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Crystal Structure and Dielectric Property of Endohedral Lithium Fullerene

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Endohedral lithium fullerene Li@C₆₀ can have a dielectric polarization by the off-centered location of the Li⁺ cation inside the C₆₀ cage. The x-ray structure analysis of the PF₆⁻ salt [Li@C₆₀](PF₆) revealed that the Li⁺ cation occupies two off-centered equivalent positions at 20 K and hence the crystal is non-polar [1]. The disordered structure at low temperature is explained by a static orientation disorder of polar Li@C₆₀ cations and/or a dynamic tunneling of the Li⁺ cation inside the C₆₀ cage. The Li⁺ tunneling would be suppressed by an intermolecular interaction at lower temperature and a dielectric phase transition might be induced. We reveal the dielectric property and crystal structure of [Li@C₆₀](PF₆) below 20 K in this study. The temperature dependence of the dielectric permittivity was measured for the single crystal down to 9 K. The dielectric permittivity increases with decreasing temperature according to the Curie-Weiss law. Such a behavior was also observed in H₂O@C₆₀ crystal but not in empty C₆₀ crystal [2]. No dielectric phase transition was observed in H₂O@C₆₀ down to 8 K. In contrast, a dielectric anomaly suggesting a phase transition was observed in [Li@C₆₀](PF₆) around 18 K. The single-crystal x-ray diffraction experiment below 20 K was also performed at SPRING-8 BL02B1. The crystal has a cubic structure at 20 K [1]. The temperature dependence of the cubic lattice constant shows no anomaly around 18 K. However, diffraction peaks that are forbidden for the given structure appear below 18 K. Thus the crystal symmetry is lowered by the dielectric phase transition. We present the result of the crystal structure analysis of the newly discovered low-temperature phase.

[1] S. Aoyagi, Y. Sado, et al., *Angew. Chem. Int. Ed.*, 2012, 51, 3377-3381, [2] S. Aoyagi, N. Hoshino, et al., *Chem. Commun.*, 2014, 50, 524-526

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