

## 4. DISCUSSIONS

### 4.1 Local structure of the photo-irradiated C<sub>60</sub> single crystals under high pressure

In this section, we attempt to make the structural picture of the PIHP materials clear. The main feature of the photo-induced structural transformation of C<sub>60</sub> single crystals is a consecutive increase in the intermolecular bonds per C<sub>60</sub> with an increase in the pressure applied at photo-irradiation. The experimental results presented in section 3.2 are markedly new phenomena concerning to the C<sub>60</sub> polymer. In spite of the novelty of the experimental results, it is difficult to visualize the structure of the PIHP materials. The difficulty arises from the fact that the photo-polymerization proceeds into random directions. The randomness is naturally understood because the C<sub>60</sub> molecule contains 30 double bonds which have the ability to form intermolecular bonds tangential to the C<sub>60</sub> ball surface. There are 30×30=900 favorable configurations for the [2+2] cycloaddition mechanism between two freely spinning C<sub>60</sub> molecules. Additionally, the basic requirements for the initiation of the [2+2] cycloaddition reaction are the intermolecular distance being less than ~ 4.2 Å with the parallel configuration of C=C bonds and the presence of photochemical assistance. Furthermore, the solid C<sub>60</sub> including C<sub>60</sub> polymers has several kinds of metastable structures due to the ductility of the lattice of molecular solid and flexible character of  $sp^2/sp^3$  carbon.

We compare the frequency of the p-A<sub>g</sub> mode of the PIHP material with that of the HPHT crystalline polymer which has the same number of the intermolecular bond. The PIHP treatment at about 20 GPa has been estimated to introduce 4 intermolecular bonds onto a C<sub>60</sub> molecule on average whose number is equal to that of the two-dimensional T polymer. The frequency of the p-A<sub>g</sub> mode of the PIHP material at 20 GPa was 1463 cm<sup>-1</sup>. This frequency of the p-A<sub>g</sub> mode is 17 cm<sup>-1</sup> higher than that of the T polymer (1449 cm<sup>-1</sup>). The difference in the frequency of the p-A<sub>g</sub> mode between the PIHP and HPHT materials suggests that the contraction of intermolecular distance in the PIHP material is greater than that in the two-dimensional HPHT polymer. The shift to the higher frequencies can be attributed to three-dimensional expansion of the intermolecular bonds of the PIHP materials. The intermolecular bonds of the PIHP

materials could prevent the structural relaxation of  $C_{60}$  lattice as observed in the c-axis (normal to the polymer plane) of 2D HPHT polymers. Meletov *et al.* have reported the *in situ* high pressure PL and Raman spectra of the T polymer under pressure [76]. They have determined the pressure dependence of the  $p-A_g$  mode of the T polymer as  $6.1 \text{ cm}^{-1}/\text{GPa}$ . According to the pressure coefficient, the frequency of the  $p-A_g$  mode of the PIHP material at 20 GPa can be reproduced by the application of  $\sim 2.5$  GPa on the T polymer. The PL spectra obtained after the PIHP treatment at  $\sim 20$  GPa is very similar to the PL spectra of the T polymer at  $\sim 2.5$  GPa as shown in Fig. 4-1 [76]. The peak energy of the main PL band of the T polymer at around  $\sim 1.4$  eV is close to the PL energy of the PIHP material obtained after the photo-irradiation at 20 GPa. As already discussed in section 3.2, the electronic properties of  $C_{60}$  polymers are mostly governed by the intermolecular distance rather than deformation of the  $C_{60}$  cage due to the formation of the intermolecular bonds. The coincidence of the PL peak energies between PIHP material and the T polymer under  $\sim 2.5$  GPa indicates that the average environment of the  $C_{60}$  molecule is similar each other. This result is consistent with the Raman data and specifies the expansion of intermolecular bonds in the PIHP materials not only into one-, and two-dimensions but also into three-dimensions.

