

Lawrence Berkeley National Laboratory

Recent Work

Title

STUDY OF NOVEL GRAPHITE-LIKE MATERIALS IN THE B-C-N SYSTEM BY ELECTRON ENERGY-LOSS SPECTROSCOPY

Permalink

<https://escholarship.org/uc/item/7s00c62h>

Author

Krishnan, K.M.

Publication Date

1987-02-01



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED
LAWRENCE
BERKELEY LABORATORY

MAR 30 1987

LIBRARY AND
DOCUMENTS SECTION

Materials & Molecular Research Division

To be presented at the Microbeam Analysis Society
Conference, Kona, Hawaii, July 13-17, 1987,
and to be published in the Proceedings

STUDY OF NOVEL GRAPHITE-LIKE MATERIALS IN THE
B-C-N SYSTEM BY ELECTRON ENERGY-LOSS SPECTROSCOPY

K.M. Krishnan

February 1987

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.*



DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

STUDY OF NOVEL GRAPHITE-LIKE MATERIALS IN THE B-C-N SYSTEM BY ELECTRON ENERGY-LOSS SPECTROSCOPY

K.M. Krishnan

Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720

Two novel graphite-like materials in the B-C-N system, synthesized by a low temperature method, have been characterized by electron energy-loss spectroscopy. Single loss profiles were extracted by the Fourier-log deconvolution method and the plasmon resonance peaks as well as the fine structure of the core-loss edges confirm that these materials are truly graphite-like, i.e., all the elements are sp^2 hybridized and occur as substitutions and not as intercalations. Finally, using SIGMAK ionization cross-sections, their compositions were determined to be $B_{0.4}C_{0.23}N_{0.37}$ and BC_4 .

Author Krishnan is at the National Center for Electron Microscopy, Lawrence Berkeley Laboratory, Berkeley, CA 94720

The author would like to acknowledge Professor N. Bartlett, Dr. Rick Kaner and J. Kouvetakis for supplying the materials and introducing him to the world of novel graphites, Ms. W. Smith for help in specimen preparation, C. J. Echer for assistance on the 200CX, Professor R. F. Egerton for supplying listings of both SIGMAK and Fourier-log deconvolution computer programs and Dr. O. Krivanek for assistance on the GATAN parallel detector. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Introduction

A wide range of novel graphite-like materials in the B-C-N system have been recently synthesized by a low temperature method^{1,2}. Although the occurrence of boron in three-fold coordination is not uncommon in ring-structures such as boron-nitride and borazine, there is very little evidence for the substitution of either boron or nitrogen for carbon in the graphite structure. Even at high temperatures (2350°C) it is reported³ that the maximum substitution of boron for carbon in graphite is only 2.5at%. However, both boron-carbon (BC) and boron-carbon-nitrogen (BCN) graphites offer the possibility of not only greater electrical conductivity and a substantially lower band gap but the possibility of achieving these properties by a controlled variation of the chemical composition. The effectiveness of this strategy is assured if and only if these materials are truly graphitic and the substituting elements occupy sites in the graphitic layers.

A wide variety of preliminary characterization methods have suggested that these materials are graphite-like. Electron micrographs show that boron graphite (BC_x) is a homogeneous product having a sheet-like character with sheets 3-4Å apart. As these materials are deposited by a non-epitaxial process at moderately low temperatures, there is no sheet-to-sheet registry and hence electron diffraction patterns, though exhibiting graphite-like symmetry, do not reveal general hkl reflections. However, the 00l and hko reflections establish the graphite-like character. Moreover, superlattice effects are weak--largely due to the similarity in the scattering factors for boron and carbon. Further, products of interaction at 300°C with chlorine indicate that boron is truly a component of the sheet and not an amorphous component of a mixture with graphite. Similarly, x-ray photoelectron spectra

have shown that $B_xC_yN_x$ materials are not simply mixtures of boron nitride and graphite⁴ and suggest that both boron and nitrogen have each other, in addition to carbon, as neighbours. Further, the ratio of boron to nitrogen has been shown by ESCA to be approximately one to one. In this paper, the characterization of these novel graphites by EELS to corroborate/confirm some of these preliminary studies are presented.

Experimental Details

All experiments were performed on a JEOL 200CX analytical electron microscope operating at an acceleration voltage of 160kV and fitted with a Gatan 607 magnetic sector electron energy-loss spectrometer. All spectra were acquired in the image mode with a 600 μ m condenser aperture ($\alpha=4.5$ mrad). No objective aperture was used to ensure a large collection angle (~ 50 - 100 mrad). A beam current of ~ 1 - 2 mA and a spectrometer entrance aperture of 1 or 2mm were used such that a fractional energy resolution of 7×10^{-6} was routinely achieved. TEM specimens were prepared by either peeling off thin films of the material followed by ion-milling or by crushing them in an agate mortar and pestle and then floating them onto a holey carbon grid. Even though the specimens used were reasonably thin ($t/\lambda \sim 0.2$ - 0.7), plural scattering was removed using a Fourier logarithmic deconvolution procedure^{5,6}. It has been shown that noise artefacts limit the straightforward application of the "complete" deconvolution procedure only to a spectrum measured with very high precision and hence the zero-loss peak in the original spectrum was removed, and replaced by a δ -function before calculating the transform. A FORTRAN code based on this simplified algorithm outlined by Egerton⁷ was adapted to run on an IBM-PCXT (640K, Intel 8087 math coprocessor chip) and all spectra were deconvoluted using this computer program.

