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## LETTER TO THE EDITOR

# Optical properties of high-pressure phases of C<sub>60</sub> fullerene

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**Abstract.** High-pressure phases of C<sub>60</sub> fullerene similar to those reported by Iwasa *et al* were obtained at a non-hydrostatic pressure of 3 GPa and different temperatures in the 100–500 °C range. The substances were investigated by means of infrared, optical and micro-Raman spectroscopies. Compared with pristine C<sub>60</sub>, the spectra of the transformed material reveal multiple changes which depend systematically on treatment conditions. They evidence a substantial modification of selection rules for allowed optical transitions apparently due to formation of C<sub>60</sub> molecules with deformed and/or partially destroyed cages.

The behaviour of C<sub>60</sub> fullerene at high pressure is rich in new phenomena. By application of non-hydrostatic pressure above 20 GPa at room (or close to room) temperature, solid C<sub>60</sub> is converted into polycrystalline cubic [1] or amorphous [2, 3] diamond. 5 GPa treatment of C<sub>60</sub> in the 300–800 °C temperature range under quasi-hydrostatic conditions results in the formation of two high-pressure phases with face-centred cubic (lattice parameter  $a_0 = 13.6 \text{ \AA}$ ) and rhombohedral structures [4, 5]. In our previous work [6] we reported transformation of C<sub>60</sub> into a very hard form of carbon which apparently comprises regions with sp<sup>3</sup> diamond-like carbon coordination. The transformation occurs under a strictly non-hydrostatic pressure of 3 GPa and a temperature 700 °C. The temperature was chosen to be close to the high-temperature limit of C<sub>60</sub> stability. As a continuation of our activity in this field we report now optical data on materials prepared from C<sub>60</sub> in a similar way at temperatures in the 100–500 °C range. Transformed substances resemble the high-pressure phases of C<sub>60</sub> obtained by Iwasa *et al* [4]. The discrepancy in conditions of the fabrication is related apparently to the non-hydrostatic pressure used in our case.

Initially, C<sub>60</sub> was prepared as described earlier, sealed in an Al<sub>2</sub>O<sub>3</sub> capsule and treated in the belt-type apparatus. Details of the treatment procedure may be found in [6]. Synthesis was carried out under a non-hydrostatic pressure of 3 GPa and at a fixed temperature in the 100–500 °C range for 2 hours. Specimens obtained at 500, 400, 300, 200 and 100 °C had the form of rather soft pellets 4 mm in diameter and 2 mm in length. They were practically insulating and insoluble in toluene. The specimens are labelled 500-C<sub>60</sub>, 400-C<sub>60</sub> and so on.

Powder x-ray diffraction spectra were taken with a Rigaku RINT 1000 diffractometer (Cu K $\alpha$  radiation). The data obtained are similar to patterns reported by Iwasa *et al*, namely, the 500-C<sub>60</sub> specimen shows distinct features of the phase indexed in [4] using the rhombohedral model, rh(pC<sub>60</sub>). All other transformed samples exhibit peaks of the second high-pressure phase, FCC(pC<sub>60</sub>). The 100-C<sub>60</sub> specimen reveals in addition reflections from the initial fullerene and should apparently be referred to a partially transformed material.

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Raman and luminescence spectra were measured using a Renishaw Raman Microscope in the region  $3500\text{--}200\text{ cm}^{-1}$  ( $640\text{--}810\text{ nm}$ ) at room temperature. The beam of the exciting He-Ne laser ( $\lambda_{\text{ex}} = 632.8\text{ nm}$ ) was focused in a  $20\text{ }\mu\text{m}$  spot; the laser power was kept at 22 mW. We concentrated mainly on broad luminescence bands as most specific for spectra of our pressure-treated samples. The measurement has shown substantial spatial inhomogeneity of the transformed material.

The powder IR absorption spectra were recorded with a Jasco FT/IR-VM7 Spectrometer (resolution  $2\text{ cm}^{-1}$ ) in the  $1600\text{--}400\text{ cm}^{-1}$  range as KBr pellets. The same pellets were used for measurements of UV and visible absorption spectra. The latter ones were carried out with a Hitachi U-3400 spectrophotometer in the  $230\text{--}800\text{ nm}$  ( $5.4\text{--}1.55\text{ eV}$ ) range. All pellets had approximately the same absorbance in the region investigated; pure KBr pellets were used as a reference. The KBr absorption may influence the shape of the spectra below  $300\text{ nm}$ .

