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Novel Ca and Ca-Li intercalated B/C and B/C/N materials with layered structures

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Prof. Kawaguchi received his Dr degree from the Kyoto University in 1984. After working at Central Glass Co. Ltd. as a researcher, he moved to Osaka Electro-Communication University (OECU) in 1994 and is currently the Dean of the Graduate School of Engineering at OECU. He has worked in the field of syntheses and application of graphite-like layered materials composed of boron, carbon, and nitrogen for 30 years.

Abstract

Boron/carbon/nitrogen (B/C/N) materials and boron/carbon (B/C) materials having graphite-like layered structures were synthesized by using chemical vapor deposition (CVD) method. Calcium (Ca) was intercalated into the B/C materials by the reaction of Ca vapor with the host B/C film to form an intercalation compound with a second stage structure as a main product. Ca was also co-intercalated with lithium (Li) into the B/C/N materials by using the liquid-alloy method to form an intercalation compound. These are the first examples of syntheses of Ca and Ca-Li intercalated B/C and B/C/N materials. The nuclear microprobe analysis (NMA) indicated the compositions of the original host B/C/N and B/C materials to be $BC_{2.6}N_{0.55}$ and $BC_{6.4}$, and the Ca-Li intercalated compound to be $Ca_{0.67}Li_{0.42}(BC_{3.3}N_{0.50})$ and suggested the homogeneity of these materials and the compound. We also found that the NMA is one of the most accurate methods for determining the compositions of air and water sensitive intercalation compounds as well as complex systems like the B/C/N and B/C materials.

Keywords: Intercalation of calcium, B/C material, B/C/N material

1. Introduction

Boron/carbon/nitrogen (B/C/N) and boron/carbon (B/C) materials with their graphite-like structure and their semiconducting properties are very attractive. Their potential applications and their ability to be considered as host material¹ are attention grabbing in several fields: batteries², capacitors³, fuel cells⁴ and semiconductors^{5,6}. These materials can be used as energy devices due to their physical and chemical properties. Indeed, it is possible to intercalate several metals such as potassium (K), lithium (Li), sodium (Na) and even magnesium (Mg) into this layered structure either by using the vapor phase reaction method or the electrochemical method⁷⁻⁹.

However, the structural organization of B/C/N and B/C

materials is poorly known and has never been fully resolved by radio crystallographic studies. In each layer of B/C/N material, 2 carbon atoms are ideally replaced by a boron atom and a nitrogen atom. However, the distance between two successive layers of B/C/N, which is very close to the interplanar distance in graphite, was experimentally determined and reaches 0.340~0.343 nm¹⁰. On the other hand, boron atoms can replace carbon atoms with the graphite structure to make the composition BC_8 ¹⁰, although the replaced boron atoms cut off the conjugated double bonds in each layer of B/C material. The distance between two layers of B/C was experimentally determined and reaches 0.340~0.343 nm which is same as that of B/C/N.

In this paper we present, after a structural and chemical study of the host B/C/N and B/C materials, the intercalation of calcium (Ca) by using a vapor phase method of Ca, and a solid-liquid method in Li-based alloys for the first time with these host materials. The novel Ca and Ca-Li intercalated compounds were studied by X-ray diffraction (XRD) and transmission electron microscope (TEM). Their chemical compositions were determined using usual elemental analyses and nuclear microprobe analysis (NMA).

2. Experimental

2.1 Syntheses of B/C/N and B/C materials as host materials

B/C/N materials were synthesized at a temperature between 1770 and 2070 K by the chemical vapor deposition (CVD) method¹¹ using an equimolecular mixture (1:1 or 1:2 as a reference) of acetonitrile and boron trichloride as starting materials⁸. B/C materials were synthesized also by the CVD method at 1170 K using an equimolecular mixture (1:1) of ethylene and boron trichloride¹⁰. The B/C/N and B/C materials films were obtained on the carbon susceptor as the substrate and then removed from the substrates. The films were formed with an orientation of *ab*-axis parallel to the susceptor, which were analyzed by using XRD and shown in the results below. The host B/C/N and B/C films were cut into thin platelets whose sizes were $0.5 \times 0.5 \times 0.01 \text{ cm}^3$ and $1.3 \times 0.6 \times 0.01 \text{ cm}^3$ for the

intercalation by using the vapor phase method and the solid-liquid method, respectively.

2.2 Intercalation reaction

The intercalation of Ca into B/C/N and B/C host materials were carried out by the vapor phase method¹². Commercially available Ca pieces (Fujifilm Wako Chemical Co. Ltd.) and B/C/N or B/C platelets were set in a stainless-steel tube, sealed with Swagelok caps at both ends under a high purity argon atmosphere in a glove box, and heated at 1070 K in an electric furnace for 2 weeks.

The intercalation of Ca-Li into B/C/N host material was carried out by the solid-liquid method in lithium-based molten alloy, developed for the intercalation of calcium into graphite¹³. The alloys were prepared in a glove box under a high purity argon atmosphere. Pure lithium and calcium metals were precisely weighed and introduced in a stainless-steel reactor which was heated to get a homogeneous liquid. The B/C/N platelet hanged on a tungsten sample-holder was then introduced in the Ca-Li liquid alloy containing 27 Ca at.%. The reactor was tightly closed and placed into a furnace outside the glove box. The reaction was performed at 620 K for a given duration (from 2 days to 3 weeks).

