INTRODUCTION

Borosilicates with leucite stoichiometry have been extensively used in glass-ceramic making. Owing to low thermal expansion coefficients, including zero values [1–3], high chemical inertness, and unique stability to a heat shock, these materials have found wide applications from manufacturing of household goods and chemical heat-resistant glassware to burial of radioactive wastes. In particular, radioactive cesium has been buried in materials based on pollucite CsAlSi2O6 and isostructural boropollucite CsBSi2O6 [4].

Borosilicates in the KBSi2O6–CsBSi2O6 series studied in our present work belong to the leucite group, i.e., the so-called ANA type. Leucites are characterized by a wide spectrum of isomorphous substitutions (R = K, Cs, Rb, H2O; X = Na; T = Si; T+ = Al, B, Fe3+) [3]. In nature, the main representatives of this group are the minerals leucite KAlSi2O6 and pollucite CsAlSi2O6. Moreover, a rubidium analog of leucite has been synthesized, which has not yet been found in nature.

In the 1970s–1980s, boron-substituted pollucite CsBSi2O6 was first to be synthesized and studied among borosilicates [1]. It was shown that the glass of this composition crystallizes at temperatures above 1073 K with the formation of a leucite-like compound. The structure of the CsBSi2O6 compound was determined in the space group Ia3d from the X-ray powder diffraction data (a = 13.01 Å) [5]; more recently, the space group Ia3d was refined from the single-crystal data (a = 13.01 Å) [6]. The structure of the synthetic boron-substituted leucite, which was referred to as the boroleucite KBSi2O6, was determined by a single-crystal X-ray diffraction analysis in the space group I43d [7, 8]. The tetragonal KBSi2O6 modification (hypothetically, with the space group I41/a, a = 12.626 Å, c = 12.745 Å, structural data are absent) synthesized by the sol–gel method at a temperature of 380°C was described by Mazza et al. [9]. The tetragonal KBSi2O6 modification was also revealed using high-temperature X-ray diffraction in our earlier work [10]. In the course of heating to temperatures...
above 350°C, the cubic modification $I\bar{4}3d$ transforms into the tetragonal modification (hypothetically, with the space group $I\bar{4}/a$). With a further increase in the temperature to 550°C, the tetragonal modification transforms again into the cubic modification but, most likely, with a higher symmetry (space group $Ia\bar{3}d$). In [11], the series of these transitions in KBSi$_2$O$_6$ was confirmed using the dilatometric technique, and their reversibility was proved using differential scanning calorimetry.

In the series of Rb$_{1-x}$Cs$_x$BSi$_2$O$_6$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$) solid solutions, the structural transformations caused by the Rb–Cs cation substitutions and variations in temperature were investigated using X-ray powder diffraction data [12, 13]. It was noted in [3, 14, 15] that the effect of an increase in the temperature on the structure is similar to the substitution of a larger cation for a smaller cation: the phase transition $I\bar{4}3d \leftrightarrow Ia\bar{3}d$ in the system occurs at room temperature in the composition range 50–60 mol % CsBSi$_2$O$_6$ through the two-phase region according to the data obtained by the Rietveld method. With an increase in the temperature, this transition in the solid solutions $I\bar{4}3d$ was revealed in the composition range $x = 0.25–0.5$ with the use of the high-temperature X-ray diffraction and dilatometric data [12, 13]. It should be noted that the transition temperature decreases upon the Rb–Cs substitution, i.e., with an increase in the cation size.

The crystal structures of the K$_{1-x}$Cs$_x$BSi$_2$O$_6$ ($x = 0.12, 0.50$) solid solutions prepared by crystallization of glasses with a nonstoichiometric composition were refined in the space group $I\bar{4}3d$, and the thermal expansion coefficients of these phases were determined in [10].

