ICOSAHEDRAL B_{12} ARRANGEMENTS IN BORON-RICH SOLIDS

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1. Introduction

Although there are several interesting aspects in the field of boron-rich solids, most research scientists working with these materials are interested in their physical and chemical properties some of which are supposed to be of technological importance. In the present paper, however, we presents structural arrangements and symmetry of icosahedral B_{12} structures in boron-rich solids. These topics are very interesting because of the unusual forms and beauty of the structures which are quite different from conventional atomic configurations.

Boron, borides and related compounds differ from conventional solids in that it is impossible to interpret their bondings in terms of the conventional rule of valence. As a result, these materials manifest a number of unique properties (such as high-hardness, high-melting points, etc.) which in many case are of possible technological importance giving rise to a growing interest in their physics and chemistry . Further, these materials are unique in that the boron atoms in their structures tend to gather to bond each other. With increase of boron concentration, the boron atoms form a pair, a (single, double and triple) zig-zag chain, a hexagonal network, B_6 octahedron, B_{12} cubooctahedron and B_{12} icosahedron.

2. B_{12} icosahedron and its derivatives

Although a great many icosahedral B_{12} compounds have so far been published, they can be classified into eight types (Table 1) according to the mode of icosahedral B_{12} arrangement (Higashi, 1986). It is not possible to utilize fivefold rotation symmetry in a two- or three-dimensional periodic network, and thus three dimensional arrangements of B_{12} icosahedra form open although rigid three dimensional frameworks. Except α-rhomboheral boron, therefor, icosahedral B_{12} crystals need additional structural entities such as B_{28}, B_{22} and B_{20} units, and isolated boron atoms to fill openings within the B_{12} frameworks.

Table I Classification of icosahedral B_{12} crystals

Structure type	Structural Formula	Reference
α-rhomb. boron	B_{12}	(Decker & Kasper, 1959)
β–rhomb. boron	$(B_{12})_4 \cdot (B_{28})_2 B$	(Hughes et al., 1963)
α-tet. boron	$(B_{12})_2 B_2 / (B_{12})_2 \cdot C \cdot B$	(Hoard et al., 1958) / (Will & Kossobutzki, 1976)
β-tet. boron / α-AlB_{12}	$(B_{12})_2 B_{22} B_x$ / $(B_{12})_2 B_{20} \cdot Al_{3.33}$	(Vlasse et al., 1979) / (Higashi et al., 1977)
AlC_4B_{24}	$(B_{12})_2 C_8 \cdot B_4 Al_{2.1} \cdot C \cdot B$	(Will, 1969)
YB_{66}	$(B_{12})_{13} B_{42} \cdot Y_3$	(Decker & Kasper, 1959)
$AlMgB_{14}$	$B_{12} B_2 \cdot AlMg$	(Matkovich & Economy, 1970) (Higashi & Ito, 1983)
γ-AlB_{12}	$(B_{12})_4 (B_{20})_2 \cdot Al_{6.66}$	(Hughes et al., 1977) (Higashi, 1983)

In Fig. 1, B_{28} and B_{20} units are presented. The B_{22} unit can be made up of B_{20} unit by filling two vacant sites with two B atoms. In addition to occurrence of these icosahedral derivatives, there are successive stages in the evolution of the basic unit (B_7, B_{12}, B_{84}, and $B_{12}(B_{12})_{12}$) of boron framework in some boron-rich solids (Fig. 2).

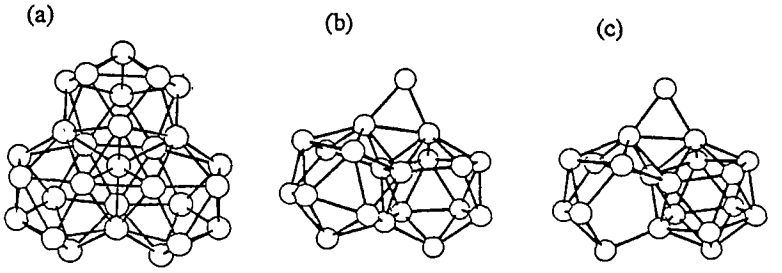

Fig. 1.(a) B_{28}, (b) B_{20}-(C_2), and (c) B_{20}-(C_s)

As shown in Fig 2, B_7 is a half-icosahedron with an additional B atom. B_{84} unit is a basic structural unit of the β-rhombohedral boron structure. This unit consists of one central B_{12} icosahedron and surrounding twelve B_6 half-icosahedra. (In the β-rhombohedral boron structure, the twelve half-icosahedra belong to six icosahedra and six B_{28} units which are directly linked to the central icosahedron.) $B_{12}(B_{12})_{12}$ unit is a basic structural unit of YB_{66}, and made up of a

