Formation and atomic structure of $B_{12}N_{12}$ nanocage clusters studied by mass spectrometry and cluster calculation

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Abstract

Boron nitride (BN) nanocage clusters of $B_{12}N_{12}$ were synthesized, and detected by laser desorption time-of-flight mass spectrometry. The $B_{12}N_{12}$ clusters consisted of 4- and 6-membered BN rings satisfying the isolated tetragonal rule, which was optimized by molecular orbital calculations. The electronic structure showed a bandgap energy of 5.1 eV, which is a little smaller than that of $B_{36}N_{36}$ cluster.

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1. Introduction

Since the discovery of $C_{60}$ [1], carbon nanocage structures, such as fullerene clusters, nanotubes, nanocapsules, nanopolyhedra, cones, cubes and onions have been reported, and they have great potential for studying materials of low dimensions in an isolated environment [1–4]. Boron nitride (BN) nanostructured materials with a bandgap energy of $\sim 6$ eV and non-magnetism are also expected to show various electronic, optical and magnetic properties such as Coulomb blockade, photoluminescence, and supermagnetism [4]. Several studies have reported on BN nanomaterials such as BN nanotubes [4,5], BN nanocapsules [4], BN nanoparticles [6,7] and BN clusters [3,4], which are expected to be useful as electronic devices, high heat-resistance semiconductors, nanocables, insulator lubricants and gas storage materials.

Some BN nanocage clusters have also been predicted theoretically [8–18], and BN clusters with sizes of $\sim 1$ nm were observed only by high-resolution electron microscopy (HREM) [3,4,19–21], which is a powerful method for direct observation of the atomic structure of cluster materials [22,23]. BN metallofullerenes, which showed the possible existence of metal atoms inside the $B_{36}N_{36}$ clusters, were also reported from HREM [4,21,24]. For these BN clusters, a $B_{12}N_{12}$ cluster was theoretically predicted to be the smallest cage cluster satisfying the isolated tetragonal rule [8–12,16], and BN cluster solids were also predicted [15,17]. Although the $B_{12}N_{12}$ clusters was reported by HREM [19,20], mass spectrum analysis has been mandatory for determining the existence of $B_{12}N_{12}$ nanocage clusters, and few such reports have been presented [25].

The purpose of the present work is to synthesize $B_{12}N_{12}$ nanocage clusters and to investigate the structure by mass spectrometry and theoretical calculation. To understand the atomic structure models and structural stabilities of the clusters, total energy calculations were carried out by molecular orbital calculations. The present study will give us a guideline for designing and synthesis of the BN clusters, which are expected as the future nanoscale devices.

2. Experimental procedures

The YB$_6$ powder (4.0 g, 99.6%, Kojundo Chemical Lab. Co., Ltd) was set on a copper mold in an electric-arc furnace, which was evacuated down to $1 \times 10^{-3}$ Pa. After introducing a mixed gas of Ar (0.025 MPa) and N$_2$ (0.025 MPa), arc-melting was applied to the samples at an
accelerating voltage of 200 V and an arc current of 125 A for 10 s [26]. Arc-melting was performed with a vacuum arc-melting furnace (NEV-AD03, Nisshin Engineering Co., Ltd), and gray to white powder were obtained around the copper mold. An AXIMA-CFR (Shimadzu/Kratos, Manchester, UK) instrument was used to obtain laser desorption time-of-flight (LD-TOF) mass spectra. The operating conditions were as follows: nitrogen laser (337 nm); linear mode; accelerating voltage at 20 kV; detection of positive ions. The sample powder (50 mg) was suspended in pyridine (C5H5N, 200 μl) with ultrasonication. The aliquot (1–2 μl) was spotted on the sample plate and dried at room temperature. The mass spectra were corrected by using C60 and C70 clusters. Cluster structures were optimized by semi-empirical molecular orbital calculations (Hamiltonian: Parameterized Model Revision 5: PM5) using CS Chem3D Ultra (CambridgeSoft, MA, USA) and WinMOPAC Professional (Fujitsu Corp., Chiba, Japan). For the prediction of electronic states, molecular orbital calculation using the discrete-variational (DV)-Xz method was carried out.

3. Results and discussion

Fig. 1(a) shows a mass spectrum for BN clusters in pyridine solution, and demonstrates the existence of 10B12−x11Bx14N12 (x=1–5) clusters. A mass spectrum for pyridine solution, which was used for matrix in LD-TOF mass spectrometry, is also shown for reference in Fig. 1(b). The mass spectrum peaks have a somewhat broad distribution because of the two isotopes of 10B and 11B. Peaks of the cluster distribution are observed at x value of 3.