For graphical understanding, we suggest the local structural model of the PIHP material. So far, structural analyses of the  $C_{60}$  photopolymer have been carried out from theoretical approach [16,17,18] because of the experimental difficulty arising from the inherent disorder in the bonding pattern of the  $C_{60}$  photopolymer. However, the polymerization will start with formation of the  $C_{60}$  dimer with the nearest neighbor molecule. We can imagine the structure of the  $C_{60}$  single crystal at the beginning of the photo-polymerization as the partially distorted FCC lattice of  $C_{60}$  single crystal where  $C_{60}$  dimer is formed between  $C_{60}$  molecules which are initially positioned at (0,0,0) and (1/2,1/2,0) while other molecules still are situated at initial lattice points. There are 18 isolated  $C_{60}$  molecules which are capable of adducting the dimer to form  $C_{60}$  trimers at the FCC lattice points in this configuration. From symmetrical consideration of  $C_{60}$  molecule, four of the  $C_{60}$  molecules will lead to an angle of  $60^\circ$  between the centers of the molecules which form  $C_{60}$  trimer, and four to  $90^\circ$ , eight to  $120^\circ$ , and two to  $180^\circ$ . Porezag and Frauenheim [18] have investigated the structure, energetics, and vibrational properties of  $C_{60}$  oligomers,  $[C_{60}]_n$  ( $n=2\sim 4$ ). They calculated the cohesive energies of

the structural candidates of  $C_{60}$  trimers whose approximate angles between the centers of the molecules bounded by ordinal [2+2] cycloadditional four-membered rings are  $60^\circ$ ,  $72^\circ$ ,  $90^\circ$ ,  $108^\circ$ ,  $120^\circ$ ,  $144^\circ$ , and  $180^\circ$ , and also  $C_{60}$  tetramers including linear chain, square-, zigzag-, T-, and star-shape. They predicted that all  $C_{60}$  oligomers are more stable than the non-interlinked  $C_{60}$  monomers and the energy differences among different oligomer structures are very small. From experimental approach, Pusztai *et al.* have investigated the structure of the  $C_{60}$  photopolymer with DSC, IR, and XRD measurements [84]. They observed doubled XRD pattern which could be assigned to the superposition of two FCC lattices having slightly different lattice constant. A lattice constant of 14.15 Å was attributed to the pristine  $C_{60}$  crystal and 13.90 Å to the  $C_{60}$  photopolymer. They also evaluated the number of the [2+2] cycloadditional bonds per  $C_{60}$  from transformation enthalpy during the decomposition of the  $C_{60}$  photopolymer into monomeric  $C_{60}$  from DSC measurements, and concluded that two intermolecular bonds per  $C_{60}$  were created out of possible 12 nearest neighbors. As structural pictures of the  $C_{60}$  photopolymer, they suggested closed triangle- and square-shaped oligomers which localized around FCC lattice points, in order to keep consistency between the results from DSC and XRD investigations. These are the possible structural models of the  $C_{60}$  photopolymer.

The structural transformation of  $C_{60}$  single crystals by PIHP treatments can be considered as an extension of the photo-polymerization at ambient condition. The intermolecular connections formed by the PIHP treatments would be achieved through the [2+2] cycloaddition mechanism at least at 3 GPa because the activation energy of the photo-polymerization at 3 GPa was equal to that of the photo-polymerization at ambient pressure. It can be considered that the external pressure applied during photo-irradiation increases the probability of the  $C_{60}$  interconnection and enlarges the size of the  $C_{60}$  oligomers. The three-dimensional structure of PIHP material would be achieved by the large-scale random polymerization as derivatives from the  $C_{60}$  oligomers formed at ambient pressure. This model can explain the continuous changes in the electronic and vibrational properties of PIHP materials which were treated in mild PIHP conditions. The PIHP materials with the 2 ~ 3 intermolecular bonds have the quasi three-dimensional structure of the aggregated small  $C_{60}$  clusters in entangled fashion. The photo-induced structural transformation of  $C_{60}$  single crystals under high

pressure can be summarized as follows:

“Three-dimensional  $C_{60}$  network structure can be achieved by the photo-irradiation under high pressure. The number of intermolecular bond increases with the pressure applied at photo-irradiation and reaches to *ca.* 5 bonds with the applied pressure of 25 GPa. The three-dimensional  $C_{60}$  network can be considered as randomly bounded  $C_{60}$  metastable phase.”

## 4.2 Doping effects on the photo-induced structural transformation of $C_{60}$ under high pressure

In this section, we discuss the doping effects on the structural transformation of  $C_{60}$ . A main focus is made on the schematic understanding of the structural transformation of iodine doped  $C_{60}$  compounds. Secondly, possible reasons for the complete suppression of photo-induced transformation of alkalis doped  $C_{60}$  are addressed.

