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Crystal structure of apatite type $Ca_{2.49}Nd_{7.51}(SiO_4)_6O_{1.75}$

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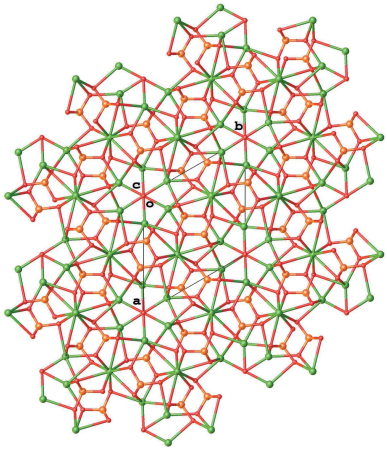
The title compound, $Ca_{2+x}Nd_{8-x}(SiO_4)_6O_{2-0.5x}$ (x = 0.49), was synthesized at 1873 K and rapidly quenched to room temperature. Its structure has been determined using single-crystal X-ray diffraction and compared with results reported using neutron and X-ray powder diffraction from samples prepared by slow cooling. The single-crystal structure from room temperature data was found to belong to the space group $P6_3/m$ and has the composition $Ca_{2.49}Nd_{7.51}(SiO_4)_6O_{1.75}$ [dicalcium octaneodymium hexakis(orthosilicate) dioxide], being isotypic with natural apatite and the previously reported $Ca_2Nd_8(SiO_4)_6O_2$ and $Ca_{2.2}Nd_{7.8}(SiO_4)_6O_{1.9}$. The solubility limit of calcium in the equilibrium state at 1873 K was found to occur at a composition of $Ca_{2+x}Nd_{8-x}(SiO_4)_6O_{2-0.5x}$, where x = 0.49.

1. Chemical context

The study of calcium rare earth oxide silicates is important because they are usually observed in nuclear waste along with rare earth silicates. So far, the calcium rare earth oxide silicates of Nd (Fahey & Weber, 1982; Fahey *et al.*, 1985), Sm (PDF 29–365; Smith, 1977), Eu (PDF 29–320; Smith, 1977), Gd (PDF 28–212; Smith, 1976), Tb (PDF 38–256; Lacout, 1986), and Ce (Skakle *et al.*, 2000) have been studied. Fahey & Weber *et al.* (1982) and Fahey *et al.* (1985) published the structure and stoichiometry limits of the $Ca_{2+x}Nd_{8-x}(SiO_4)_{2-0.5x}$ system using X-ray and neutron powder diffraction. In that study, the samples were synthesized at 1523 or 1873 K and cooled at a rate of 250 K per hour. However, such a slow cooling process may lead to undesired modifications of the obtained specimens since the solubility of calcium does not remain constant but decreases with decreasing temperature. This problem is avoided in the present work by rapid quenching of the $Ca_{2+x}Nd_{8-x}(SiO_4)_6O_{2-0.5x}$ samples in their equilibrium state at 1873 K to room temperature within a few seconds. Consequently, compositions of the samples can be preserved better.



2. Structural commentary

The single crystal structure determined from room temperature data was found to belong to the space group $P6_3/m$ and has the composition $Ca_{2.49}Nd_{7.51}(SiO_4)_6O_{1.75}$ and is isotypic with natural apatite and the previously reported $Ca_2Nd_8(SiO_4)_6O_2$ and $Ca_{2.2}Nd_{7.8}(SiO_4)_6O_{1.9}$ (Fahey & Weber, 1982; Fahey *et al.*, 1985). The solubility limit of calcium in the equilibrium state at 1873 K was found to occur at a composition of $Ca_{2+x}Nd_{8-x}(SiO_4)_6O_{2-0.5x}$, where x = 0.49.

