Possibility of Semiconducting Quasicrystal in Boron-Rich Solids —Cohesive Energy Calculation and Transformation from Amorphous Phase—

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Boron-rich solids are great candidates for a semiconducting quasicrystal because they have various semiconducting crystalline structures with icosahedral clusters (B_{12}). Analyzing the crystalline structure of α - and β -rhombohedral boron as an approximant structure of quasicrystal, the atomic structure of two unit cells (prolate and oblate rhombohedra) of the icosahedral quasicrystal are constructed. The cohesive energies of the α -, β -boron and α -boron type quasicrystal are estimated using molecular orbital total energy calculation. According to the calculation, the realization of α -boron type quasicrystal is expected. A neutral $B_{12}H_{12}$ icosahedral cluster is distorted to a cubic or rhombohedral one by the Jahn-Teller effect. The distortions of B_{12} cluster in the $K_2B_{12}H_{12}$ and β -rhombohedral boron have the same signs as the lowest energy distortions in the calculation. Among the α -rhombohedral type structures, the distortion of B_{12} is correlated with the rhombohedral axis angle. The angle is close to the icosahedral angle and the distortion is smallest around 10 at% of carbon in B_4C structure. Search for semiconducting quasicrystal has been done experimentally in the B-C system. A meta-stable phase has been found in the annealing process of the $B_{100-x}C_x$ ($x=3, 5$ and 7) amorphous phases.

(Received November 6, 1992)

Keywords: boron carbide, semiconductor, cohesive energy, molecular orbital calculation, amorphous phase, meta-stable phase, icosahedral phase, phase transformation, Jahn-Teller effect, quasicrystal

I. Introduction

Quasicrystals have been found in many kinds of, but only metallic alloy systems⁽¹⁾. It is very interesting to inquire whether a quasicrystalline structure can be stable in a covalent bonding system⁽²⁾⁽³⁾. Though several reports about semiconducting quasicrystals in $Ge^{(4)-(6)}$, $BN^{(7)}$ and $C_{60}^{(8)}$ materials have been published, they have not been established yet. Boron-rich solids are great candidates for semiconducting quasicrystals because they have various semiconducting crystalline structures with icosahedral clusters (B_{12})⁽⁹⁾. And some of them have unit cells almost the same as the prolate rhombohedra (PR), one of the building blocks of the three-dimensional Penrose pattern⁽²⁾⁽³⁾. The B_{12} in crystalline structure is distorted from the icosahedral symmetry; one of the origins of the distortion is considered to be the Jahn-Teller effect⁽¹⁰⁾.

In the present paper, 1) several crystalline structures of boron-rich solids are analyzed as approximant structures of a quasicrystal. As a result of these analyses, quasicrystalline structures of boron are conceived, and their stability is estimated using a molecular orbital calculation. 2) The distortion of B_{12} is estimated by using crystallographic data and the molecular orbital calculation. If B_{12} is taken to be distorted spontaneously, there is no reason why the icosahedral symmetry grows. 3) The search for quasicrystals is done in a non-equilibrium proc-

ess because most quasicrystals have been found as meta-stable phases in metallic alloy systems. Some boron-rich amorphous films are prepared and examined the transformation by heat treatment.

II. Method and Experiment

For the estimation of the cohesive energies of crystalline and quasicrystalline structures of boron, molecular orbital calculations by the MNDO method were performed with MOPAC Ver. 5.01⁽¹¹⁾. *Ab initio* molecular orbital calculation⁽¹²⁾ was used to investigate the Jahn-Teller effect of the $B_{12}H_{12}$ cluster. Atomic orbitals as basis functions were Slater-type orbitals expressed by the sum of three Gaussian-type functions.

The amorphous films were prepared by an electron-beam evaporation of pure boron and boron-carbon compound powder. The films were deposited on quartz glass substrates and then removed from them. The amorphous powder was heated up to 1400°C in BN crucibles, in Ar-sealed quartz tubes. Phases and composition of these films were determined by a transmission electron microscope (TEM), X-ray diffraction and an electron probe micro analyzer (EPMA).

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III. Stability of the Quasicrystalline Structure of Boron

1. Cohesive energies of α - and β -rhombohedral boron

To examine the stability of crystalline and quasicrystalline arrangements, the cohesive energies of the structures are estimated using the molecular orbital total energy calculation. Usually, the cohesive energy of a crystalline structure can be derived using energy band structure calculations, but these methods cannot be applied for quasicrystalline structures because they have no periodicity. In this paper, the cohesive energy is derived to be divided into two parts: the cohesive energy of the clusters and the bonding energy between the clusters. Each dangling bond in the cluster is treated to be terminated by a hydrogen atom.

