SHORT COMMUNICATIONS

Thermal Decomposition of \( K_{1-x}Cs_xBSi_2O_6 \) Borosilicates

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Abstract—Thermal decomposition of mixed \( K_{1-x}Cs_xBSi_2O_6 \) borosilicates by the methods of thermal analysis, annealing, and quenching, with the following refining of the structure by the Rietveld method on the example of solid solutions with \( x = 0.3 \) and 0.7 crystallizing in the space groups \( I4d \) and \( Ia3d \), respectively, is studied. It is shown that the solid-phase decomposition of borosilicates proceeds with the release of the gaseous phase and formation of cristobalite and/or tridymite of SiO\(_2\) at the final stage. In this case the solid solutions enriched by potassium decompose in one stage with the formation of SiO\(_2\), while the solutions enriched by cesium decompose with the formation of the intermediate zeolite-like CsBSiO\(_{12}\) borosilicate, which also decomposes during further thermal treatment. According to the data of the structure, the refining of \( K_{1-x}Cs_xBSi_2O_6 \) solid solutions obtained by thermal treatment at 1000°C for 20, 65, 80, and 100 h, it is detected that for the samples with \( x = 0.3 \) and 0.7 the parameter of the cubic cell of the leucite-like phase decreases and the vacancies in the position of alkaline cation appear. During the solid-phase decomposition of \( K_{1-x}Cs_xBSi_2O_6 \) solid solutions the structure degrades.

Keywords: borosilicates, Rietveld method, solid-phase decomposition, crystalline structure

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INTRODUCTION

The solid solutions of \( K_{1-x}Cs_xBSi_2O_6 \) borosilicates crystallize in an ANA structural type in two space groups \([1–3]\): samples enriched by potassium crystallize in the cubic group \( I4d \) similar to KBSiO\(_6\) \([4]\); phases enriched by cesium crystallize in the \( Ia3d \) group corresponding to CsBSiO\(_6\) \([5]\). The phase transition \( I4d \rightleftharpoons Ia3d \) in the compositions with \( x = 0.35–0.40 \) was revealed and the transformation of the crystalline structure under the action of temperature and isomorphous substitutions was investigated \([1–3]\). The structure refined at high temperatures was established that KBSiO\(_6\) boroleucite is subjected to the polymorphic transition \( I4d \rightleftharpoons Ia3d \) in the temperature interval of 525–575°C \([6]\). According to \([7]\), in the series of \( K_{1-x}Rb_xBSi_2O_6 \) the sample with \( x = 0.20 \) obtained by crystallization from glass at 900°C contains both polymorphic modifications \( I4d \) and \( Ia3d \). At high temperatures, CsBSiO\(_6\) decomposes in a solid state with the formation of the zeolite-like phase CsBSiO\(_{12}\) and release of the gaseous phase: CsBSiO\(_6\) \( \rightarrow \) CsBSiO\(_{12}\) + CsBO\(_2\) \([5, 8]\); the CsBSiO\(_{12}\) borosilicate structure was determined by the Rietveld method in \([8]\); the compound is isomorphous to CsAlSiO\(_{12}\) zeolite of the CAS-type; it was shown that it also decomposes in the solid state; and as a result the modifications of SiO\(_2\) remain in the solid phase.

The solid-phase decomposition of some \( Rb_{1-x}Cs_xBSi_2O_6 \) solid solutions were studied by the methods of annealing and quenching at different temperatures, DSC, and TGA in \([9]\); the decomposition of CsBSiO\(_6\) with the structure refined after thermal treatment (1000°C) was studied in \([10]\).

In the present work, the process of the thermal solid phase decomposition of \( K_{1-x}Cs_xBSi_2O_6 \) borosilicates was investigated by the methods of thermal analysis, annealing, and quenching (1000°C), with the following structure refining by the Rietveld method on the example of two solid solutions with \( x_{Cs} = 0.3 \) and 0.7 referring to different space groups \( I4d \) and \( Ia3d \), respectively.

EXPERIMENTAL

The samples of \( K_{1-x}Cs_xBSi_2O_6 \) compositions with \( x = 0.3 \) and 0.7 under investigation were obtained by crystallization from glass. The synthesis of the samples was described in \([2, 3]\). The thermal treatment temperature (1000°C) was chosen according to the data on weight loss in the series of \( K_{1-x}Cs_xBSi_2O_6 \) occurring before melting (Fig. 1). The holding time was varied from 20 to 100 h.