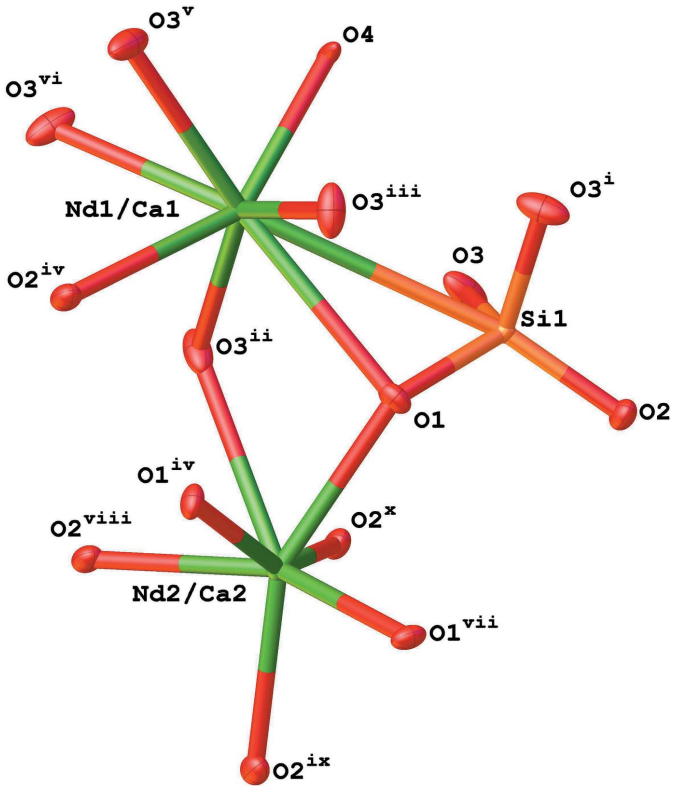


Figure 1
View of the coordination spheres of the Nd/Ca and Si atoms [displacement ellipsoids shown at the 50% probability level; symmetry codes: (i) $x, y, -z+\frac{1}{2}$; (ii) $y, -x+y, -z$; (iii) $y, -x+y, z+\frac{1}{2}$; (iv) $-y+1, x-y, z$; (v) $y-x, -x, -z+\frac{1}{2}$; (vi) $y-x, -x, z$; (vii) $y-x+1, -x+1, z$; (viii) $y, -x+y, z-\frac{1}{2}$; (ix) $-y+x+1, x, z-\frac{1}{2}$; (x) $-x+1, -y+1, z-\frac{1}{2}$].

There are two metal positions in the asymmetric unit of the structure (Fig. 1) and both contain disordered Nd and Ca ions: Nd1/Ca1 occupies the lower symmetry site 6*h* and Nd2/Ca2 the higher symmetry site 4*f*. The occupancies of these metal sites were refined resulting in 0.887 (5)/0.113 (5) for Nd1/Ca1 and 0.546 (4)/0.454 (4) for Nd2/Ca2. The majority (80%) of calcium is situated at the *4f* site. In the structures of $Ca_2Nd_8(SiO_4)_6O_2$ and $Ca_{2.2}Nd_{7.8}(SiO_4)_6O_{1.9}$, these values are 89 and 73%, respectively (Fahey *et al.*, 1985). The refined value of the amount of Nd in the structure gives a value of 0.49 for x in the equation $Ca_{2+x}Nd_{8-x}(SiO_4)_6O_{2-0.5x}$. For charge-balance purposes, the occupancy of O^{2-} in the structure must be $2 - 0.5x$ or 1.755. Initially, the occupancy of the O^{2-} position O4 in the structure was allowed to refine freely and its value was close to what is required for charge balance; however, it was fixed at 0.146 as the refinement of heavy-atom positions is the most reliable and exact charge balance is required.

The Nd1/Ca1 site is seven coordinate and the Nd/Ca—O bond lengths vary between 2.3909 (19) and 2.721 (3) Å for oxygen atoms of the SiO_4^{2-} unit but the shortest bond length of 2.2681 (2) Å is to the O^{2-} ion, O4 (Fig. 1; Table 1). The Nd2/Ca2 site is nine coordinate and only bonds to SiO_4^{2-} units with six short distances [Nd—O = 2.4231 (17), 2.4715 (18) Å] and three long distances [Nd—O = 2.830 (2) Å] (Fig. 1; Table 1) are observed. The distances are similar to those reported by

Table 1
Selected bond lengths (Å).

