MS15-1-9 Closing some gaps of knowledge: single crystals of $Pr_2O[SiO_4]$ and $Sm_2O[SiO_4]$ with the A-type structure
#MS15-1-9

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Abstract
Syntheses with lanthanoid metals in glassy silica ampoules often tend to yield oxosilicates as by-products. Thus, the two presented silicates $Pr_2O[SiO_4]$ and $Sm_2O[SiO_4]$ were also obtained from different reactions including the elemental lanthanoids, but with other target compounds. Both crystallize isostructurally to the $Ln_2O[SiO_4]$ series with *Ln* = La, Nd, Eu, Gd, Ho – Tm and Lu [1–6] in the monoclinic space group $P2_1/c$ with the lattice parameters *a* = 925.49(8) pm, *b* = 733.97(6) pm, *c* = 692.06(5) pm, β = 108.382(3)° for $Pr_2O[SiO_4]$ (CSD-2127743) and *a* = 915.92(8) pm, *b* = 717.19(6) pm, *c* = 679.42(5) pm, β = 107.825(3)° for $Sm_2O[SiO_4]$ (CSD-2127807) adapting the $Gd_2O[SiO_4]$- or A-type structure with *Z* = 4.
The Ln^{3+} cations occupy two crystallographically different positions (Figure 1). $(Ln1)^{3+}$ resides in a distorted capped square hemiprism with 8+1 oxygen atoms, while $(Ln2)^{3+}$ centres a capped trigonal prism with just seven of them. The lanthanoid-oxygen distances, namely *d*(Pr–O) = 234 – 269 pm and *d*(Sm–O) = 231 – 259 pm, fall into the usual range when compared with similar praseodymium and samarium oxosilicates such as apatite-type $Ln_{4.667}O[SiO_4]_3$ (*Ln* = Pr and Sm) [7], for example. Silicon is surrounded by a slightly distorted tetrahedron of four oxygen atoms as *ortho*-oxosilicate anion $[SiO_4]^{4-}$ with silicon-oxygen distances ranging from 159 to 166 pm, which remains isolated. The fifth oxygen atom works as an O^{2-} anion, which is coordinated by four Ln^{3+} cations as $[OLn_4]^{10+}$ tetrahedron (*d*(O–*Ln*) = 230 – 243 pm). Their connectivity via edges and corners leads to corrugated $^2_\infty\{[O(Ln1)_{1/1}(Ln2)_{3/3}]^{4+}\}$ layers spreading out parallel to the (100) plane (Figure 2).

References
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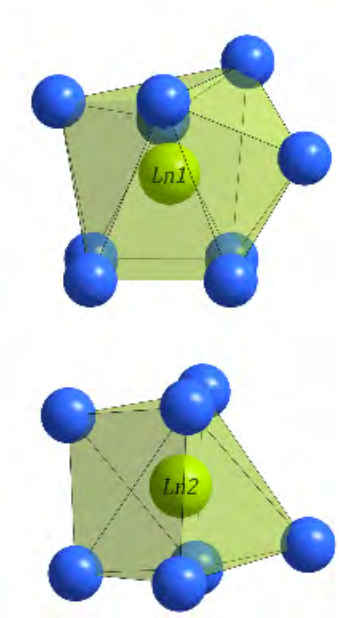
Coordination polyhedra of $(Ln1)^{3+}$ and $(Ln2)^{3+}$.



Unit cell of the A-type structure of $Ln_2O[SiO_4]$.