The thermal expansion of leucites was first investigated for the natural leucite, synthetic leucites KAlSi$_2$O$_6$ and RbAlSi$_2$O$_6$, and pollucite CsAlSi$_2$O$_6$ [16]. At room temperature, the first three phases were assigned to the tetragonal crystal system and the pollucite CsAlSi$_2$O$_6$ was attributed to the cubic crystal system. As the temperature increases, the tetragonal modifications transform into the cubic modifications at 690, 605, and 310°C, respectively. For the cubic modifications of the synthetic leucites and pollucite, Taylor and Henderson [16] revealed two ranges characterized by different slopes of the temperature dependence of the lattice parameter $a$ and, correspondingly, by different thermal expansion coefficients $\alpha$. The tetragonal phase and the cubic phase in the first range exhibit a considerable expansion: the thermal expansion coefficients $\alpha$ are equal to $8.548 \times 10^{-6}$°C$^{-1}$ for the KAlSi$_2$O$_6$ phase and $7.980$ and $4.653 \times 10^{-6}$°C$^{-1}$ for the RbAlSi$_2$O$_6$ phase. The second range of the cubic phase is characterized by a low thermal expansion: the thermal expansion coefficients for leucite and rubidium-substituted leucite are equal to $0.921 \times 10^{-6}$ and $1.215 \times 10^{-6}$°C$^{-1}$, respectively. The thermal expansion of the cubic pollucite CsAlSi$_2$O$_6$ occurs in two stages with the thermal expansion coefficients $\alpha = 4.8 \times 10^{-6}$°C$^{-1}$ and $\alpha = 0$ [16]. More recently, it was found that the synthetic pollucite also has a tetragonal phase, which transforms into the cubic modification at temperatures of 273 and 373°C according to the data obtained in [17, 18], respectively. Different structural mechanisms of thermal expansion in phases with a leucite structure in terms of rotation of tetrahedra with an increase in the temperature were discussed in [3, 16, 18, 19].

With the aim of searching for materials with a low thermal expansion, Richerson and Hummel [1] and Bayer [2] synthesized and investigated various substituted leucites in which Al was replaced by B, Fe$^{3+}$, and Ga, as well as in equimolar amounts by Si and Be, Zn, Co, Mg, and Ni, and K was replaced by Rb and Cs. Taylor and Henderson [16] were the first to note that cesium-containing phases have the lowest thermal expansion. In particular, the replacement of Al by Si and Be, as well as the replacement of Al by B, leads to a drastic decrease in the thermal expansion: $\alpha = 2.2 \times 10^{-6}$°C$^{-1}$ for the CsBe$_{0.8}$Si$_{2.8}$O$_6$ phase and $\alpha = 2.4 \times 10^{-6}$°C$^{-1}$ for the CsBSi$_2$O$_6$ phase. Yanase et al. [20] revealed that, among the cesium-containing phases based on pollucite, the lowest thermal expansion is observed for the Cs$_{0.9}$Al$_{0.1}$Si$_2$O$_6$ ($\alpha = 2.05 \times 10^{-6}$°C$^{-1}$ in the temperature range 298–1273 K) and CsB$_{0.2}$Al$_{0.8}$Si$_2$O$_6$ compositions.

To date, structural deformations, phase transitions, and thermal expansion in the leucite-like borosilicate solid solutions Rb$_{1-x}$Cs$_x$BSi$_2$O$_6$ [12, 13] and K$_{1-x}$Rb$_x$BSi$_2$O$_6$ [11] have been thoroughly investigated by varying the composition $x$ and temperature $T$. However, the K$_{1-x}$Cs$_x$BSi$_2$O$_6$ solid solutions with the largest difference between the cation sizes have been studied only fragmentarily: in fact, known are crystal structures of the solid solutions with $x = 0.12$ and 0.50, which were prepared by the crystallization of glasses with compositions displaced with respect to the stoichiometry of the phases [10]. For the purpose of a further development of the high-temperature crystal chemistry of borosilicates, we investigated the isomorphism, polymorphism, and thermal expansion in the series of solid solutions KBSi$_2$O$_6$–CsBSi$_2$O$_6$.

**SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE**

The main methods for investigating samples of the K$_{1-x}$Cs$_x$BSi$_2$O$_6$ compositions are described in our earlier work [11] devoted to the study of the thermal expansion and phase transitions in the K$_{1-x}$Rb$_x$BSi$_2$O$_6$ solid solutions with a leucite structure.

**Synthesis and Heat Treatment of Samples**

Polycrystalline samples of the K$_{1-x}$Cs$_x$BSi$_2$O$_6$ compositions with $x = 0.20, 0.30, 0.35, 0.40, 0.50$, 0.60, 0.80, 0.90, and 1.00 were prepared by the conventional melt technique.