

## FIGURE CAPTIONS

- Fig.1-1. Structural view of a  $C_{60}$  molecule drawn by Burgi *et al* [2].
- Fig.1-2. Structure view of a FCC unit cell of a  $C_{60}$  single crystal drawn by Burgi *et al* [2].
- Fig.1-3. A schematic view of tetrahedral and octahedral regular interstitial sites in a FCC unit cell of a  $C_{60}$  single crystal. Solid circles represent  $C_{60}$  molecules.
- Fig.1-4. (a) A schematic energy level diagram for the  $C_{60}$  molecule. S and T indicate the singlet and triplet states, respectively. M and D indicate molecule and dimer states, respectively. (b) The bimolecular chemical reaction model of the [2+2] cycloaddition mechanism [19].
- Fig.1-5. A NaCl structure of an  $A_1C_{60}$  compound. Intermolecular bonds are created in the temperature lower than *ca.* 400K in [110] directions. Large and small balls represent  $C_{60}$  molecules and alkali ions, respectively.
- Fig.1-6. Structural model of  $C_{60}$  polymers fabricated by high-pressure and high-temperature treatments.
- Fig.1-7. Structural model of three-dimensional  $C_{60}$  polymer reported by Okada *et al.* [40]. Red spheres denote the four-coordinated  $sp^3$  carbon atoms.
- Fig. 2-1. A schematic picture of electric furnace and a quartz tube.  $T_1$  and  $T_2$  denote the temperatures at the cold and hot ends of the quartz tube, respectively.
- Fig. 2-2. (a) A schematic illustration for weighing alkali metals. (b) A schematic illustration for the *in situ* Raman measurements during potassium doping process to  $C_{60}$  thin film.
- Fig. 2-3. Optical arrangement for optical transmittance measurements.
- Fig. 2-4. Optical arrangement for photoluminescence measurements.
- Fig. 2-5. Optical arrangement for Raman scattering measurements.
- Fig. 2-6. A set of diamond anvil cell of the Mao-Bell type used in the present study.
- Fig. 2-7. An illustration of pressure generation with a diamond anvil cell.
- Fig. 2-8. The pressure dependence of ruby florescence lines when paraffin oil is used for the pressure transmitting medium. The FWHMs of the R1 line are plotted as a function of pressure in the upper part of the figure.
- Fig. 3-1. X-ray diffraction (XRD) patterns of pure- $C_{60}$  and  $I_xC_{60}$  compounds. XRD

patterns show that the structure of the  $I_xC_{60}$  varies from FCC to hexagonal lattice.

- Fig. 3-2. A structural model of an  $I_4C_{60}$  compound with hexagonal lattice [30]. The small closed circles denote iodine atoms. Large open circles denote  $C_{60}$  molecules.
- Fig. 3-3. (a) Raman scattering spectra of the  $C_{60}$  single crystal, fcc- $I_xC_{60}$ , and hex- $I_xC_{60}$  in the frequency region from 120 to 800  $\text{cm}^{-1}$  at 80 K and room temperature. (b) Raman scattering spectra of the  $C_{60}$  single crystal, fcc- $I_xC_{60}$ , and hex- $I_xC_{60}$  in the frequency region from 1380 to 1600  $\text{cm}^{-1}$  at room temperature.
- Fig. 3-4. (a) Raman scattering spectra of the hex- $I_xC_{60}$  in the temperature range from 4 K to 250 K. (b) The result of the peak fitting to data using some Gaussian components. A broken line denotes the Raman spectrum which was obtained at 18 K. Asterisks indicate the plasma lines of an  $\text{Ar}^+$  laser. (c) Temperature dependence of the frequencies of Raman bands obtained by the peak fittings in the same way as illustrated in (b).
- Fig. 3-5. Structural models of alkali metal doped  $C_{60}$  compounds. Large and small balls denote  $C_{60}$  molecules and alkali ions, respectively. A FCC  $C_{60}$  single crystal is drawn in an equivalent body centered tetragonal representation (bct) in order to describe structural changes to body centered cubic (bcc) structure of  $A_6C_{60}$  compound. Body centered cubic representation of a FCC unit cell has been shown in Fig. 1-5.
- Fig. 3-6. *In situ* Raman scattering spectra of  $A_xC_{60}$  film during potassium doping at 140 °C.
- Fig. 3-7. A schematic picture of the  $A_g(2)$  intramolecular vibrational mode and changes in the Raman spectrum of a  $C_{60}$  single crystal caused by photo-polymerization. Dotted and solid lines represent the Raman data and Gaussian components fitted to data.
- Fig. 3-8. Changes in photoluminescence spectrum of a  $C_{60}$  single crystal caused by photo-polymerization. (a) and (b) correspond to the PL spectra of the pristine and photo-polymerized  $C_{60}$ , respectively.
- Fig. 3-9. Photoluminescence spectra of PIHP materials. All PL spectra were recorded

at ambient pressure. Dots denote PL data. Solid and dotted lines denote Gaussian components fitted to data.

