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Photoluminescence Study of the Two-Dimensional Tetragonal and Rhombohedral Polymers of C_{60} at High Pressure

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ABSTRACT

The pressure behavior of the photoluminescence (PL) spectra of the planar polymeric phases of C_{60} have been studied at pressure up to 4 GPa. The PL spectra and the pressure-induced shift of the principal bands differ considerably for the pristine C_{60} , two-dimensional tetragonal (2D-T) and rhombohedral (2D-R) polymers of C_{60} . The changes in the PL spectra may be related with the transformation of the electron energy spectrum of polymers.

Key Words: Photoluminescence; Tetragonal polymers; Rhombohedral polymers; C_{60} ; Pressure.

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The optical transitions to the lowest excited singlet state of C_{60} (symmetry $^1T_{1g}$) are dipole forbidden, whereas the first allowed transition to $^1T_{1u}$ state has noticeably higher energy.^[1] The quantum yield of fluorescence is related to vibronically assisted transitions and increases from solution to solid due to the impurities and defects. The polymerization of C_{60} under high pressure and high temperature treatment changes the crystal structure and phonon spectrum of material and one can expect also changes in the electron energy spectrum of polymers.^[2,3] In view of this we have measured carefully the photoluminescence (PL) spectra of the planar C_{60} polymers, namely crystalline two-dimensional rhombohedral (2D-R) and tetragonal (2D-T) polymeric phases, at pressures up to 4.0 GPa and at room temperature.

The 2D-R polymer was obtained by subjecting 99.99% pure C_{60} powder to a pressure of $P \approx 5$ GPa at a temperature $T \approx 773$ K. The x-ray analysis confirmed the rhombohedral crystal structure (space group: $R\bar{3}m$).^[2] The 2D-T polymer (space group: $P4_2mmc$) was obtained in a similar way at $P \approx 2.2$ GPa and $T \approx 820$ K. The PL spectra were recorded with spatial resolution ~ 20 μm by the use of microscope arrangement for excitation and a single monochromator for registration, the spectral width of the system was

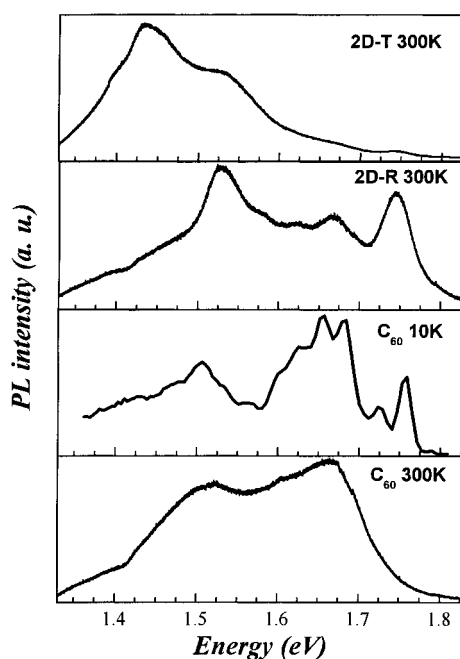


Figure 1. The PL spectra of the pristine C_{60} , 2D-R and 2D-T polymers at ambient pressure.



~0.5 meV. The samples were tested in order to identify the 2D-T and 2D-R phases by means of by micro-Raman probing. Measurements at high pressures were carried out using the diamond anvil cell of Mao-Bell type.

The PL spectra of the pristine C₆₀, 2D-R and 2D-T polymers at $T \approx 300$ K are shown in Fig. 1. The spectrum of the pristine C₆₀ at room temperature is rather diffuse but becomes well structured at $T = 10$ K due to the trapping of excitations on shallow defect levels.^[4] The PL spectrum of the 2D-R polymer at $T \approx 300$ K is structured while the spectrum of the 2D-T polymer is diffuse. Figure 2 shows the pressure dependence of the principal bands in the PL spectra of the 2D-R, 2D-T polymers and pristine C₆₀. The intensity distributions in the PL spectra and the pressure-induced shifts of the principal bands are quite different for the pristine C₆₀, 2D-T and 2D-R polymers. The pressure coefficients $\partial E/\partial P$ are equal to -80 , -25 , and -11 meV/GPa for main bands of the pristine C₆₀, 2D-R and 2D-T polymers, respectively. The deformation potential, $D = \partial E_g/\partial \ln(V_0/V) = -B_0 \times \partial E_g/\partial P$ where E_g is the direct gap and B_0 the bulk modulus of a material, drops from 1.15 eV for C₆₀ to

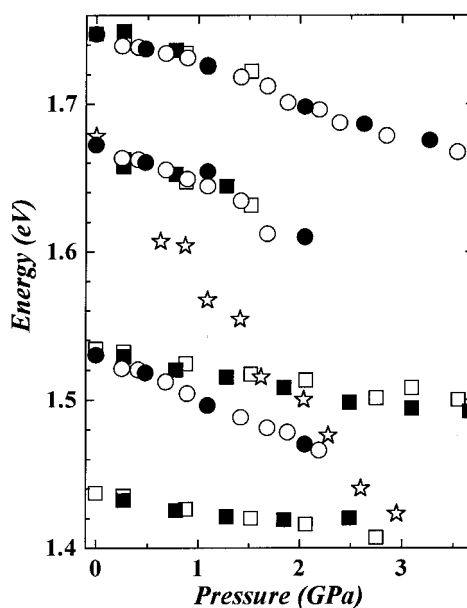


Figure 2. The pressure dependence of the principal bands in the PL spectra of the pristine C₆₀, 2D-R and 2D-T polymers. Circles and squares represent the data for 2D-R and 2D-T polymer, respectively; stars show the pressure dependence of the fluorescence band in the pristine C₆₀; open and solid symbols show increasing and decreasing pressure runs, respectively.



0.7 eV for 2D-R and to 0.33 eV for 2D-T. The decrease of the pressure coefficients is related with the increase of the bulk moduli B_0 of the C_{60} polymers (14.4, 28.1, and 29.9 GPa for the pristine C_{60} , 2D-R and 2D-T, respectively).^[5,6] Despite of proximity of B_0 the two planar polymers have rather different pressure coefficients and deformation potentials. In addition, the intensity distribution in the PL spectra of the 2D-R and 2D-T polymers is quite different. Taking into account the changes in the crystal structure and phonon spectra we suppose that polymerization of C_{60} transforms also the electron energy spectra in a way specified by the number and location of the intermolecular covalent bonds.

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