

## B K-Edge XANES Spectra of Borosilicon Carbonitrides

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Borosilicon carbonitride (BSiCN) materials composed of four light elements of boron, silicon, carbon, and nitrogen have been reported to be quite stable amorphous materials at high temperatures.

Recently, Hasegawa prepared BSiCN materials by a distinctive method using the precursor and investigated their excellent resistance against the oxidation at high temperatures with a view to their application to space materials such as heat insulators and rocket engines [1,2]. These materials have characteristics of little mass loss up to 1700 °C under ambient pressure and outstanding resistance to oxidation under the oxygen partial pressure ranging from 0.4 to  $2 \times 10^5$  Pa.

Hasegawa investigated their structure by XRD, TEM, electron energy-loss spectroscopy, electron probe microanalysis and IR spectroscopy [1,2]. However, there are few reports on the local structure around the boron atom using X-ray absorption near-edge structure (XANES) measurements [3]. In the present study, we measured B K-edge XANES spectra of these BSiCN materials.

B K-edge XANES spectra for the BSiCN and reference samples (elemental boron, B<sub>2</sub>O<sub>3</sub>, B<sub>4</sub>C, hexagonal boron nitride (h-BN), and cubic boron nitride (c-BN)) were measured using a beamline BL-2 of the SR Center at Ritsumeikan University [4]. All samples were powdered to collect their XANES spectra in the total electron yield (TEY) mode. The vacuum level in the sample chamber was higher than  $1.0 \times 10^{-5}$  Pa during measurements. A background absorption calculated by a Victoreen-type function was subtracted from a measured XANES spectrum, and then normalized to the fundamental absorption intensity around 230 eV where no peaks due to electronic transitions were observed.

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Figure 1 shows the B *K*-edge XANES spectra of the BSiCN and reference samples. For h-BN, an intense peak at 192.0 eV and a structured absorption band of 197 - 201 eV are assigned to the transitions from B1s to the unoccupied B2p  $\pi^*$  and  $\sigma^*$  states, respectively, of the trigonal [BN<sub>3</sub>] unit [5,6]. For B<sub>2</sub>O<sub>3</sub>, a sharp peak located at 194.0 eV and a broad absorption band around 203 eV are assigned to the transitions from B1s to the unoccupied B2p  $\pi^*$  and  $\sigma^*$  states, respectively, of the trigonal [BO<sub>3</sub>] unit [5,7]. For c-BN, only a broad absorption band due to the transition from B1s to the unoccupied 2p  $\sigma^*$  of the tetrahedral [BN<sub>4</sub>] unit is observed [6]. For B<sub>4</sub>C, sharp peaks located at 191.3 and 192.0 eV are assigned to the transitions from B 1s to unoccupied B2p states of the C-B-C bond, and a broad absorption band of 195-207 eV to the continuum state [5,8]. For elemental boron, a broad absorption band reveals its continuum electronic state.

For the BSiCN samples, the obtained spectra are similar to those reported in ref. 3, sharp peaks at 192.0 (peak A) and 194.1 eV (peak B) being probably due to the h-BN- and B<sub>2</sub>O<sub>3</sub>-like structures, respectively. A broad absorption band of 196 - 207 eV (band C) is contributed from both structures. The peak B became weak relative to the peak A and the h-BN-like feature in the band C was strengthened with increase in the calcination temperature. Two weak peaks at 192.8 and 193.5 eV located between the peaks A and B can be assigned to the transitions from B1s to the unoccupied B2p  $\pi^*$  for nitrogen-void defects of [BN<sub>2</sub>] and [BN<sub>1</sub>] units, respectively [9]. For BSiCN materials, this is probably the first report of the existence of these kinds of defects. No B-C bonds were detected in the present measurements.

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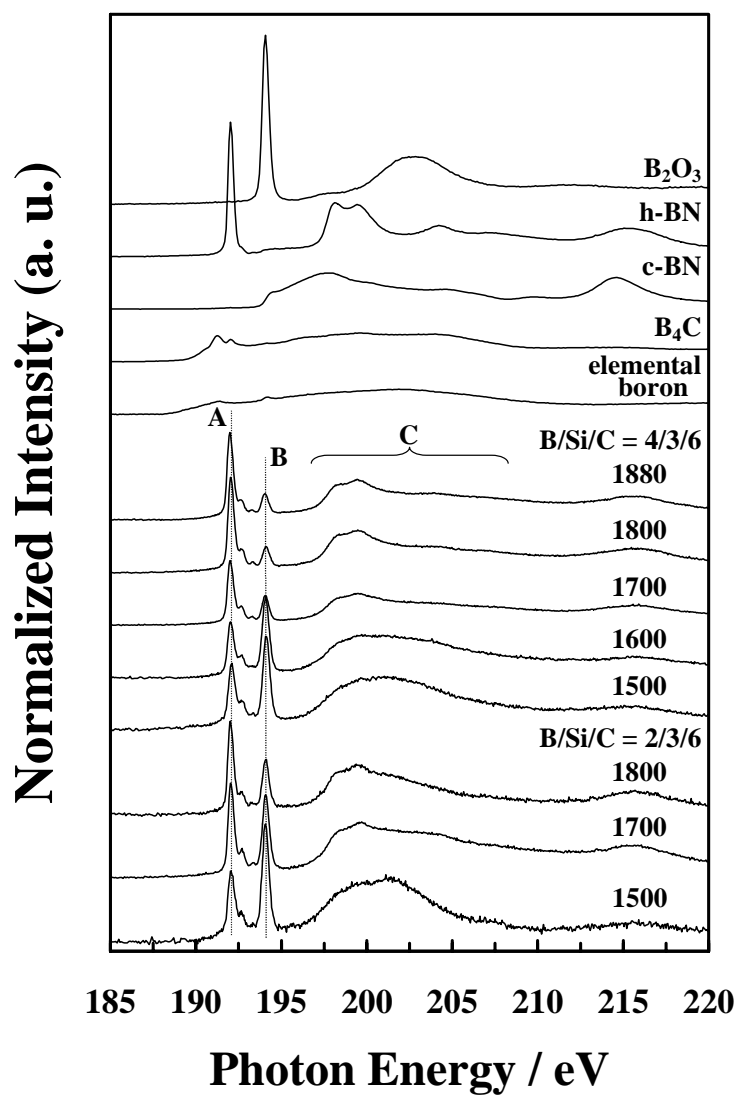


Figure 1. B *K*-edge XANES spectra of BSiCN and reference samples.