- Fig. 3-10. Applied pressure dependence of PL peak energy and band gap energy of  $C_{60}$  samples.  $\circ$  and  $\bullet$  denote the band gap energy of the PIHP materials at ambient pressure obtained from PL (Fig. 3-9) and OT data (Fig. 3-11), respectively. A broken line denotes the energy shifts of the  $C_{60}$  single crystals under pressure obtained by *in situ* PL measurements (Fig. 3-12).  $\square$  indicates the PL peak energy of  $C_{60}$  samples obtained after the pressure treatments without photo-irradiation (Fig. 3-13).
- Fig. 3-11. Optical transmittance spectra of PIHP materials: (a) original, (b) 7.7 GPa, (c) 10.6 GPa, (d) 18.9 GPa, (e) 30.0 GPa. All spectra were recorded at ambient pressure. The straight lines attached to spectrum (a) illustrate an estimation of the energy gap,  $E_g$ .
- Fig. 3-12. PL spectra of  $C_{60}$  single crystal under high pressure up to 5 GPa. The left and right hand side graphs correspond to pressure increase and decrease runs, respectively.
- Fig. 3-13. PL spectra of  $C_{60}$  single crystal at ambient pressure after subjecting to the pressure treatment up to 26 GPa without photo-irradiation.
- Fig. 3-14. Raman scattering spectra of PIHP materials at ambient pressure.
- Fig. 3-15. Results of peak fitting with Gaussian components to data which are presented in Fig. 3-14. Dots and solid lines denote Raman data and the Gaussian components, respectively.
- Fig. 3-16. Peak frequencies and FWHM (full width at half maximum) of the  $A_g(2)$  mode and the p- $A_g$  mode of the PIHP materials at ambient pressure as functions of the applied pressure at PIHP treatments. The  $A_g(2)$  and p- $A_g$  modes are denoted by circles and squares, respectively.
- Fig. 3-17. Photoluminescence spectra of HPHT polymers in the temperature range from 15 to 300 K [72].
- Fig. 3-18. Raman spectra of the pristine  $C_{60}$  (a),  $C_{60}$  dimer (b), 1D orthorhombic (c) and (d), 2D tetragonal (e), and 2D rhombohedral (f) structures [33]. Spectra (a)~(c) were excited with the 1064 nm line, and spectra (d)~(f) were excited with the 568.2 nm line.

- Fig. 3-19. Pressure dependence of the frequency of the p-A<sub>g</sub> mode (●) and the energy of the PL band (■) of the C<sub>60</sub> photopolymer, and the applied pressure dependence of the frequency of the p-A<sub>g</sub> mode (○) and the energy of the PL band (□) of PIHP materials. The solid and broken lines are the least squares fits to the data.
- Fig. 3-20. The fictive pressures which were obtained from Raman and PL data. Circles and squares denote the  $P_f^R$  and  $P_f^{PL}$ , respectively.
- Fig. 3-21. *In situ* high pressure PL spectra of the C<sub>60</sub> photopolymer. The PL peak energies which are obtained in the same way as described in Fig. 3-9 are plotted as a function of pressure in the right figure.
- Fig. 3-22. *In situ* high pressure Raman spectra of the C<sub>60</sub> photopolymer. Thick and thin arrows indicate the p-A<sub>g</sub> and A<sub>g</sub>(2) mode, respectively. The frequency of the p-A<sub>g</sub> mode is plotted as a function of pressure in the right figure.
- Fig. 3-23. Schematic pictures of the two factors in the formation of intermolecular bonds.
- Fig. 3-24. The comparison of the energy gap shift ( $\Delta E_g$ ) between a C<sub>60</sub> crystal and 2D HPHT polymers. Open and solid circles denote the  $\Delta E_g$  based on the absorption measurement of a C<sub>60</sub> crystal under pressure [73] and the theoretically obtained  $\Delta E_g$  of 2D polymers [75], respectively.
- Fig. 3-25. Conversion of the fictive pressures (left axis) to the Raman frequencies (right axis) in accordance with the pressure coefficient of the p-A<sub>g</sub> mode of the C<sub>60</sub> photopolymer, 6.3 cm<sup>-1</sup>/GPa. Squares and circles correspond to the PL and Raman results, respectively.
- Fig. 3-26. A pressure-temperature phase diagram for HPHT C<sub>60</sub> polymers [78].
- Fig. 3-27. (a) PL and (b) Raman spectra at ambient condition of C<sub>60</sub> single crystals which were subjected to HPHT treatments.
- Fig. 3-28. Temperature and photo-irradiation time dependence of the PL spectra of C<sub>60</sub> samples. (A), (B), and (C) correspond to the results of the PIHP treatments at room temperature, 75 °C, and 100 °C, respectively. All PL spectra were recorded at ambient condition after the photo-irradiation at HPHT condition.
- Fig. 3-29. Illustration of the PL analysis for the PIHP treatments at room temperature using two PL elements, I<sub>BeF</sub> and I<sub>Aft</sub>. (a) PL spectra of the pristine C<sub>60</sub> single