Nd1—O1	2.721 (3)	Nd2—O2^{iv}	2.4715 (18)
Nd1—O2^{i}	2.463 (3)	Nd2—O3^{v}	2.830 (2)
Nd1—O3^{ii}	2.3909 (19)	Si1—O1	1.621 (3)
Nd1—O3^{iii}	2.547 (2)	Si1—O2	1.623 (3)
Nd1—O4	2.2681 (2)	Si1—O3^{vi}	1.629 (2)
Nd2—O1^{i}	2.4231 (17)		

Symmetry codes: (i) $-y+1, x-y, z$; (ii) $y, -x+y, z+\frac{1}{2}$; (iii) $-x+y, -x, -z+\frac{1}{2}$; (iv) $x-y+1, x, z-\frac{1}{2}$; (v) $-x+1, -y+1, -z$; (vi) $x, y, -z+\frac{1}{2}$.

Fahey *et al.* (1985) for the structures of $Ca_2Nd_8(SiO_4)_6O_2$ and $Ca_{2.2}Nd_{7.8}(SiO_4)_6O_{1.9}$ determined by powder X-ray diffraction.

The O4 atom (O^{2-} ion) is coordinated to three different Nd1/Ca1 ions whilst the SiO_4^{4-} group has eight contacts to different Nd/Ca positions. The O1 atom coordinates one Nd1/Ca1 position and two Nd2/Ca2 positions, the O2 atom coordinates one Nd1/Ca1 position and two Nd2/Ca2 positions and the O3 position coordinates one Nd1/Ca1 and one Nd2/Ca2 positions. These contacts generate the packing, which can be seen viewed down the *c* axis in Fig. 2.

3. Synthesis and crystallization

A mixture of appropriate amounts of fine powders of Nd_2O_3 (99.99%), CaO (99.9%) and SiO_2 (99.9%) was put into a sealed Pt-20%Rh tube and heated to 1873 K in an argon atmosphere and maintained at that temperature for 24 h. CaO

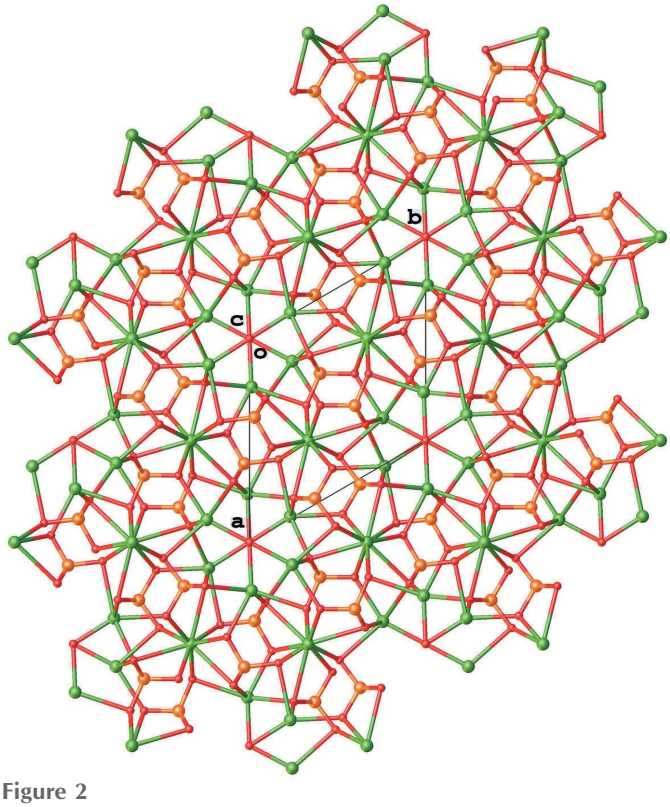


Figure 2
View along the *c* axis of the packing arrangement.