First, the cohesive energies of α - and β -rhombohedral boron are estimated to check the accuracy of this method, and they are compared with the cohesive energy of the quasicrystalline structure. As illustrated in Fig. 1(a), α -rhombohedral boron is composed of boron icosahedra (12-atoms cluster, B_{12}) located at the corners of a rhombohedral unit cell⁽¹³⁾. The icosahedron has 12 outer bonds along the five-fold axis. Each of the six atoms in the icosahedron is directly connected to another icosahedron via two-center bond along the unit cell edge. Each of the remaining six atoms directly bonds to other two icosahedra through three-center bond (the shaded triangles in Fig. 1(a)).

The calculated cohesive energy of icosahedral cluster ($E[B_{12}]$), the inter-icosahedral two-center bonding energy ($E[B_{12}-B_{12}]$) and the three-center bonding energy ($E[\Delta]$) are listed in Table 1, and the numbers of clusters and bonds in a unit cell are listed in the third column. For example, the inter-icosahedral bonding energy ($E[B_{12}-B_{12}]$) was examined as follows:

Table 1 Calculated cohesive energy of B_{12} cluster and two-center and three-center bonding energy for the α -rhombohedral boron.

	Cohesive and bonding energy in aJ [eV]	Number of clusters and bonds per unit cell
$E[B_{12}]$	8.097 [50.54]	1
$E[B_{12}-B_{12}]$	0.125 [0.78]	3
$E[\Delta]$	1.520 [9.49]	2

Fig. 2 A model of bonding clusters to calculate the bonding energy between B_{12} clusters. The black atoms are hydrogen atoms which terminate dangling bonds. The bonding energy was estimated by subtracting twice the total energy of $B_{12}H_5$ from that of this model.

$$E[B_{12}-B_{12}] = E(B_{12}H_5 - B_{12}H_5) - 2E(B_{12}H_5) \\ = 0.125 \text{ aJ [0.78 eV]}$$

where $E(B_{12}H_5 - B_{12}H_5)$ is the total energy of directly bonding two $B_{12}H_5$ clusters (Fig. 2) and $E(B_{12}H_5)$ is that of $B_{12}H_5$ cluster. Each two-center bond of $B_{12}-B_{12}$ cluster is terminated by a hydrogen atom, but three-center bonds are not, as shown in Fig. 2. As the three-center bonding energy ($E[\Delta]$) is too large compared with the two-center bonding energy ($E[B_{12}-B_{12}]$), the treatment of the dangling bond of three-center bond may have a question. The α -rhombohedral boron has 12 atoms, 1 icosahedral cluster, 3 two-center bonds and 2

Fig. 1 Atomic structures of two unit cells of the icosahedral quasicrystal, (a) prolate and (b) oblate rhombohedra, constructed by analyzing that of the α -rhombohedral boron. (c) Two icosahedra located at the both ends of short body diagonal of the oblate rhombohedron.

Fig. 3 (a) Atomic structure of the β -rhombohedral boron, and (b) B_{57} unit on the long body diagonal of the unit cell.

three-center bonds in a unit cell. Thus the cohesive energy of the α -rhombohedral boron is

$$E_{\text{coh}}(\alpha) = (E[B_{12}] + 3E[B_{12}-B_{12}] + 2E[\Delta]) / 12 \\ = 578 \text{ kJ/mol [5.99 eV/atom]}.$$

Although this is a rough estimation, the calculated cohesive energy agrees fairly well with the experimental value⁽¹⁴⁾ of 561 kJ/mol [5.81 eV/atom].

Figure 3(a) shows the β -rhombohedral boron⁽¹⁵⁾, B_{105} , which has 105 atoms in a unit cell. This is composed of two kinds of icosahedra and B_{57} unit (Fig. 3(b)). The icosahedra are located at the corners and the edge centers of the unit cell, and the B_{57} unit resides along the longest diagonal of the unit cell. Different from the case of the α -boron, each cluster is connected to the other clusters via only two-center bonds. Every dangling bond is terminated by a hydrogen atom, *e.g.* the icosahedron has 12 H atoms ($B_{12}H_{12}$). Calculated cohesive and bonding energies are listed in Table 2. The first three are the

Table 2 Calculated cohesive and bonding energies of clusters in the β -rhombohedral boron.