crystal ( $I_{\text{Bef}}$ ) and (b) PL spectra of  $C_{60}$  sample which was subjected to photo-irradiation under HPHT condition for 90 minutes ( $I_{\text{Aft}}$ ). In the left figure, dotted and chain lines denote  $I_{\text{Bef}}$  and  $I_{\text{Aft}}$  components, respectively.

Fig. 3-30. PL analyses for the PIHP treatment at 75 °C, and 100 °C. These analyses were performed in the same way described in Fig. 3-29.

Fig. 3-31. The ratios,  $I_{\text{Aft}}/I_{\text{Bef}}$ , as functions of the photo-irradiation time at room temperature ( $\blacktriangle$ ), 75 °C ( $\bullet$ ), and 100 °C ( $\blacksquare$ ). The dashed lines indicate fits to the data using exponential functions to obtain time constants  $\tau$ . Arrhenius plots are shown in the inset.

Fig. 3-32. *In situ* high pressure Raman scattering spectra of the hex- $I_xC_{60}$  up to 11 GPa. Raman spectra relevant to iodine molecules and  $C_{60}$  molecules are shown by dots in (a) and (b), respectively. The up and down arrows in parentheses denote the pressure increase and decrease process, respectively. Solid lines denote Gaussian components fitted to data.

Fig. 3-33. Pressure dependence of the peak frequency of the peak-A and  $A_g(2)$  mode. Open and closed notations indicate pressure increase and decrease runs, respectively.

Fig. 3-34. The photo-irradiation time dependence of Raman spectra of the (a)  $C_{60}$  single crystal, (b) fcc- $I_xC_{60}$  and (c) hex- $I_xC_{60}$  at ambient pressure. Solid lines denote Lorentz functions fitted to Raman data represented by dots.

Fig. 3-35. Intensity ratios,  $I_{\text{p-Ag}}/(I_{\text{p-Ag}}+I_{\text{Ag}(2)})$ , as functions of photo-irradiation time at ambient pressure. The ratios obtained from  $C_{60}$  single crystal, fcc- $I_xC_{60}$  and hex- $I_xC_{60}$  are denoted by circles, squares and triangles, respectively.

Fig. 3-36. Photo-irradiation time dependence of Raman spectra of the fcc- $I_xC_{60}$  at ambient pressure.

Fig. 3-37. Graphitic particle size,  $La$ , as a function of the photo-irradiation time. The diameter,  $La$ , was estimated using equation 3.1.

Fig. 3-38. Raman spectra of the fcc- $I_xC_{60}$  which were obtained after the PIHP treatments up to ~37 GPa. The 488.0 nm (a) and 514.5 nm (b) lines were used for the photo-irradiation.

Fig. 3-39. Raman spectra of the hex- $I_xC_{60}$  which were obtained after the PIHP treatments up to ~30 GPa. The 457.9 nm (a), 514.5 nm (b) and the 647.1 nm

(c) lines were used for the photo-irradiation.