At the end of the reaction by the both methods, the reactor was opened in the glove box and the intercalated sample was recovered and then placed in a well-adapted air-tight sample-holder for each characterization.

2.3 Elemental analysis

Elemental analyses for the host B/C/N and B/C materials were carried out by the usual combustion method for carbon and nitrogen, and ICP emission spectroscopic method for boron using a boron containing solution made by a decomposition of the host materials in an alkali solution.

2.4 Ion beam analysis

The host materials and the intercalated compounds were characterized by ion beam analysis using NMA. This technique based on the interactions between a high energy ion beam in the MeV domain and the probed material were used to determine the chemical composition, but also the homogeneity of the samples laterally as well as in-depth^{14,15}. A proton beam of 3050 keV and a particle detector at 170° from beam axis were used. To determine the nature and the concentration of the elements likely to be present (B, C, N, Ca, Li), elastic scattering and nuclear reactions were considered. A single spectrum led to the whole information for Li, B, C, N, and Ca laterally and in-depth. The analyzed map is typically of 200 × 200 μm², with lateral resolution at a few micrometers level (beam size 3.5 × 4 μm²). Samples composition was determined by adjustment between simulated spectra and experimental data using the SimNRA software. The simulated spectrum was made up of the superimposed contributions of all the interactions, with each isotope of each element of each sublayer of the defined solid. (More information concerning Li, B, C, N, O and Ca cross-sections for both backscattering and nuclear reactions are given in Supporting Information 1.)

2.5 X-ray diffraction

X-ray diffraction experiments were realized with a XRD

apparatus (RIGAKU RINT-Ultima) using Cu-Kα radiation. Since the intercalation compounds were air and water sensitive, a platelet sample was used for the measurement and placed on a sample holder in a sealed equipment with a Be window under pure argon atmosphere or was covered with a polymer film on it.

2.6 TEM and EDX

The intercalation compounds were analyzed by using scanning transmission electron microscopy (STEM) and energy-dispersive X-ray (EDX) as the following. The obtained intercalation compound film was cut into a small piece by using the focused ion beam (FIB) manipulation under argon atmosphere. The small piece was then set in a TEM apparatus (JEOL, JEM-ARM200F). The STEM observation and the EDX analyses were made from the direction of *ab*-axis for the cross section of the intercalation compound.

3. Results and Discussion

3.1 Host B/C/N materials

The precise chemical composition of this type of material is difficult to determine with the elemental analyses. One of the reasons is due to the combustion difficulty of the materials under oxygen to determine the carbon and nitrogen contents by the usual combustion method. Therefore, we firstly determined boron content by the ICP emission spectroscopy. Then the rest of the contents (100 % - boron content %) was proportionally divided with the carbon and nitrogen contents measured by the combustion method.

We also used the NMA to determine the composition and study the homogeneity of the samples. Table 1 indicates the results of the composition determined by the elemental analyses and the NMA. For the NMA, many samples were studied in several regions and a representative spectrum has been selected and modeled (Figure 1). The numerous recorded spectra are superimposable (not shown), which attests to the good homogeneity of the BCN material. Despite the proximity of the three elements (B, C, N), this spectrum clearly shows three steps. In details, a first step is observed at 2290 keV, which is attributed the ¹⁴N(p,p)¹⁴N reaction. Then, the signal measured around 2172 keV is attributed to the ¹²C(p,p)¹²C reaction. Finally, the last step at 2105 keV corresponding to the ¹¹B(p,p)¹¹B and ¹⁰B(p,p)¹⁰B reaction is observed. We can also see a small step at 2370 keV characteristic of the presence of oxygen in-depth of the sample. All steps are horizontal and do not present any accident indicating that the sample is homogeneous in depth, which is confirmed by the modeling. The amount of boron, carbon and nitrogen is the same throughout the sample and corresponds to a chemical formula BC_{2.6}N_{0.55} (indicated in Table 1) with a slight presence of oxygen (6 at. %) in the whole sample. The difference of the compositions analyzed by using the elemental analyses and the NMA could be due to the estimation of carbon and nitrogen contents by using the elemental analyses. Therefore, we represent the compositions of the host B/C/N and B/C materials, and the Ca-Li intercalated B/C/N material by using the NMA in this paper.

Table 1. Composition of B/C/N material analyzed by elemental analysis and nuclear microprobe analysis (NMA).

