

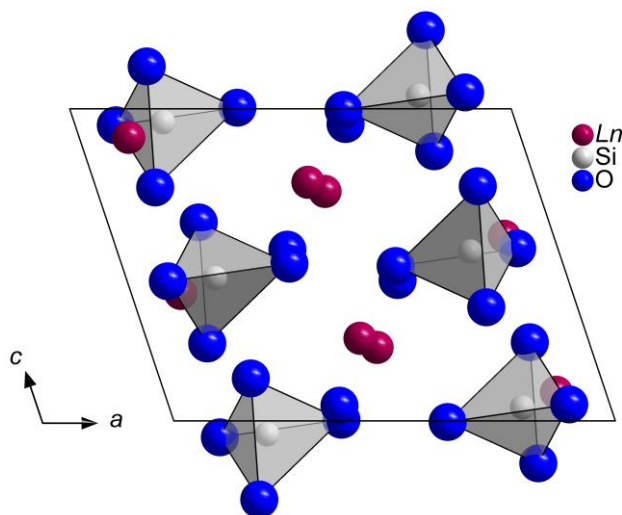
## Closing Some Gaps of Knowledge: Single Crystals of $\text{Pr}_2\text{O}[\text{SiO}_4]$ und $\text{Sm}_2\text{O}[\text{SiO}_4]$ with the A-Type Structure

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Syntheses with lanthanoid metals in glassy silica ampoules often tend to yield oxosilicates as by-products. Thus, the two presented silicates  $\text{Pr}_2\text{O}[\text{SiO}_4]$  and  $\text{Sm}_2\text{O}[\text{SiO}_4]$  were also obtained from different reactions including the elemental lanthanoids, but with other target compounds. Both crystallize isostructurally to the  $\text{Ln}_2\text{O}[\text{SiO}_4]$  series with  $\text{Ln} = \text{La}, \text{Nd}, \text{Eu}, \text{Gd}, \text{Ho} - \text{Tm}$  and  $\text{Lu}^{[1-6]}$  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,  $\beta = 108.382(3)^\circ$  for  $\text{Pr}_2\text{O}[\text{SiO}_4]_2$  (CSD-2127743) and  $a = 915.92(8)$  pm,  $b = 717.19(6)$  pm,  $c = 679.42(5)$  pm,  $\beta = 107.825(3)^\circ$  for  $\text{Sm}_2\text{O}[\text{SiO}_4]_2$  (CSD-2127807) adapting the  $\text{Gd}_2\text{O}[\text{SiO}_4]_2$ - or A-type structure with  $Z = 4$ .

The  $\text{Ln}^{3+}$  cations occupy two crystallographically different positions.  $(\text{Ln}1)^{3+}$  resides in a distorted capped square hemiprism with 8+1 oxygen atoms, while  $(\text{Ln}2)^{3+}$  centers a capped trigonal prism with seven of them. The lanthanoid-oxygen distances, namely  $d(\text{Pr}-\text{O}) = 234 - 269$  pm and  $d(\text{Sm}-\text{O}) = 231 - 259$  pm, fall into the usual range when compared with similar praseodymium and samarium oxosilicates such as apatite-type  $\text{Ln}_{4.667}\text{O}[\text{SiO}_4]_3$  ( $\text{Ln} = \text{Pr}$  and  $\text{Sm}$ )<sup>[7]</sup>. Silicon is surrounded by a slightly distorted tetrahedron with four oxygen atoms as oxosilicate anion  $[\text{SiO}_4]^{4-}$  with silicon-oxygen distances ranging from 159 to 166 pm, which remains isolated. The fifth oxygen atom works as an  $\text{O}^{2-}$  anion, which is coordinated by four  $\text{Ln}^{3+}$  cations as  $[\text{OLn}_4]^{10+}$  tetrahedron ( $d(\text{O}-\text{Ln}) = 230 - 243$  pm). Their connectivity via edges and corners leads to  $\infty^2\{[\text{O}(\text{Ln}1)_{1/1}(\text{Ln}2)_{3/3}]^{4+}\}$  layers spreading out parallel to the (100) plane.



**Figure 1.** Projection of the monoclinic crystal structure of  $\text{Ln}_2\text{O}[\text{SiO}_4]$  ( $\text{Ln} = \text{Pr}$  and  $\text{Sm}$ ) onto (010) showing the isolated  $[\text{SiO}_4]^{4-}$  tetrahedra.

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