trial 3
Starting Composition:			
%C_{60}	74.70	95.90	98.00
%C_{70}	19.65	0.97	0.70
%Other[b]	5.65	3.13	1.30[c]
Highest Purity C_{60} Obtained	99.20	99.80	99.97
% Yield at Highest Purity	1	3.8	16.6
% Yield > 98% C_{60}	2.3	100	100
% Yield Between 90% - 98% C_{60}	15.8	0	0

[a] Fullerene purities accurate to ± 0.05%
[b] Includes $C_{60}O$, C_{76}, C_{78} and C_{84}
[c] Remaining 1.30% $C_{60}O$

Table 1. Tabulated results of the molecular distillation method.

The results of several purification procedures are shown in Table 1. In each case, the composition of the fullerene mixture both before and after distillation was obtained using High Pressure Liquid Chromatography (HPLC). Trials 2 and 3 were conducted with fullerene starting material that was rated as greater than .99 % and 99.4 % pure, respectively. Note that the highest purities obtained are greater than what is currently commercially available. The dramatic increase in yield at the highest purities of C_{60} for a starting material of over 90 % purity appears to be due to deviations from ideality (Raoult's law) particularly in the vapor pressure mixtures of high mole fraction C_{60}.

III. High Purity Solvent Free C_{60} Films: Optical Properties

The high purity source material obtained as described in the above section was then grown into films on sapphire substrates by sublimation in vacuum at growth pressures of 10^{-8} to 10^{-9} torr. The optical properties of these high purity C_{60} films were studied with the samples under vacuum or inert gas. In addition to films grown with solvent free high purity source material, solid C_{60} films were also grown which had been intentionally doped with toluene. The toluene molecules were incorporated into the solid via cosublimation with the C_{60} during the film growth process. From raman spectroscopic data, the amount of solvent impurities is estimated as less than 10 %. Purity of these films were also measured destructively, by HPLC analysis, to ensure that no chemical modification of the C_{60} constituent molecules of the solid had occurred during growth and subsequent handling.

Photoluminescence spectroscopy has been performed on C_{60} and mixed fullerene films by numerous workers.[5] In addition, several interesting effects, such as intensity-dependent white light luminescence,[6] and temperature-dependent luminescence,[5] have also been reported.

In Figure 2 the photoluminescence spectrum of high purity solvent free C_{60} is displayed. The photoluminescence spectrum was obtained using 514.5 nm photoexcitation wavelength, and illumination intensities between 1 to 10 W/cm^2. The photoluminescence is linear with excitation intensity, and no evidence of polymerization was seen at these intensities in either the photoluminescence or the raman spectroscopic features of these films. The PL spectrum obtained from these films is consistent with PL spectra of C_{60} that have been previously published. The main features of this spectrum are the two peaks shown at 1.69 and 1.53 eV, which vary as a function of temperature. The previously reported temperature dependence of the integrated PL spectrum is also confirmed here. The temperature dependence of the integrated PL intensity for solvent free high purity C_{60} is displayed in Figure 3.

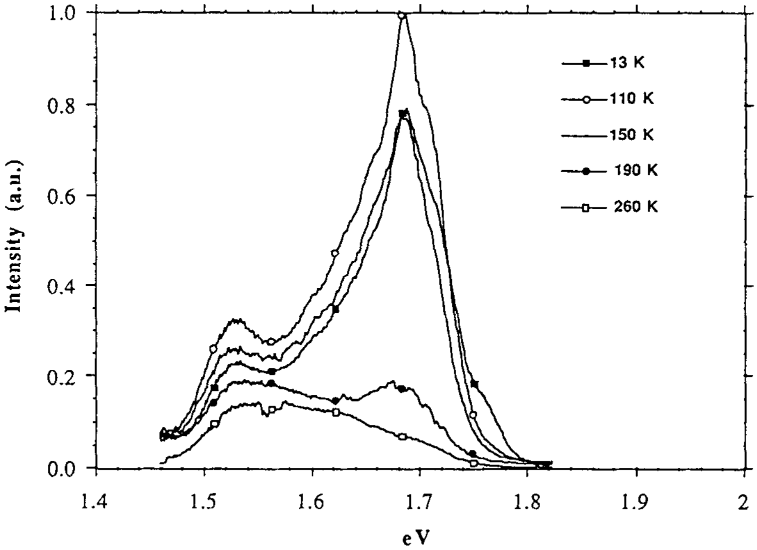

Figure 2. Photoluminescence spectrum of solvent free C_{60}.