Table 2
Experimental details.

Crystal data	
Chemical formula	$Ca_{2.49}Nd_{7.51}(SiO_4)_6O_{1.75}$
M_r	1763.24
Crystal system, space group	Hexagonal, $P6_3/m$
Temperature (K)	298
a, c (Å)	9.5507 (3), 7.0513 (3)
V (Å^3)	557.03 (3)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	18.18
Crystal size (mm)	0.05 × 0.05 × 0.05
Data collection	
Diffractometer	Agilent SuperNova (single source at offset, Eos detector)
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2012)
T_{min}, T_{max}	0.717, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2616, 878, 813
R_{int}	0.024
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.821
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.019, 0.035, 1.11
No. of reflections	878
No. of parameters	42
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.79, −0.86

Computer programs: *CrysAlis PRO* (Agilent, 2012), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *OLEX2* (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010).

was made by calcination of $CaCO_3$ at 1373 K for 12 h. The sample was then quenched in a cold-water bath to give a light-blue crystalline solid, from which a single crystal of the title compound was selected. The sample was further analyzed by EPMA–WDS, giving a composition of 20.2% SiO_2, 72.1% Nd_2O_3 and 7.7% CaO. The converted formula according to the EPMA–WDS result was $Ca_{2.45}Nd_{7.45}Si_6O_{25.775}$ (O was calculated).

4. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 2. There are two metal positions in the structure and the Nd and Ca ions are disordered on both of these sites. Nd/Ca occupancy on each of the two positions was refined and the occupancy of Nd was found to be 88.7 (5)% for one site and 54.6 (4)% for the other, giving a value of 0.49 for x in $Ca_{2+x}Nd_{8-x}(SiO_4)_6O_{2-0.5x}$. The occupancy of the anionic O atom was fixed at $2 - 0.5x$. Constraints were applied so that the Nd and Ca on the same site had identical positional and displacement parameters.

Acknowledgements

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supporting information

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Computing details

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO* (Agilent, 2012); data reduction: *CrysAlis PRO* (Agilent, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010).

Dicalcium octaneodymium hexakis(orthosilicate) dioxide

Crystal data

$Ca_{2.49}Nd_{7.51}(SiO_4)_6O_{1.75}$
M_r = 1763.24
Hexagonal, $P6_3/m$
Hall symbol: -P 6c
a = 9.5507 (3) Å
c = 7.0513 (3) Å
V = 557.03 (3) Å^3
Z = 1
$F(000)$ = 790
D_x = 5.256 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1649 reflections
θ = 4.3–35.5°
μ = 18.18 mm^{-1}
T = 298 K
Block, light blue
0.05 × 0.05 × 0.05 mm

Data collection

Agilent SuperNova (single source at offset, Eos detector) diffractometer
Radiation source: SuperNova (Mo) X-ray Source
Mirror monochromator
Detector resolution: 15.9631 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2012)
T_{min} = 0.717, T_{max} = 1.000
2616 measured reflections
878 independent reflections
813 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 35.7°, θ_{min} = 3.8°
h = −15→15
k = −15→15
l = −11→5

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.035
S = 1.11
878 reflections
42 parameters
0 restraints
4 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0072P)^2 + 0.3232P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.79 e Å^{-3}
$\Delta\rho_{min}$ = −0.86 e Å^{-3}

Extinction correction: *SHELXL2014* (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0062 (2)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Nd1	0.24279 (2)	0.01102 (2)	0.2500	0.00756 (7)	0.887 (5)
Ca1	0.24279 (2)	0.01102 (2)	0.2500	0.00756 (7)	0.113 (5)
Nd2	0.6667	0.3333	−0.00110 (5)	0.00906 (10)	0.546 (4)
Ca2	0.6667	0.3333	−0.00110 (5)	0.00906 (10)	0.454 (4)
Si1	0.37185 (11)	0.40114 (11)	0.2500	0.0077 (2)	
O1	0.4886 (3)	0.3232 (3)	0.2500	0.0127 (5)	
O2	0.4707 (3)	0.5974 (3)	0.2500	0.0144 (5)	
O3	0.2528 (2)	0.3424 (3)	0.0659 (3)	0.0209 (5)	
O4	0.0000	0.0000	0.2500	0.0141 (10)	0.88

