

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

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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 Cs_2O - and $\text{BaO-B}_2\text{O}_3-\text{SiO}_2$ 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 $\text{Cs}_2\text{O-B}_2\text{O}_3-\text{SiO}_2$ system substitutions in tetrahedral site are observed in the probes obtained by glass crystallisation around boropollucite CsBSi_2O_6 . CsBSi_2O_6 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 $\text{Cs}_{0.4}\text{Ba}_{0.3}\text{BSi}_2\text{O}_6$ initialize the crystallization of a new low-temperature CsBSi_2O_6 modification at 700 °C which transforms into cubic CsBSi_2O_6 on further heat treatment at 800 °C. In the samples with compositions $\text{Cs}_{0.4}\text{Ba}_{0.3}\text{BSi}_2\text{O}_6$ and $\text{Cs}_{0.6}\text{Ba}_{0.2}\text{BSi}_2\text{O}_6$ cubic form of CsBSi_2O_6 crystallizes mixed with $\text{Ba}_3\text{B}_6\text{Si}_2\text{O}_{16}$ at 800 °C.

In $\text{BaO-B}_2\text{O}_3-\text{SiO}_2$ system the formation and thermal stability of $\text{BaB}_2\text{Si}_2\text{O}_8$ and $\text{Ba}_3\text{B}_6\text{Si}_2\text{O}_{16}$ borosilicates was investigated. Synthetic maleevite, $\text{BaB}_2\text{Si}_2\text{O}_8$ was obtained by slow cooling of the stoichiometric melt from 1000 to 900 °C for 2.5 hours with admixture of BaSi_2O_5 . It is shown that $\text{BaB}_2\text{Si}_2\text{O}_8$ could not be obtained by solid-state reaction at 800, 900 and 950 °C in a wide range of compositions. In the field of $3\text{BaO} \times 3\text{B}_2\text{O}_3 \times 2\text{SiO}_2$ composition the compound $\text{Ba}_3\text{B}_6\text{Si}_2\text{O}_{16}$ mixed with borates and/or barium silicates is formed at 800, 900 and 950 °C depending on the composition of initial mixture. Pure compound $\text{Ba}_3\text{B}_6\text{Si}_2\text{O}_{16}$ 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. $\text{Ba}_3\text{B}_6\text{Si}_2\text{O}_{16}$ 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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