

Phase Formation and Thermal Stability in Cs, Ba-borosilicate systems

M. Krzhizhanovskaya (1), R. Bubnova (1,2), E. Derkacheva (1), L. Gorelova (1,2), L. Galafuntik (2), and S. Filatov (1)

(1) Saint Petersburg State University, Geological Faculty, Crystallography, St. Petersburg, Russian Federation (krzhizhanovskaya@mail.ru), (2) Grebenshchikov Institute of Silicate Chemistry RAS, St. Petersburg, Russia

The problem of immobilization of high level waste (HLW) rose especially sharply at the turn of the 20-21st centuries. Vitrification, in particular with the use of borosilicates, is the main method of immobilization of HLW at present. This fact causes numerous studies of glassy borosilicates. Compared with glass, crystalline borosilicates and, particularly, Cs- and Ba-containing phases, which can be formed in the process of immobilization, are poorly studied. The main object of this work is the search for new phases, their crystal chemical characterization, study of phase formation and their thermal stability in Cs₂O- and BaO-B₂O₃-SiO₂ systems.

Totally about 50 probes of about 20 compositions for every system were synthesized by solid state reactions and glass crystallization methods. Long-term heat treatments at temperatures of 800-1000 °C and short annealings at 1000-1400 °C were performed. Phase analysis was carried out by X-ray powder diffraction.

In Cs₂O-B₂O₃-SiO₂ system substitutions in tetrahedral site are observed in the probes obtained by glass crystallization around boropollucite CsBSi₂O₆. CsBSi₂O₆ tetrahedral substitutions and high temperature decomposition is studied by Rietveld method.

Taking into account the great ability of pollucite structure to the cationic substitution, we tried to prepare Ba-exchanged boropollucite. It was shown that up to 800 °C cubic boropollucite structure does not adopt Ba during solid state reaction. Addition of Ba to the initial mixture up to the nominal composition Cs_{0.4}Ba_{0.3}BSi₂O₆ initialize the crystallization of a new low-temperature CsBSi₂O₆ modification at 700 °C which transforms into cubic CsBSi₂O₆ on further heat treatment at 800 °C. In the samples with compositions Cs_{0.4}Ba_{0.3}BSi₂O₆ and Cs_{0.6}Ba_{0.2}BSi₂O₆ cubic form of CsBSi₂O₆ crystallizes mixed with Ba₃B₆Si₂O₁₆ at 800 °C.

In BaO-B₂O₃-SiO₂ system the formation and thermal stability of BaB₂Si₂O₈ and Ba₃B₆Si₂O₁₆ borosilicates was investigated. Synthetic maleevite, BaB₂Si₂O₈ was obtained by slow cooling of the stoichiometric melt from 1000 to 900 °C for 2.5 hours with admixture of BaSi₂O₅. It is shown that BaB₂Si₂O₈ could not be obtained by solid-state reaction at 800, 900 and 950 °C in a wide range of compositions. In the field of 3BaO×3B₂O₃×2SiO₂ composition the compound Ba₃B₆Si₂O₁₆ mixed with borates and/or barium silicates is formed at 800, 900 and 950 °C depending on the composition of initial mixture. Pure compound Ba₃B₆Si₂O₁₆ was crystallized from the melt of stoichiometric composition by slow cooling from 1000 to 900 °C for 2.5 hours. The probe contained small colorless single crystals suitable for X-ray single crystal diffractometry. Ba₃B₆Si₂O₁₆ crystallizes in triclinic system with the cell parameters: $a=5.062(2)$, $b=7.721(3)$, $c=8.564(2)$ Å, $\alpha=77.70(3)$, $\beta=78.05(3)$, $\gamma=86.53(3)$ °. The powder XRD pattern is well indexed in this unit cell.

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