Crystal Chemistry and Thermal Behavior of Cs and Sr Borosilicates

M. Krzhizhanovskaya[^1], R. Bubnova[^2][^1], S. Filatov[^1]

[^1]: Department of Crystallography, St. Petersburg State University, Russia
[^2]: Grebenshchikov Institute of Silicate Chemistry RAS, St. Petersburg, Russia
E-mail: krzhizhanovskaya@mail.ru

In spite of great technological importance of Cs and Sr borosilicate systems for many applications including their potential usage for immobilization of radioactive wastes no systematical studies of these systems have been performed. Here we present the data on phase formation, crystal structures, thermal behavior, phase equilibria and summarize structural temperature-dependent behavior in the mentioned systems. The investigation was done by means of single crystal and powder X-ray diffraction (XRD) at room and elevated temperatures.

Up to now in Cs$_2$O-B$_2$O$_3$-SiO$_2$ system two synthetic compounds CsBSi$_2$O$_6$ and CsBSi$_2$O$_{12}$ were structurally characterized in [1-2, 3-4]. Recently mineral kirchhoffite, CsBSi$_2$O$_6$, isostructural to tetragonal pollucite was found in Darai-Pioz alkaline massif, Tadzhikistan, and structurally described in [5]. Our investigation in the system concerns mainly the phase formation and various substitutions (Cs-K, Cs-Ba, B-Si) in CsBSi$_2$O$_6$ boropollucite structure. Interesting to note that CsBSi$_2$O$_6$ was synthesized many times in a wide range of temperature by both solid state reaction and glass crystallization and we neither obtained its tetragonal modification; Cs-deficient cubic $Ia3d$ phase is reported in [2] from single crystal experiment. Although in nature Cs-K substitution is rare observed, we have studied cubic ↔ cubic structural transformation of $Ia3d$ (CsBSi$_2$O$_6$) ↔ $I-43d$ (KBSi$_2$O$_6$) under the Cs-K substitutions. It should be noted that no immiscibility have been observed between CsBSi$_2$O$_6$ and KBSi$_2$O$_6$ [6]. The ability of CsBSi$_2$O$_6$ structure to the Cs-Ba substitution was tested during the heat treatment at 700 and 800 °C of the series of mixtures included Cs$_2$O/BaO in different proportion. Up to now we have not been able to insert Ba into boropollucite structure. The substitution B-Si in CsBSi$_2$O$_6$ structure is studied by both solid state reaction and glass crystallization methods. It is shown that the B-Si substitution could be easier obtained by glass crystallization than by solid state reaction as it was also found before in Rb$_2$O-B$_2$O$_3$-SiO$_2$ [7].

First the subsolidus relations in SrO–B$_2$O$_3$–SiO$_2$ system were investigated in 1976 [8]: a stable Sr$_3$B$_2$SiO$_8$ compound and a metastable SrB$_2$Si$_3$O$_8$ were reported and unindexed XRD data were presented. Twenty years later the structure of SrB$_2$Si$_2$O$_8$ isotypical to danburite was solved in [9]. Not long ago naturally occurring Sr-dominant analogue of danburite (pekovite, SrB$_2$Si$_2$O$_8$) was found in alkaline massif and structurally characterized in [10].

Single crystals of Sr$_3$B$_2$SiO$_8$ were obtained by solid state reaction of stoichiometric mixture at 1200 °C. Crystal structure was solved in orthorhombic $Pnma$ group [11]. The structure contains zigzag pseudo-chains running along the $b$ axis and built up from corner sharing (Si,B)–O polyhedra. Boron and silicon are statistically distributed over one site with their coordination strongly disordered.

A new series of solid solutions Sr$_{3-x}$B$_2$Si$_{1-x}$O$_{8-3x}$ have been crystallized from melt in the pseudobinary Sr$_3$B$_2$O$_5$–Sr$_3$B$_2$SiO$_8$ system [11]. In Sr$_{3-x}$B$_2$Si$_{1-x}$O$_{8-3x}$ unit cell parameters decrease along with decrease of SiO$_2$ content. Crystal structures of Sr$_2$B$_2$O$_5$ and Sr$_3$B$_2$SiO$_8$ are similar (Fig. 1). When compared to Sr$_3$B$_2$SiO$_8$, Sr$_2$B$_2$O$_5$ has the $a$ parameter increasing twice, whereas other parameters are the practically the same. Substitution of B by Si is accompanied by intercalation of additional oxygen atoms to form disordered tetrahedra in Sr$_{3-x}$B$_2$Si$_{1-x}$O$_{8-3x}$.
solid solutions. It could be assumed that isolated B$_2$O$_5$ groups in Sr$_2$B$_2$O$_5$ (Fig. 1, left) are transformed to pseudo-tetrahedral chains in our structure due to the incorporation of silicon (Fig. 1, right). The Sr$_{3-x}$B$_2$Si$_1-x$O$_{8-3x}$ (x ≈ 0–0.9) solid solutions are extended almost to Sr$_2$B$_2$O$_5$. Immiscibility is caused by the difference in symmetry of Sr$_2$B$_2$O$_5$ and Sr$_3$B$_2$SiO$_8$ and nonexistence of silicon atoms in triangles.

The anisotropic character of thermal expansion of Sr$_3$B$_2$SiO$_8$ has been observed using powder high-temperature XRD in the range 20–900 °C: $\alpha_a = -1.3$, $\alpha_b = 23.5$, $\alpha_c = 13.9$, and $\alpha_V = 36.1 \times 10^{-6}$ °C$^{-1}$ (25 °C). Maximal thermal expansion of the structure along of the chain direction [010] is caused by partial straightening of chain zigzag. Sr$_2$B$_2$SiO$_8$ decomposes above 770 °C.

Finally the thermal expansion of two cesium (CsBSi$_2$O$_6$ and CsBSi$_5$O$_{12}$) and two strontium (Sr$_3$B$_2$SiO$_8$ and SrB$_2$Si$_2$O$_8$) borosilicates are discussed comparing to Cs and Sr borates.

![Fig. 1. The comparison of Sr$_2$B$_2$O$_5$ and Sr$_3$B$_2$SiO$_8$ structures.](image)

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References