At first, we discuss the structure of the photo-irradiated  $I_xC_{60}$  compounds and the mechanism of the photo-induced transformation of the  $I_xC_{60}$  compounds. As presented in section 3.3, the  $I_xC_{60}$  was insensitive to the photo-irradiation in contrast to the  $C_{60}$  single crystal. The Raman investigations for the compounds which had been subjected to the PIHP treatments up to 37 GPa revealed that the frequency of the  $p-A_g$  mode of neither  $fcc-I_xC_{60}$  nor  $hex-I_xC_{60}$  did depend on the pressure applied during the photo-irradiation. The average frequency of the  $p-A_g$  mode was  $1463\text{ cm}^{-1}$  for both  $fcc-I_xC_{60}$  and  $hex-I_xC_{60}$ . It is well known that the frequencies of the  $p-A_g$  mode in neutral  $C_{60}$  materials sensitively depend on the number of the intermolecular [2+2] cycloaddition bonds per  $C_{60}$  molecule. The frequency of the  $p-A_g$  mode of the HPHT  $C_{60}$  dimers has been determined to be  $1462\text{ cm}^{-1}$  [33,34]. This value is very close to the average frequency of the  $p-A_g$  modes observed after PIHP treatment for the iodine doped  $C_{60}$ . Furthermore, there was no charge transfer or formation of chemical bonds between iodine and  $C_{60}$  molecules. Therefore the number of intermolecular bond of the  $I_xC_{60}$  compounds can be estimated from the frequency of the  $p-A_g$  mode in the same way as neutral  $C_{60}$  polymers. As a result, it can be said that the photo-irradiated  $I_xC_{60}$  compounds consist of  $C_{60}$  dimers and iodine molecules. The iodine molecular vibrations give us an insight into the mechanism of the photo-transformation of  $I_xC_{60}$  compounds as well as the  $p-A_g$  mode. The appearance of the isolated  $I_2$  molecules will originate from the irreversible polyiodine chain breaking followed by the polymerization of  $C_{60}$  molecules. We consider the structural transformation taking place in the  $I_xC_{60}$  during the photo-irradiation under pressure as follows. The polyiodine molecules ( $I_5^-$ ,  $(I_2)_n$ ) are thermally activated by the absorption of photon by the  $hex-I_xC_{60}$  and partially decompose into  $I_2$  molecules. Then the photo-polymerization of  $C_{60}$  lattice occurs and

prevents  $I_2$  molecules from forming polyiodine chain again. The problem is how the isolation of  $I_2$  molecules is kept in the  $C_{60}$  dimers. On analogy of the fact that the Raman band of the isolated  $I_2$  molecule is dominant in the fcc- $I_xC_{60}$ , thermal activation by photo-irradiation might drive iodine molecules from the vicinity of the photo-polymerized region and decrease iodine molecules from the  $C_{60}$  interstitials. Consequently, the isolation of iodine molecules is kept after PIHP treatments in the hex- $I_xC_{60}$ .

Secondly, we consider the photo-induced graphitic transformation of the fcc- $I_xC_{60}$ . In order to elucidate the iodine doping effects on the photo-induced graphitization, important features of the graphitization of  $C_{60}$  single crystal [20,85] are briefly addressed. The photo-induced graphitization of  $C_{60}$  single crystals is dependent on the crystallinity of solid  $C_{60}$ , presence of  $O_2$  molecule in the lattice, and sample temperature. In a high quality  $C_{60}$  single crystal without air exposure, photo-induced structural transformation of the  $C_{60}$  single crystal is governed by Jahn-Teller distortion of  $C_{60}$  molecule: The distorted  $C_{60}$  in the excited state due to the electron-phonon interaction would be recovered by emitting light. In the solid form of  $C_{60}$ , however, Jahn-Teller distortion would remain semi-permanently in the electronic ground state without formation of chemical bonds. Metastable states of  $C_{60}$  could exist in the solid state with modification of the lattice in the crystal. On the other hand, once oxygen molecules are introduced into the interstitial of the  $C_{60}$  crystal, the Jahn-Teller distortion of the  $C_{60}$  molecule was completely suppressed at low temperature. At the room temperature, the photo-induced graphitization of  $C_{60}$  single crystals occurred. The presence of oxygen is considered to promote the destruction of  $C_{60}$  molecule by the photo-excitation of  $C_{60}-O_2$  configuration in which the oxygen forms carbonyl-like bonding with  $C_{60}$  molecule. In addition, the electron in the excited state could non-radiatively decay to the ground state of an  $sp^2$  amorphous graphite by getting over the activation barrier when the system possessed sufficient thermal energy. Temperature and the photo-oxidization cooperatively promote the destruction of  $C_{60}$  molecule. The grain size of the  $C_{60}$ -derived  $sp^2$  amorphous graphite reportedly increased up to 250 Å by the photo-irradiation with the 514.5 nm of 1.9 kW/cm<sup>2</sup>. In the present study, estimated grain size of the photo-transformed fcc- $I_xC_{60}$  saturated at about 80 Å by the 90 minutes of irradiation with the 514.5 nm of 750 W/cm<sup>2</sup>. The grain size for the