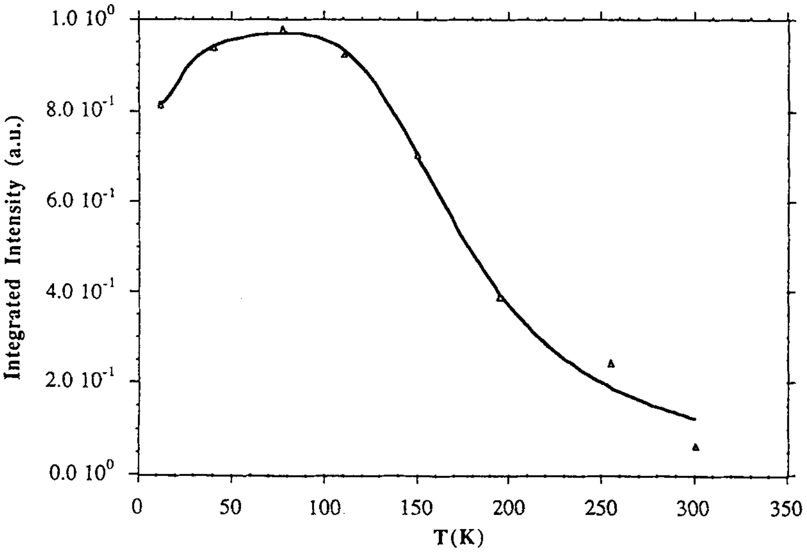

Figure 3. Photoluminescence temperature dependence of solvent free C_{60} films.

This unique temperature dependence of the integrated photoluminescence intensity of C_{60} can be described by the following model, shown in Figure 4. This is an extension of the picture that describes polaron formation for photoexcited C_{60}.[7] A small barrier exists between the free exciton and the self-trapped exciton (polaron). This barrier is responsible for the increase in luminescence as a function of intensity in the low temperature range (up to 100 degrees Kelvin). The two primary spectral features at 1.69 and 1.53 eV are assigned to a repopulation of the vibrational sublevels of the ground state. At higher temperatures, the relative peak heights of the 1.69 and 1.53 eV spectral features reduce in intensity due to the Franck-Condon effect and nonradiative processes.

This model yields the following expression for the PL efficiency:

$$\eta = \frac{c_1 + c_2 exp(-E_F/kT)}{1 + c_2 exp(-E_F/kT) + c_3 exp(-E_R/kT)} \tag{3.1}$$

where the coefficients are the normalized relative rates for each individual recombination process. In the temperature dependent fit shown in Figure 3, values are obtained for the small barrier to self-trapped exciton formation of $E_F = 0.007eV$, and to the overall temperature dependent luminescence quenching of $E_R = 0.080eV$. ($c_1 = 0.813, c_2 = 16.4, c_3 = 2157$).

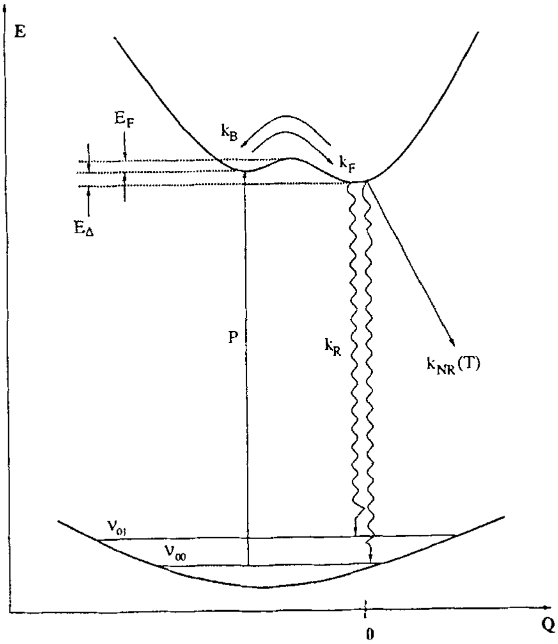

Figure 4. Proposed shallow barrier model for PL temperature dependence. P = photoexcitation, E_F is the barrier height between the free and the self-trapped exciton. The k's are rates for the various radiative and nonradiative processes described in the text.