Synthetic temperature / K	Molar ratio BC ₁₃ : CH ₃ CN	Composition	
		Elemental analysis	NMA
1770	2:1	BC _{2.2} N _{0.76}	BC _{1.8} N _{0.69}
2070	2:1	BC _{2.5} N _{0.79}	BC _{2.0} N _{0.81}
2070	1:1	BC _{3.6} N _{0.87}	BC _{2.6} N _{0.55}

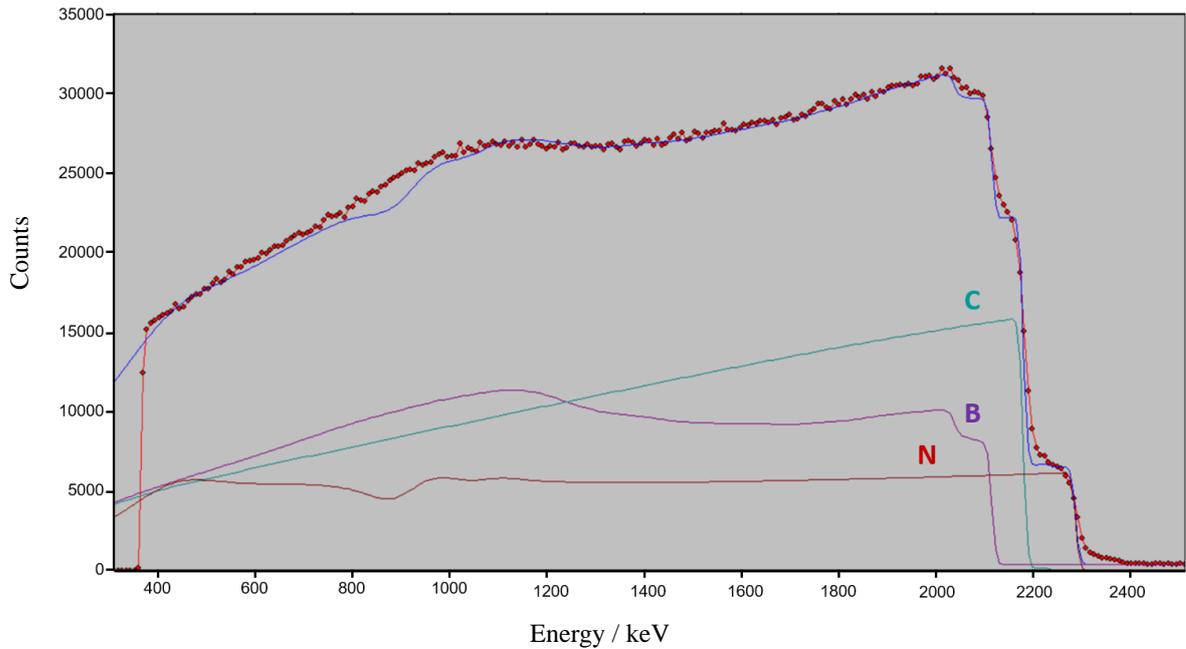


Figure 1. NMA(RBS/NRA) spectrum of the B/C/N material, compared with the simulated spectrum. Each elementary contribution to the simulation is individually indicated. Red spots: experimental result. Blue solid line: simulated result.

The crystal structure of this B/C/N material has been studied. For this purpose, a film sample was reduced to powder in order to record an X-ray powder diffraction pattern. The corresponding pattern (Figure 2) reveals a strong and sharp diffraction line at 26.12° in 2θ ($d = 0.341$ nm), a diffraction line at 53.94° in 2θ ($d = 0.170$ nm), and a weak diffraction line at 85.72° in 2θ ($d = 0.113$ nm), which are the positions close to the graphite (002), (004), and (006) diffraction lines, respectively. Weak and broad diffraction lines at 42.28° and 77.12° in 2θ ($d = 0.214$ nm and 0.124 nm, respectively) were observed in Figure 2, which are the positions close to the (10) and (11) diffraction line of graphite with the turbostratic structure¹⁶. These attributions suggest that the B/C/N material had a layered structure like the graphite. Although the (00 l) diffraction index depends on the stacking sequence (AB, AA, or turbostratic stacking), the diffraction line at 26.12° in 2θ ($d = 0.341$ nm) is called the (002) diffraction line as a usual understandable indexing in this paper.

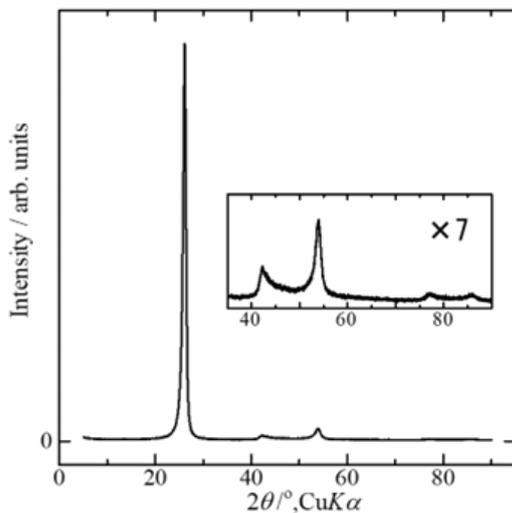


Figure 2. X-ray powder diffraction of B/C/N material ($BC_{2.6}N_{0.55}$).

3.2 Host B/C material

In the case of B/C material, we firstly determined boron content by the ICP emission spectroscopy and assumed the rest of the contents (100 % - boron content %) to be carbon content. We analyzed carbon and hydrogen contents by using the combustion method and found negligible amounts of hydrogen in the materials.

We also used NMA to determine the composition and study the homogeneity of the samples. Table 2 indicates the results of the composition determined by the elemental analyses and the NMA. As is the case of B/C/N material, we represent the composition $BC_{6.4}$ analyzed by using NMA for the B/C material used in the present paper. For the NMA, many samples were studied in several regions and a representative spectrum has been selected and modeled (Figure 3).