Results and Discussion

Microanalysis. The compositions of both of these novel graphites were determined by EELS. The ionization cross-sections required for the analysis were calculated using an approximate model employing hydrogenic wavefunctions⁸. This cross-section program (SIGMAK) has been shown to have surprisingly good agreement with experimental K-shell data. From our measurements of electron energy-loss intensities integrated over an energy window of 65eV and using well established quantification procedures⁹, these two novel graphites were shown to have a composition of $B_{0.40}N_{0.37}C_{0.23}$ (Fig.1) and BC_4 . These analyses are in error by 10-15 percent due to the difficulty in modeling the background of such closely spaced edges and the inaccuracy inherent in the cross-section calculations. The former compound was predicted to have a composition of $B_{0.35}C_{0.30}N_{0.35}$ based on the measurements of boron to nitrogen ratios by ESCA and boron to carbon ratios from fluorine combustion products. The latter compound produced by the reaction of BCl_3 with benzene at 800°C should ideally have a composition of BC_3 . Our observation of a larger carbon content is probably due to a greater pyrolyzation of carbon than expected at this temperature.

Low-loss spectra. The low loss regions of deconvoluted single scattered spectra from both BC and BCN graphites, and two reference standards--highly oriented pyrolytic graphite (HOPG) and boron-nitride, are shown in Fig. 2. In all cases two prominent resonance peaks are found. These plasmon peaks are associated with the two groups of valence bands (a π band close to the Fermi level and a σ band lying deeper and energetically separated from the former). In the case of HOPG¹⁰ and BN¹¹ it has been concluded that the lower energy peak corresponds to plasmon oscillations in which one π electron

per atom having $2p_z$ orbitals is involved and the higher energy peak is a hybrid resonance involving all four valence electrons per atom including the three σ electrons of the strong coplanar bond joining atoms to their neighbours on the same layer. Similar interpretations can be made for the plasmon oscillations of BC and BCN shown in Fig. 2.

The plasmon resonance energies for HOPG (6.9eV and 27.1eV) which are in agreement with earlier experimental observations¹⁰ differ from those calculated for graphite (12.5eV and 25.1eV) using a simple free electron or "jellium" model¹². The difference is attributed to a "screening" of the plasmon resonance by the σ electrons. However, the plasmon resonance energy, E_p is proportional to $n^{1/2}$, where n is the number of valence electrons per unit volume⁷. Using this proportionality the shifts in the peak positions of BC (6.36eV and 24.8eV) and BCN (7.5eV and 24.54eV) with respect to HOPG and BN (8.04eV and 26.5eV) are consistent with the former two being electron deficient with respect to the latter pair. However, the ratio of the localized to the delocalized electrons, calculated using the plasmon resonance energies in Fig. 2, in BC and BCN are identical to those in HOPG and BN, respectively. These observations confirm that all these compounds are structurally similar.

Core-loss edges. The core-loss edges for these four materials (HOPG, BN, BC graphite and BCN graphite) studied also showed remarkable similarity. The relevant energy region of the spectra for boron, carbon and nitrogen K edges are shown in Figs. 3, 4 and 5 respectively. It is clear that these edges show prominent features corresponding to both π^* and σ^* antibonding levels corresponding to the unoccupied bound states of the conduction band, for all the elements in all the four materials. These observations along with the features of the plasmon resonances discussed earlier confirm that

