Crystal chemistry of halide containing silver borates

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The excellent optical properties and versatile crystal chemistry make borates outstanding candidates for application as nonlinear optical (NLO) materials. These properties are enhanced by introducing “extra” anions, halides yielding the best performances. Introducing halides increases the abundance of non-centrosymmetric structures. As constituents of ionic lattices, halide ions readily contribute to the formation of salt-inclusion structures, which are generally defined as structures comprised of two parts, of varied dimensionality, exhibiting one, covalent, and the other, ionic character of chemical bonding. The ionic part generally fills the channels and/or cavities of porous covalent networks, while the cases where these parts constitute interpenetrating frameworks are scarce.

We have successfully synthesized and characterized several new silver halide borates, Ag₄B₄O₇X₂ (X = Br, I), Ag₃B₆O₁₅I, and Ag₄B·O₁₂Br, which were prepared by slow cooling stoichiometric melts jr glass crystallization. The crystal structure of Ag₄B₄O₇X₂ is non-centrosymmetric (s.g. P₆₁₂) and comprised of coalesced pentaborate groups or so-called “kernite” chains 5B : 2Δ₃□ : (<Δ2□ > – <Δ2□ > – )sharing vertices to form a framework with equal content of BO₃ triangles and BO₄ tetrahedra. Their thermal expansion is strongly anisotropic due to the orientation of rigid kernite chains aligned parallel to ab plane. The calculated band structures indicate that Ag₄B₄O₇Br and Ag₄B₄O₇I are direct semiconductors with a band gap of about 2.0 and 2.4 eV, respectively.

The crystal structure of Ag₄B·O₁₂Br is triclinic (s.g. P-1), and formed by unique layers comprised of vertex-sharing triborate and tetraborate groups. Ag₃B₆O₁₅I is orthorhombic (s.g. Pnma) and isostructural to Na₃B₆O₁₀Br. The structure contains two interpenetrating frameworks one of them comprised of vertex shearing B₆O₁₃ hexaborate groups; the metal-halide anti-ReO₃ framework is strongly distorted towards formation of isolated Ag₄I²⁺ groups with relatively short Ag×××Ag contacts indicative of “argentophilic” interactions.

Crystal structures of these borates are comprised of two porous interpenetrating frameworks and demonstrate a further development of the “salt-inclusion” architecture toward a “covalent-inclusion” structure. The AgX sublattices exhibit strong anharmonic vibrations. The joint-probability density function was calculated from the inverse Fourier transform of the anharmonic ADPs approximated by the third-order expansion of the Gram–Charlier series [1]. This indicates the presence of structural analogies between borate nitrates and borate halides and indicates further directions in the search for new compounds in these families.


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