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Synthesis and Structure of Ba_xC_{70}

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We have investigated the structural sequence of Ba_xC_{70} binary systems. X-ray diffraction measurements revealed that there exist at least four stable phase at x=3, 4, 6, and 9. Among them, structural models are presented for Ba_3C_{70} and Ba_9C_{70}. Ba_3C_{70} takes an analogous structure to A15-Ba_3C_{60}, but the unit cell is distorted to tetragonal with the cell doubling. Ba_9C_{70} is fcc, involves a distorted cube of Ba8 in the octahedral interstices. This x=9 structure is also known in K_9C_{70} as a saturated phase.

Keywords: fullerene; C_{70}; intercalation chemistry; structural sequence

INTRODUCTION

One of the unique properties of C_{60} fulleridesis the wide reduction states from $(C_{60})^{0-}$ to $(C_{60})^{12-}$. Because of such a wide tunability of the valence states, C_{60} can be regarded as an "electron sponge". The wide range of reduction states is achieved by the alkali or alkaline earth metal intercalation compounds, M_xC_{60} ($1 \le x \le 6$). In the case of barium doped C_{60}, three distinct doped phases have been identified, namely the A15 cubic phase at x=3[1], the non-cubic superconducting orthorhombic phase at x=4[2] and the saturated bcc phase at x=6[3]. The occurrence of superconductivity in the non-cubic Ba_4C_{60} is in sharp contrast with the absence of superconductivity in the alkali fullerides, A_4C_{60} (A=K,Rb,Cs), despite the similar or identical structures[4,5]. In alkali doped systems, in which the metallic state is known to be unstable to several purtabations, such as structural deformations. In these Ba-compounds, on the other hands, the metallic state is much more robust due to the hybridization between the metal *d* orbitals and the C_{60} $p\pi$ levels which is suggested theoretically[6]. The stabilization of metallic and superconducting

states in Ba-intercalated systems leads us to expect the metallic states of intercalated higher fullerenes. However, to the best of our knowledge, there has been no reports on the intercalation of Ba into C_{70} or higher fullerenes.

C_{70} is the second abundant fullerene and the intercalation of alkali metals has been investigated by many researchers. Such studies also report the possible character of an "electron sponge", where the valence state is changeable from $(C_{70})^{0-}$ to $(C_{70})^{9-}$ in the alkali metals intercalated compounds A_xC_{70} $(1 \leq x \leq 9)$[7]. Among these compounds, K_4C_{70} is known to be a granular metal[8], there has been no reported on the conducting properties for other band-filling states. For other higher fullerenes, no metallic properties have been found in intercalated compounds. Therefore, we are searching for metallic states by the intercalation of Ba into C_{70}. Considering the existence of A_9C_{70} phase, higher reduction states look also accessible by intercalation of alkaline earth metals A^{2+}. And such a high reduction state is of great interest from the view point of intercalating chemistry.

In this paper we present the result of a study in the intercalation chemistry of the ellipsoidal D_{5h} C_{70} with the barium metal and report the structure sequence of Ba-doped C_{70}. The x-ray measurements revealed that the nominal composition of x=3, 4, 6, and 9 yield stable phases. Among these, we present the structure models for the tetragonal Ba_3C_{70} and the fcc Ba_9C_{70}. A doubled unit cell of the modified A15 Ba_3C_{60} structure explains the diffraction pattern of Ba_3C_{70}. Ba_9C_{70} has the similar structure to K_9C_{70} that contains a distorted Ba8 cube in the octahedral site of the fcc lattice[7].

EXPERIMENTAL

Samples with the nominal concentration of Ba_xC_{70} $(0.5 \leq x \leq 12)$ were prepared by a reaction of C_{70} powder and Ba metals (99.9%) sealed in a quartz tube at a vacuum of 2×10^{-6} torr. Heat treatments were carried out at temperatures between 550 and 600 °C for periods ranging from a few days to weeks. Highly uniform samples are synthesized by a two week annealing with frequent intermittent grindings.

To obtain an x-ray diffraction pattern, powder samples of Ba_xC_{70} were sealed in a 0.5-mm diameter glass capillary. A synchrotron radiation x-ray powder diffraction experiment was carried out with imaging plates as

detectors at the BL-6A2, Photon Factory, KEK. The wavelength of incident X-rays was 1.000 Å and data was rebinned in the 2θ range 2.0-77.0° at a step of 0.02°.