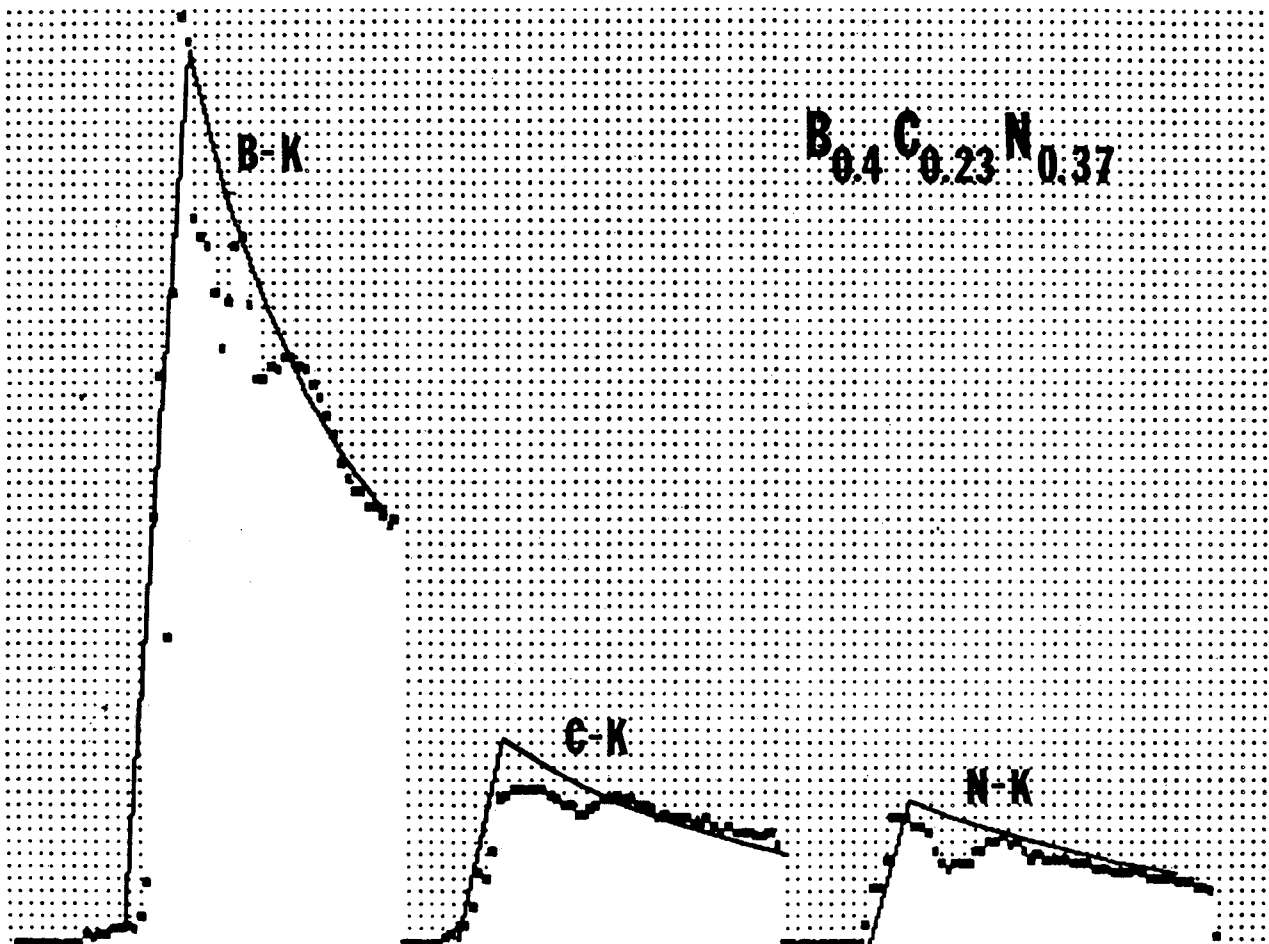
all the elements (B,C,N) in all the materials are sp^2 hybridized and occupy sites in the graphitic layers. The features of the B K edge in BC graphite are confirmed to be real by taking the second difference of four different spectra collected at 1eV shifts in rapid succession using a prototype parallel detector mounted on a JEOL 1200FX at 120keV¹³. Further, the energy values of the fine structures of the C K edge (284eV, 290eV, 295eV) in HOPG and the BK edge (191eV, 197.5eV, 202.5eV) and N K edge (397.5eV, 399eV, 404.0eV, 405.5eV, 410.5eV) are in good agreement with the band structure calculation^{14,15} at symmetry points of the Brillouin zone (BZ)¹¹. As both BC and BCN graphites are structurally similar to HOPG and BN, it should be possible to do the reverse, i.e. obtain information about their band structure at the symmetry points of the BZ using the observed energy values of the fine structure of the K edges. This is currently in progress.

References

1. Neil Bartlett, J. Kouvetakis, R. B. Kaner and Kannan M. Krishnan, Science, in press.
2. J. Kouvetakis, R. B. Kaner, M. L. Sattler and N. Bartlett, J. Chem. Soc., Chem. Comm., in press.
3. C. E. Lowell, J. Amer. Cer. Soc. 50, 142 (1967).
4. R. B. Kaner, J. Kouvetakis, C. E. Warble, M. L. Sattler and N. Bartlett, Mat. Res. Bull., in press.
5. D. W. Johnson and J. C. H. Spence, J. Phys. D7, 711 (1974).
6. R. D. Leapman and C. R. Swyt, AEM-1981, R. H. Geiss, ed., S.F. Press (1981), 164.
7. R. F. Egerton, EELS in the electron microscope, pp. 229, 362 (1986).
8. R. F. Egerton, Ultramicroscopy 4, 169-179 (1979).
9. R. F. Egerton, SEM/II, 505 (1984).
10. W. Y. Liang and S. L. Cundy, Phil. Mag. 19, 1031 (1969).
11. J. Hosoi, T. Oikawa, M. Inoue, Y. Matsui and T. Endo, J. Elec. Spec. and Rel. Phen. 27, 243 (1982).
12. D. Pines, Elementary excitation in solids, Benjamin, N.Y. (1963).
13. O. L. Krivanek, C. C. Ahn and R. B. Keeny, Ultramicroscopy, in press.
14. H. Nagayoshi, M. Tsukada, K. Nakao and Y. Uemura, J. Phys. Soc. Japan 35, 396 (1973).
15. K. Doni and G. P. Parravicini, Nuovo Cimento 64B, 117 (1969).

