High-Temperature Study of K- and Rb-Boroleucite Crystal Structures by Rietveld Method

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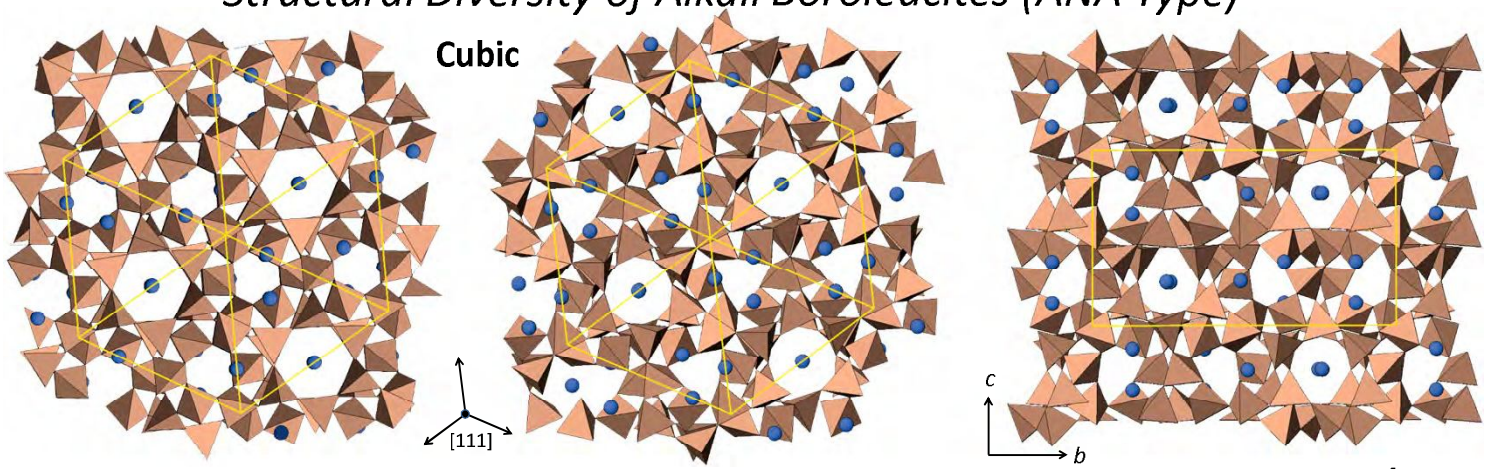
Up to now three modifications of $KBSi_2O_6$ (cubic *I*-43*d* [1], *Ia*3*d* [2] and monoclinic $P2_1/a$ [3]) and cubic (*I*-43*d*) modification of $RbBSi_2O_6$ [4] determined with ANA type of three dimensional framework structure are known. Present study is focused on high-temperature structural investigation of cubic modifications of K- and Rb-boroleucites. High-temperature powder X-ray diffraction (HTPXRD) study has been performed in air in the temperature range 20-1000 °C. Crystal structures were refined using the Rietveld method (Topas program).

Structural Diversity of Alkali Boroleucites (ANA Type)



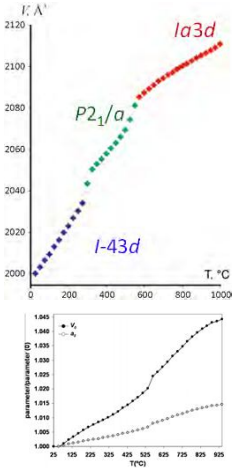
Ia3d
$RbBSi_2O_6$ (HT), $KBSi_2O_6$ (HT) [2], $CsBSi_2O_6$ [5]

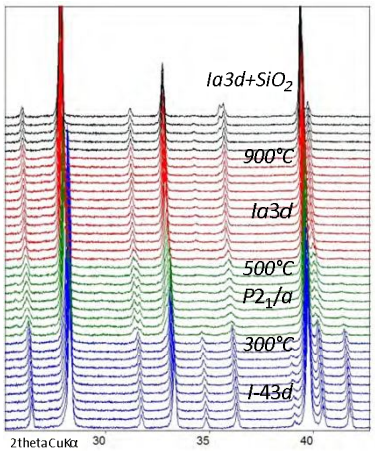
I-43d
$KBSi_2O_6$ [1], $RbBSi_2O_6$ [4]