Table 2. Composition of B/C material analyzed by elemental analysis and NMA.

Synthetic temperature / K	Molar ratio $BCl_3 : C_2H_4$	Composition	
		Elemental analysis	NMA
1170	4:3	$BC_{8.0}$	$BC_{6.4}$

The crystal structure of this B/C material has been studied. Figure 4 indicates a powder X-ray diffraction pattern of B/C material ($BC_{6.4}$). Like that of B/C/N material, it shows very few reflections and are very close to those of graphite. A strong and sharp diffraction line at 26.16° in 2θ ($d = 0.341$ nm), a diffraction line at 54.02° in 2θ ($d = 0.170$ nm), and a weak diffraction line at 85.78° in 2θ ($d = 0.113$ nm), which are the positions close to the graphite (002), (004), and (006) diffraction lines, respectively. Weak and broad diffraction lines at 42.30° and 77.42° in 2θ ($d = 0.214$ nm and 0.123 nm, respectively) were observed on Figure 4, which are the positions close to the (10) and (11) diffraction lines of graphite with the turbostratic structure¹⁶. In the similar manner to the B/C/N material, the B/C material had a layered structure¹⁷ like the graphite.

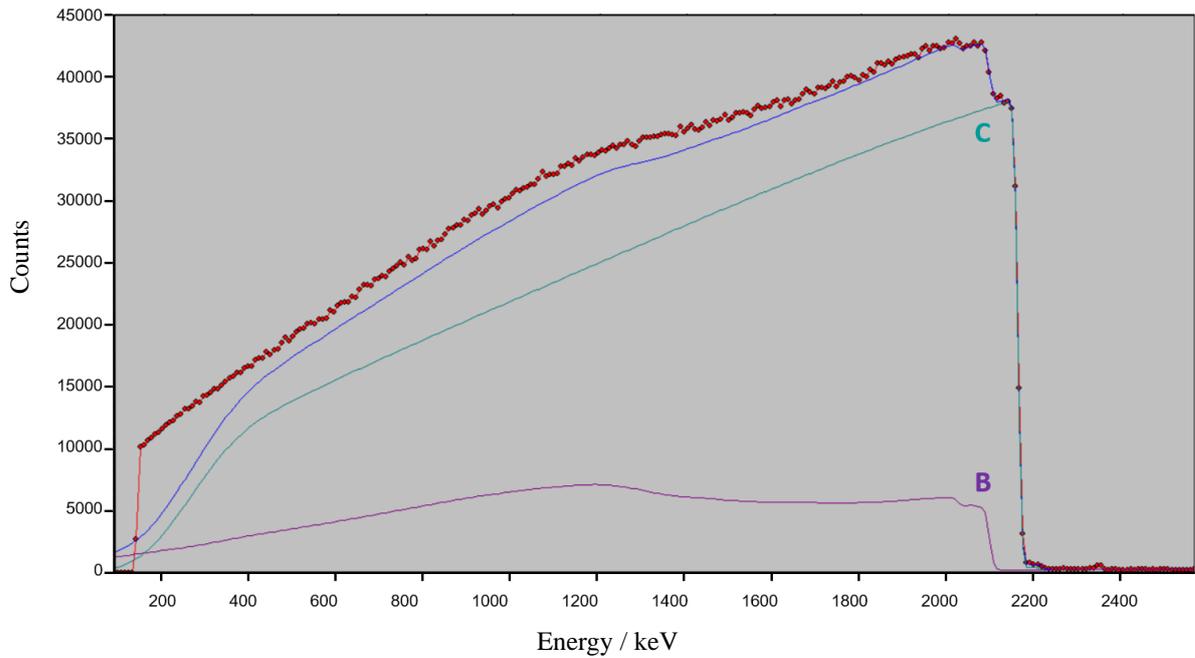


Figure 3. NMA(RBS/NRA) spectrum of the B/C material, compared with the simulated spectrum. Each elementary contribution to the simulation is individually indicated. Red spots: experimental result. Blue solid line: simulated result.

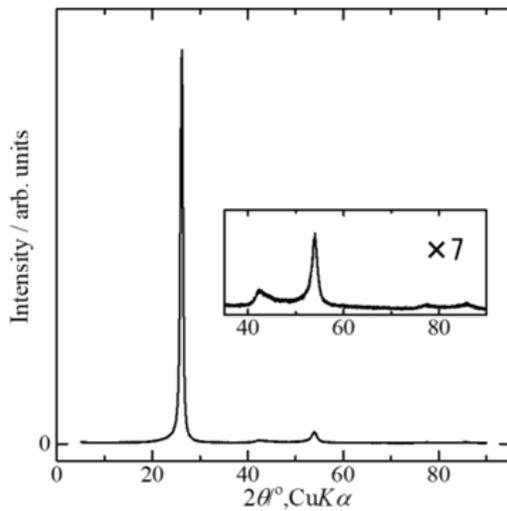


Figure 4. X-ray powder diffraction pattern of B/C material (BC_{6.4}).