An atomic structure model of the B12N12 cluster viewed along hexagonal BN ring, tetragonal BN ring and hexagonal BN bonding is shown in Fig. 2(a)–(c), respectively. Although carbon fullerenes satisfy the isolated pentagon rule, the present B12N12 cluster consists of 6 tetragonal and 8 hexagonal BN rings satisfying the isolated tetragonal rule. The structural optimization of the BN clusters was performed by molecular orbital calculations (PM5), and the results are summarized in Table 1, comparing with a B36N36 cluster [4,24]. Total energy of the B12N12 cluster was calculated to be −12.4 kcal/atom, which is fairly large compared to the B36N36 cluster. Lengths of the BN bonding are as follows (Fig. 2(a) and Table 1): six-membered rings closed to four-membered rings (BN6,4=0.1527 nm) and six-membered rings closed to six-membered rings (BN6,6=0.1462 nm), which are larger than hexagonal BN rings (0.144 nm) in ordinary BN crystal. Since distortion of BN rings would be mitigated for six-membered rings, the hexagonal BN bonding would have the smallest value.

In the present work, a peak of the cluster distribution in LD-TOF mass spectrometry is observed for 10B911B314N12. For localized structures of BN clusters, it should be noted that the isotopic ratio of boron atoms might be different from the natural averaged ratio (10B:11B=19.9:80.1) because of the minimization of the clusters’ structural energy. Atomic structure model of 10B911B514N12 is proposed as shown in Fig. 2(d). All boron atoms are 10B, and only 11B atoms are indicated by arrows.

An electronic structure of the B12N12 cluster was investigated as shown in Fig. 3. The B36N36 cluster was also calculated for comparison, which was optimized by a molecular orbital calculation as listed in Table 1. An energy level diagram is shown in Fig. 3(a). The B12N12 cluster shows a large energy gap of 5.1 eV between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Although the HOMO–LUMO gap of the B36N36 cluster was calculated to be 5.4 eV, the present B24N24 cluster shows lower energy gap of 5.1 eV, which indicates reduction of the energy gap by decreasing the BN cluster size. According to previous theoretical calculations, the energy gap of a B36N36 cluster is reduced by introducing a metal atom inside the B36N36 cluster, which indicates controllability of the bandgap.
Further studies are needed for the properties of the BN cage clusters. The BN cluster is a molecule with polarity because of a positive charge at boron atom positions and a negative charge at nitrogen atom positions; so an electrophilic or nucleophilic reagent would work as a solution for BN clusters. In the present work, pyridine (C₅H₅N) did work well for the extraction of the BN clusters because of an electrophilic

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![Fig. 2. (a–c) Atomic structure models of B₁₂N₁₂ cluster viewed along (a) hexagonal BN ring, (b) tetragonal BN ring and (c) hexagonal BN bonding. (d) Proposed structure model of ¹⁰B₇⁺¹¹B₃⁺N₁₂. Only ¹¹B atoms are indicated by arrows.](image)

![Fig. 3. (a) Energy level diagram and (b) density of states for B₁₂N₁₂ cluster.](image)

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### Table 1

|                    | B₁₂N₁₂ | B₃₆N₃₆ |
|--------------------|--------|--------|
| Heat of formation (kcal/mol) | -298.3 | -1597.8 |
| Heat of formation per atom (kcal/mol·atom) | -12.4 | -22.2 |
| Tetragonal BN rings | 6      | 6      |
| Hexagonal BN rings  | 8      | 32     |
| BN₆₋₄ (nm)         | 0.1527 | 0.1509 |
| BN₆₋₆ (nm)         | 0.1462 | 0.1487 |
| d̂ max (nm)         | 0.488  | 0.743  |
| d̂ min (nm)         | 0.488  | 0.882  |
| ϵHOMO (eV)         | -3.1   | -3.1   |
| ϵLUMO (eV)         | 2.0    | 2.3    |
| Energy gap Eᵦ (eV) | 5.1    | 5.4    |
reaction; pyrrole (C₅H₇NH) would also work as a nucleophilic reagent. Since C₆₀ fullerene clusters have no polarity and are soluble in nonpolar solvents such as toluene [27] and benzene, they have difficulty in solvating in a polar solvent. Other octahedral BN clusters could also be extracted by using a polar solvent. In order to investigate these BN nanocage clusters further, separation technique using high performance liquid chromatography should also be developed.

4. Conclusion

BN nanocage clusters of B₁₂N₁₂ were synthesized by an arc-melting method from YB₆ powder in N₂/Ar mixture gas, and detected by LD-TOF mass spectrometry. The B₁₂N₁₂ clusters consisted of 6 tetragonal and 8 hexagonal BN rings satisfying the isolated tetragonal rule, which was optimized by molecular orbital calculations with formation energy of −298.3 kcal/mol. The electronic structure showed bandgap energy of 5.1 eV, which is smaller than that of B₃₆N₃₆ cluster.

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