Figure Captions

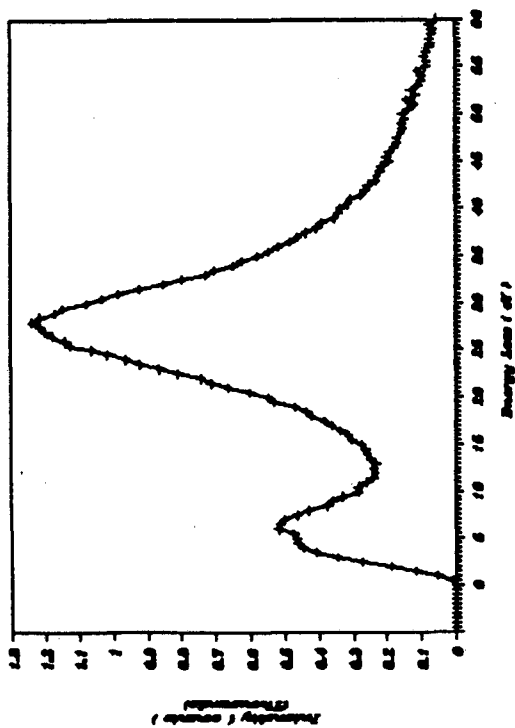
- Fig. 1. Typical spectrum of $B_{0.4}C_{0.23}N_{0.37}$ after background subtraction. The calculated energy loss spectra for identical experimental conditions using hydrogenic wavefunctions (SIGMAK ionization cross-sections) are also superimposed.
- Fig. 2. Low-loss spectra of HOPG, BN, BC graphite and BCN graphite. All profiles are single loss extractions obtained by a Fourier-log deconvolution method. The lower energy features on the π plasmons are artefacts of the deconvolution procedure.
- Fig. 3. Core loss fine structure: B K edges.
- Fig. 4. Core loss fine structure: C K edges.
- Fig. 5. Core loss fine structure: N K edges.



