Soft x-ray emission and absorption study of boron carbides.

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Boron carbide is a solid with a structure based on B_{12} icosahedra and 3-atom linear chain forming units,[1,2] which exhibits very interesting physical properties: B_4C is a light, hard, semiconductor and refractory material.[3] Although the stoichiometric compound is nominally B_4C, the boron to carbon ratio can vary over a broad range by partial substitution of B by C atoms both in the chains and in the icosahedra. Near the carbon rich limit, i.e. 20 at. % carbon and B_4C stoichiometry, the solid is composed of $B_{11}C$ icosahedra and CBC chains. As the composition becomes more boron rich, CBB chains replace the CBC ones. With further carbon reduction the $B_{11}C$ icosahedra are replaced by B_{12} units.[4,5] Figure 1 sketches the structure of boron carbide.

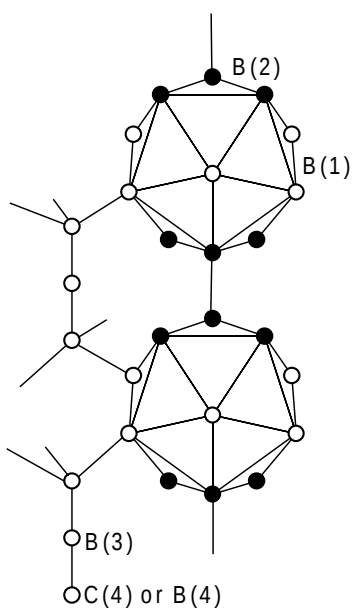

Figure 1. Structure of boron carbide.

The electronic structure of this solid is poorly known, due to the large number of atoms in the unit cell, the complexity of the atomic structure and the lack of experimental results available so far for comparison. Among the problems to perform angle resolved photoemission are the difficulty to grow single crystals and obtain clean surfaces, and the small size of the Brillouin zone that poses problems of angular resolution. Moreover, calculations of the electronic structure of boron carbide show a complicated dispersion of the multiple bands with momentum, indicating that it can be difficult to extract useful information from angle resolved experiments.[6]

An interesting question is how much of the electronic structure of the boron icosahedra remains in the solid. Boron carbide is not a molecular solid, since it is a hard and refractory material, but its atomic structure is based on the B_{12} unit. It is interesting to compare the density of states in different solids based on B_{12} icosahedra, like boron carbides with different stoichiometries, with molecules based on B_{12} cages like boranes and carboranes.[7]

X-ray absorption spectroscopy (XAS) and soft x-ray emission spectroscocpy (SXF) can be used to obtain information on the partial density of unoccupied and occupied electronic states corresponding to the different elements, respectively. Since the signal is not restricted to the surface area, surface cleanliness is not a limiting factor. This allows the study of polycrystalline and amorphous specimens in the form of bulk samples, powders, and thin films. A complete study of the electronic structure, with a comparison of theoretical and experimental results is being performed.[8] Some experimental results are described below.

Figure 2 shows from bottom to top, the x-ray absorption spectra at the B(1s) edge from: (a) a polycrystalline B_4C-bulk sample, (b) a B_4C powder, (c) a non-stoichiometric B_xC (x>4) thin film grown by sputtering, (d) a B_xC film grown by pulsed laser depositon, (e) an amorphous boron powder and (f) a crystalline boron powder. Curve (a) is used as a reference for comparison purposes.

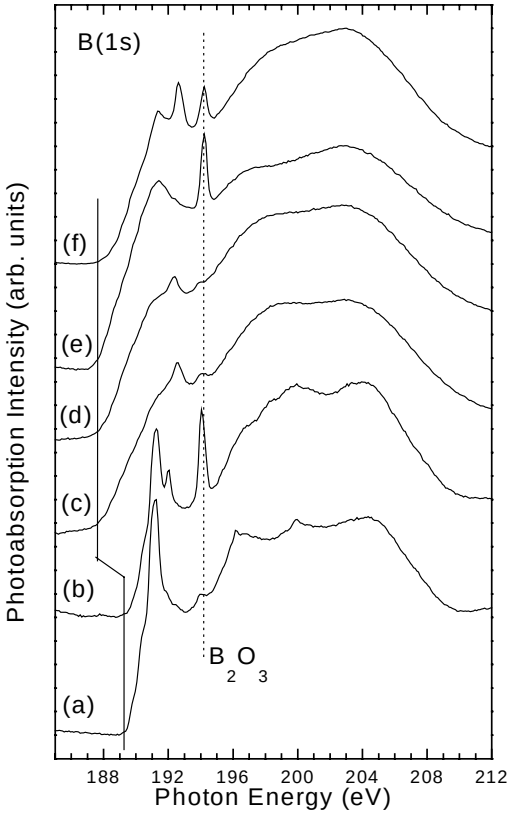

Figure 2. X-ray absorption spectra at the boron edge from: (a) B_4C-bulk sample, (b) B_4C-powder, (c) B_xC film grown by sputtering, (d) B_xC film grown by pulsed laser deposition, (e) amorphous B, and (f) crystalline B

