Crystal structure of boralsilite and its relation to a family of boroaluminosilicates, sillimanite, and andalusite

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ABSTRACT

Boralsilite, Al16B6Si2O37, is monoclinic, space group C2/m, with \( a = 14.767(1) \) Å, \( b = 5.574(1) \) Å, \( c = 15.079(1) \) Å, \( \beta = 91.96(1)^\circ \), and \( Z = 2 \). The structure was solved with direct methods and refined to an unweighted residual of 0.026 using 1193 observed reflections. The structure is closely related to those of sillimanite, andalusite, grandidierite, synthetic aluminum borate (Al18B4O33), and werdingite. These structures are all based on a backbone of chains of edge-sharing AlO6 octahedra arranged parallel to \( c (\cong 5.6 \) Å) and at the vertices and center of a pseudo-tetragonal subcell having \( a \equiv b \equiv 7.5 \) Å. In the boralsilite structure, AlO6 octahedral chains are cross-linked by Si2O7 disilicate groups, BO4 tetrahedra, BO3 triangles, and AlO4 trigonal bipyramids. A given BO4 or SiO4 tetrahedron or BO3 triangle shares two vertices with two adjacent AlO6 octahedra of one chain and a third vertex with an octahedron vertex of an adjacent chain, thus cross-linking the AlO6 octahedral chains. Further linkage is provided through vertex-sharing of AlO4 trigonal bipyramids. These bipyramids alternate with B or Si polyhedra parallel to AlO6 octahedral chains to form four kinds of cross-linking chains of polyhedra, with alternate atom pairs \([5] Al1-Si, [5] Al2-[4] B2, [5] Al3-[3] B1, \) and \([5] Al4-[3] B3 \). The units which cross-link between chains of AlO6 octahedra can alternatively be viewed as consisting of SiO4 dimers, trimers of edge-sharing AlO4 trigonal bipyramids (plus a triangle and B tetrahedron), and dimers of edge-sharing AlO4 trigonal bipyramids (plus B triangles and tetrahedra). Variations on these themes are found in the structures of sillimanite, andalusite, grandidierite, werdingite, mullite, and synthetic Al16B6O37. The interchangeability and variety of the various interchain units appears to result in part from the flexibility produced by the ability of Al and B to assume a variety of coordinations by oxygen and from the potential for partial vacancy of some anion and cation sites.

INTRODUCTION

Boralsilite (Al16B6Si2O37) was described as a new mineral by Grew et al. (1998), in part based on the results of the crystal structure analysis that is described in detail here. Its structure is closely related to that of sillimanite and thus to a large group of aluminosilicates and boroaluminosilicates which includes sillimanite, andalusite, mullite, werdingite, grandidierite, and synthetic aluminum borate (Al18B4O33) (Table 1). All of these phases have closely related structures based on similar arrays of chains of edge-sharing AlO6 octahedra. The relation between boralsilite and these phases is suggested not only by similarities in composition and lattice parameters, but also by parallel intergrowths of boralsilite with werdingite and grandidierite and by a scalariform (ladder-like) werdingite-boralsilite intergrowth resembling textures derived through exsolution.

It is well known that the crystal structures of andalusite and sillimanite (Burnham and Buerger 1961; Burnham 1963) are based on a common theme of chains of edge-sharing Al-octahedra oriented parallel to the \( c \)-axis, chains that have \((x,y)\) coordinates \((0,0)\) and \((1/2,1/2)\) and that are linked by fourfold- or fivefold-coordinated Al and tetrahedrally coordinated Si. The mullite structure, for which there is a range of solid solution, is derivative to the sillimanite structure, but it retains the octahedral chains virtually unchanged. Synthetic ternary solid solutions with compositions between those of mullite and Si-free aluminum borates, and apparently having the same basic unit of structure as sillimanite, have been called “boron-mullites” (Werding and Schreyer 1984; 1996; Grew et al. 1998). The structure of synthetic Al borate, whose composition is given variously as Al19BO6 and Al15B4O37, also has octahedral chains cross-linked by units related to those in sillimanite, andalusite, and mullite (Sokolova et al. 1978; Ihara et al. 1980; Garsche et al. 1991). The structures of the Fe- and Mg-bearing minerals werdingite, Al₁[(Mg,Fe)₂₋₃]Al₄[Si₂(B,Al)₄]O₃⁷, and grandidierite, Al₁₂[AlₓMgₓBSi]O₃₇, have similar subunits, with cross-linking polyhedra which display even greater variety due to the presence of Mg and Fe.

Table 1 summarizes the compositions and unit-cell data for the relevant phases whose structures have been determined. A translation of approximately \( 2.8 \) Å or multiples thereof reflects periodicity in the chain of AlO6 octahedra, one octahedron having an O-O edge approximately \( 2.8 \) Å in length. Similarly, the simple relations between the values of the cell dimensions within the plane perpendicular to the chains of octahedra are a measure of the distribution of chains in this plane; i.e., with coordinates \((0,0)\) and \((1/2,1/2)\) relative to a cell with \( A \equiv B \equiv 7.5 \) Å.