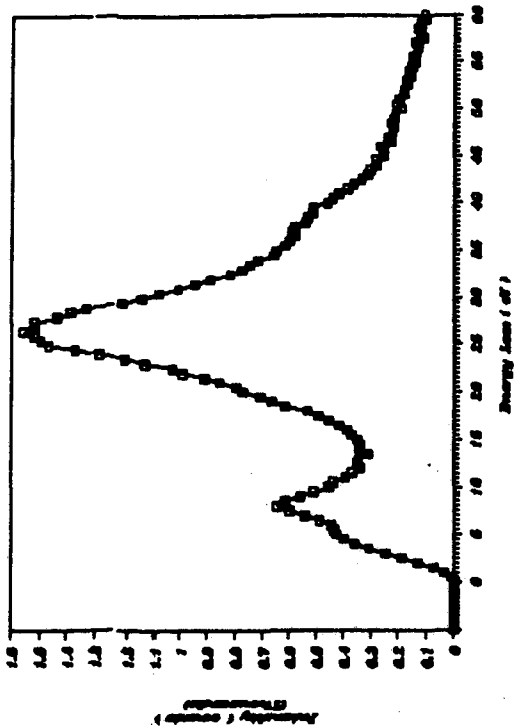
XBL 871-285

Fig. 1

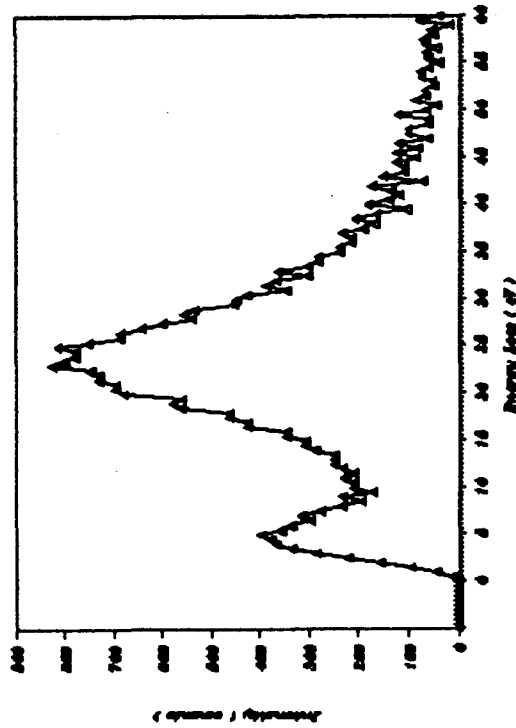
HOPG, Low Loss, SSD, 160 kV



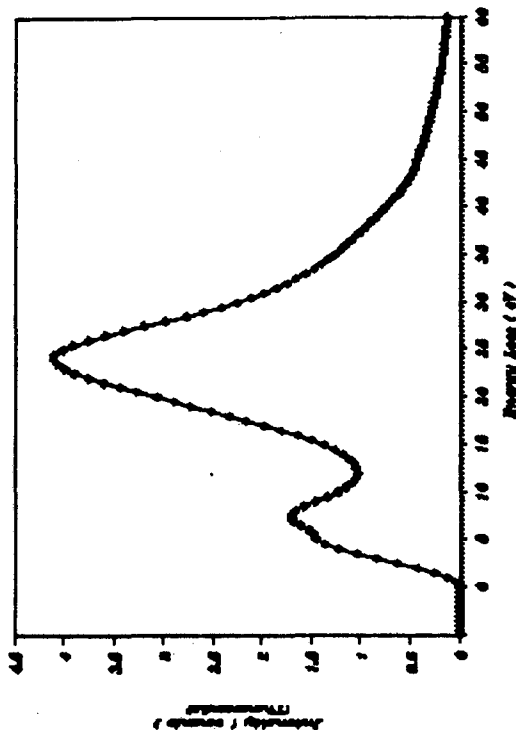
BN, Low Loss, SSD, 160 kV



BC Graphite, Low Loss, SSD, 160 kV