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Nd1	0.00740 (10)	0.00713 (10)	0.00733 (9)	0.00301 (7)	0.000	0.000
Ca1	0.00740 (10)	0.00713 (10)	0.00733 (9)	0.00301 (7)	0.000	0.000
Nd2	0.00913 (12)	0.00913 (12)	0.00892 (15)	0.00456 (6)	0.000	0.000
Ca2	0.00913 (12)	0.00913 (12)	0.00892 (15)	0.00456 (6)	0.000	0.000
Si1	0.0069 (4)	0.0079 (4)	0.0085 (4)	0.0039 (3)	0.000	0.000
O1	0.0116 (12)	0.0187 (13)	0.0123 (12)	0.0108 (10)	0.000	0.000
O2	0.0120 (12)	0.0085 (11)	0.0222 (14)	0.0049 (9)	0.000	0.000
O3	0.0158 (9)	0.0382 (13)	0.0131 (9)	0.0166 (9)	−0.0042 (7)	−0.0098 (8)
O4	0.0052 (12)	0.0052 (12)	0.032 (3)	0.0026 (6)	0.000	0.000

Geometric parameters (Å, º)

Nd1—Nd1^{i}	3.9284 (3)	Si1—Nd2^{viii}	3.2527 (8)
Nd1—Nd1^{ii}	3.9284 (3)	Si1—Nd2^{xi}	3.2527 (8)
Nd1—Nd2^{iii}	4.0666 (3)	Si1—Ca2^{xi}	3.2527 (8)
Nd1—Si1	3.2877 (9)	Si1—Ca2^{viii}	3.2527 (8)
Nd1—Si1^{i}	3.1738 (9)	Si1—O1	1.621 (3)
Nd1—O1	2.721 (3)	Si1—O2	1.623 (3)
Nd1—O2^{iv}	2.463 (3)	Si1—O3^{xii}	1.629 (2)
Nd1—O3^{v}	2.3909 (19)	Si1—O3	1.629 (2)

Nd1—O3^{vi}	2.3909 (19)	O1—Nd2^{iii}	2.4230 (17)
Nd1—O3^{i}	2.547 (2)	O1—Ca2^{iii}	2.4230 (17)
Nd1—O3^{vii}	2.547 (2)	O2—Nd1^{iii}	2.463 (3)
Nd1—O4	2.2681 (2)	O2—Ca1^{iii}	2.463 (3)
Nd2—Si1^{vi}	3.2527 (8)	O2—Nd2^{viii}	2.4715 (18)
Nd2—Si1^{viii}	3.2527 (8)	O2—Nd2^{xi}	2.4715 (18)
Nd2—Si1^{ix}	3.2527 (8)	O2—Ca2^{xi}	2.4715 (18)
Nd2—O1^{iii}	2.4231 (17)	O2—Ca2^{viii}	2.4715 (18)
Nd2—O1^{iv}	2.4231 (17)	O3—Nd1^{ii}	2.547 (2)
Nd2—O1	2.4230 (17)	O3—Nd1^{xiii}	2.3909 (19)
Nd2—O2^{viii}	2.4715 (18)	O3—Ca1^{xiii}	2.3909 (19)
Nd2—O2^{ix}	2.4715 (18)	O3—Ca1^{ii}	2.547 (2)
Nd2—O2^{vi}	2.4715 (18)	O3—Nd2^{viii}	2.830 (2)
Nd2—O3^{x}	2.830 (2)	O3—Ca2^{viii}	2.830 (2)
Nd2—O3^{viii}	2.830 (2)	O4—Nd1^{ii}	2.2681 (2)
Nd2—O3^{vi}	2.830 (2)	O4—Nd1^{i}	2.2681 (2)
Si1—Nd1^{ii}	3.1738 (9)	O4—Ca1^{ii}	2.2681 (2)
Si1—Ca1^{ii}	3.1738 (9)	O4—Ca1^{i}	2.2681 (2)

