

BEHAVIOR OF B-CONTAINING CERAMIC MATERIALS AT EXTREME CONDITIONS OF TEMPERATURE AND PRESSURE

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Boron is a fundamental resource for the modern society, as confirmed by the doubling in the world production of ore minerals during the last decade (US Geological Survey, 2007, 2017). The applications of boron in the ceramic industry mainly concerns the production of: *i*) super-hard light ceramics (*e.g.*, B₄C), *ii*) ultra-high temperature ceramics for extreme refractories applications, and *iii*) composite materials for the shielding of neutron radiation, due to the large absorption capacity of ¹⁰B (Carter *et al.*, 1953). The understanding of the technical properties of materials at non-ambient conditions of T and P, requires the understanding of the (T, P)-induced deformation of the crystal structure at the atomic scale. In this contribution are reported three examples concerning B-containing compounds: I) synthetic mullite-type Al₅BO₉, II) natural londonite, and III) natural colemanite. I) The synthetic Al₅BO₉ compound is a commercially relevant ceramic material (Fischer & Schneider, 2008). It belongs to the group of mullite-type compounds, with crystal structures characterized by infinite chains of edge-sharing AlO₆ octahedra. Al₅BO₉ shares with mullite (*sensu stricto*) several technical properties, among those: a low thermal expansion coefficient ($\alpha_{T0} = 1.36(2) \cdot 10^{-5} \text{ K}^{-1}$, Fisch & Armbruster, 2012) and high thermal and pressure stability. In addition provides lower density (for aerospace ceramics applications) and neutron absorption capacity. Its high-P behavior was studied up to 26 GPa (Gatta *et al.*, 2010, 2013), disclosing that the low compressibility ($K_{T0} = 1/\beta_{T0} = 164(4) \text{ GPa}$, $\beta_{T0} = 0.0061(1) \text{ GPa}^{-1}$) and the anisotropic compression are strictly controlled by the mullite-type crystal structure. The chains of AlO₆ octahedra act as pillars, which counteract the compression along the [100] direction. On the contrary, the higher compressibility on the plane perpendicular to the chains direction (100) is controlled by the occurrence of inter-polyhedral tilting mechanisms. II). The high-P behavior of Al₅BO₉ suggests that inhibiting the tilting among the coordination polyhedra may be adopted for tuning lower compressibilities. In this respect, suitable structures can be searched among the materials provided by Nature (*i.e.* minerals). Londonite, for example, is a rare mineral with ideal chemical formula (Cs,K)Al₄Be₅B₁₁O₂₈, with Cs > K. Londonite is characterized by high symmetry (space group: *P*-43*m*) and a highly close-packed structure. Its high-T (Gatta *et al.*, 2011) and high-P behaviors (Gatta *et al.*, 2017) have been investigated by means of *in situ* diffraction techniques. High-P data showed that londonite is stable in its cubic symmetry at least up to 24 GPa and disclosed a significantly low compressibility ($K_{T0} = 212(7) \text{ GPa}$), approaching that of carbide ceramic compounds ($K_{T0} \sim 250 \text{ GPa}$). Such a stiffness is controlled by the high symmetry and close-packing of the structure, which prevent the inter-polyhedral tilting and allow the accommodation of the bulk compression only through the compression and distortion of the polyhedra. In this light, synthetic counterparts of londonite are promising materials for neutron shielding and Cs-disposal applications. III) Colemanite, CaB₃O₄(OH)₃·H₂O, is not a ceramic compound, but a relevant B-ore mineral. Its high-P behavior (Lotti *et al.*, 2017) provides a window on the behavior of boron at extreme conditions. The experimental diffraction data collected up to ~ 24 GPa show the occurrence of a reconstructive phase transition at ~ 14.5 GPa. Remarkably, the phase transition induces a fraction of the boron atoms to increase their coordination from triangular to tetrahedral, by making new bonds with close H₂O-oxygen atoms.

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