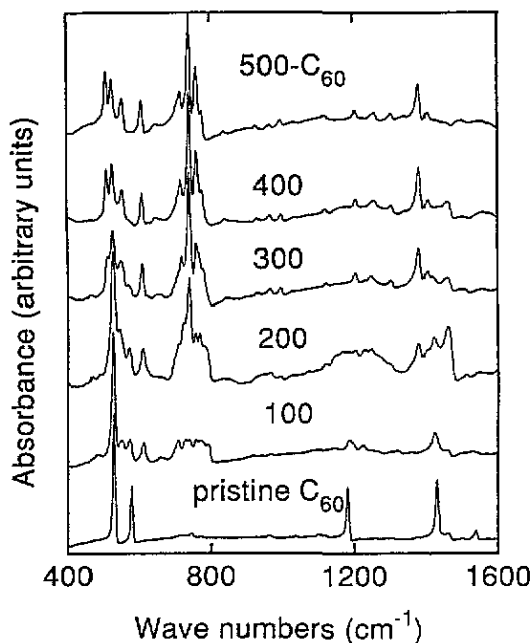


Figure 1. Infrared powder spectra of pristine  $\text{C}_{60}$  and specimens pressure-treated at different temperatures. The inclined background was subtracted.

IR and Raman spectra of the transformed material are shown in figures 1 and 2 correspondingly. The first of them is in good qualitative agreement with the data of Iwasa *et al* [4]. Raman spectra recorded by us in different microregions of our samples varied and therefore are not so distinct. This is related probably to a spatial inhomogeneity of the transformed material. Especially strong differences in the Raman data were observed for the  $500\text{ }^\circ\text{C}$  pressure-treated specimen. In order to reveal all details of the spectra, additional measurements are necessary.

It is well known that spectra of pristine  $\text{C}_{60}$  exhibit four IR-active  $\text{F}_{1u}$  modes at  $1429$ ,  $1183$ ,  $576$  and  $527\text{ cm}^{-1}$  (figure 1) and ten Raman-active vibrations with  $\text{A}_g$  and  $\text{H}_g$  symmetry at  $1572$ ,  $1469$ ,  $1425$ ,  $1249$ ,  $1099$ ,  $774$ ,  $709$ ,  $494$ ,  $431$  and  $273\text{ cm}^{-1}$ , see [7] for instance. IR spectra of the fullerene treated at  $100$  and  $200\text{ }^\circ\text{C}$  have some common features of the pristine compound and a new phase (figure 1). Indeed, four IR peaks of  $\text{C}_{60}$  may

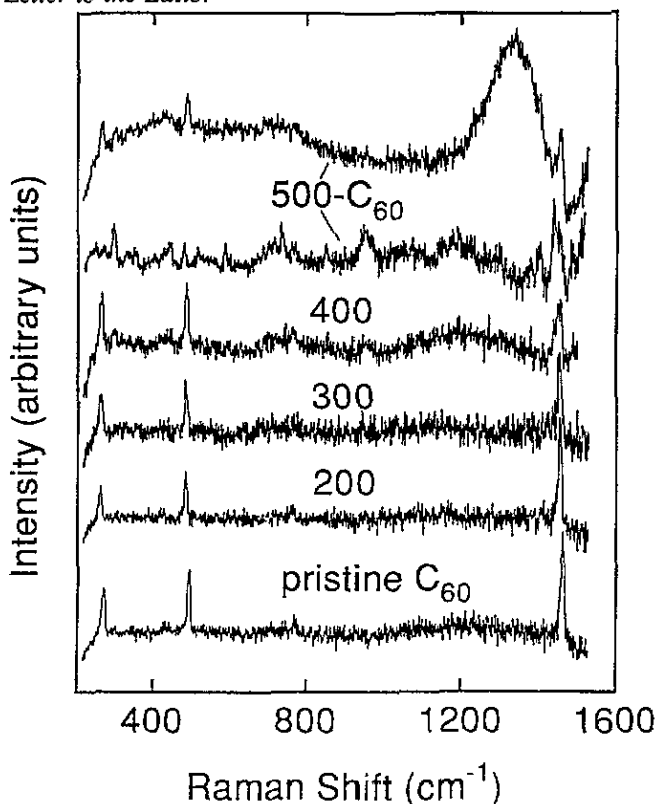


Figure 2. Micro-Raman spectra for pellets of pristine  $C_{60}$  and specimens pressure-treated at different temperatures. The luminescence background was subtracted.

