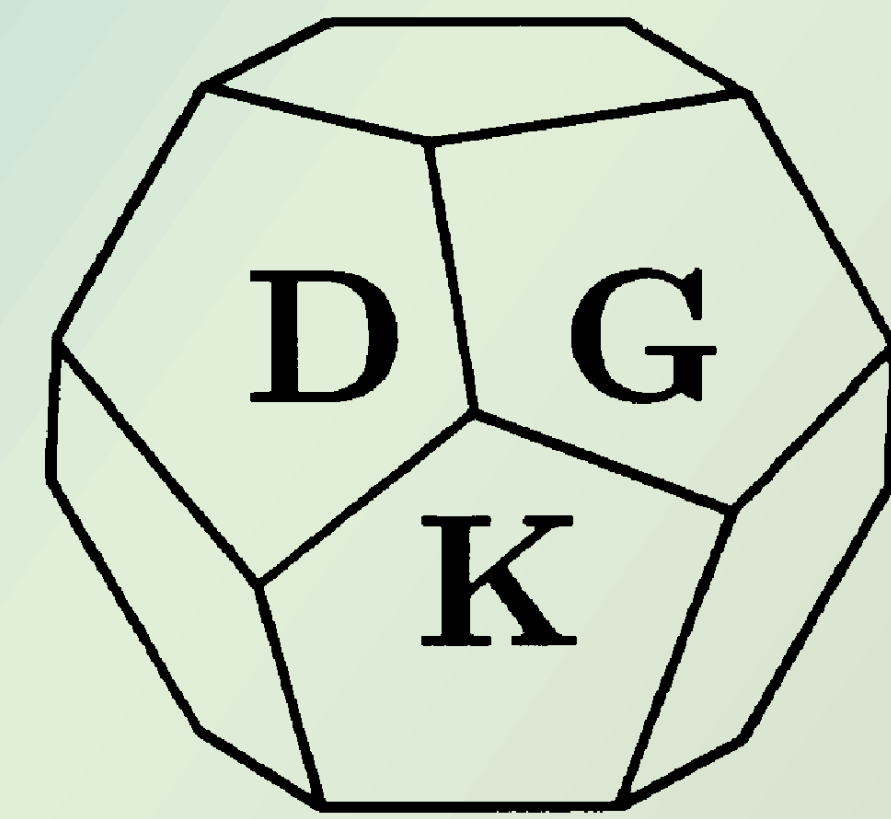


Closing Some Gaps of Knowledge: Single Crystals of $\text{Pr}_2\text{O}[\text{SiO}_4]$ and $\text{Sm}_2\text{O}[\text{SiO}_4]$ with the A-Type Structure

Patrik Djendjur, Ralf J. C. Locke, Marion C. Schäfer and Thomas Schleid*



Institute for Inorganic Chemistry, University of Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart

Introduction

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, $b = 717.19(6)$ 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) adopting the $\text{Gd}_2\text{O}[\text{SiO}_4]_2$ - or A-type structure with $Z = 4$.

Atomic Positions and Equivalent Isotropic Displacement Parameters

Atom	Wyckoff site	$\text{Pr}_2\text{O}[\text{SiO}_4]$				$\text{Sm}_2\text{O}[\text{SiO}_4]$			
		x/a	y/b	z/c	$U_{\text{eq}}/\text{pm}^2$	x/a	y/b	z/c	$U_{\text{eq}}/\text{pm}^2$
<i>Ln1</i>	4e	0.38805(7)	0.15075(9)	0.09143(9)	167(2)	0.38706(7)	0.14851(8)	0.08820(8)	147(2)
<i>Ln2</i>	4e	0.01579(7)	0.12457(9)	0.23538(9)	157(2)	0.02097(7)	0.12454(8)	0.23477(8)	140(2)
Si	4e	0.2988(4)	0.5825(5)	0.0420(5)	156(6)	0.2985(4)	0.5836(5)	0.0421(5)	147(6)
O1	4e	0.2935(10)	0.0714(14)	0.3644(12)	194(17)	0.2935(10)	0.0722(13)	0.3598(12)	167(16)
O2	4e	0.3659(10)	0.4617(12)	0.2509(12)	190(17)	0.3650(10)	0.4584(12)	0.2500(12)	194(18)
O3	4e	0.8801(10)	0.3649(13)	0.0039(13)	198(19)	0.8822(10)	0.3635(11)	0.0060(13)	183(17)
O4	4e	0.5926(10)	0.2528(14)	0.4468(13)	204(19)	0.5941(10)	0.2604(13)	0.4473(12)	233(19)
O5	4e	0.1127(10)	0.3742(12)	0.4500(14)	191(17)	0.1139(10)	0.3775(11)	0.4506(13)	177(18)

Experimental Procedure

The oxidation of praseodymium or samarium metal with oxidizing agents such as selenium dioxide in the presence of sodium chloride as fluxing agent at 900 °C for 10 days in evacuated silica ampoules led to the formation of colorless, needle-shaped single crystals of $\text{Pr}_2\text{O}[\text{SiO}_4]$ and $\text{Sm}_2\text{O}[\text{SiO}_4]$ as a by-products after some reaction with the SiO_2 container material. The insoluble single crystals could be collected after removal of the fluxing agent by washing the crude batches several times with demineralized water.