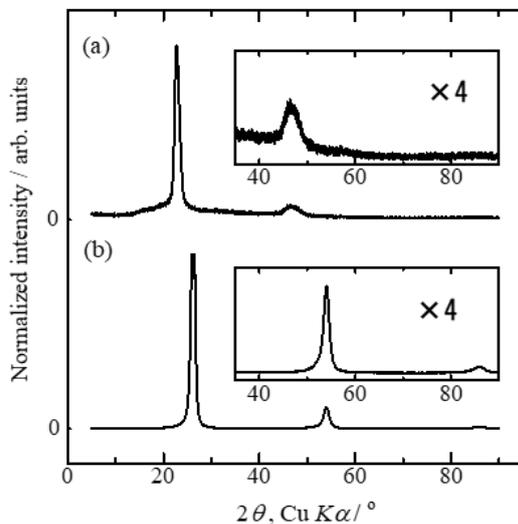


Figure 5. XRD patterns of (a) the Ca intercalated BC_{6.4} film and (b) the original BC_{6.4} host film¹².

3.3 Ca intercalated B/C material

The vapor-phase reaction of Ca with the B/C film (BC_{6.4}) resulted in the formation of Ca intercalated B/C material (called as “Ca intercalated BC_{6.4}” thereafter). Figure 5 shows an XRD pattern of the Ca intercalated BC_{6.4} film (a), compared with that of the original BC_{6.4} host film (b)¹². (00 l) diffraction lines of the original BC_{6.4} film were strongly observed in relative to the (10) diffraction (Figure 5b), compared to the relative intensity for the powder (Figure 4). This is because the original film was deposited by the CVD method with an orientation of ab -axis in parallel to the substrate. The (002) and (004) diffraction peaks at 26.16° ($d = 0.341$ nm) and 53.94° ($d = 0.170$ nm) of the original BC_{6.4} film disappeared after the reaction. Then we observed new diffraction peaks at 22.72° ($d = 0.391$ nm) and 45.84° ($d = 0.198$ nm) (Figure 5a). These changes in XRD diffraction patterns suggested that the BC_{6.4} host film reacted with Ca vapor to form the intercalation compound (Ca intercalated BC_{6.4}).

Figure 6 indicates an expected structural view of the c -axis stacking of the compound which has the second stage structure. The layer spacing of the Ca intercalated BC_{6.4}, d_i : 0.461 nm (= 0.341 + 0.120 nm), is assumed from the Ca intercalated graphite (first stage CaC₆: $d_i = 0.455 = 0.335 + 0.120$ nm)¹⁸. A (002) diffraction peak of the second stage Ca intercalated BC_{6.4} can be estimated to be 0.401 nm $\{= (0.461 + 0.341)/2\}$, which is close to the diffraction peak observed at 22.72° ($d = 0.391$ nm) in Figure 5a. The diffraction peak at 45.84° ($d = 0.198$ nm) in Figure 5a should be a (004) diffraction of the second stage compound. The Van der Waals radius of B/C layers overlaps with the Ca^{δ+} ion can be explained in the same manner as the alkali metal intercalated graphite by using the theory of “nestling”¹⁹.

When we used the B/C material powder as the starting material, we couldn’t observe the XRD pattern like Figure 5a, but observed an XRD pattern showing a lot of diffraction lines which couldn’t be identified. This means that we couldn’t obtain the intercalation compound by using the B/C powder as the starting material. This is probably because the B/C powder having large surface area violently reacted with Ca vapor to form an unexpected compound such as a carbide.

Figure 7 shows the cross-section image of main part of the Ca intercalated BC_{6.4} observed with STEM. The second stage

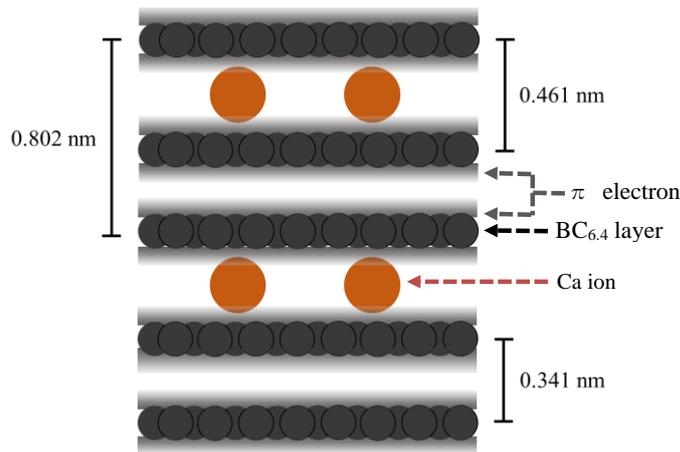


Figure 6. Expected structural view of the c -axis stacking of Ca intercalated $BC_{6.4}$ with the second stage structure.