- Fig. 3-40. Illustration of the peak fitting with Gaussian components to Raman spectra of the fcc- $I_xC_{60}$  and hex- $I_xC_{60}$  after PIHP treatments. The Raman spectra of the fcc- $I_xC_{60}$  and hex- $I_xC_{60}$  correspond to those shown in Fig. 3-38 (b) and Fig. 3-39 (b), respectively.
- Fig. 3-41. The frequency of the  $p-A_g$  mode of (a) fcc- $I_xC_{60}$  and (b) hex- $I_xC_{60}$  as functions of pressure applied at PIHP treatments. (a)  $\square$  and  $\circ$  correspond to the results of the PIHP treatments with 514.5 nm and 488.0 nm lines, respectively.  $\Delta$  denotes the results of the PIHP treatment for the  $C_{60}$  single crystal with the 488.0 nm line. (b)  $\bullet$ ,  $\square$  and  $\circ$  correspond to the results of the PIHP treatments with 647.1 nm, 514.5 nm and 457.9 nm lines, respectively.  $\Delta$  is same as in the case of (a).
- Fig. 3-42. Changes in the Raman spectra of the  $I_xC_{60}$  compounds which were subjected to pressure treatments (a) without and (b) with photo-irradiation. The original Raman spectra of the  $I_xC_{60}$  compounds are shown in the upper graph in (b).
- Fig. 3-43. Raman spectra of  $K_3C_{60}$  at ambient condition after subjecting to the PIHP treatment at 200 °C. Experimental conditions are presented in the upper part of each graph.
- Fig. 3-44. Raman spectra of  $K_6C_{60}$  at ambient condition after subjecting to photo-irradiation under HPHT conditions. Experimental conditions are presented in the upper part of each graph. In the left graph, two different PIHP treatments were performed onto the same sample continuously at room temperature (RT).
- Fig. 3-45. *In situ* high pressure Raman scattering spectra of  $Rb_3C_{60}$  and  $K_3C_{60}$  in the frequency range from  $1350\text{ cm}^{-1}$  to  $1520\text{ cm}^{-1}$ .
- Fig. 3-46. *In situ* high pressure Raman scattering spectra of  $Rb_6C_{60}$  and  $K_6C_{60}$  in the frequency range from  $1350\text{ cm}^{-1}$  to  $1550\text{ cm}^{-1}$ .
- Fig. 3-47. Peak frequencies of the  $H_g(7)$ ,  $H_g(8)$ , and  $A_g(2)$  mode of the  $C_{60}$  single crystal [77] and  $A_xC_{60}$  ( $A=Rb, K$   $x=3, 6$ ) as functions of pressure. Explanations of notation and pressure coefficients are given in the figure.
- Fig. 3-48. *In situ* high pressure Raman scattering spectra of  $Rb_3C_{60}$  and  $K_3C_{60}$  in the

frequency range from  $230\text{ cm}^{-1}$  to  $720\text{ cm}^{-1}$ .

Fig. 3-49. *In situ* high pressure Raman scattering spectra of  $\text{Rb}_6\text{C}_{60}$  and  $\text{K}_6\text{C}_{60}$  in the frequency range from  $230\text{ cm}^{-1}$  to  $720\text{ cm}^{-1}$ . Asterisks indicate the plasma lines of an  $\text{Ar}^+$  laser.

Fig. 3-50. Peak frequencies of the  $\text{H}_g(1)$  and  $\text{A}_g(1)$  modes of the  $\text{C}_{60}$  single crystal and  $\text{A}_x\text{C}_{60}$  ( $\text{A}=\text{Rb}$ ,  $\text{K}$   $x=3, 6$ ) as functions of pressure. Explanations of notation and pressure coefficients are given for  $\text{A}_g(1)$  modes in the right figure.

Fig. 3-51. Stereographic representation of the  $\text{H}_g(1)$ ,  $\text{A}_g(1)$ , and  $\text{A}_g(2)$  modes of the  $\text{C}_{60}$  molecule [81].

Fig. 3-52. Normalized frequencies of  $\text{H}_g(1)$ ,  $\text{A}_g(1)$ , and  $\text{A}_g(2)$  mode are plotted as functions of normalized volumes of  $\text{C}_{60}$  single crystal and  $\text{A}_x\text{C}_{60}$  compounds ( $\text{A}=\text{Rb}$ ,  $\text{K}$   $x=3, 6$ ). The Grüneisen parameters are tabulated for  $\text{A}_g(1)$  and  $\text{A}_g(2)$  modes.

Fig. 4-1. *In situ* high pressure PL spectra of the T polymer. [76]