The Novel Structure of I_h-$La_2@C_{80}$

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More and more varieties of endohedral metallofullerenes are coming up as variety of encapsulated metal atoms increase. Attractive behaviors of metal atoms inside carbon cage; giant thermal motion, metal cluster formation, etc., have been revealed by structural characterization, so far. Those characteristic features were found to be closely related to the cage symmetry and the electrostatic-interaction between the metal atoms and carbon cage caused by the charge transfer from metals to carbon cage. Here, we reported the striking novel feature of endohedral metallofullerene, which is a virtual metal-carbon double cage revealed for $La_2@C_{80}$ by synchrotron radiation (SR) structural study. The result reveals that two La atoms form dodecahedral charge distribution inside the highly symmetric C_{80} cage (I_h).

A soot sample containing $La_2@C_{80}$ and other La metallofullerenes was produced in direct-current (300～400 A) spark mode under He flow at 50-80 Torr. The separation and isolation of $La_2@C_{80}$ were done by the two-stage high-performance liquid chromatography (HPLC) method. The purity of $La_2@C_{80}$ relative to other fullerenes was more than 99.9%. $La_2@C_{80}$ powder specimen was grown from toluene solvent. The obtained powder sample was sealed in a silica glass capillary (0.3mm int. diam.).

The synchrotron radiation x-ray powder experiment with imaging plate (IP) as detectors was carried out by Large Debye-Scheerer Camera at SPring-8 BL02B2. The exposure time was 6 hours. The wavelength of incident x-rays was 1.0 Å. The x-ray powder pattern of $La_2@C_{80}$ was obtained with a 0.02° step from 3.0° to 35.0° in 2θ, which corresponds, to 1.66 Ă resolution in *d*-spacing.

The experimental data were analyzed by the MEM/Rietveld[1)] analysis, which is a self-consistent iterative analysis of combination of the maximum entropy method (MEM) and Rietveld analysis. Most of the metallofullerenes' structures; $Y@C_{82}$[1)], $Sc@C_{82}$[2)].. $La@C_{82}$[3)], $Sc_2@C_{84}$[4)], $Sc_3@C_{82}$[5)], $Sc_2@C_{66}$[6)] and $Sc_2C_2@C_{84}$[7)] have been successfully visualized as the charge densities by the method using synchrotron radiation powder data. The detail of this method is described in the previous studies. The cell parameters are determined as a=18.2872(8) Ă, b=11.2120(4) Ă, c=11.1748(4)Ă and β=107.91(1)° (monoclinic: $P2_1$), by the Rietveld analysis. The reliability factor(R-factor) based on the Bragg intensities, R_I, and weighted profile R-factor, *Rwp*, were 6.3% and 2.6%, respectively. The MEM charge density based on Rietveld analysis was derived with 502 observed structure factors by dividing unit cell into 128×72×72 pixels. The reliable factor of the final MEM charge density was 3.8%.

The obtained MEM charge density clearly exhibits six- and five-membered rings revealing the I_h symmetry of C_{80} cage. The clear pentagon-dodecahedral cage, which should be due to the La atom, is recognized inside the C_{80} cage. To confirm that the charge density of this dodecahedral cage stems from the La atoms encapsulated in the C_{80} cage, the total charge of this internal cage is counted. The obtained result is 108.8*e*, which is close to the number of electrons of triply charged state of two La ions (108.0*e*). This is consistent with the result of the previous study[8)]. It is concluded that the dodecahedral internal cage represents the two La atoms' distribution encapsulated inside the C_{80} cage having the formal electronic structure, $(La^{3+})_2@C_{80}^{6-}$.

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