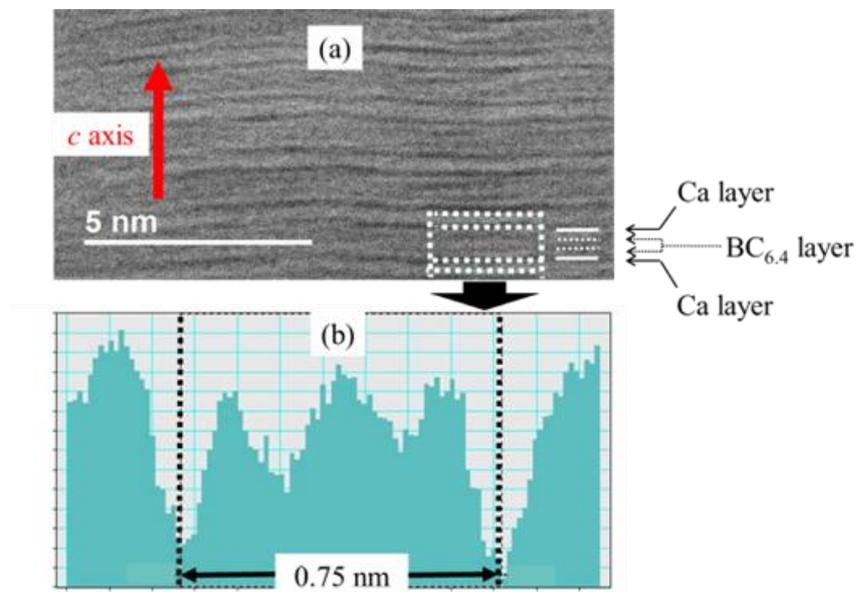


Figure 7. (a) Cross-section image of main part of the Ca intercalated $BC_{6.4}$ film observed with STEM and (b) contrast change image in the direction of c -axis. These indicate the second stage structure¹².

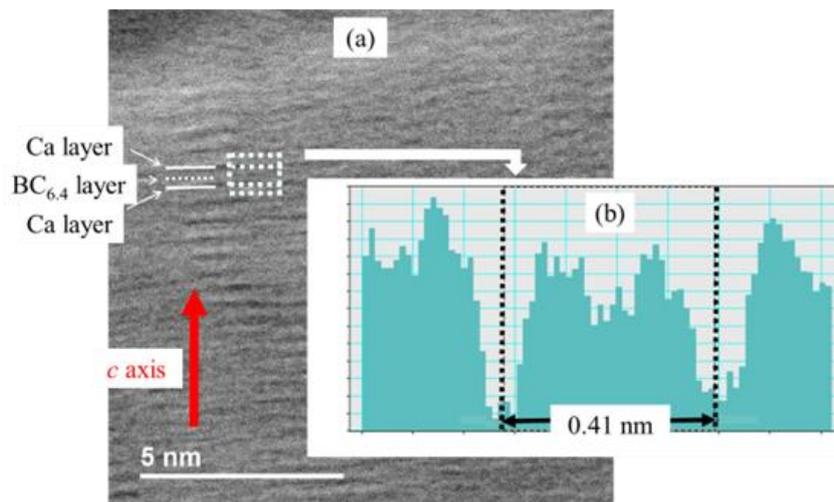


Figure 8. (a) Cross-section image of the Ca intercalated $BC_{6.4}$ film observed with STEM and (b) contrast change image in the direction of c -axis. These indicate the first stage structure¹².

structure was observed on the image. Layers including the heaviest Ca atoms are indicated with the darkest lines, while $BC_{6.4}$ layers are indicated with the next dark lines. In Figure 7a, two separated Ca layers sandwich two continuous $BC_{6.4}$ layers, which suggests the second stage structure. Figure 7b indicates the contrast change image in the direction of c -axis. Although the distances measured by STEM are not so accurate as those measured by XRD, the distance between the Ca layers in Figure 7 is approximately 0.75 nm, which is close to the value of 0.80 nm for second stage structure calculated from the XRD result (Figure 5) and shown in Figure 6.

Figure 8 shows the cross-section image of a different part of the Ca intercalated $BC_{6.4}$ observed with STEM. The first stage structure was observed on the image. In Figure 8a, two separated Ca layers sandwich one $BC_{6.4}$ layer, which suggests the first stage structure. Figure 8b indicates the contrast change image in the direction of c -axis. An approximate distance between the Ca layers (darkest lines) is 0.41 nm, which is close to the value of 0.46 nm for the first stage structure predicted from the distance of second stage one (Figure 6).

In the XRD pattern of Ca intercalated $BC_{6.4}$ film (Figure 5a), the (002) diffraction line was broader compared with that of the original $BC_{6.4}$ (Figure 5b). This result suggests that the crystallinity of Ca intercalated $BC_{6.4}$ was lower than that of the

original $BC_{6.4}$, and it was composed of several stage structures shown in Figs. 7 and 8. Probably Ca intercalated $BC_{6.4}$ had not only the second stage structure but also the first stage one.

The Ca intercalated $BC_{6.4}$ had a Ca content in the range between 18 and 27 wt% (6 and 10 at%), which was observed through the EDX analyses. This result is consistent with the metal contents of general graphite intercalation compounds (GICs) with second stage structures (compositions between $C_{12}M$ and $C_{24}M$, where M is Li, K, or CS)¹⁸.

From the above results made by using XRD, STEM, and EDX analyses, we concluded that the obtained compound "Ca intercalated $BC_{6.4}$ " was composed of the second stage compound as the main product and the first stage one as the sub-product.

We have checked the intercalation of Ca vapor into graphite under the same reaction conditions used in the present study and found that Ca couldn't be intercalated into graphite. Also, we have recognized that Ca intercalation into B/C/N materials under the same reaction condition used in the present study resulted in the formation of intercalation compounds with higher stage structure having a small amount of Ca in the layers. From these results, we found that B/C material with the composition $BC_{6.4}$ intercalated Ca in their layers more efficiently than the cases of graphite and B/C/N materials.