Crystallographic Data

	$\text{Pr}_2\text{O}[\text{SiO}_4]$	$\text{Sm}_2\text{O}[\text{SiO}_4]$
Crystal system	monoclinic	
Space group	$P2_1/c$ (no. 14)	
Lattice parameters		
a/pm	925.49(8)	915.92(8)
b/pm	733.97(6)	717.09(6)
c/pm	692.06(5)	679.34(5)
$\beta/^\circ$	108.382(3)	107.815(3)
Number of formula units	$Z = 4$	
Calculated density (D_x in g/cm^3)	5.805	6.392
Molar volume (V_m in cm^3/mol)	446.12	424.79
Diffractometer	κ -CCD (Bruker-Nonius)	
Wavelength	Mo-K α : $\lambda = 71.07$ pm	
Diffractometer limit ($2\theta_{\text{max}}$ in deg)	65.83	56.62
Index range ($\pm h_{\text{max}}, \pm k_{\text{max}}, \pm l_{\text{max}}$)	13 / 11 / 10	12 / 9 / 9
Number of e^- per unit cell ($F(000)$)	688	712
Absorption coefficient (μ in mm^{-1})	21.76	27.56
Number of collected / unique reflections	7503 / 1564	9487 / 1051
Data set residuals ($R_{\text{int}} / R_\sigma$)	0.089 / 0.063	0.088 / 0.037
Structure residuals (R_1 / wR_2)	0.057 / 0.147	0.044 / 0.102
Goodness of Fit ($GooF$)	1.108	1.096
Residual electron density (max. / min.)	3.16 / -3.49	2.37 / -2.40
Structure solution and refinement	Program package SHELX-97 [8]	

Structure Description

The Ln^{3+} cations occupy two crystallographically different positions. (Ln1) $^{3+}$ resides in a distorted capped square hemiprism with 8+1 oxygen atoms, while (Ln2) $^{3+}$ 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 Sm) $^{[7]}$. Silicon is surrounded by a slightly distorted tetrahedron with four oxygen atoms as *ortho*-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 O^{2-} anion, which is coordinated by four Ln^{3+} cations as $[\text{OLn}_4]^{10+}$ tetrahedron ($d(\text{O}-\text{Ln}) = 230 - 243$ pm). Their interconnection via edges and corners leads to $\infty^2\{[\text{O}(\text{Ln1})_{1/1}(\text{Ln2})_{3/3}]^{4+}\}$ layers spreading out parallel to the (100) plane.