A first observation is the position of the absorption edge, at 189 eV for stoichiometric B_4C and at 187 eV for boron and non-stoichiometric boron carbide. Also, there are additional peaks in the non-stoichiometric and boron samples compared to the B_4C reference, that cannot be assigned to B_2O_3 contamination.

Regarding the density of occupied states, Figure 3 (left pannel) shows the soft x-ray emission spectra out of resonance from the same set of samples. The overall lineshape is very similar, suggesting that the density of occupied states is given mostly by the B_{12} units present in all the samples. However, there are small changes in the density of states that are evident in the difference spectra presented in the right pannel. Here, the x-ray emission signal corresponding to the reference B_4C sample (a) have been subtracted from all other spectra. The extra features appear consistenly in the two non-stoichiometric films, and in the two boron powders,and are not present in the B_4C powder. This shows that there is a clear relationship between the density of states and the B to C stoichiometry, and that the presence of long range order is only a secondary effect.

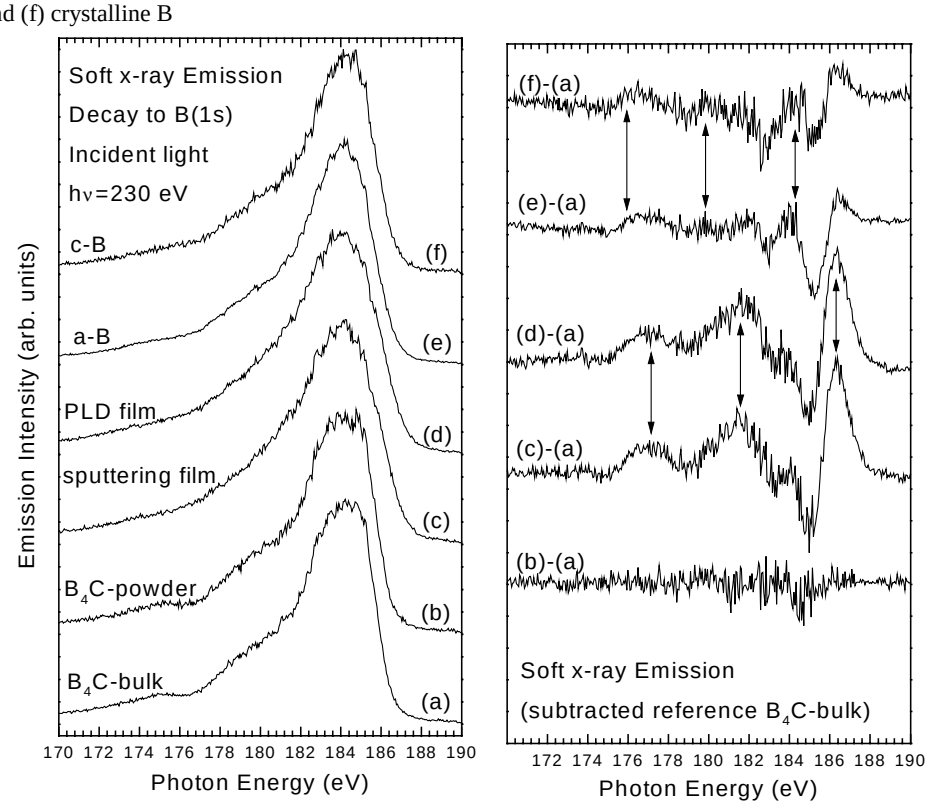

Figure 3. Left pannel: soft x-ray emission spectra from the same samples considered in Fig. 2. Right pannel: difference spectra obtained from subtraction of the bulk-B_4C spectrum.

ACKNOWLEDGMENTS

This work has been supported by the Division of Materials Sciences, Office of Basic Energy Science, and performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48 and the NSF under contract No. DMR-9632527. The work was performed at the Stanford Synchrotron Radiation Laboratory, which is supported by the Department of Energy, Office of Basic Energy Sciences, and at the Advanced Light Source, LBNL under Contract No. DE-AC03-76SF00098. I. J. acknowledges financial support from the Spanish CICYT project PB94-53 and NATO project CRG-971539.

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