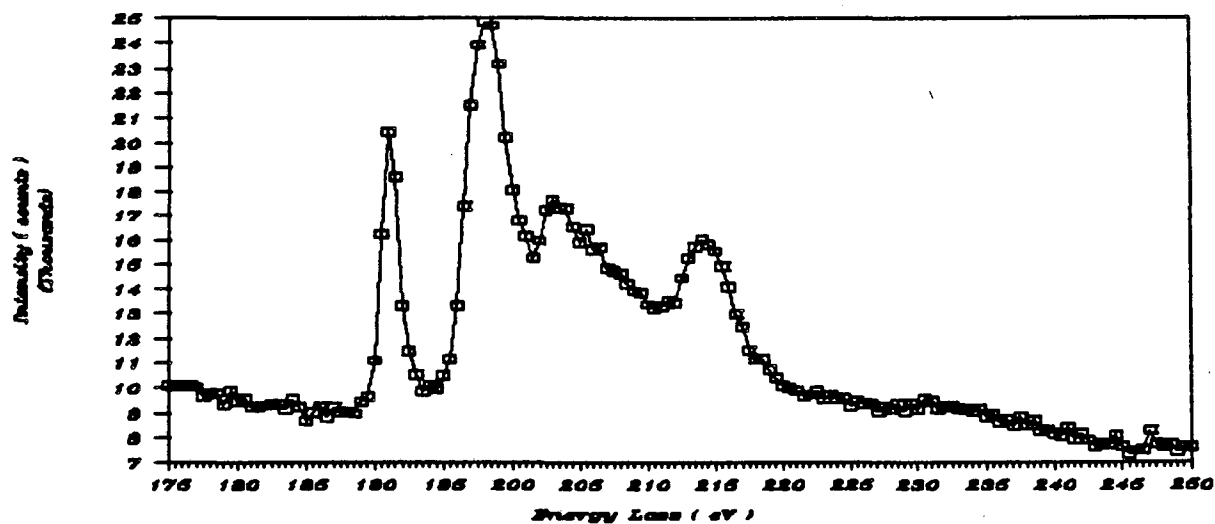
BCN Graphite, Low Loss, SSD, 160 kV



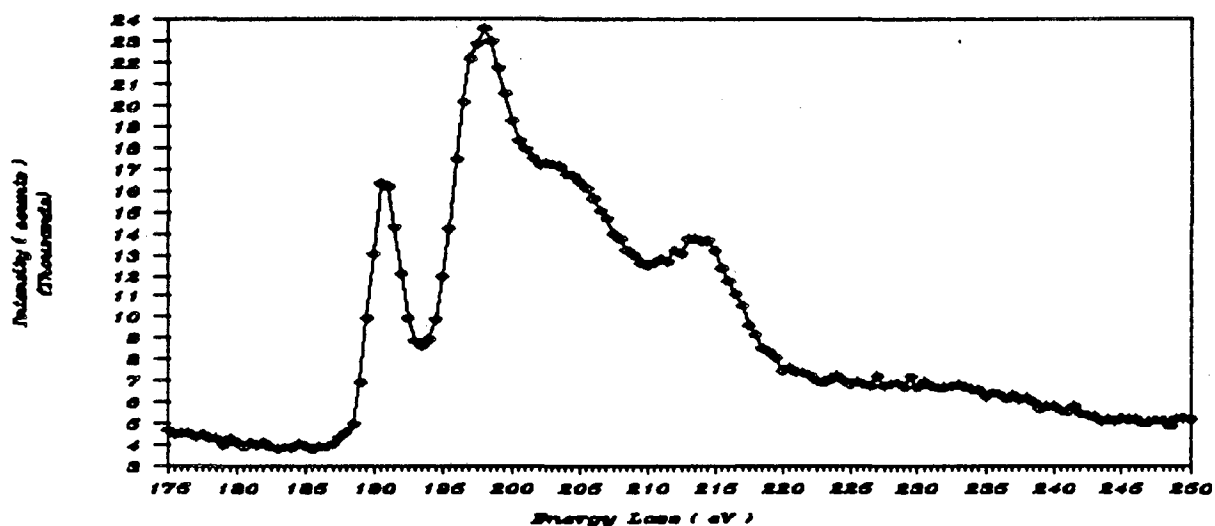
XBL 871-286

Fig. 2

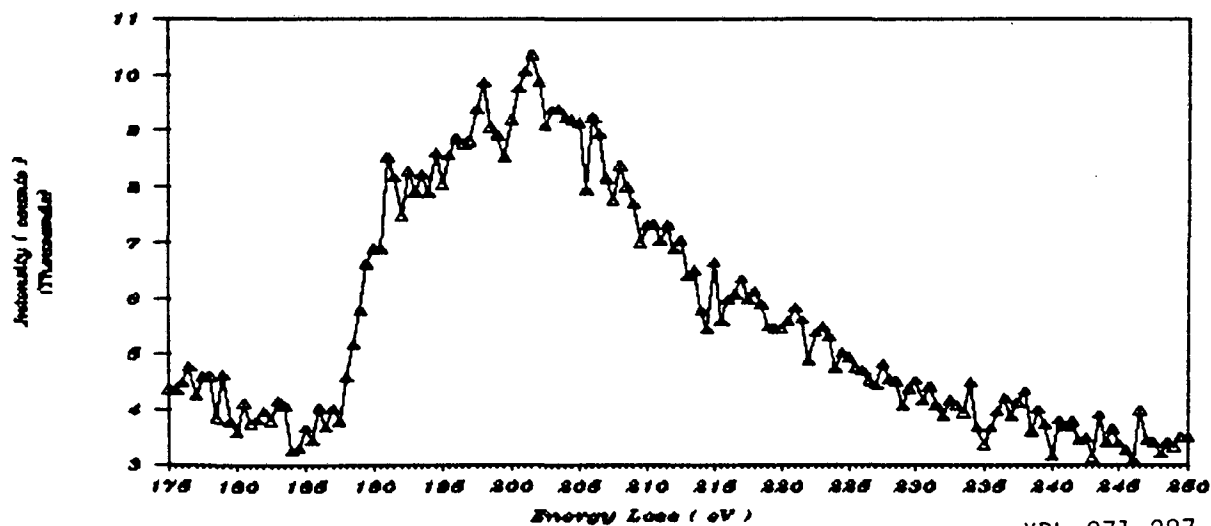
BN, B K edge, SSD, 160 kV



BCN Graphite, B K edge, SSD, 160 kV