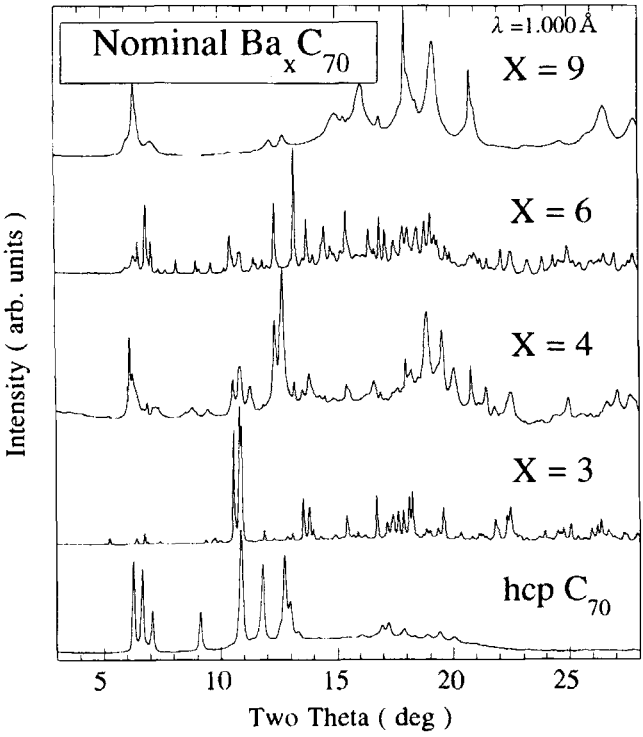

FIGURE 1. XRD patterns for hcp C_{70} and the nominal x=3,4,6,and 9 in Ba_xC_{70}.

RESULTS AND DISCUSSION

Fig.1 shows the x-ray diffraction patterns for the nominal x=3, 4, 6 and 9 compounds. These compositions seem to yield stable phases, since the diffraction patterns of the other composition are explained by mixtures of these stable phases. Among them, the nominal Ba_3C_{70} is a rather stable phase. This phase can be synthesized only by a few days annealing. Most of the diffraction peaks of Ba_3C_{70} except for lower angle peaks could be indexed

as a tetragonal cell with a lattice constant of a=11.738(3) Å and c=12.222(4) Å. This unit cell dimension and the intensity distribution are quite similar to those for Ba_3C_{60}[1], indicating that the structure of Ba_3C_{70} is a modified version of A15-type Ba_3C_{60} structure. Figure 2 shows the observed and calculated diffraction pattern for the nominal Ba_3C_{70}. Intensity calculations were made using the LAZY-PULVERIX program[9]. In this calculation, we used the A15-like tetragonal cell (Pmmm space group), where the configuration of Ba-site is similar to that of the A15-cubic Ba_3C_{60}, and the C_{70} cage was hypothetically treated as a spherical shell (Fig.2). Interestingly, all the peaks which are not indexed with the above unit cell, can be explained by doubling the unit cell to a=23.47(1) Å and c=24.45(1) Å. The amazing similarity for the main peak position and the intensity distributions means that Ba_3C_{70} has a doubled cell in each direction of the calculated A15-like tetragonal structure. Superlattice structures have been reported on the rare-earth doped C_{60}, Sm_xC_{60}[10] and Yb_xC_{60}[11](x=2.75), where the vacancy in the tetrahedral site is ordered so that the unit cell is doubled. Our results suggest the possibility of vacancy-ordering like $Sm_{2.75}C_{60}$ and $Yb_{2.75}C_{60}$ in Ba_3C_{70}. Another possible reason for the superstructure is a long range orientational ordering of C_{70} molecules, since the shape of C_{70} is not spherical like C_{60} but ellipsoidal. The analysis of superstructure is now in progress.

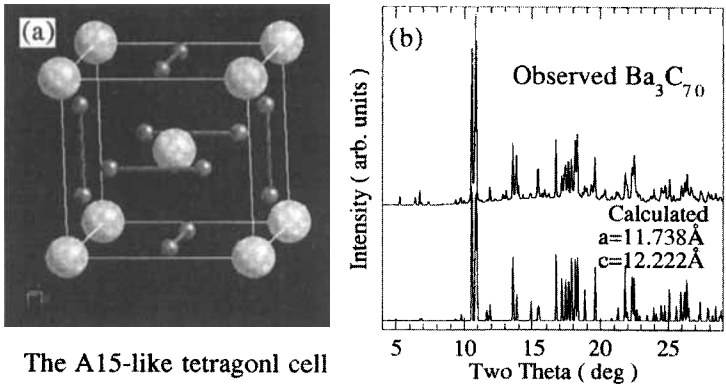

FIGURE 2. (a) the A15-like tetragonal cell. (b) the observed and calculated diffraction patterns for the nominal Ba_3C_{70}.

Both Ba_4C_{70} and Ba_6C_{70} are less stable phases. For synthesizing these compounds, a long time annealing with frequent grindings is crucial. Otherwise we obtain only mixtures. However, we have not succeeded to determine the unit cell of these phases so far. A remarkable feature of Ba_4C_{70} is the lowest peak in the diffraction pattern (2θ=3.54°). It is equivalent to 16.19 Å d-spacing which might suggest a cell doubling with some kinds of ordering, similarly to Ba_3C_{70}.

