In metal borides, the bonding of boron varies depending on the atomic ratio B/M. Diborides have B/M = 2, as in the well-known superconductor MgB$_2$; they crystallize in a hexagonal AlB$_2$-type layered structure. Hexaborides have B/M = 6 and form a three-dimensional boron framework based on a boron octahedron (Fig. 1a). Tetraborides, i.e. B/M = 4, are mixtures of diboride and hexaboride structures. Cuboctahedron (Fig. 1b) is the structural unit of dodecaborides, which have a cubic lattice and B/M = 12. When the composition ratio exceeds 12, boron forms B$_{12}$ icosahedra (Fig. 1c) which are linked into a three-dimensional boron framework, and the metal atoms reside in the voids of this framework.[1][2][3]

This complex bonding behavior originates from the fact that boron has only three valence electrons; this hinders tetrahedral bonding as in diamond or hexagonal bonding as in graphite. Instead, boron atoms form polyhedra. For example, three boron atoms make up a triangle where they share two electrons to complete the so-called three-center bonding. Boron polyhedra, such as B$_6$ octahedron, B$_{12}$ cuboctahedron and B$_{12}$ icosahedron, lack two valence electrons per polyhedron to complete the polyhedron-based framework structure. Metal atoms need to donate two electrons per boron polyhedron to form boron-rich metal borides. Thus, boron compounds are often regarded as electron-deficient solids.[4]

Icosahedral B$_{12}$ compounds include[2] α-rhombohedral boron (B$_{13}$C$_2$), β-rhombohedral boron (MeB$_x$, 23≤x), α-tetragonal boron (B$_{48}$B$_2$C$_2$), β-tetragonal boron (β-AlB$_{12}$),[5] AlB$_{10}$ or AlC$_4$B$_{24}$, YB$_{25}$, YB$_{66}$, NaB$_{15}$ or MgAlB$_{14}$, γ-AlB$_{12}$,[5] BeB$_3$[6] and SiB$_6$.[7]

Fig. 2. Relationship between the ionic radius of trivalent rare-earth ion and chemical composition of icosahedron-based rare-earth borides.

YB$_{25}$ and YB$_{60}$ decompose without melting that hinders their growth as single crystals by the floating zone method. However, addition of a small amount of Si solves this problem and results in single crystals[8] with the stoichiometry of YB$_{41}$Si$_{1.2}$.[9] This stabilization technique allowed the synthesis of some other boron-rich rare-earth (RE) borides.

Albert and Hillebrecht reviewed binary and selected ternary boron compounds containing main-group elements, namely, borides of the alkali and alkaline-earth metals, aluminum borides and compounds of boron and the nonmetals C, Si, Ge, N, P, As, O, S and Se.[10] They, however, excluded the described here icosahedron-based rare-earth borides. Note that
rare-earth elements have \( d \)- and \( f \)-electrons that complicates chemical and physical properties of their borides. Werheit et al. reviewed Raman spectra of numerous icosahedron-based boron compounds.\(^{[11]}\)

Figure 2 shows a relationship between the ionic radius of trivalent rare-earth ions and the composition of some rare-earth borides. Note that scandium has many unique boron compounds, as shown in figure 2, because of the much smaller ionic radius compared with other rare-earth elements.\(^{[3][12]}\)

In understanding the crystal structures of rare-earth borides, it is important to keep in mind the concept of partial site occupancy, that is, some atoms in the described below unit cells can take several possible positions with a given statistical probability. Thus, with the given statistical probability, some of the partial-occupancy sites in such a unit cell are empty, and the remained sites are occupied.\(^{[13]}\)