	Cohesive and bonding energy in aJ [eV]	Number of clusters and bonds per unit cell
$E[B_{12v}]$	8.052 [50.26]	1
$E[B_{12e}]$	7.991 [49.88]	3
$E[B_{57}]$	39.959 [249.43]	1
$E[B_{12v}-B_{12e}]$	0.359 [2.24]	6
$E[B_{12e}-B_{12e}]$	0.226 [1.41]	6
$E[B_{57}-B_{57}]$	0.449 [2.80]	6
$E[B_{57}-B_{12v}]$	0.433 [2.70]	6
$E[B_{57}-B_{12e1}]$	0.460 [2.87]	6
$E[B_{57}-B_{12e2}]$	0.489 [3.05]	12

cohesive energies of icosahedral clusters ('v' and 'e' stand for the vertex and edge center clusters, respectively) and the B_{57} unit. The next three are the inter-cluster and inter-unit bonding energies. The last three are the bonding energies between the B_{57} unit and the icosahedral clusters; there are two different bond lengths between the B_{57} unit and the edge center cluster ($E[B_{57}-B_{12e1}]$ and $E[B_{57}-B_{12e2}]$). Then the cohesive energy of the β -rhombohedral boron was estimated as follows:

$$E_{\text{coh}}(\beta) = \{ E[B_{12v}] + 3E[B_{12e}] + E[B_{57}] \\ + 6E[B_{12v}-B_{12e}] + 6E[B_{12e}-B_{12e}] \\ + 6E[B_{57}-B_{12v}] + 6E[B_{57}-B_{12e1}] \\ + 12E[B_{57}-B_{12e2}] + 6E[B_{57}-B_{57}] \} / 105 \\ = 512 \text{ kJ/mol [5.31 eV/atom]}.$$

The cohesive energy of the α -rhombohedral boron is larger than that of the β -rhombohedral boron. This is consistent with the fact that α -boron is more stable than β -boron below 1200°C⁽¹⁶⁾.

2. Cohesive energy of α -rhombohedral type quasicrystal (I)

The structure of the α -rhombohedral boron is considered to be a rhombohedral crystalline approximant of the icosahedral quasicrystal. Considering the unit cell as the prolate rhombohedron (PR), corresponding structure of the oblate rhombohedron (OR) can be constructed (Fig. 1(b)). The question of the structure is the too short distance between the two icosahedra located at the both ends of short body diagonal. Since these icosahedra are too close to each other, three black atoms in Fig. 1(c) must be removed. The remaining three atoms on the interface of two icosahedra in Fig. 1(c), which are equivalent to three removed atoms, were rotated 30° along the three-fold axis and displaced to the outside along the radial direction in order to stabilize the cluster (B_{21}). After removing the three atoms and relaxing the other three atoms, the total energy of the cluster increases 299 kJ/mol [3.10 eV/atom] and 30 kJ/mol [0.31 eV/atom], respectively.

The cohesive energy of the OR was estimated with the following assumptions. 1) The OR is composed of B_{12} and B_{21} clusters. 2) The OR has 9 (=12-3) atoms in a unit cell; 3.6 of 9 belong to B_{12} cluster because each B_{12}

Table 3 Calculated cohesive and bonding energies of the oblate rhombohedron for the α -boron type quasicrystalline structure.

	Cohesive and bonding energy in aJ [eV]		Number of clusters and bonds per unit cell
$E[B_{12}]$	8.097	[50.54]	3.6/12
$E[B_{21}]$	15.124	[94.41]	5.4/21
$E[B_{12}-B_{21}]$	0.250	[1.56]	2.4
$E[B_{12}-B_{12}]$	0.125	[0.78]	0.6

locates at the vertex with $4\pi/20$ solid angle ($12 \times 1/20 \times 6 = 3.6$), and the rest are from B_{21} cluster. 3) In a unit cell, there are 0.6 of $B_{12}-B_{12}$ bond and 2.4 of $B_{12}-B_{21}$ bond. The calculated cohesive and bonding energies are listed in Table 3, and then the cohesive energy of the OR is estimated as follows:

$$E_{\text{coh}}[\text{OR}] = \left\{ \frac{3.6}{12} E[B_{12}] + \frac{5.4}{21} E[B_{21}] + 0.6 E[B_{12}-B_{12}] + 2.4 E[B_{12}-B_{21}] \right\} / 9$$

$$= 468 \text{ kJ/mol [4.85 eV/atom]}.$$

The 3-dimensional Penrose pattern, i.e. the icosahedral quasicrystalline structure, is constructed of the PR and OR, and number of the PR is τ times more than that of the OR. The symbol τ is the golden mean (≈ 1.618). Using the $E_{\text{coh}}[\alpha]$ as the cohesive energy of the PR and the $E_{\text{coh}}[\text{OR}]$, the cohesive energy of α -boron type quasicrystal is estimated as follows.

$$E_{\text{coh}}[\alpha - \text{QC}] = \{12\tau E_{\text{coh}}[\alpha] + 9E_{\text{coh}}[\text{OR}]\} / (12\tau + 9)$$

$$= 543 \text{ kJ/mol [5.63 eV/atom]}.$$

3. Cohesive energy of α -rhombohedral type quasicrystal (II)

The cohesive energy of the α -boron type quasicrystal was estimated by another method. Because all environments around the clusters are not equivalent in a quasicrystalline structure, main six sites of them were accounted for the estimation (Table 4). The cohesive energy is estimated by

$$E_{\text{coh}}[\alpha - \text{QC}] = (\langle E_{\text{bond}} \rangle + \langle E_{3c} \rangle + \langle E_{\text{clst}} \rangle) / \langle N \rangle$$

where $\langle E_{\text{bond}} \rangle$ is the average two-center bonding energy, $\langle E_{3c} \rangle$ is the average three center bonding energy, $\langle E_{\text{clst}} \rangle$ is the average cohesive energy of clusters and $\langle N \rangle$ is the average number of atoms on a site. These averages are estimated as follows:

$$\langle N \rangle = \sum_i P_i N_i$$

where P_i and N_i are frequency (Table 4) and number of atoms per site for site i ; $N_1=9$, $N_2=N_3=10.5$ and $N_4=N_5=N_6=12$.

$$\langle E_{\text{bond}} \rangle = \frac{1}{2} \sum_i \sum_j P_i Z_i P_j E_{ij}$$

where Z_i is the coordination number of site i (Table 4)

Table 4 Definition of sites in three dimensional Penrose pattern.

	Number of vertex (See Fig. 4)				Frequency (P_i) (%)	Coordination number (Z_i)
	$\angle A$	$\angle B$	$\angle C$	$\angle D$		
Site 1	2	2	0	0	26.5	4
Site 2	1	4	0	1	26.5	5
Site 3	1	3	1	3	6.3	6
Site 4	0	6	0	2	26.5	6
Site 5	0	5	1	4	6.3	7
Site 6	0	4	2	6	7.8	8

Fig. 4 Definition of four vertices, A, B, C and D, of (a) oblate and (b) prolate rhombohedra. Their solid angles are $7\pi/5$, $3\pi/5$, $\pi/5$ and $\pi/5$, respectively.Table 5 Calculated bonding energies for the α -boron type quasicrystalline structure.

E_{14}	0.272 aJ	[1.70 eV]
E_{24}	0.250 aJ	[1.56 eV]
E_{34}	0.292 aJ	[1.82 eV]
E_{25}	0.199 aJ	[1.24 eV]
E_{26}	0.242 aJ	[1.51 eV]

and E_{ij} is a bonding energy between site i and j . Because these bonding energies are not so different, some major E_{ij} are calculated for this estimation (Table 5).

$$\langle E_{3c} \rangle = \frac{1}{3} E[\Delta] \sum_i P_i N_{Bi}$$

where N_{Bi} is the number of vertex B (in Table 4) around site i , because vertex B has one-third of the three center bond.

$$\langle E_{\text{clst}} \rangle = \sum_i P_i E_{ci}$$

where E_{ci} is a cohesive energy of a cluster located at site i . For site 1, E_{c1} is 9/30 of the cohesive energy of B_{30} cluster (Fig. 5) located at site 1; $E_{c1} = 9E[B_{30}]/30$ where $E[B_{30}] = 20.07 \text{ aJ [125.3 eV]}$. This cluster is constructed of three icosahedra located at the ends of short body diagonals of two OR, and each three atoms are removed from two interfaces between icosahedra similarly to the B_{21} cluster. For site 2 and 3, $E_{c2} = E_{c3} = E[B_{21}]/2$. For the other sites, $E_{ci} = E[B_{12}]$. The cohesive energy estimated by this method is

$$E_{\text{coh}}[\alpha - \text{QC}] = 567 \text{ kJ/mol [5.88 eV/atom]}.$$

Fig. 5. B_{30} cluster located at site 1. The cohesive energy, $E[B_{30}]$, was estimate to be 20.07 aJ [125.53 eV].

