Theoretically Predicted Soft X-ray Emission and Absorption Spectra of Graphitic-Structured BC$_2$N

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Abstract

Theoretical B K, C K and N K x-ray emission/absorption spectra of three possible graphitic-structured BC$_2$N clusters are predicted based on the B2p-, C2p-, and N2p- density-of-states (DOS) calculated by discrete variational (DV)-Xα molecular orbital calculations. Several prominent differences in DOS spectral features among BC$_2$Ns, h-BN, and graphite are confirmed from comparison of calculated B2p-, C2p-, and N2p-DOS spectra. These variations in the spectra allow BC$_2$N structures to be positively identified by high-resolution x-ray emission/absorption spectroscopy in the B K, C K, and N K regions.

Keywords

BC$_2$N, soft x-ray spectra, x-ray emission, x-ray absorption, molecular orbital calculations, electronic structure, density of states

1. INTRODUCTION

In the search for advanced materials with novel physical and chemical properties, boron/carbon/nitrogen materials are attractive targets. A new and particularly exciting area for such BCN materials is the synthesis and characterization of graphitic-structured BC$_2$N [1]. The graphitic network structure of BC$_2$N should be similar to graphite and hexagonal boron nitride (h-BN), yet should exhibit very different physical and chemical properties. It is well known that graphite and h-BN have contrasting properties; for example, graphite is a semimetal and excellent host material while h-BN is an insulator and generally
does not form intercalation materials. Thus, graphitic-structured BC$_2$N may exhibit novel semiconducting and intercalation properties that could prove useful in many applications including light-emitting materials, thermoelectric conversion materials, lightweight electrical conductors, electrode material for batteries, high-temperature lubricants, and coating materials.

In the synthesis of graphitic-structured BC$_2$N materials, structural characterization is important because various structural isomers are possible and the properties of each exhibit strong structural dependence. For the characterization of composite materials consisting solely of light elements, high-resolution soft x-ray emission and absorption spectroscopy using synchrotron radiation is a powerful tool that reveals detailed information regarding the electronic and chemical structure [2]. Spectroscopic analysis of these x-ray spectra can best be achieved using discrete variational (DV) Xα molecular orbital (MO) calculations [3], which approximately reproduce the x-ray spectral features from the calculated density-of-states (DOS) spectra [4 - 6]. The present author has successfully characterized several carbon nitride films as covalent C$_n$N$_4$ materials using soft x-ray spectroscopy and DV-Xα MO calculations, demonstrating the power of this method in the characterization of light-element composite materials [7].

Characterizing graphitic-structured BC$_2$N materials using soft x-ray emission and absorption spectroscopy requires theoretically calculated x-ray spectra in order to identify the x-ray spectral features of the various structural isomers. Here, the author reports theoretically predicted x-ray emission and absorption spectra calculated from the occupied and unoccupied DOS for the possible structural isomers of BC$_2$N using DV-Xα MO calculations.

2. DV-Xα MO CALCULATIONS

2.1. CONFIRMATION OF DV-Xα MO CALCULATIONS FOR GRAPHITE AND h-BN CLUSTER MODELS

To confirm the validity of DV-Xα MO calculations for graphitic-structured BC$_2$N materials, the x-ray emission/absorption spectra of graphite and h-BN are compared to the corresponding DOS spectra obtained by DV-Xα MO calculations. Cluster models of graphite (C$_{26}$H$_{24}$) and h-BN (B$_{48}$N$_{48}$H$_{24}$) used in the DV-Xα MO calculations are illustrated in Figure 1. These structures were optimized using molecular mechanics (MM2) [8] with commercially available Chem3D Plus software. DV-Xα MO calculations for these cluster models were conducted on the electronic structure of the ground states with a basis set of 1s, 2s, and 2p orbitals for B, C, and N atoms. Calculations were performed using the SCAT program [3] as part of commercially available DV-Xα software running on a DOS/V computer.
Density of state (DOS) spectra of BC$_2$N

![Cluster models of three possible structural isomers of graphitic-structured BC$_2$N (B$_{24}$C$_{48}$N$_{24}$H$_{24}$) with references h-BN (B$_{48}$N$_{48}$H$_{24}$) and graphite (C$_{90}$H$_{24}$). Hydrogen atoms terminating the edge atoms in the cluster models are not shown in the figure.](image)

Fig. 1. Cluster models of three possible structural isomers of graphitic-structured BC$_2$N (B$_{24}$C$_{48}$N$_{24}$H$_{24}$) with references h-BN (B$_{48}$N$_{48}$H$_{24}$) and graphite (C$_{90}$H$_{24}$). Hydrogen atoms terminating the edge atoms in the cluster models are not shown in the figure.