Harigaya predicted that the presence of intercalated impurities in the solid would give rise to site disorder potentials on the order of 1 eV.[8] This is an effect which should be readily observed in the optical properties of solid C_{60}. When toluene molecules are intentionally cosublimed as the C_{60} solid is grown, the photoluminescence spectrum of the resulting film is dramatically changed relative to pristine films. The cosublimation results in a toluene concentration that has been estimated as approximately 10 %. The spectrum becomes distinctly broadened about the $v = 0$ peak of the photoluminescence, and is quite symmetric and featureless, as shown in Figure 5. Note that the peak of this broad luminescence still corresponds to the 1.69 eV peak found in the photoluminescence of the solvent free film. The temperature dependence is also modified relative to the pristine film.

This broad, featureless photoluminescence spectrum is a direct observation of the effect of impurity-induced site disorder on the optical properties of solid C_{60}. The broadening can be described by a gaussian distribution convolved with the luminescence lineshape. This is also shown in Figure 5.

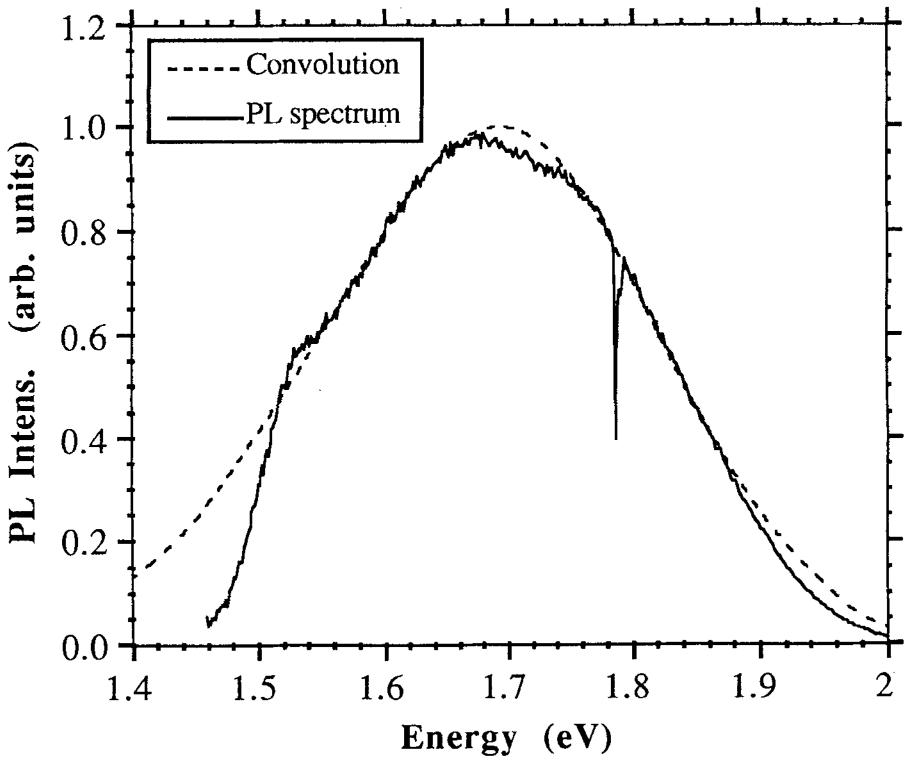

Figure 5. Photoluminescence spectrum of Toluene-doped C_{60} films.

In contrast to other reports of spectrally broad photoluminescence in solid C_{60}, the strong intensity-dependent broadening previously reported was not observed in these films.[6]

In conclusion, we have developed a method for obtaining high purity solvent free C_{60}. We have grown films of solvent free C_{60} and films of C_{60} intentionally doped with toluene impurity molecules. The photoluminescence of the pristine films agrees with earlier reported results, and we have suggested an interpretation of the temperature dependence of the observed photoluminescence spectrum in terms of an extension of the proposed exciton-polaron model for photoexcited C_{60}. We have in addition reported the effect of intentionally added solvent impurities on the photoluminescence properties. These spectra indicate the effect of impurity-induced site disorder on the optical properties of C_{60}. The manipulation and control of the degree of disorder in C_{60} solids through the controlled addition of impurities has important implications in the understanding of the relaxation dynamics of C_{60} films.

We acknowledge particularly fruitful discussions with P. Nordlander. We acknowledge the Office of Naval Research, the Texas Advanced Technology Program, the Robert A. Welch Foundation, and the National Science Foundation for support of this project (NJH is the recipient of an NSF Young Investigator Award.)

*Permanent address: Institute for Physical Research of Armenian Academy of Sciences, Ashturak 2, 378410 Armenian Republic.

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