be found in the spectra at very similar positions (table 1). Besides, an additional structure in the IR spectra reveals itself in the vicinity of Raman-active vibrations. This is observed in particular for the  $A_g$  'pentagonal pinch' mode near  $1469\text{ cm}^{-1}$  and  $H_g$  vibrations in the region  $710\text{--}780\text{ cm}^{-1}$  (figure 1). Changes in the Raman spectrum of the  $200\text{ }^\circ\text{C}$  treated specimen seem to be less drastic:  $1469$ ,  $494$  and  $273\text{ cm}^{-1}$  bands of pristine  $C_{60}$  move down to  $1453$ ,  $482$  and  $262\text{ cm}^{-1}$  correspondingly (figure 2). Substantially shifted strong IR peaks appear also near  $1381$ ,  $741$ ,  $608$  and  $542\text{ cm}^{-1}$ . The latter ones become dominant in the  $500\text{ }^\circ\text{C}$  treated specimen. Changes quite similar in shape in the IR spectra were observed earlier at photopolymerization of  $C_{60}$  [8].

Two different kinds of Raman spectra were recorded from the  $500\text{-}C_{60}$  specimen. The first of them has a broad (about  $200\text{ cm}^{-1}$ ) band with a maximum near  $1320\text{ cm}^{-1}$  (figure 2, upper curve). Sometimes, a similar peculiarity was also observed from samples pressure-treated at lower temperature. The band in this region is typical for the hard carbon converted from the  $C_{60}$  fullerene at  $700\text{ }^\circ\text{C}$  and  $3\text{ GPa}$  [6]. It may apparently be ascribed to a disordered graphite peak which, however, is normally located at  $1355\text{ cm}^{-1}$  [9]. The band is also close to the position of the diamond peak ( $1332\text{ cm}^{-1}$ ), but is essentially broader. The spectrum recorded (figure 2) consists of several narrow  $C_{60}$  peaks; nevertheless we believe that it originates mainly from an amorphous carbon phase of an apparently non-molecular nature. The Raman spectrum from the specimen of the second type (figure 2, lower curve) shows a lot of narrow bands which differ in position from the bands of pristine fullerene. Frequencies of these bands are included in table 1 and are probably related to a new  $C_{60}$  structure.

The transformation of the recorded IR spectra with the treatment conditions may be ascribed to a gradual reduction of the icosahedral symmetry of the  $C_{60}$  molecule. It should occur in particular if the spheroidal shape of the  $C_{60}$  cage is deformed with the uniaxial pressure. Appearance of planar disk-shaped fragments can result in an inter-molecular carbon-carbon  $\pi$ -bonding, like in graphite [9]. A distortion of the axial symmetry of the cages at the highest temperatures may also take place, resulting in formation of pear-shaped molecules. The structures are stable, probably due to strong covalent C-C (as proposed in [8]) or weaker  $\pi$ -bonding of adjacent cages. According to Raman data, one also cannot exclude a partial destruction of closed  $C_{60}$  shells as well as formation of an amorphous carbon phase. The analysis of molecular vibrations with variation of the symmetry of the  $C_{60}$  cages is now under way.

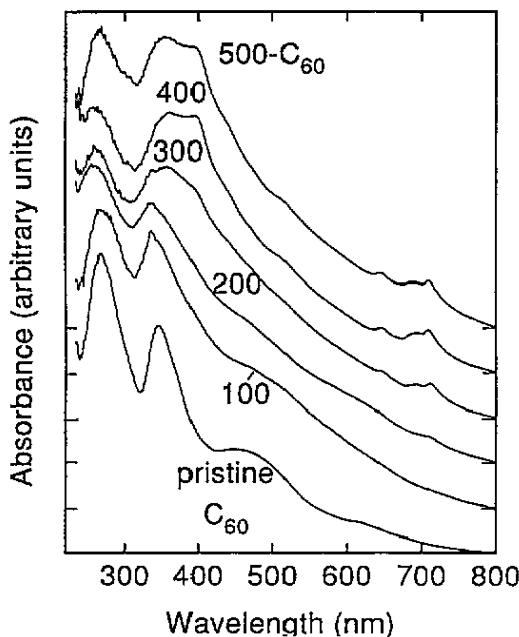


Figure 3. Powder optical absorption spectra of pristine  $C_{60}$  and specimens pressure-treated at different temperatures. In order to compare overall profiles of the spectra the relative differences in absorbance are not shown.

