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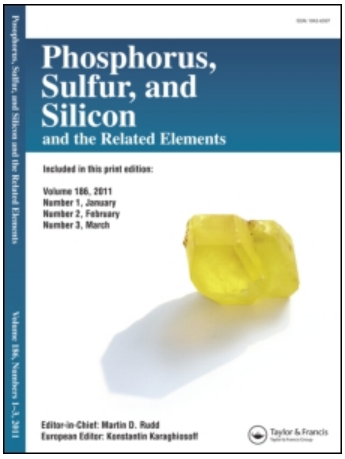

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ISOLATED $B_{10}Se_{20}$-MACROTETRAHEDRA IN THE NOVEL QUATERNARY SELENOBORATE $Li_{6-2x}Sr_{2+x}B_{10}Se_{20}$ ($x \approx 0.7$)

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ISOLATED $B_{10}Se_{20}$-MACROTETRAHEDRA IN THE NOVEL QUATERNARY SELENOBORATE $Li_{6-2x}Sr_{2+x}B_{10}Se_{20}$ ($x \approx 0.7$)

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We report the synthesis and crystal structure of $Li_{6-2x}Sr_{2+x}B_{10}Se_{20}$ ($x \approx 0.7$). $Li_{6-2x}Sr_{2+x}B_{10}Se_{20}$ ($x \approx 0.7$) crystallizes tetragonal and its lattice parameters are $a = 14.735(1)$ Å, $c = 14.144(2)$ Å. The structure solution in space group $I4_1/a$ (No. 88) yielded residuals of $R1 = 0.036$ and $wR2 = 0.078$.

Keywords: Boron; crystal structure; selenoborates

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Practical applications of lithium containing solids in batteries, fuel cells and related devices have drawn interest on the mechanisms of cationic conductivity and the relations to structural features. Lithium thioborates have shown ionic conductivity in the glassy state.[1] A wide variety of chalcogenoborates,[2–6] especially those containing smaller cation species, are candidates for closer investigations in the context of solid state ionics. Furthermore, electron densities (i.e., diffusion pathways) can be extracted from the SXRD experiments and dynamical properties of ionic motion are visible on the much shorter NMR timescale.

EXPERIMENTAL

$Li_{6-2x}Sr_{2+x}B_{10}Se_{20}$ ($x \approx 0.7$) was synthesized by reaction of stoichiometric amounts of the lithium selenide, strontium, amorphous boron, and selenium. The reaction mixture was filled into a carbon coated silica

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tube, evacuated, sealed, and inserted into metal cylinders which fit into a horizontal one zone furnace. During the reaction and subsequent annealing, respectively, a specific temperature profile was applied to the reaction mixture. As some of the starting compounds as well as the product are moisture and air sensitive, all steps of the preparation were carried out under inert gas atmosphere.

CRYSTAL STRUCTURE

The structure of $Li_{6-2x}Sr_{2+x}B_{10}Se_{20}$ ($x \approx 0.7$) contains isolated $B_{10}Se_{20}$-entities (Figure 1), which we observed for the first time in selenoborate chemistry. Hitherto $B_{10}Se_{20}$-units are known, which are polymerized to three-dimensional network structures as in $Li_9B_{19}Se_{33}$, $Li_{6-x}M_xB_{10}Se_{18}$ with M = K, Rb, Cs ($x \approx 0.9$), and $Li_{6-2x}Ba_{1+x}B_{10}Se_{19}$ ($x \approx 0.21$), while $Li_{3+x}Na_{5-x}B_{10}Se_{19}$ contains one-dimensional zigzag chain anions.[7,8] A macrotetrahedron found in the present $Li_{6-2x}Sr_{2+x}B_{10}Se_{20}$ ($x \approx 0.7$) exhibits nearly T_d-symmetry. The average boron-selenium bond length is calculated to 2.055 Å which is in good agreement to the ones found in other selenoborates where

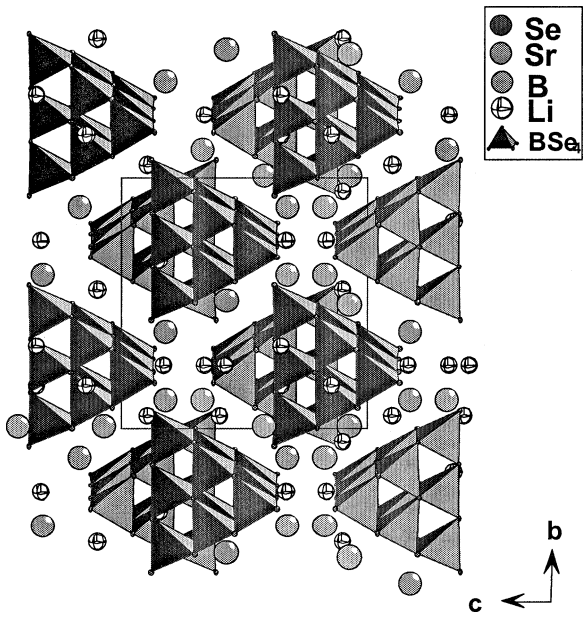

FIGURE 1 Projection of the unit cell of $Li_{6-2x}Sr_{2+x}B_{10}Se_{20}$ ($x \approx 0.7$) along [100].

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$B_{10}Se_{20}$-entities occur. However the B—Se bonds can be divided into three categories: μ_3-Se (2.066 Å: B—Se(1)), μ_2-Se (2.057 Å: B—Se(2); 2.043 Å: B–Se(3); 2.059 Å: B—Se(4)) and terminal Se (2.031 Å: B–Se(5)). The packing of the anions in the crystal structure offers wide cavities for the cations. Lithium and strontium both exhibit large thermal displacement parameters and partial occupation respectively. Sr(1) is nine-fold coordinated by selenium in an irregular geometry with Sr···Se distances from 2.980 to 3.952 Å while Li(1) and Li(2) are four- and five-fold coordinated by selenium with an average Li···Se distance of 2.89 Å. However, $Li_{6-2x}Sr_{2+x}B_{10}Se_{20}$ ($x \approx 0.7$) is a promising candidate for ionic conductivity due to the possible cation pathway in the structure. Li-NMR and conductivity measurements are underway.

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