The X-ray patterns of the samples were obtained in air (powder diffractometer Bruker Phaser D2, CuK_{α}. The interval of the reflection angles was 2θ = 10−
The structure was refined by the Rietveld method using the Topas software package; the details of the refining are given in [3].

Thermal analysis (DSC and TGA) was performed on the STA 429 apparatus of NETZSCH. A piece of glass of mass $(30 \pm 0.05) \text{ mg}$ was placed in the platinum crucible and heated in the temperature interval of $23–1200^\circ \text{C}$ in air at $10 \text{ K/min}$. The DSC method was used to determine the effects of the temperature.

RESULTS AND DISCUSSION

Glasses of compositions $x = 0.3$ and $0.7$ of the $\text{K}_{1-x}\text{Cs}_x\text{BSi}_2\text{O}_6$ series was investigated by the DSC and TGA methods (Fig. 1). The first endothermic peak in the interval of $600–660^\circ \text{C}$ corresponds to the glass transition process. The next peak of crystallization is double. Thus, for example, the crystallization of the sample of composition $x = 0.3$ begins at $758^\circ \text{C}$ and ends at $924^\circ \text{C}$; the maximum of the first exo-effect is at $819^\circ \text{C}$ and the maximum of the second exo-effect is at $880^\circ \text{C}$. According to the data of the X-ray diffraction, the sample after the first peak of crystallization ($842^\circ \text{C}$) was quenched in the DSC oven and contained two phases: an $Ia\overline{3}d$-boroleucite phase with $a = 12.794(3) \text{ Å}$ and an X-ray amorphous phase. It might be supposed that the second exo-effect ($880^\circ \text{C}$) corresponds to the crystallization of the remaining glass and transition of the $Ia\overline{3}d$ phase into the $I\overline{4}3d$ phase. The samples of this composition investigated by methods of annealing and quenching with the following study by the Rietveld method crystallize in the space group $I\overline{4}3d$; with the rise of the temperature and holding time, the unit cell parameter changes from $a = 12.765(2) \text{ Å} (850^\circ \text{C}/10 \text{ h})$ to $a = 12.7785(1)$ and $12.74224(1) \text{ Å} (1000^\circ \text{C}/20 \text{ h}$ and $100 \text{ h}$, respectively).

The melting point slightly changes in the series of $\text{K}_{1-x}\text{Cs}_x\text{BSi}_2\text{O}_6$ solid solutions: for $x = 0.3$ it equals $1120^\circ \text{C}$ and for $x = 0.7$ it equals $1123^\circ \text{C}$. The weight losses increase with the rise of the Cs content on the sample from 2 wt % for $\text{KBSi}_2\text{O}_6$ to 16 wt % for $\text{CsBSi}_2\text{O}_6$; for the samples under investigation, the losses were 4.9 ($x = 0.3$) and 7.8 ($x = 0.7$) wt % (Fig. 1).

SOLID-PHASE DECOMPOSITION OF $\text{K}_{1-x}\text{Cs}_x\text{BSi}_2\text{O}_6 (x = 0.3, 0.7)$ BOROSILICATES

The samples of $\text{K}_{0.7}\text{Cs}_{0.3}\text{BSi}_2\text{O}_6$ and $\text{K}_{0.3}\text{Cs}_{0.7}\text{BSi}_2\text{O}_6$ compositions were subjected to thermal treatment at $1000^\circ \text{C}$; and the holding time was varied from 20 to 100 h. According to the data of the X-ray diffraction (with the following refining of the structure by the Rietveld method), in the sample $x = 0.3$, after annealing at $1000^\circ \text{C}$ for 20 h, only the cubic phase of boroleucite (space group $I\overline{4}3d$) is contained. With the increase of the annealing time up to 100 h, the traces of cristobalite ($\sim 12\%$) appeared in the sample. There is only cubic phase $Ia\overline{3}d$ in the sample enriched by cesium ($x = 0.7$) at $1000^\circ \text{C}$ and annealing time of 20 h (see table), while the annealing of pure $\text{CsBSi}_2\text{O}_6$ leads to the formation of the traces of zeolite-like $\text{CsBSi}_5\text{O}_{12}$ borosilicate ($\sim 10\%$) in the sample after 20 h of annealing [9]. In the sample with $x = 0.7$ held for 65 h, the amount of the zeolite-like phase increases approximately up to $32\%$, and holding for 100 h leads to the rise of its amount up to $35\%$ and traces ($\sim 4\%$) of cristobalite appear. By the examples of