On the synthesis of GICs, it has long been known that

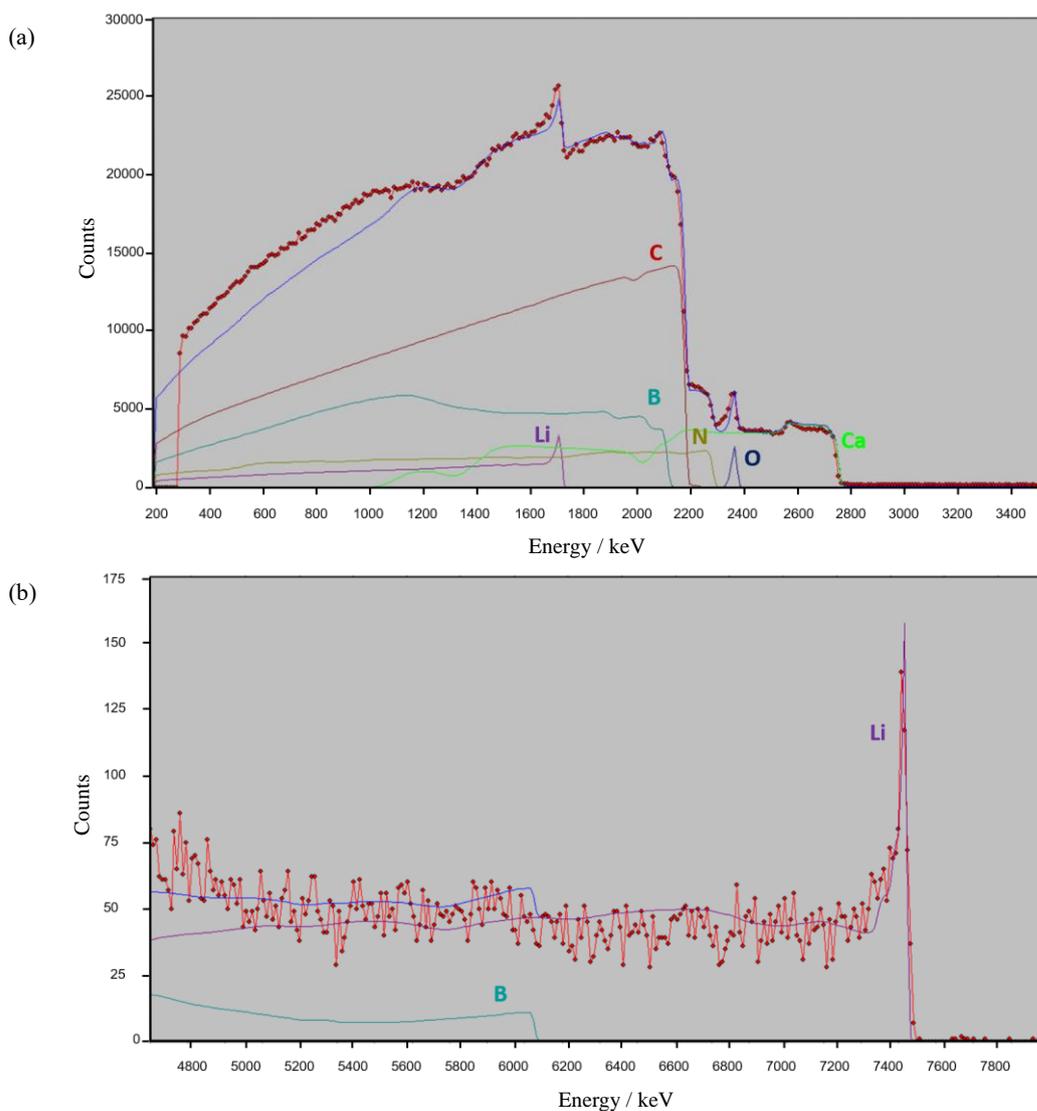


Figure 9. NMA(RBS/NRA) spectrum of the Ca-Li intercalated B/C/N material, compared with the simulated spectrum. Each elementary contribution to the simulation is individually indicated. (a) Total spectrum, (b) high energy part. Red spots: experimental result. Blue solid line: simulated result.

the synthesis of low-stage Na-GIC is difficult compared with those of low-stage other alkali metals-GICs. It has been also known that Mg cannot be intercalated into graphite. On the other hand, Na and Mg have been intercalated into B/C/N materials^{8,9} and Na has been intercalated into B/C materials¹⁰. Several members (Kawaguchi and Ishikawa) of the present authors explained these results in terms of the ionization potentials of the metals and the electron affinities of the host materials^{9,17}. They reported that the bottoms of the conduction bands of B/C and B/C/N materials were ca. 1.1 eV lower than that of graphite, which was evaluated from the results of the X-ray absorption near-edge structures (XANES)¹⁷. This means that the electron affinities of B/C and B/C/N materials are ca. 1.1 eV larger than that of graphite (4.6 eV). Also, Yamada reported that Na could be intercalated more efficiently into B/C materials by using electrochemical method probably because of the larger electron affinity of B/C material compared with that of graphite¹⁰. The present authors consider that this mechanism can also explain the intercalation of Ca into BC_{6.4} observed in the present study. The larger electron affinity of B/C material resulted in the efficient Ca intercalation into the B/C material with the composition BC_{6.4}, compared with the difficult intercalation of Ca into graphite through the solid gas reaction²⁰.