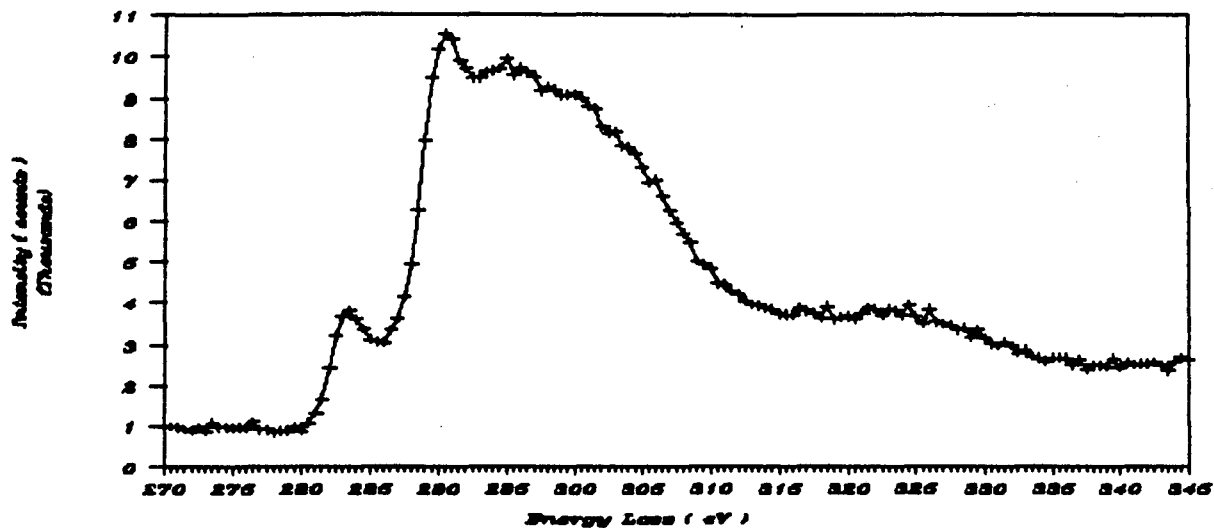
BC Graphite, B K edge, SSD, 160 kV



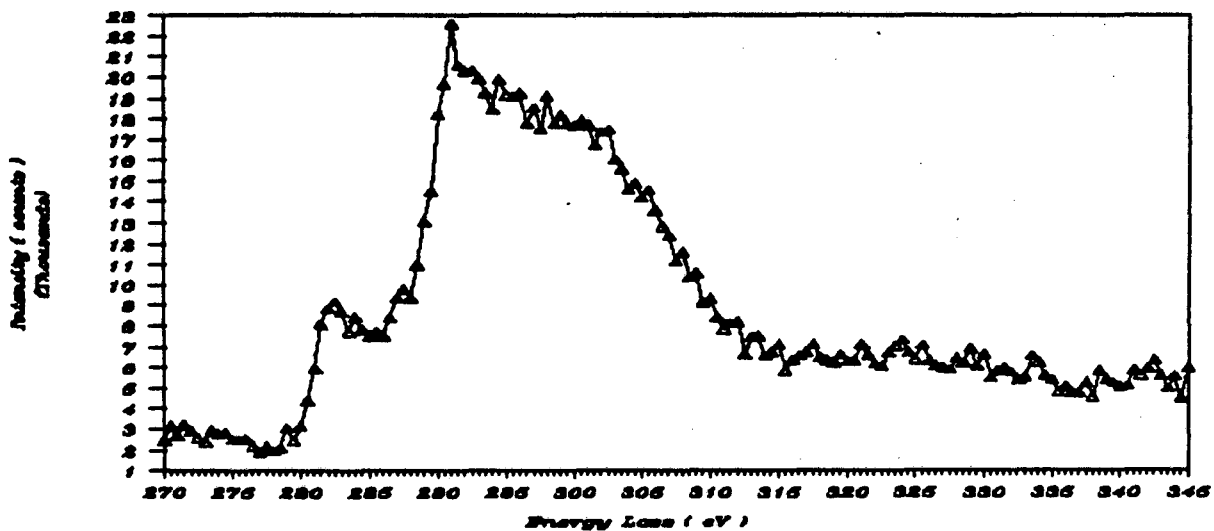
XBL 871-287

Fig. 3

HOPG, C K edge, SSD, 160 kV



BC Graphite, C K edge, SSD, 160 kV



BCN Graphite, C K edge, SSD, 160 kV

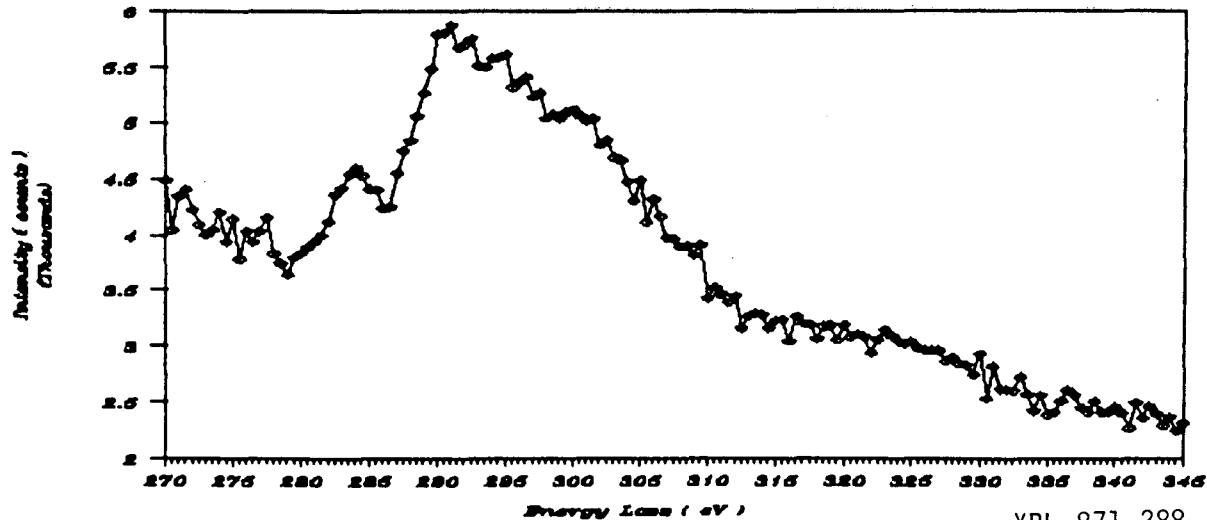
