Microsymposium

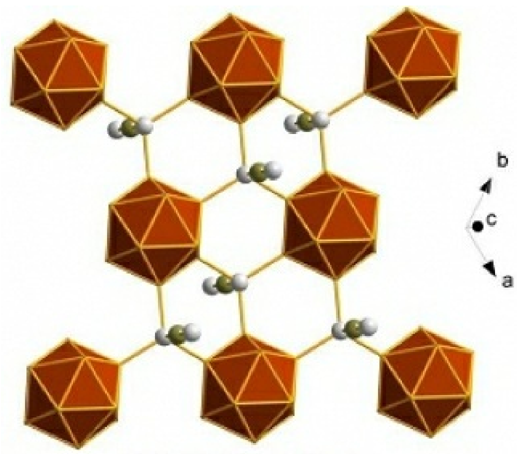
MS035.O06

New insights into the bonding mechanism of boron carbide

Swastik Mondal[1]
[1]*Sensor And Actuator Division, CSIR-Central Glass And Ceramic Research Institute, Kolkata, India*
E-mail: swastik_mondal@cgcri.res.in

Boron carbide has a mysterious power to accommodate a large variation of atomic proportions (with a general formula of $B_{12+x}C_{3-x}$, 0.06 > x > 1.7) within the same general rhombohedral crystal structure [1]. The structure of stoichiometric boron carbide ($B_{13}C_2$ or $B_{12}CBC$) consists of the 12-atom icosahedral B_{12} clusters and the 3-atom linear CBC chains. The mystery of chemical bonding in this structure is that the icosahedral B_{12} unit is deficient by two electrons and the CBC chain with a divalent boron atom can provide only one electron; thus there seems to be a net deficiency of one electron in $B_{13}C_2$ composition. One solution to this problem is replacing any boron atom in $B_{13}C_2$ by a carbon atom, which will result in a stoichiometry $B_{12}C_3$ or B_4C. However, the so-called electron precise $B_{12}C_3$ could never been experimentally isolated [1]. This puzzle of chemical bonding in boron carbide has remained unsolved since many decades. A high-resolution aspherical electron density study has been undertaken in order to get more insights into the enigma of chemical bonding in boron carbide. The study was performed on the basis of a multipole model of electron density distribution in $B_{13}C_2$ constructed using low-temperature, high-resolution, single-crystal synchrotron X-ray diffraction data [2]. Electron densities have been analyzed using the Bader's quantum theory of atoms in molecules [3]. The study reveals existence of an unprecedented electron-deficient bond and a charge transfer between structural units of boron carbide. The bonding model successfully explains the origin of a range of physical and chemical properties of boron carbide. A Comparison of electron density distributions in boron-rich materials related to boron carbide reveals a generalized bonding mechanism of B_{12} icosahedra that explains why boron carbide and related materials can preserve the same crystal structure over a range of compositions.

[1] Balakrishnarajan, M. M. et al. (2007). New. J. Chem. 31, 473-485.
[2] Mondal, S., et al. (2016). Sci. Rep. 6, 19330.
[3] Coppens, P. (1997). X-ray Charge Densities and Chemical Bonding. Oxford University Press, New York, USA.



Crystal structure of $B_{13}C_2$.

Keywords: Boron-rich materials, Electron-density analysis, Structure-property relationship