X-ray spectral measurements of graphite and h-BN powders were carried out using high-brilliance synchrotron radiation at the Advanced Light Source (ALS; Berkeley, USA). High-resolution x-ray emission spectra in the B K, C K, and N K regions were obtained using a grating x-ray spectrometer installed on beamline 8.0 [9], and absorption spectra were obtained using beamline 6.3.2 [10] by the total-electron-yield method. The resolving power (E/ΔE) was estimated to be approximately 270 for emission measurements and 1600 for absorption in the C K region.

Measured x-ray emission/absorption spectra in the B K and N K regions of h-BN and those in the C K region of graphite are shown in Figure 2. Superimposed upon these measured spectra are the individual DOS spectra for centered atoms (denoted by asterisks) of B$_2$p and N$_2$p in h-BN and C$_2$p in graphite. The calculated spectra are obtained by broadening individual DOS with 0.5 eV-wide Lorentzian functions. The occupied B$_2$p-, C$_2$p-, and N$_2$p-DOS spectra well reproduce measured x-ray emission spectra. This suggests that the generation of DOS spectra from DV-Xα MO calculations is an appropriate method for...
simulating x-ray emission spectra. However, the calculated unoccupied DOS spectral features do not exactly agree with the experimental absorption spectra at the B K, C K, and N K threshold. This is reasonable in that the final state relaxation effects, which should be considered in exact calculations of core photoabsorption spectroscopy, were not taken into account. However, outline features such as $\pi^*$ and $\sigma^*$ peaks in the x-ray absorption spectra were roughly reproduced by the calculated DOS spectra. These results confirm that DV-Xα MO calculations on monolayer models composed of nearly 100 atoms reproduce x-ray emission spectra with good accuracy [12] and may also be useful in assigning the absorption spectral features for graphitic-structured BC$_2$N materials.

Fig. 2. Soft x-ray emission spectra (a) and absorption spectra (b) in the B K and N K regions of h-BN and those in the C K region of graphite. Corresponding occupied and unoccupied C2p-DOS spectra of the h-BN and graphite cluster models calculated with DV-Xα MO calculations are superimposed on the x-ray emission and absorption spectra.
2.2. DV-Xα MO CALCULATIONS FOR BC₂N CLUSTER MODELS

Three possible structures of BC₂N were predicted by Liu et al. [11] as shown in Fig. 1. Carbon atoms in model (a) form poly-acylene-like structures. Each carbon atom in model (b) is bound to carbon, boron, and nitrogen atoms. There are two kinds of carbon atoms in model (c): one carbon atom is bound to one carbon atom and two boron atoms, while the other is bound to one carbon atom and two nitrogen atoms. Based on these structures, DV-Xα MO calculations were performed for the three cluster models of B₂₄C₄₈N₂₄H₂₄. Atoms on the edges of the clusters are terminated by hydrogen atoms. The geometries of these model structures were initially optimized by the MM2 method. DV-Xα MO calculations of these cluster models were performed on the electronic ground states with a basis set of 1s, 2s, and 2p orbitals for B, C, and N atoms. DOS spectra were obtained by broadening the calculated individual DOS of the centered atoms (denoted by asterisks in Fig. 1) using 0.5 eV-wide Lorentzian functions.

3. RESULTS AND DISCUSSION

Figure 3 shows the occupied and unoccupied DOS spectra of 2s- and 2p-orbitals in B, C, and N atoms of the three BC₂N cluster models. DOS spectra for B and N atoms in h-BN and for C in graphite are also shown as references. In these DOS spectra, the energy levels of the highest occupied molecular orbitals (HOMOs) are defined as zero eV on the MO energy scale.