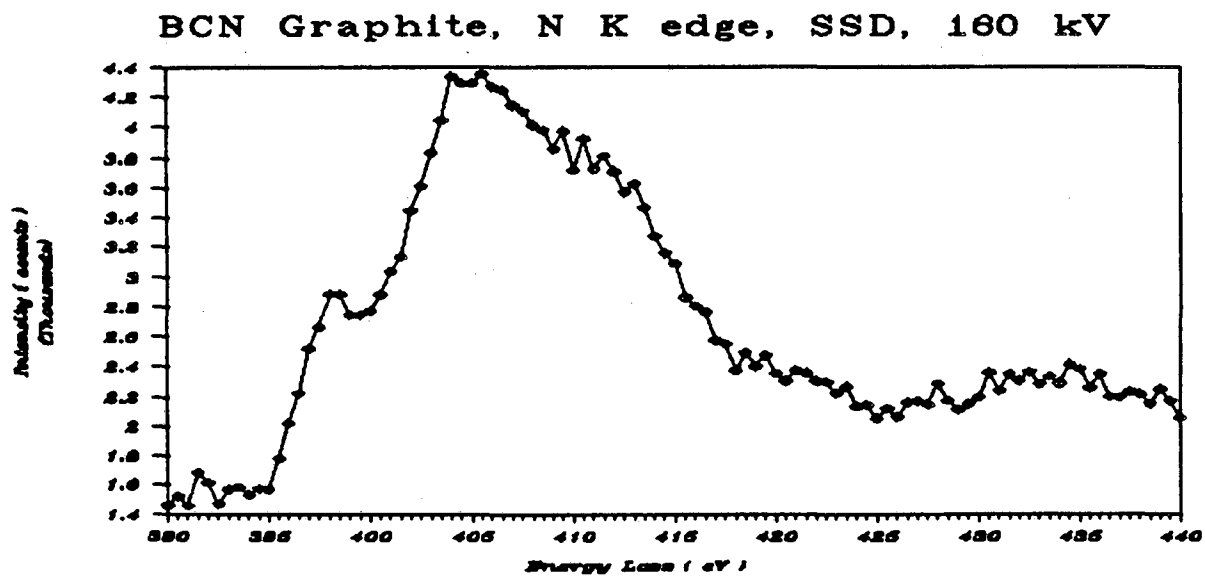
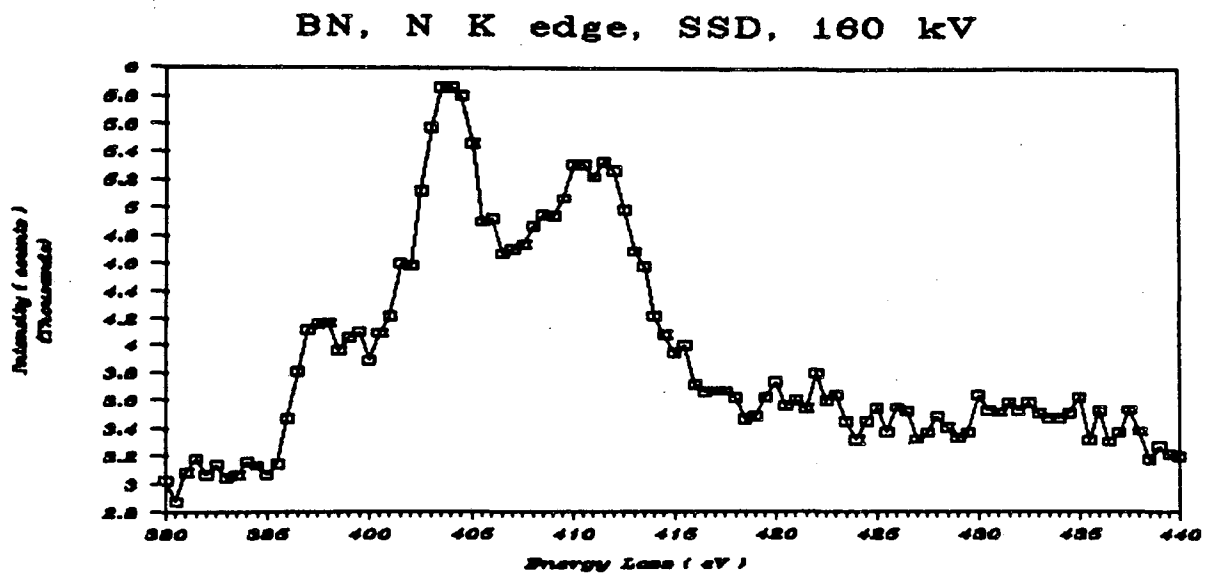


Fig. 4

XBL 871-288



XBL 871-289

Fig. 5

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

*LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720*