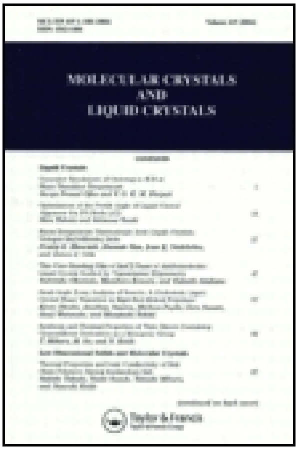

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Recently we have succeeded to synthesize solvent-free single crystals of endohedral metallofullerene La@C_{82} with the size of 0.5x0.2x0.2mm^3 for the first time. The low temperature (T) x-ray diffraction measurements (20K-300K) have elucidated successive phase transitions and the existence of four phases, (I) the face-centered cubic (fcc) structure (300K-180K), (II) the rhombohedral structure (180K-140K), (III) the triclinic structure (140K-20K) and (IV) the simple cubic (sc) structure (132K-20K). The rhombohedral and triclinic phases are characterized by the C_{82}-cage orientational order, while the sc phase is characterized by the molecular electric dipole order. In the fcc phase, both are not in order. As for the two lowest-T phases, the crystal remains in the triclinic phase for slow cooling below 132K. On the other hand with rapid cooling, the crystal undergoes the phase transition to the sc phase at 115K, which is stable up to 132K. The sc phase is more stable than the triclinic phase, contrary to the usual cases.

Keywords: metallofullerene; single crystal; phase transition

INTRODUCTION

The endohedral metallofullerene has a novel structure, namely, the metal atom being contained in the fullerene cage. In addition to the structural feature of the molecule, much attention is paid to the structural properties of the crystal, because the metallofullerene has a large molecular electric dipole moment[1] which should play an important role in contrast to the "empty" fullerene crystals.

Actually our previous results of powder x-ray diffraction study[2] showed that the solvent-free crystal of La@C_{82} has the fcc lattice structure at room temperature (T), and the molecules tend to take an orientation that the long axes of the Rugby-ball shaped C_{82}-cage face away to each other and simultaneously minimizing the electrostatic interaction between the electric dipoles of the La@C_{82} molecule, and turn their direction between the preferable orientations with jumping motion[2]. So, it is expected that the ordered phase of the cage long axis orientation or the electric dipole direction is appeared at low T. However, no sign of such phase transition was observed with use of the powder sample. So we prepared the solvent-free single crystals of La@C_{82}, which enable us to obtain the high resolution data. In this paper, we will report the successive structural phase transitions of the solvent-free La@C_{82} crystal.

EXPERIMENTAL

We synthesized solvent-free single crystals of La@C_{82} by the sublimation method. First, the high purity powder samples were isolated from other fullerenes, metallofullerenes and isomers by the three-step HPLC technique. In order to remove the solvent, we baked the dried powder sample of 0.2mg in a small quartz glass tube of 2mm in a diameter under high vacuum ($<1\times10^{-6}$ torr). Then, we sealed the tube in a vacuum of 3×10^{-7} torr and heated it up to 600°C at the side of the powder sample and to 580°C at the other side. After three weeks, we obtained the single crystals with the largest size of 0.5x0.2x0.2mm^3 at the lower temperature side.

Low temperature x-ray diffraction experiments (20K-300K) were performed both at the synchrotron radiation source of Photon Factory (BL6C_1 and BL1B), KEK, Tsukuba (λ=1.1 Å) and at the ISSP rotating-anode source (CuKα). We used a scintillation counter and an imaging plate for detection.

