

Crystal chemistry of halide containing silver borates

Sergey Volkov¹, Dmitri Charkin², Manelis Lev², Rimma Bubnova¹

¹*Grebenshchikov Institute of Silicate Chemistry, Saint-Petersburg, Russian Federation;*

²*Department of Chemistry, Lomonosov Moscow State University, Moscow, Russian Federation;*

s.n.volkov@inbox.ru

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, $\text{Ag}_4\text{B}_4\text{O}_7\text{X}_2$ ($\text{X} = \text{Br}, \text{I}$), $\text{Ag}_3\text{B}_6\text{O}_{10}\text{I}$, and $\text{Ag}_4\text{B}_7\text{O}_{12}\text{Br}$, which were prepared by slow cooling stoichiometric melts or glass crystallization. The crystal structure of $\text{Ag}_4\text{B}_4\text{O}_7\text{X}_2$ is non-centrosymmetric (s.g. $P6_122$) and comprised of coalesced pentaborate groups or so-called “kernite” chains $5\text{B} : 2\Delta 3\Box : (\langle \Delta 2\Box \rangle - \langle \Delta 2\Box \rangle)$ sharing vertices to form a framework with equal content of BO_3 triangles and BO_4 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 $\text{Ag}_4\text{B}_4\text{O}_7\text{Br}_2$ and $\text{Ag}_4\text{B}_4\text{O}_7\text{I}_2$ are direct semiconductors with a band gap of about 2.0 and 2.4 eV, respectively.

The crystal structure of $\text{Ag}_4\text{B}_7\text{O}_{12}\text{Br}$ is triclinic (s.g. $P-1$), and formed by unique layers comprised of vertex-sharing triborate and tetraborate groups. $\text{Ag}_3\text{B}_6\text{O}_{10}\text{I}$ is orthorhombic (s.g. $Pnma$) and isostructural to $\text{Na}_3\text{B}_6\text{O}_{10}\text{Br}$. The structure contains two interpenetrating frameworks one of them comprised of vertex shearing B_6O_{13} hexaborate groups; the metal-halide *anti*- ReO_3 framework is strongly distorted towards formation of isolated Ag_3I^{2+} groups with relatively short $\text{Ag}^{\times\times\times}\text{Ag}$ 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.

[1] Kuhs, W. F. (1992). *Acta Cryst.* **A109**, 80–98.

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