UV and visible absorption spectra of the pristine substance measured relative to a KBr pellet (figure 3) are similar to those reported by Kazaoui *et al* for  $C_{60}$  film [10]. The assignment of electronic transitions in the substance was carried out by Leach *et al* using solution data [11]. According to the work [11], intense peaks in the 230–410 nm region (5.4–3.0 eV) should be interpreted as allowed  ${}^1T_{1u} \rightarrow {}^1A_g$  transitions (C and E bands). The region 410–620 nm (3.0–2.0 eV) is related to several forbidden singlet–singlet transitions in the  $C_{60}$  molecule. One of them,  ${}^1T_{1g} \rightarrow {}^1A_g$  (labelled  $\gamma$  in [11]), is responsible for the hump near 620 nm. Very weak bands in the  $C_{60}$  solution near 680 and 700 nm (1.82 and 1.77 eV) are due to forbidden transitions involving  ${}^3T_{1g}$  and  ${}^3T_{2g}$  triplet electronic states. Sharp bands at 670 and 750 nm (1.85 and 1.65 eV) from  $C_{60}$  in benzene were recorded by Bensasson *et al* [12] using a pulse radiolysis technique. They were interpreted as  ${}^3H_u \rightarrow {}^3T_{2g}$  and/or  ${}^3G_u \rightarrow {}^3T_{2g}$  triplet–triplet transitions. It was also pointed out that the transition from the ground  ${}^1A_g$  to  ${}^3T_{2g}$  state becomes allowed if the  $C_{60}$  cage exhibits a static Jahn–Teller

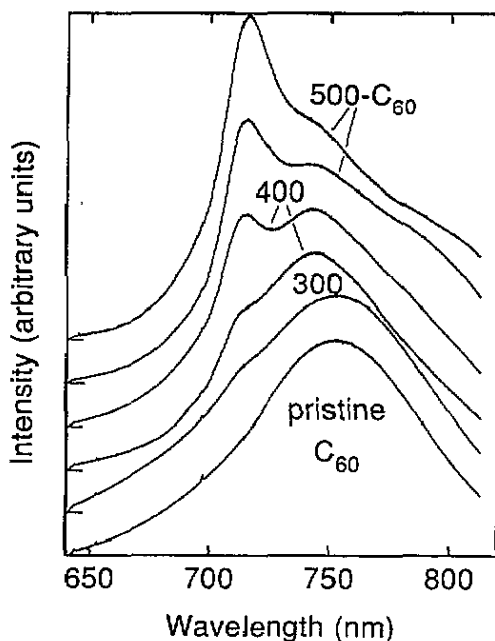
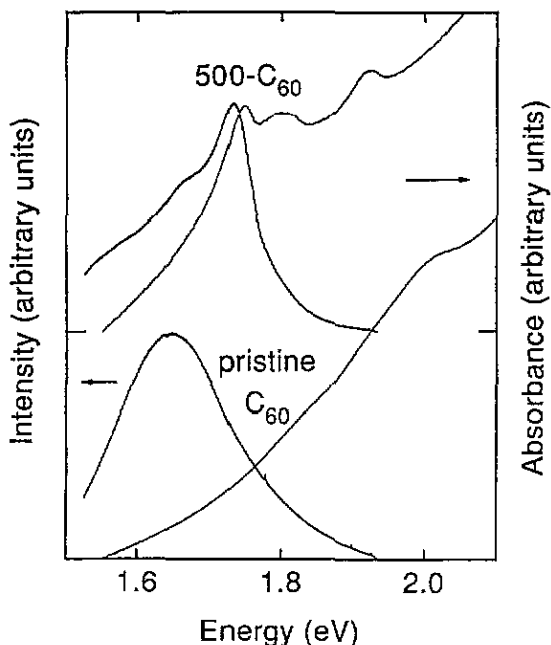


Figure 4. Room temperature luminescence spectra for pellets of pristine  $C_{60}$  and specimens pressure-treated at different temperatures. In order to compare overall profile of the spectra the relative differences in intensity are not shown.

distortion. Steep increase of the absorption coefficient of the  $C_{60}$  single crystal in 830–720 nm (1.5–1.7 eV) region was also observed by Wen *et al* with the constant photocurrent method [13].

Figure 3 shows that UV and visible spectra are sensitive to the high-pressure treatment of  $C_{60}$ . Weak but distinct bands in the 640–710 nm (1.94–1.75 eV) region already appear for the 200- $C_{60}$  specimen. The material treated at higher temperatures reveals three distinct bands at 643, 688, 709 nm (1.93, 1.80, 1.75 eV). This is accompanied by the dramatic transformation of the spectrum near 395 nm (3.14 eV). The new strong band appears in the region of transitions allowed for  $C_{60}$  molecule. Its position in the spectrum is close to A and B  ${}^1T_{1u}-{}^1A_g$  transitions, which in the pristine substance have a relatively small oscillator strength [11]. Positions of two other strong bands (C and E) in 500- $C_{60}$  (267 and 355 nm or 4.64 and 3.49 eV) do not change substantially compared with the solid state spectrum of the starting material (267 and 346 nm or 4.64 and 3.58 eV correspondingly). A weak peculiarity in the 500- $C_{60}$  spectrum is observed also at 508 nm (2.44 eV).