RESULTS AND DISCUSSION

Figure 1 shows the temperature (T) dependence of the peak intensity of the 022 reflection. All Bragg reflections behave in the same way. We observed an anomaly at 180K. Above 180K, the crystal takes the fcc structure as shown in the rotation photograph (Fig.2a). Below 180K, the peak intensity steeply decreases with T decreasing, and simultaneously we observed the peaks broadening in the tangential direction of the reciprocal space and also splitting in the radial direction (Fig.2b). From the splitting width of each reflection, the crystal structure is determined as the rhombohedral structure. And below 150K, further splitting was observed, which indicates the crystal takes the triclinic structure. The tangential broadening observed in the rhombohedral and triclinic phase indicates that the crystal is divided into the micro-domains. Below 132K we observed two different structures depending on cooling rate. When slowly cooled from 132K to 110K, the crystal remains in the triclinic structure down to the lowest-T (20K). On the other hand, on rapid cooling, the peak intensity returns to the same level as in the fcc phase, and the crystal which was once divided into the micro-domains returns to the single domain again. The diffraction pattern is similar to the fcc phase, but we observed the super lattices indicating the sc structure (Fig.2c). This phase transition is accompanied by the large hysteresis, and after transformed to the sc phase, it is stable up to 132K. Such a cooling rate dependence appears only in the T-region of 132K to 110K. In another T-region or in the heating process, the structural feature depends only on T, and the above processes are reversible. With respect to the two phases below 132K, we can conclude that the sc phase appearing on rapid cooling is more stable than the triclinic phase for slow cooling, because the triclinic phase can turn to the sc phase as mentioned above, but the inverse process did not occur.

As for the molecular orientation in the rhombohedral phase, judging from the uniaxial lattice symmetry, we think that the orientational order of the C_{82}-cage long axis occurs and the molecular motion is restricted around its long axis. And in the triclinic phase, we also think that the orientational order of the C_{82}-cage short axis also occurs and the molecular rotational motion is frozen. In the sc phase, however, we have concluded that the order of the molecular electric dipoles occurs, which is shown by the analysis of the super lattice intensity. Such competition of two kinds of interaction, the elastic and dipole-dipole ones, is one of the striking feature of the metallofullerene in comparison to the "empty" fullerene.

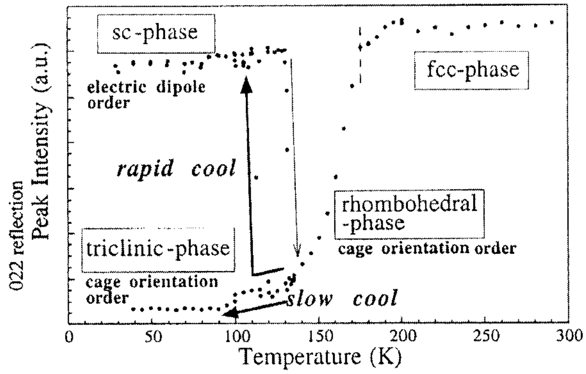

FIGURE 1 Temperature dependence of the peak intensity of 022 reflection. All Bragg peaks behave in the same way.

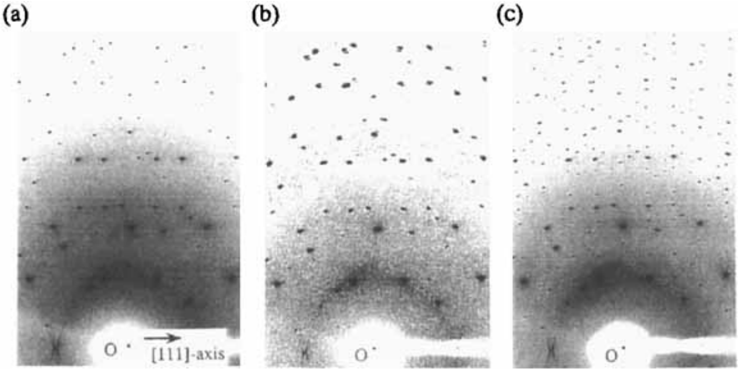

FIGURE 2 Rotation photographs of the La@C_{82} single crystal. (a) the fcc-phase at 300K (b) the triclinic-phase at 135K (c) the simple cubic phase at 100K.

Acknowledgments

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