

**BORON INCORPORATION IN RARE-EARTH SILICATE APATITES:
A SINGLE-CRYSTAL X-RAY STUDY**

by

U. Kolitsch

Institut für Mineralogie und Kristallographie
Geozentrum, Universität Wien, Althanstrasse 14, A-1090 Wien

As part of studies of the system Y_2O_3 - TiO_2 - SiO_2 , a B-rich Y silicate apatite has been grown as whitish hexagonal prisms with the help of a PbO_2 - PbF_2 - MoO_3 - $B(OH)_3$ flux (for details see Refs. [1],[2]). The crystal structure has been refined in space group $P6_3/m$ typical of rare-earth (RE) silicate apatites ($RE_{3.33}\square_{0.67}^{IX}RE_6^{VII}(Si^{IV}O^{IV}_4)_6O^{III}_2$ (\square = cation vacancy; roman numbers = coordination numbers). For the refinement single-crystal X-ray diffraction data were used (Mo- $K\alpha$ radiation, CCD area detector, room temperature).

Crystal data and R factors are: $a = 9.260(1)$, $c = 6.748(1)$ Å, $V = 501.10(11)$ Å³, $R_1 = 2.88$ % for 743 'observed' reflections [$F_o > 4\sigma(F_o)$]. SEM-EDS analyses showed only the presence of Y and Si. The refinement provided convincing evidence that ~20 % of the Si has been replaced by B, with a concomitant filling-up of the cation-deficient Y 4f site. The charge-balanced formula, $(Y_{3.73}\square_{0.27})_{\Sigma 4.00}Y_6[(SiO_4)_{4.80}(BO_4)_{1.20}]_{\Sigma 6.00}O_2$, is also in accordance with a refinement of the occupancies of the two Y sites (4f, 6h). As expected, the B incorporation results in a considerably decreased average (Si,B)-O bond length of 1.592 Å, and in decreased unit-cell parameters by comparison to B-free Y silicate apatites. A strong decrease is especially observed for the a parameter.

The present results confirm the work of ITO (1968)[3] who prepared polycrystalline B-bearing Y silicate oxyapatites at 1150°C and inferred the existence of two complete solid solution series $Y_{10}Si_4B_2O_{26} \Leftrightarrow Mg_2Y_8Si_6O_{26}$ and $Y_{10}Si_4B_2O_{26} \Leftrightarrow Ca_2Y_8Si_6O_{26}$, based on the observation of linear changes of unit-cell parameters along the respective series. The given formula, $Y_{10}Si_4B_2O_{26}$, can be rewritten as $Y_4Y_6[(SiO_4)_4(BO_4)_2]_{\Sigma 6}O_2$, thus demonstrating that this apatite is characterised by completely filled Y sites and a replacement of every third SiO_4 tetrahedron by a BO_4 tetrahedron. A comparison of the unit-cell parameters of $Y_{10}Si_4B_2O_{26}$, $a = 9.15$, $c = 6.75$ Å [3], with those of $(Y_{3.73}\square_{0.27})_{\Sigma 4.00}Y_6[(SiO_4)_{4.80}(BO_4)_{1.20}]_{\Sigma 6.00}O_2$, $a = 9.260(1)$, $c = 6.748(1)$ Å, shows that the further increase of the incorporated amount of B leads to a distinct decrease of the a parameter, but apparently does not affect the c parameter to any significant degree.

Very recently, a B-rich La silicate apatite was prepared and characterised by Rietveld refinement of neutron powder diffraction data.[4] The given formula, $\text{La}_5\text{Si}_2\text{BO}_{13}$, can be reformulated as $\text{La}_4\text{La}_6[(\text{SiO}_4)_4(\text{BO}_4)_2]_{\Sigma 6}\text{O}_2$, again demonstrating that in rare-earth silicate apatites every third SiO_4 tetrahedron can be replaced by a BO_4 tetrahedron. Similar B incorporation could also occur in natural (RE,Ca)-silicate-phosphate apatites (britholites).

Further comparisons are drawn with the solid solutions series $\text{RE}_{9,33+2x}(\text{Si}_{1-x}\text{Al}_x\text{O}_4)_6\text{O}_2$ [5].

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References

- [1] KOLITSCH, U. (2001): Flux growth, crystal data and crystal chemistry of silicates, titanates, titanate-molybdates and molybdates of Nd, Gd, Y and Sc. - To be submitted.
- [2] KOLITSCH, U. (2001): Crystal chemistry of four flux-grown neodymium, gadolinium and yttrium silicate apatites: incorporation of Pb, Li and B, and implications for ionic conductivity. - To be submitted.
- [3] ITO, J. (1968): Silicate apatites and oxyapatites. - *Am. Mineral.*, 53, 890-907.
- [4] MAZZA, D., TRIBAUDINO, M., DELMASTRO, A. & LEBECH, B. (2000): Synthesis and neutron diffraction study of $\text{La}_5\text{Si}_2\text{BO}_{13}$, an analog of the apatite mineral. - *J. Solid State Chem.*, 155, 389-393.
- [5] KOLITSCH, U., SEIFERT, H. J. & ALDINGER, F. (1998): Phase relationships in the systems $\text{RE}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ (RE = rare earth element, Y, and Sc). - *J. Phase Equilibria* 19, 426-33.