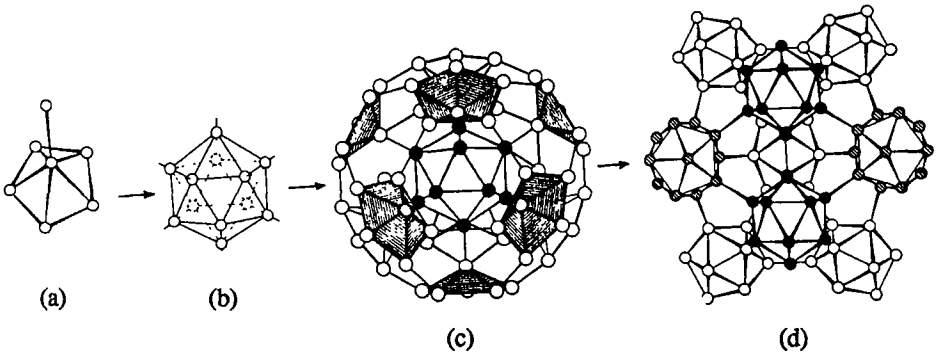

Fig. 2. Evolution of the basic unit of the boron framework in some boron-Rich phases: (a) B_7, (b) B_{12}, (c) B_{84}, (d) $B_{12}(B_{12})_{12}$ (From Naslain, 1977).

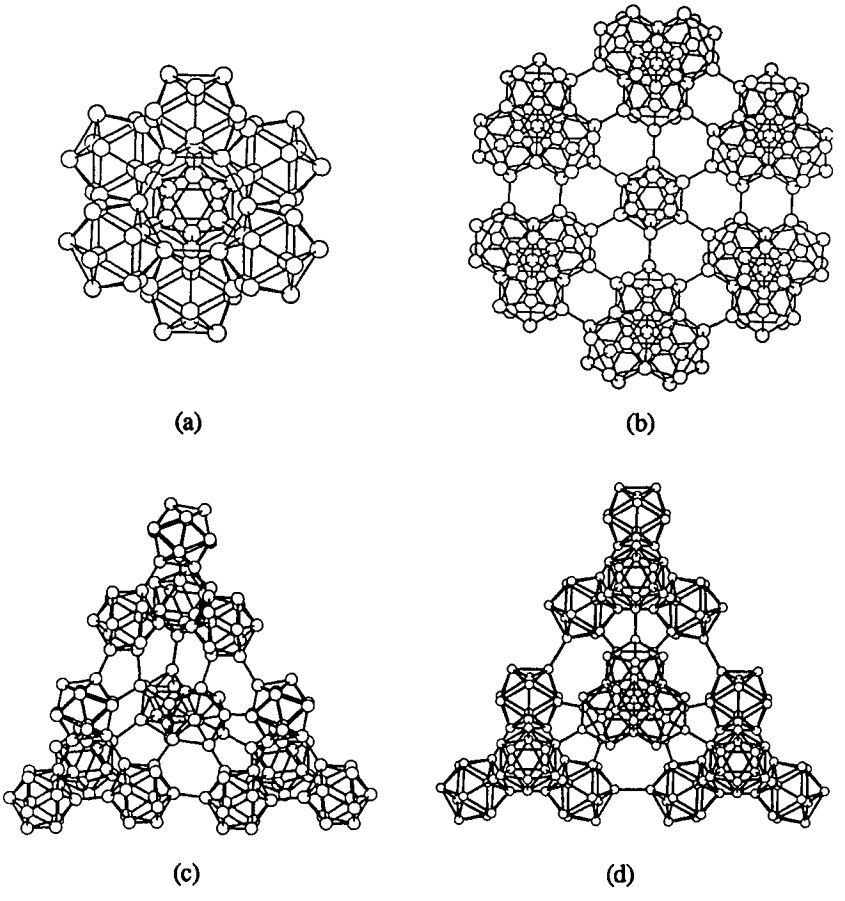

Fig. 3. Features of the linkages, (a) B_{12}-$6B_{12}$, (b) B_{12}-$6B_{28}$, (c) B_{20}-$9B_{12}$, (d) B_{28}-$9B_{12}$

central B_{12} icosahedron and surrounding twelve B_{12} icosahedra. All the linkages between neighboring icosahedra within the giant $B_{12}(B_{12})_{12}$ unit are formed along the fivefold axes of icosahedra. Construction of any structural unit greater than $B_{12}(B_{12})_{12}$ by linking B_{12} icosahedra through their fivefold axes seems to be impossible, since five-fold rotation symmetry can not be utilized in constructing three dimensional periodic space. Therefore, in the YB_{66} structure (Cubic; Space group, Fm3c; a = 23.44 Å) the giant $B_{12}(B_{12})_{12}$ unit is situated at the lattice point of the face-centered cubic unit cell, resulting in the occurrence of large openings, which are filled with Y atoms and irregularly shaped B_{42} units having considerable number of vacant sits.

In Fig. 3, features of the linkages, B_{12}-$6B_{12}$ (β-rhombohedral boron) , B_{12}-$6B_{28}$ (β-rhombohedral boron), B_{28}-$9B_{12}$ (β-rhombohedral boron), and B_{20}-$9B_{12}$ (α-AlB_{12}), are presented. The beauty of the structures of icosahedral B_{12} crystals is in that all the linkages between the structural units are effected along their fivefold axes of icosahedra or similar axes of the icosahedral derivatives, neatly constructing infinite three dimensional rigid frameworks.

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