

## 5. SUMMARY AND CONCLUSION

In this thesis, the main focus has been made on the elucidation of the nature of structural transformation of  $C_{60}$  based on the cooperative effects of photo-irradiation, pressure, and impurity doping.

We have investigated systematically the photo-induced structural transformation of  $C_{60}$  single crystals under high pressure up to 30 GPa. We found that the photoluminescence, optical transmittance, and Raman spectra showed continuous changes depending on the applied pressure at the photo-irradiation. These results indicated that formation of intermolecular bonds imprinted the contracted structures where  $C_{60}$  intermolecular distance was kept short. The number of intermolecular bonds per  $C_{60}$  molecule was estimated by the comparative analyses based on the fictive pressure using the high pressure optical spectra of  $C_{60}$  photopolymer which had been subjected to the photo-irradiation at ambient pressure. The number of the intermolecular bond increases up to around 5 with an increase in the applied pressure to 25 GPa. From the PL analysis of the photo-induced structural transformation at HPHT conditions ( $P \approx 3$  GPa,  $T \leq 100$  °C), the activation energy of the photo-polymerization under 3 GPa was estimated 0.23 eV. The result revealed the formation of intermolecular connections to be achieved by the [2+2] cycloaddition mechanism. A possible structural picture has been proposed on the basis of the structural models of the  $C_{60}$  photopolymer. The noncrystalline random structure of the photo-irradiated  $C_{60}$  was tunable by magnitude of the applied pressure at photo-irradiation. The random network would expand not only into one- and two-dimensions, but also into three-dimensions.

We have investigated the iodine and alkali metal doping effects on the photo-induced structural transformation of  $C_{60}$  by means of Raman scattering measurements. Firstly, there was no indication of the charge transfer or formation of chemical bonds between iodine and  $C_{60}$  molecules in Raman spectra under pressure and after the PIHP treatments, although incorporation of guest species into  $C_{60}$  lattice was expected to modulate the bonding structure and electronic property of  $C_{60}$  polymers. The presence of iodine molecules suppressed the photo-polymerization of  $C_{60}$  lattice. The polyiodine molecules in  $I_xC_{60}$  partially dissociated and moved from the vicinity of the dimerization area by thermal effect due to absorption of light by the  $I_xC_{60}$ . The photo-irradiated  $I_xC_{60}$  formed only  $C_{60}$  dimer irrespective of the structure of the  $C_{60}$  lattice and the pressure at the photo-irradiation. In other words, iodine molecules play a role of a structural template for  $C_{60}$  dimerization. Secondly, alkali metal doping has

completely suppressed the structural change of  $C_{60}$  molecules in contrast to some previous studies bringing a hopeful view on the new polymeric  $C_{60}$  compounds.

We have investigated the structural transformation of  $C_{60}$  which originates from the cooperative effects. We conclude that the tunable photo-polymerization which reaches to three-dimensional network structure is a new phenomenon achieved by the combination of pressure and photo-excitation.