The occupied DOS spectra of B atoms for all three BC₂N models exhibit a low-energy tail feature in B2p-DOS, which hybridizes with the B2s orbital. However, the low-energy peak observed in h-BN is not observed in the BC₂N. This low-energy peak feature therefore represents an index for distinguishing BC₂N from h-BN. The high-energy features differ among the three BC₂N models: model (a) has small shoulder peaks, model (b) has a sharp peak, and model (c) exhibits no high-energy fine structures. These differences in high-energy features will provide useful indices for identifying BC₂N structures in B K x-ray emission spectra. In the occupied DOS spectra of N atoms, the N2p-DOS spectrum of h-BN is the main peak feature with a high-energy peak and a low-energy step-like shoulder. However, such fine structure is not observed in the BC₂N models. This difference in N2p-DOS spectra between BC₂N and h-BN is another clear index for distinguishing BC₂N from h-BN. In the BC₂N models, the main peak feature in model (c) is slightly sharper than that of models (a) and (b). However, there is little significant difference in the N2p-DOS spectra among the three BC₂N models.
Fig. 3. Occupied and unoccupied DOS spectra of 2s- and 2p-orbitals in B, C and N atoms of the three BC2N cluster models. Molecular structures of the BC2N models (a – c) are shown in Fig. 1.
It therefore appears difficult to distinguish between the three BC$_2$N structures based solely on N K x-ray emission spectra. In the occupied DOS spectra of C atoms, there are clear differences in C2p-DOS spectral features of the main peak and high-energy shoulder/peak between the BC$_2$N models and graphite. These main-peak and high-energy-shoulder/peak features can therefore be used to distinguish BC$_2$N from graphite. In the BC$_2$N models, there are clear differences among the three models: a broad main peak with a high-energy peak in model (a), a main peak with a small high-energy peak in (b), and a broad main peak with a prominent high-energy peak in (c). Spectral features of the main peak and high-energy peak in C K x-ray emission can also be used as indices for identifying BC$_2$N structures.

![DOS spectra for BC$_2$N models](image)

Fig. 4. Occupied and unoccupied C2p-DOS spectra drawn by separating the components of C(1) and C(II) atoms in BC$_2$N cluster models (a) and (c). Molecular structures of (a) and (c) models are shown in Fig. 1.
In the unoccupied DOS spectra, there are distinctive differences in B2p-, N2p-, and C2p-DOS among the three BC2N models and the reference h-BN and graphite in the fine threshold structures. This demonstrates that BC2N structures can be identified from high-resolution x-ray absorption spectra at the B K, C K, and N K thresholds, in addition to identification using the above-mentioned x-ray emission spectra.

There are two kinds of C atoms in BC2N models (a) and (c). In model (a), one C atom (denoted by I in Fig. 1) is bound to two C atoms and one N atom, while C (II) is bound to two C atoms and a single B atom. In model (c), one C (I) is bound to a single C atom and two B atoms, while C (II) is bound to one C atom and two N atoms. The clear difference in the C2p-DOS spectra between (a) and (c) results from these variations in chemical bonding. Figure 4 shows the occupied and unoccupied C2p-DOS spectra after separation of the components of C (I) and C (II) atoms in (a) and (c). In the occupied spectra, high-energy peak features are assigned primarily to hybridization with B atoms. Consequently, the prominent high-energy peak in (c) can be well explained by strong hybridization with two B atoms of the C (I) atom. In the unoccupied spectra, the prominent low-energy peaks in (a) and (c) are due to hybridization with N atoms.

4. CONCLUSIONS

The author has obtained B2p-, C2p-, and N2p-DOS spectra for the three possible graphitic-structured BC2N models ($B_2C_4N_2H_4$) based on DV-Xα MO calculations in order to predict the B K, C K and N K x-ray emission/absorption spectra. From a comparison of the occupied/unoccupied DOS spectra of BC2N models with graphite ($C_{96}H_{24}$) and h-BN ($B_{48}N_{48}H_{24}$) references, clear differences in the individual DOS spectra of the BC2N and reference models were identified. In addition, clear variations in both occupied and unoccupied DOS spectra were discovered, with the exception of occupied N2p-DOS, among the three BC2N models. Thus, the author demonstrated that high-resolution soft x-ray emission and absorption spectral measurements in the B K, C K, and N K regions for graphitic-structured BC2N compounds are a useful tool for structure identification.

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6. REFERENCES