The nominal x=9 sample is a Ba-saturated phase. This is because the systematic synthesis of Ba_xC_{70} showed that all the samples of $12 \geq x \geq 9$ yielded the same diffraction pattern shown in Fig.1. The diffraction pattern indicates a cubic symmetry and systematic absences are consistent with face-centering. Le Bail extraction[12] gives a lattice parameter a=15.562(2) Å. Since the diffraction pattern of Ba_9C_{70} is very similar to K_9C_{70}[7] and $K_{8+x}C_{84}$[13], it is very likely that Ba_9C_{70} has a similar crystal structure. A common feature of both materials is a K8 cube in the octahedral site of the fcc fullerene lattice. We tried a preliminary intensity calculation according to the structure model of K_9C_{70}[7] with a spherical C_{70} shell. In this model, the Ba8 cluster is a distorted cubic. From the fcc $Ba_{10}C_{70}$ with the Ba8 cube in the octahedral site, this model is explained as follows. Four Ba atoms at the diagonally opposite sites of cube is moved along the diagonal lines to outside and the position of the other four Ba atoms is adjusted on the moving directions with keeping its distances between atoms. Finally, the stoichiometry of this structure becomes Ba_9C_{70} by removing the half of Ba atoms in the tetrahedral sites that are close to first four atoms. The simulation successfully agrees with the observed diffraction patterns, indicating that the composition of nominal x=9 sample in Ba_xC_{70} is really Ba_9C_{70} and also that it is isostructual to K_9C_{70}. If we assume that the barium metal is Ba^{2+} in the crystal, the charge state of C_{70} is estimated to be $(C_{70})^{18-}$. Such a high valence state is of significant interest to be investigated in the future.

CONCLUSIONS

We succeeded to synthesize Ba_xC_{70} with the nominal x=3, 4, 6, and 9. Ba_3C_{70} had the tetragonal cell with the superlattice that is explained as a doubled unit cell of the A15-like tetragonal cell. Ba_4C_{70} and Ba_6C_{70} were less stable phases and a superlattice structure was suggested for Ba_4C_{70}. The fcc

Ba_9C_{70} has the similar structure to K_9C_{70} that contains the distorted Ba8 cube in the octahedral site of the fcc C_{70} molecules. Experiments on the Raman spectroscoply and the electrical resistivity are in progress in order to clarify the valence state of C_{70} and the electronic properties.

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References

[1] A. R. Kortan, N. Kopylov, R. M. Fleming, O. Zhou, F. A. Thiel, and R. C. Haddon, *Phys. Rev. B,* **47,** 13070 (1993).
[2] M. Baenitz, M. Heinze and K. Luders, *Solid State Commun.*, **96,** 539 (1995).
[3] A. R. Kortan, N. Kopylov, S. Glarum, E. M. Gyorgy, A. P. Ramirez, R. M. Fleming, O. Zhou, F. A. Thiel, P. L. Trevor, and R. C. Haddon, *Nature,* **360,** 566 (1992).
[4] C. A. Kuntscher, G. M. Bendele, and P. W. Stephens, *Phys. Rev. B,* **55,** R3366 (1997).
[5] P. Dahlke, P. F. Henry, and M. J. Rosseinsky, *J. Mater. Chem.*, **8,** 1571 (1998).
[6] C. M. Brown, S. Tage, B. Gogia, K. Kordatos, S. Margadonna, K. Prassides, Y. Iwasa, K. Tanigaki, A. N. Fitch, and P. Pattision, preprint.
[7] M. Kobayashi, Y. Akahara, and H. Kawamura, *Phys. Rev. B,* **48,** 16877 (1993).
[8] Z. H. Wang, K. Ichimura, M. S. Dresselhaus, G. Dresselhous, W.-T. Lee, K. A. Wang, and P. C. Eklund, *Phys. Rev. B,* **48,** 10657 (1993).
[9] K. Yvon, W. Jeitschko, and E. Parthe, unpublished software.
[10] X. H. Chen and G. Roth, *Phys. Rev. B,* **52,** 15534 (1995).
[11] E. Özdas, A. R. Kortan, N. Kopylov, A. P. Ramirez, T. Siegrist, K. M. Rabe,H. E. Bair, S. Schuppler, and P. H. Critrin, *Nature,* **357,** 126 (1995).
[12] A. LeBail, H. Duroy, and J. L. Fourquet, *Mater. Res. Bull.*, **23,** 447 (1988).
[13] K. M. Allen, T. J. S. Dennis, M. J. Rosseinsky, and H. Shinohara, *J. Am. Chem. Soc.*, **120,** 6681 (1998).