Table 6 Cohesive energy of each structure.

	Cohesive energy in kJ/mol [eV/atom]	
	Calculated	Experimental
α -rhombohedral crystal	578 [5.99]	561 [5.81]
β -rhombohedral crystal	512 [5.31]	—
α -rhombohedral type quasicrystal	543 [5.63] (method I) 567 [5.88] (method II)	—

These calculated results are summarized in Table 6. For both estimations, the α -boron type quasicrystal has a value of cohesive energy between that of α - and β -rhombohedral borons. For this reason, the realization of α -boron type quasicrystal is expected.

IV. Distortion of B_{12} Clusters

Since a B_{12} icosahedron has 12 outer bonds along five-fold axes, 12 hydrogen atoms are located to terminate these bonds. The highest occupied molecular orbital (HOMO) of neutral $B_{12}H_{12}$ has 4-fold degeneracy and only 6 electrons. As a result, the $B_{12}H_{12}$ cluster is distorted to a cubic or rhombohedral type by the Jahn-Teller effect. The maximal sub group of the icosahedral symmetry group is a cubic, rhombohedral or pentagonal one. The cubic and rhombohedral distortions of $B_{12}H_{12}$ are stable on the basis of the molecular orbital calculation, but the pentagonal one is not (Table 7). The distortions of B_{12} in the $K_2B_{12}H_{12}$ crystal and the β -rhombohedral boron, cubic and rhombohedral ones, respectively, have the same signs as the lowest energy ones in the calculation (Table 7) and can be considered to be caused by the Jahn-Teller effect. Two electrons for each B_{12} must be supplied to suppress the Jahn-Teller effect and to grow the icosahedral symmetry.

On the other hand, the distortion of B_{12} can be controlled by adding another element in the α -rhombohedral boron. In the structure of B_6O , $B_{100-x}C_x$ ($9 < x < 20$) or $B_{13}P_2$, O, C or P is located on the body diagonal of the

Table 7 Comparison between the lowest energy distortion of $B_{12}H_{12}$ in molecular orbital calculation and distortion of B_{12} in real crystalline structure.

	Calculated distortion	Real distortion
Cubic	$\Delta\theta = -8\%$	$\Delta\theta = -1.25\%$ ($K_2B_{12}H_{12}$)
Rhombohedral	$\Delta\theta_1 = +8\%$ $\Delta\theta_2 = -3\%$	$\Delta\theta_1 = +1.5\%$ $\Delta\theta_2 = -1.3\%$ (β -rhomb. boron)
Pentagonal	Unstable	Nothing

Fig. 6 (a) Unit cell structures of α -rhombohedral type crystal. (b) Correlation between distortion of B_{12} ($\Delta\theta_1$ and $\Delta\theta_2$) and rhombohedral axis angle in these structures. The θ_1 and θ_2 are angles between six icosahedral basic vectors and a three-fold axis⁽³⁾.

unit cell of the α -rhombohedral boron (Fig. 6(a)). In these α -rhombohedral type structures, the distortion of B_{12} is correlated to the angle of rhombohedral axis (Fig. 6(b))⁽³⁾. The angle is closest to that of icosahedral basic vectors and the distortion of B_{12} is the smallest in the B-C system.

V. Phase Transformation of B-C Amorphous Phases

Based on the consideration of the previous two sections, the α -boron type quasicrystalline structure can be formed and the distortion of B_{12} should be smallest in the B-C system. For the above reasons, we have tried to search for semiconducting quasicrystal in the B-C system. In the equilibrium phase diagram of B-C system, the boron carbides exist as a single-phase material with B_4C structure, from about 9 to 20 at% C⁽¹⁷⁾ and the distortion of B_{12} is reduced with decreasing C content (Fig. 7)⁽¹⁸⁾⁻⁽²⁰⁾. In addition, because the oblate rhombohedron of Fig. 1(b) has no inside C site like the chain sites of the prolate one (the B_4C unit cell) of Fig. 6(a), the composition of the quasicrystalline structure should be C poor compared with that of the B_4C structure. Therefore, the quasicrystalline composition is expected to be between 0 and 9 at% C.

