Crystal growth and structure of a new yttrium titanate, Y$_{5+x}$Ti$_{2+y}$O$_{12}$, related to rutile.

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Flux growth experiments were run to investigate phase relations in the systems RE$_2$O$_3$-TiO$_2$-SiO$_2$ (RE = Nd, Gd, Y, Sc), which contain phases related to trimounsite-(Y) [(Y,RE)$_2$Ti$_2$SiO$_7$] and the RE-(Mg,Fe)-titanosilicates perrierite/checkevinite. Crystals of the new yttrium titanate Y$_{5+x}$Ti$_{2+y}$O$_{12}$ (with $x = 0.03$ or $y = 0.25$) were grown from a LiF-MoO$_3$ flux at 1050 - 850°C in air. The crystal structure (space group C2/m, $a = 12.226(2)$, $b = 5.885(1)$, $c = 7.135(1)$ Å, $\beta = 106.99(3)^\circ$, $Z = 8$) was determined using single-crystal diffractometer data (CCD area detector, MoK$\alpha$ X-radiation) and refined to $R = 2.24\%$.

The structure contains three Y-O polyhedra and infinite chains of edge-sharing TiO$_6$ octahedra along the $b$-axis (with alternating short and long Ti-Ti distances, 2.839 and 3.046 Å). Apical O atoms of the Y(3)O$_6$ octahedra link the TiO$_6$ chains within the (100) plane. Sheets of YO$_7$ polyhedra parallel to (100) link the chains along the $a$-axis. Y$_{5+x}$Ti$_{2+y}$O$_{12}$ shows the basic topology of Y$_3$Mo$_{10.5}$O$_{24.5}$ and RE$_3$Re$_{2.5}$O$_{22}$ compounds$^2$. However, it contains an additional, octahedrally coordinated and partially occupied cation site at (0,0,0.5), which is needed for charge compensation. This site is probably occupied by a mixture of major Y and minor Ti, and was designated Y(4). The suggested general formula is Y$_{5+x}$Ti$_{2+y}$O$_{12}$, with possible structures equivalent molybdenum atoms, J. Solid State Chem., (1985), 60: 332-342.

A new, lintisite-related titanosilicate mineral from Russia: crystal structure, occurrence and properties.

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The new mineral, which is closely related to lintisite (Na$_3$LiTi$_6$Si$_{14}$O$_{42}$H$_2$O), was found at Malyi Punkarauiv Mountain, Lovozero alkaline massif, Kola Peninsula, Russia. It occurs in a hydrothermally altered hyperalkaline pegmatite. Electron microprobe analyses show only Ti and Si (Ti:Si ratio close to 0.5) and very low Na contents (0.2-0.3, rarely up to 1 wt.% Na$_2$O); the Li content has not been determined yet. The IR spectrum is clearly different from spectra of the related minerals lintisite, vinogradovite [(Na$_3$Ca$_2$)$_6$Ti$_4$Si$_{20}$O$_{68}$H$_2$O], kukisvumite [Na$_3$Zn$_4$Si$_{28}$O$_{88}$H$_4$O] and lorenenite [Na$_3$Ti$_6$Si$_{14}$O$_{46}$]. The mineral forms colourless, elongate {100} prism (C2/c, $a = 26.68$, $b = 8.77$, $c = 5.22$ Å, $\beta = 91.2^\circ$), similar to that of lintisite (C2/c, $a = 28.58$, $b = 8.60$, $c = 5.22$ Å, $\beta = 91.0^\circ$), but with a distinctly smaller $a$ parameter. A structure determination of a crystal fragment of mediocre quality showed the mineral to contain basically the same polyhedral titanosilicate slabs found in lintisite (R ~10% - a triclinic refinement resulted in the same model; twinning was not evident). The slabs consist of chains of edge-sharing TiO$_6$ octahedra extended along {010}, which are connected to pyroxene-like chains of SiO$_4$ tetrahedra via shared O ligands. These slabs are oriented // to {010} and separated by a widely open space which contains a somewhat disordered and partially occupied, [4]-coordinated Li ion. Its position is identical to the Li position in lintisite. Two O atoms shared by the LiO$_4$ and Si(2)O$_4$ tetrahedra are disordered, too. There is also evidence that the Si(2) position is only partially occupied. Very small residual electron densities are found close to disordered atoms and the Ow and Na(2) positions of lintisite. The wide spacing between the titanosilicate slabs explains the excellent cleavage // to {010}. The spacing is smaller in the new mineral than in lintisite because there are no two 'space-consuming' Na sites as in lintisite. The relation to the structures of lintisite and vinogradovite will be discussed.