fcc-I<sub>x</sub>C<sub>60</sub> was one-third of that for the C<sub>60</sub> single crystal. However, the grain size of 80 Å correspond to the 5~6 times of the lattice constant of the fcc-I<sub>x</sub>C<sub>60</sub>. The photo-induced graphitization of fcc-I<sub>x</sub>C<sub>60</sub> at ambient pressure involves larger number of C<sub>60</sub> molecule than the photo-polymerization of the fcc-I<sub>x</sub>C<sub>60</sub> under pressure. It contradicts to the photo-polymerization of C<sub>60</sub> sub-lattice which could not expand beyond the dimer structure due to the presence of iodine molecules. The photo-graphitization would occur through desorption of iodine molecules followed by incorporation of oxygen molecules, because existence of oxygen is favorable for the graphitization of C<sub>60</sub> molecules through formation of carbonyl-like C<sub>60</sub>-O<sub>2</sub> bond. Since the photo-irradiation for the photo-graphitization is performed in the atmosphere, desorption of I<sub>2</sub> molecule effectively take place. Consequently, the graphite grains could grow up to ~ 80 Å.

We next present explanations for the insensitivity of the alkali doped C<sub>60</sub> compound against the photo-irradiation under HPHT conditions. The potassium doping effect on polymerization has been suggested to increase the photo-absorption efficiency of C<sub>60</sub> molecules due to the reduction of the molecular symmetry to C<sub>2v</sub> symmetry of C<sub>60</sub><sup>3-</sup>, that is, the removals of the degeneracy of the t<sub>1u</sub> (LUMO) and t<sub>1g</sub> (LUMO+1) levels into a<sub>1</sub>+b<sub>2</sub>+b<sub>1</sub> and b<sub>2</sub>+b<sub>1</sub>+a<sub>2</sub>, respectively [50]. The activation of Stone-Wales rearrangement has also been suggested for enhancement of the reactivity of the C<sub>60</sub><sup>3-</sup> anion which promotes the formation of C<sub>120</sub> peanuts structure. The stability of (C<sub>60</sub><sup>n-</sup>)<sub>N</sub> poly-anion isomers (0≤n≤6) have been calculated by Pekker *et al.* [86]. They showed that the [2+2] cycloadduct polymers are the most stable in the neutral and low-charge states while singly bonded polymers are favored in the high charge states. They also showed that the singly bonded (C<sub>60</sub><sup>n-</sup>)<sub>N</sub> isomers (n=3, 6) are more stable than the neutral C<sub>60</sub> dimer and/or C<sub>60</sub> one-dimensional polymers. Therefore, the combination of photo-irradiation, HPHT treatments, and alkali doping was a potential candidate for a new network structure. However, no structural change of A<sub>x</sub>C<sub>60</sub> was observed by photo-irradiation under several HPHT conditions and with the application of pressure. A serious problem for the polymerization must be expansion of C<sub>60</sub> sub-lattice because of presence of alkali ions. Alkali ions would interrupt formation of intermolecular bonds due to geometrical restriction and short range repulsion between ion core and π orbital of C<sub>60</sub> molecule. The doping effects on photo-induced structural transformation of C<sub>60</sub> under high pressure are summarized for iodine and alkali metals as follows:

“Thermally activated polyiodine molecules are dissociated into isolated iodine molecules and driven from the vicinity of the  $C_{60}$  lattice where the photo-dimerization proceeds. Alkali metal doping completely suppresses the structural transformation of  $C_{60}$  lattice.”