The composition of the evaporated B_4C film is confirmed by EPMA to be almost the same as that of the starting powder material. The powder X-ray diffraction spectra for the evaporated films of B and B_4C show broad maxima characteristic of amorphous phases. The four diffraction maxima for the amorphous B and B_4C films are corresponding to the four groups of the strongest diffraction peaks for the α -rhombohedral boron and B_4C , respectively. The third maximum corresponds to the B-B bond length. The first and second maxima show the existence of structural correlation in larger units, i.e. B_{12} , in these amorphous films.

Figure 8 shows X-ray diffraction patterns of $B_{100-x}C_x$ ($x=3, 5, 7$ and 10) after heating of amorphous phase at several temperatures for 10 min. The compositions determined by EPMA are 6.74, 7.34 and 9.65 at% C for the specimens with $x=3, 5$ and 7 , respectively. Phase

Fig. 8 Powder X-ray diffraction spectra from Cu K α radiation for $B_{100-x}C_x$, (a) $x=10$, (b) $x=7$, (c) $x=5$ and (d) $x=3$, after heating of amorphous phases for 10 min at 1300°C or 1200°C. Bars in (a) show the positions of the diffraction peaks of the B_4C phase, and the black arrows show that of BN phase which is contamination from a crucible.

Fig. 7 Correlation between distortion of icosahedral cluster ($\Delta\theta_1$ and $\Delta\theta_2$) and carbon content in boron carbides⁽¹⁸⁾⁻⁽²⁰⁾.

transformation starts at 1200°C for $B_{90}C_{10}$ and at 1150°C for the others. As shown in Fig. 8(a), $B_{90}C_{10}$ amorphous phase crystallizes to the B_4C phase, the peak positions of which are indicated by segments in the figure. According to the equilibrium phase diagram, the $B_{100-x}C_x$ ($0 < x < 9$) amorphous phase would be expected to be decomposed into the elemental boron (α - or β -rhombohedral boron) and the B_4C after heating. However, the observed diffraction patterns (Fig. 8(b), (c) and (d)) show the B_4C phase and a phase which is not in the diagram. We try to identify the diffraction peaks of the unknown phase marked by white arrows in Fig. 9, by the $B_{25}C$ tetragonal structure or the quasicrystalline one. These peaks can be explained by the $B_{25}C$ tetragonal structure inflated by 3.7% along the a -axis and by 0.5% along the c -axis. To explain them by the icosahedral quasicrystalline structure as shown in Fig. 9, the quasilattice constant must be 0.53 nm, which is 1.6% larger than the lattice constant of the $B_{19}C_2$ (B_4C structure) rhombohedral crystal. However, the following problems exist: the peak A cannot be explained by the icosahedral structure, and inversion of rel-

Fig. 9 Powder X-ray diffraction spectrum from Cu $K\alpha$ radiation for $B_{95}C_5$ after heating of amorphous phase for 10 min at 1360°C . Bars show the positions of the diffraction peaks of the icosahedral quasicrystalline phase with a quasilattice constant of 0.53 nm. The white and black arrows show those of unknown and BN phases, respectively.

active intensities between peak A and B at 3 at% C has not been understood yet. To determine the structure of this unknown phase, TEM observation, electron diffraction pattern analysis and the study of phase transformation processes for other compositions, $B_{100-x}C_x$ ($0 < x < 9$), are in progress.

VI. Conclusions

The molecular orbital calculation shows that the cohesive energy for the α -boron type quasicrystal lies between that for α - and β -boron, suggesting the realization of the structure. A neutral $B_{12}H_{12}$ icosahedral cluster is distorted to a cubic or rhombohedral one by the Jahn-Teller effect. Among the α -rhombohedral type structures, the distortion of B_{12} is correlated with the rhombohedral axis angle and the distortion is smallest for B-C system. In the annealing process of $B_{100-x}C_x$ ($x=3, 5$ and 7) amorphous phases, a meta-stable phase, diffraction peaks of which are possibly related to a quasicrystalline structure, has been found.

Acknowledgments

This research has been supported by Special Coordination Funds for Promoting Science and Technology from the Science and Technology Agency and by Iketani Science and Technology Foundation.

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