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SYNTHESIS OF BOROLEUCITE $K[BSi_2O_6]$ SINGLE CRYSTALS

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Single crystals of boroleucite have been isolated from specimens prepared by slow cooling of a melt of the composition $K_2O \cdot B_2O_3 \cdot 4\,SiO_2$ *with addition of 5—10 %* KHF_2, *between temperatures 1 300—1 100 K.*

Recently, during his investigations of glasses in the system K_2O—B_2O_3—SiO_2, Voldán [1] observed in the concentration range 15—30 % K_2O, 15—30 % B_2O_3, 50—70 % SiO_2 (wt. %) an intense crystallization of a ternary compound hitherto unknown. The glasses crystallized in a wide temperature range (923—1 373 K), yielding dendritic and spherolitic crystals. Any attempt to grow bigger crystals a) by slow cooling of the batch from 1 418 to 1 263 K at the rate 1.5 K/hour, and b) by annealing the glass in a sealed Pt tube, 76 hours at 1 341 K, resulted in idiomorphous crystals (cubes, icositetrahedra and their combinations) but their size did not exceed 1 μm. The powder diffraction pattern of the new phase could be interpreted in terms of a cubic structure with $a = 12.615\,(3) \cdot 10^{-10}$ m. Due to its close similarity to that of the high-temperature leucite $K[AlSi_2O_6]$ ($a = 13.40 \cdot 10^{-10}$ m), Voldán assigned the new phase the composition $K[BSi_2O_6]$ and called it "boroleucite". Such a structural analogy is remarkable from the point of view of the coordination of B atoms in the new phase. Voldán pointed out that the Al atoms in the leucite structure are tetrahedrally coordinated and thus also B atoms in the boroleucite structure might appear in $[BO_4]$ tetrahedra. This would imply that such tetrahedra should prevail also in glasses from which boroleucite crystallizes.

In order to obtain more detailed structural information on boroleucite by means of an X-ray structure analysis, suitable single crystals were needed. The results of Voldán indicated that the crystallization of boroleucite may be obstructed by high viscosity of the corresponding glass melt. On the other hand, it is known from literature [2], [3] that the viscosity of silicate melts can be considerably reduced by addition of fluorides. We attempted therefore to grow boroleucite crystals from glass melts with the addition of KF, which has the appropriate melting point (1 125 K) and which does not bring foreign cations into the system K_2O—B_2O_3—SiO_2.

This decision was supported by the fact that the phase diagram of a similar system KF—K_2SiO_3 [5] (eutectic temperature 1 003 K at 59 wt. % KF) as well as those of other related systems [6] are of a simple eutectic type so that we could assume a similar behaviour also in the system KF—$K[BSi_2O_6]$.

A glass with the composition 24.6 % K_2O, 17.55 % B_2O_3 and 57.8 % SiO_2 (wt. %), prepared in the State Glass Research Institute in Hradec Králové (Czechoslovakia), was used as starting material. A piece of this glass (~30 g) was heated 5 hours at 1 170 K and subsequently quenched in water. The product was ground to a powder

with particles below 0.2 mm—its powder diffraction pattern was identical with that of boroleucite given by Voldán [1]. The powder thus obtained was mixed with 5 or 10 wt. % KHF_2 and the mixture (~15 g) was melted by heating it up to 1 300 K in Pt crucibles at the rate of 300 K/hour. After a one-hour soaking period the samples were cooled down to 1 100 K at the rate of 30 K/hour, then removed from the furnace and let to cool spontaneously. The potassium fluoride-rich phase was then leached out from the cooled samples by hot distilled water leaving individual isometric crystals (about 0.1—2 mm in size) as well as their aggregates, the dominant form being icositetrahedron {211}. The identity of these crystals with Voldán's boroleucite was confirmed by an X-ray powder analysis. The melting point of boroleucite determined in a high-temperature microscope was 1 368(5) K, in agreement with the maximum liquidus temperature in the ternary system K_2O—B_2O_3—SiO_2 [1].

The work on the crystal structure analysis of boroleucite and an investigation of its physical properties goes on [7].

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SYNTÉZA MONOKRYŠTÁLOV BOROLEUCITU $K[BSi_2O_6]$

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Pripravili sa kryštály kubického boroleucitu — $K[BSi_2O_6]$ s cieľom študovať kryštálovú štruktúru a ďalšie vlastnosti tejto fázy.

Prášok boroleucitu, pripravený kryštalizáciou skla zloženia 24,6 % K_2O, 17,55 % B_2O_3 a 57,8 SiO_2 pri 1.170 K sa zmiešal s 5, resp. 10 % hmotn. KHF_2, zmes sa zahriala na 1 300 K a ochladzovala pri poklese teploty 30 K . h^{-1} na 1 100 K. Z ochladenej vzorky sa pôsobením horúcej destilovanej vody izolovali kubické, väčšinou agregované kryštály veľkosti 0,1—2 mm. Ich identita s boroleucitom sa potvrdila rtg práškovou analýzou. Individuálne kryštály majú väčšinou tvar tetragón-trioktaédrov {211}. Teplota topenia kryštálov boroleucitu je 1 368 ±5 K.

СИНТЕЗ МОНОКРИСТАЛЛОВ БОРОЛЕЙЦИТА $K[BSi_2O_6]$

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Приготовили кристаллы кубического боролейцита $K(BSi_2O_6)$ с целью исследовать кристаллическую структуру и дальнейшие свойства данной фазы.

Порошок боролейцита, полученный кристаллизацией стекла составом 24,6 % K_2O, 17,55 % B_2O_3 и 57,8 SiO_2 при 1170 K перемешивали с 5 или 10 % по весу KHF_2, смесь нагревали до 1300 K и охлаждали при понижении температуры 30 K . $ч^{-1}$ до 1100 K. Из охлаждаемого образца под действием горячей дистиллированной воды изолировали кубические, в большинстве случаев агрегированные кристаллы размером 0,1—2 мм. Их идентичность с боролейцитом доказали с помощью рентгеновского порошкового анализа. Отдельные кристаллы имеют в большинстве случаев форму тетрагон-триоктаэдров {211}. Температура плавления кристаллов боролейцита — 1368 ± 5 K.