Intense bands in the region of forbidden transitions for the pristine substance are consistent with the assumption of appearance of a stable static deformation of  $C_{60}$  cages at the pressure–temperature treatment. This results in changes of selection rules for allowed optical transitions and rather modest variation of their energies. The room temperature luminescence spectra of compounds investigated are shown in figure 4. The spectrum of pristine  $C_{60}$  coincides with multiple data reported previously (with a restriction only on the wavelength range available), see [10, 12, 13] and references therein. A broad maximum is located near 750 nm. The overall profile of the spectrum does not change much in 100 °C and 200 °C pressure-treated samples. Sometimes only its maximum is recorded at approximately 740 nm. The shift however lies within an uncertainty in the luminescence



**Figure 5.** The comparison of luminescence (on the left) and absorption (on the right) spectra of pristine  $C_{60}$  and specimen pressure treated at 500 C. Relative differences in intensity and absorbance are not shown.

peak position observed for  $C_{60}$  films and crystals [10,13]. The substantial deviation in the shape of the spectrum appears for the 300- $C_{60}$  specimen (figure 4). A new, quite narrow peak near 715 nm increases its strength in 400 °C treated material and becomes dominant in 500 °C treated  $C_{60}$ . The relative intensity of the 715 nm peak compared with the 740 nm band depends on the spatial position of the laser excitation spot on the sample surface. The intensity ratio of the band is usually equal to 0.7–1.0 for 400- $C_{60}$  and 0.9–1.5 for 500- $C_{60}$ ; corresponding typical spectra are presented in figure 4.

The blue-shifted peak was earlier observed in low-temperature luminescence spectra of  $C_{60}$  crystals and ascribed to defect-related luminescence originated from X traps [13]. It appears, however, that the defects can be easily created with the pressure–temperature treatment. They sharply reveal themselves not only in the room temperature luminescence but also in IR, Raman and optical absorption spectra. In our opinion, the defects may be related to  $C_{60}$  molecules with deformed or partially destroyed cages.

The comparison of luminescence and related absorption data for the pristine and 500 °C treated material is shown in figure 5. One can see that lack of mirror symmetry between the spectra in the pristine material is restored for the 500- $C_{60}$  specimen. In the latter case, allowed electronic states probably contribute to both emission and absorption spectra.

In summary, high-pressure phases of  $C_{60}$  were obtained at non-hydrostatic pressures of about 3 GPa and temperatures in the 100–500 °C range. The material was characterized with IR, Raman, optical absorption and luminescence spectra which comprise a lot of new bands compared with the pristine fullerene. The bands can tentatively be explained by the assumption that the spheroidal shape of the  $C_{60}$  molecule is deformed and/or partially destroyed with the pressure–temperature treatment. The structures obtained are stable, probably due to linking of adjacent  $C_{60}$  cages with strong covalent C–C or weaker  $\pi$

**Table 1.** Infrared and Raman spectra of specimens pressure-treated at 200 °C and 500 °C ( $\text{cm}^{-1}$ )<sup>a</sup>.

200-C <sub>60</sub>		500-C <sub>60</sub> <sup>b</sup>	
Infrared	Raman	Infrared	Raman
1462 s	1453 s		
1422 m			1437 m, br
1404 w		1406 w	1400 w
1381 m		1383 m	
1306 vw		1306 w	
1250 w		1260 w 1229 w	
1206 w		1206 w	
1152 vw			
1173 vw			
1119 w		1123 w	
993 vw		997 w	
966 vw		960 w	947 w, br
		932 w	
		841 vw	848 w
783 m		777 m	
770 m	764 vw	762 s	759 vw
758 m			
741 vs		743 vs	733 w
725 sh			
710 m		717 m	715 vw ?
			700 vw ?
		646 w, br	685 vw ?
608 m		608 m	585 w
571 m			
542 s		554 m	
525 vs		525 m	
		509 s	512 vw ?
486 vw	482 m		477 w
465 w		441 w	
	426 vw		
	262 m		295 w

<sup>a</sup> Relative intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

<sup>b</sup> Shape of the spectrum varies in different spatial regions on the surface of the sample.

bonds. Similar species with distorted and/or dimerized molecules may also be created in small quantities at photopolymerization of C<sub>60</sub> or growing of C<sub>60</sub> crystals. A mechanically hard inorganic structure with apparently sp<sup>3</sup> coordinated diamond-like regions is converted from C<sub>60</sub> fullerene with 3 GPa pressure treatment at 700 °C.

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