3.4 Ca-Li intercalated B/C/N material

For the B/C/N host material, intercalation reactions using calcium-lithium alloys were performed using several experimental conditions. After the reaction of a B/C/N film in the Ca-Li alloy (27 Ca at. %) during 2 days at 620 K, the X-ray (00 l) diffraction lines of the host structure completely disappeared, indicating that an intercalation phenomenon occurred (Supporting Information 2 represents the (00 l) X-ray diffraction pattern of the sample obtained after the reaction of a B/C/N film in the Ca-Li alloy during 2 days at 620 K, compared with that of the B/C/N host structure). The (00 l) diffraction lines of the new intercalation compound allow to estimate d -spacings of 0.376 nm and 0.188 nm, although the stage structure hasn't been identified yet. When the reaction time was increased to 5 days, the d -spacings slightly increased to 0.381 nm and 0.191 nm, respectively. However, the d -spacings didn't change any more after 10 days or 21 days, corresponding to the thermodynamic equilibrium. In the case of using graphite host, the intercalation of Ca-Li alloy took longer time to reach the equilibrium¹³. From the comparison of the experimental results between the two kinds of host materials, the B/C/N film reacted with the Ca-Li alloy more smoothly than the case of graphite under the same reaction condition used in the present study. This is probably because the reaction mechanism described in the section 3.3 (Ca intercalated B/C material).

The chemical composition of this new B/C/N intercalation compound was studied by ion beam analysis. Many areas of the sample were analyzed, and a representative spectrum was selected and modelled (Figure 9). Figure 9a indicates a total spectrum showing all parts of analyzed zone. In addition to the boron, carbon and nitrogen steps of the host structure, the spectrum shows the Ca step at 2745 keV and the Li one at 1705 keV. The spectrum shows a characteristic peak of the interaction between protons and oxygen corresponding to the presence of oxygen on the surface of the sample. This oxidation can be explained by the exposure of the sample to the air during its transfer into the analysis chamber of the nuclear microprobe. Since we quickly transfer the sample, oxygen cannot diffuse into the bulk material that is why only a peak is observed (whereas steps are characteristics of the elements present in the bulk material). Figure 9b indicates a high energy part in which Li is recognized. In both spectra Figure 9a and 9b, it is easy in the modelling to distinguish the surface and the bulk of the sample

whose chemical composition is Ca_{0.67}Li_{0.42}(BC_{3.3}N_{0.50}). This analysis confirms the intercalation of both lithium and calcium, using the solid-liquid method in lithium-based alloys.

By using B/C film (composition: BC_{6.4}) as the starting material for the intercalation of Ca-Li alloy, a part of the film dissolved in the alloy solution and small pieces of compounds were obtained probably because of a rapid reaction of B/C material with the alloy solution.

The Ca and Ca-Li intercalated B/C and B/C/N compounds were air and water sensitive material, which is like the case of alkali metal or Ca intercalated graphite²¹. The Ca intercalated BC_{6.4} film slowly decomposed in air to expand in the thickness direction. The Ca-Li intercalated B/C/N film rapidly decomposed in water to show broad X-ray diffraction pattern.

In summary, Ca and Ca-Li were intercalated into B/C and B/C/N materials in this study, while they couldn't be intercalated into graphite under the same experimental condition. The NMA is useful tool to determine the compositions not only the host B/C/N and B/C materials but also the water sensitive Ca and Ca-Li intercalated materials. The efficient intercalation of Ca and Ca-Li into the B/C and B/C/N materials reported in this study suggests the application of these intercalation phenomena to the Ca secondary batteries²² and superconductors^{13,23} as the future energy systems.

4. Conclusion

The B/C material having the graphite-like layered structure with the composition of BC_{6.4} can intercalate Ca in their layers to form the second stage compound "Ca intercalated BC_{6.4}". The d -spacing of the intercalated layer was 0.461 nm, which is the value like that of the Ca intercalated GIC CaC₆. B/C/N material having the graphite-like layered structure with the composition of BC_{2.6}N_{0.55} can intercalate Ca-Li metals by using the Ca-Li liquid alloy to form the intercalation compound having the composition of Ca_{0.67}Li_{0.42}(BC_{3.3}N_{0.50}). The intercalation of Ca and Ca-Li into B/C and B/C/N host materials could be explained by considering the relationships between the ionization potentials of metals and the electron affinities of B/C and B/C/N materials. The authors also found that the NMA is one of the most accurate methods for the composition analyses of the host materials and the intercalation compounds. The efficient intercalation of Ca and Ca-Li into the B/C and B/C/N materials, which has been found in the present study, is expected toward the application to the Ca secondary batteries and the superconductors as the future energy systems.

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Supporting Information 1: Li, B, C, N, O and Ca cross-sections for both backscattering and nuclear reactions.

Supporting Information 2: (00 l) X-ray diffraction patterns of the compound film obtained after reaction of B/C/N film in the Ca-Li alloy during 2 days at 620 K and the original B/C/N host film.

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