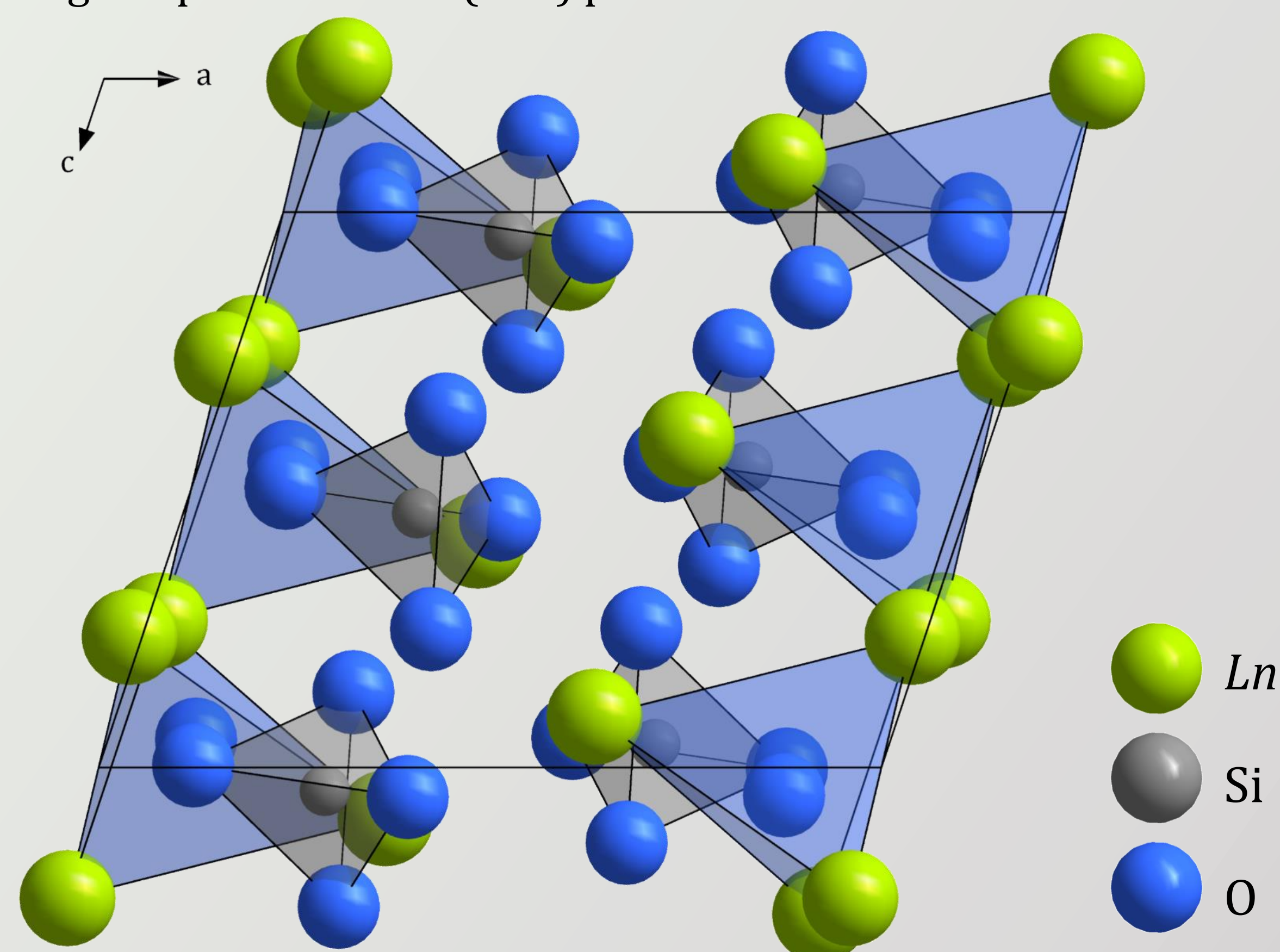


Figure 1. Projection of the monoclinic crystal structure of $\text{Ln}_2\text{O}[\text{SiO}_4]$ ($\text{Ln} = \text{Pr}$ and Sm) onto (010) showing the isolated $[\text{SiO}_4]^{4-}$ tetrahedra.

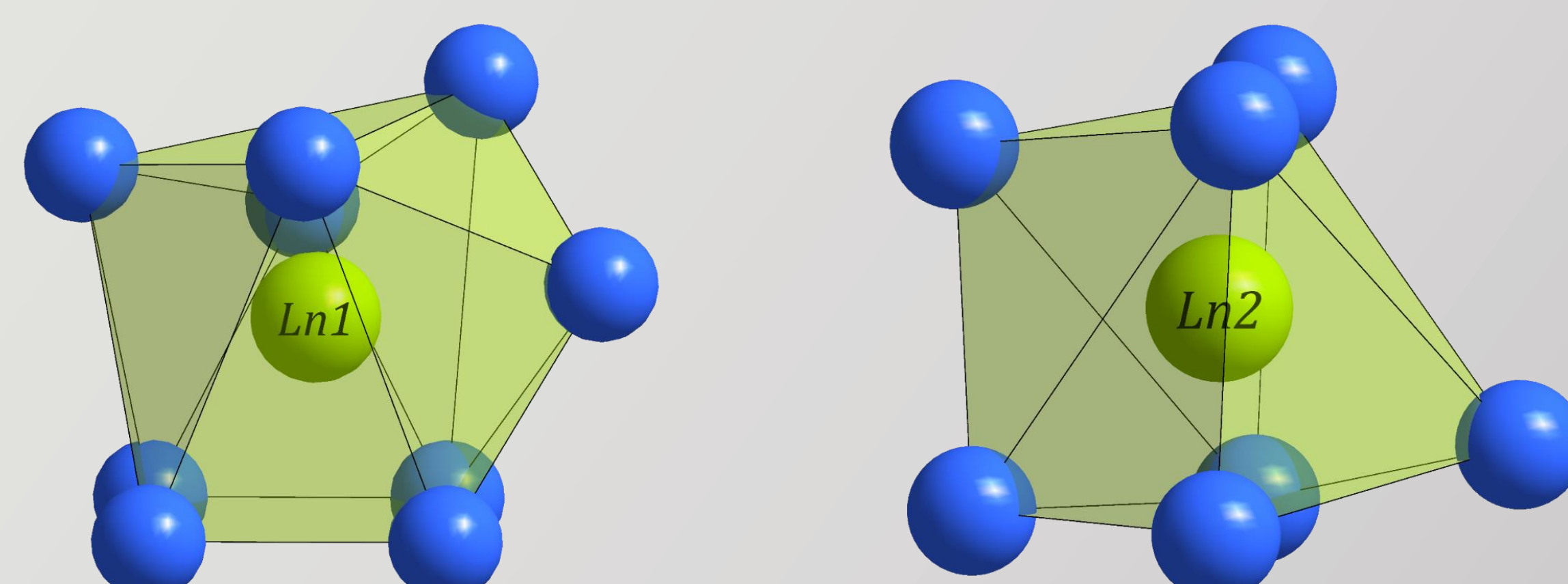


Figure 2. Anionic coordination polyhedra of the two crystallographically different Ln^{3+} cations in $\text{Pr}_2\text{O}[\text{SiO}_4]$ and $\text{Sm}_2\text{O}[\text{SiO}_4]$.

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