Monoclinic *P2₁/a*
$KBSi_2O_6$ [3]

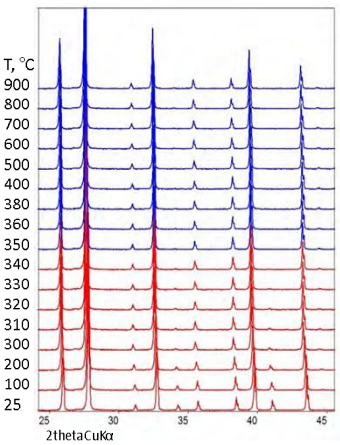
Reversible $KBSi_2O_6$ Transformation I-43d ↔ P2₁/a ↔ Ia3d

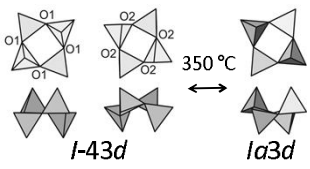
As it was noted recently by us [6] cubic $KBSi_2O_6$ structure undergoes reversible transformation into a lower symmetrical modification in the temperature range 300-500 °C. Present Rietveld refinement showed that over 300 °C cubic $KBSi_2O_6$ (*I*-43*d*) transforms reversibly into intermediate monoclinic modification which transforms later at 500 °C into *Ia*3*d* cubic phase. Thus the thermal polymorphic transformation of $KBSi_2O_6$ looks like: *I*-43*d* ↔ $P2_1/a$ ↔ *Ia*3*d*. These three phases are very similar to each other and belong to ANA type of structure. Consequently the transformation has displacive character and occurs continuously without breaking bonds. In [2] continuous transformation from *I*-43*d* directly to *Ia*3*d* space group in the temperature range 565-700 °C has been reported for slightly hydrated $KBSi_2O_6$ boroleucite from Rietveld refinement of synchrotron powder diffraction data.



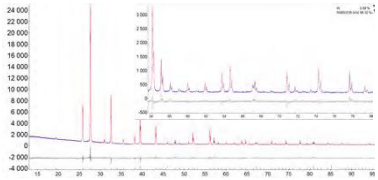


High-Temperature Structural I-43d ↔ Ia3d Transformation of $RbBSi_2O_6$

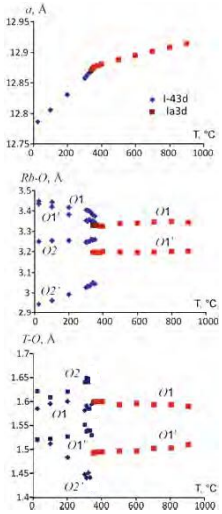


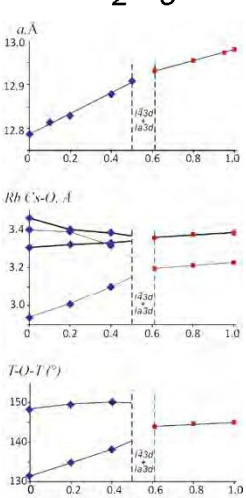


$RbBSi_2O_6$ 25 °C *I*-43*d* $a = 12.785364(70)$ (Å)
Rwp: 7.64 Rp : 5.41
Rexp: 4.34 GOF: 1.73
R-Bragg : 3.01



$RbBSi_2O_6$ 400 °C *Ia*3*d* $a = 12.878926(85)$ (Å)
Rwp: 6.68 Rp : 4.92
Rexp: 4.33 GOF: 1.55
R-Bragg : 2.09





According to HTPXRD data cubic $RbBSi_2O_6$ (*I*-43*d*) transforms over 300 °C directly into higher symmetrical *Ia*3*d* phase; Rietveld refinement of low- and high-temperature modifications at 25 and 400 °C are presented, respectively. Evolution of boroleucite structure under temperature and chemical composition changes looks very similar.

$RbBSi_2O_6$ Solid Solutions $Rb_{1-x}Cs_xBSi_2O_6$

Literature

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