Nd1^{ii}—Nd1—Nd1^{i}	60.0	O3^{viii}—Nd2—Si1^{ix}	92.88 (4)
Nd1^{ii}—Nd1—Nd2^{iii}	103.981 (6)	O3^{vi}—Nd2—Si1^{viii}	92.88 (4)
Nd1^{i}—Nd1—Nd2^{iii}	150.673 (5)	O3^{vi}—Nd2—Si1^{vi}	30.06 (4)
Si1—Nd1—Nd1^{ii}	51.249 (17)	O3^{x}—Nd2—Si1^{viii}	123.63 (4)
Si1^{i}—Nd1—Nd1^{ii}	113.889 (17)	O3^{vi}—Nd2—O3^{viii}	117.44 (2)
Si1^{i}—Nd1—Nd1^{i}	53.889 (17)	O3^{x}—Nd2—O3^{vi}	117.45 (2)
Si1—Nd1—Nd1^{i}	111.249 (17)	O3^{x}—Nd2—O3^{viii}	117.45 (2)
Si1—Nd1—Nd2^{iii}	58.326 (14)	Nd1^{ii}—Si1—Nd1	74.86 (2)
Si1^{i}—Nd1—Nd2^{iii}	134.034 (14)	Nd1^{ii}—Si1—Nd2^{viii}	81.18 (2)
Si1^{i}—Nd1—Si1	165.14 (2)	Nd1^{ii}—Si1—Nd2^{xi}	81.18 (2)
O1—Nd1—Nd1^{ii}	80.66 (5)	Nd1^{ii}—Si1—Ca2^{xi}	81.18 (2)
O1—Nd1—Nd1^{i}	140.66 (5)	Nd1^{ii}—Si1—Ca2^{viii}	81.18 (2)
O1—Nd1—Nd2^{iii}	35.26 (3)	Ca1^{ii}—Si1—Nd1	74.86 (2)
O1—Nd1—Si1^{i}	165.45 (5)	Ca1^{ii}—Si1—Nd1^{ii}	0.000 (8)
O1—Nd1—Si1	29.41 (5)	Ca1^{ii}—Si1—Nd2^{xi}	81.18 (2)
O2^{iv}—Nd1—Nd1^{i}	120.15 (6)	Ca1^{ii}—Si1—Nd2^{viii}	81.18 (2)
O2^{iv}—Nd1—Nd1^{ii}	179.85 (6)	Ca1^{ii}—Si1—Ca2^{xi}	81.18 (2)
O2^{iv}—Nd1—Nd2^{iii}	75.88 (5)	Ca1^{ii}—Si1—Ca2^{viii}	81.18 (2)
O2^{iv}—Nd1—Si1	128.60 (6)	Nd2^{xi}—Si1—Nd1	139.386 (19)
O2^{iv}—Nd1—Si1^{i}	66.27 (6)	Nd2^{viii}—Si1—Nd1	139.386 (19)
O2^{iv}—Nd1—O1	99.18 (8)	Nd2^{xi}—Si1—Nd2^{viii}	65.31 (2)
O2^{iv}—Nd1—O3^{i}	71.01 (7)	Nd2^{xi}—Si1—Ca2^{viii}	65.31 (2)
O2^{iv}—Nd1—O3^{vii}	71.01 (7)	Ca2^{xi}—Si1—Nd1	139.386 (19)
O3^{v}—Nd1—Nd1^{i}	110.42 (6)	Ca2^{viii}—Si1—Nd1	139.386 (19)
O3^{i}—Nd1—Nd1^{i}	58.32 (5)	Ca2^{xi}—Si1—Nd2^{xi}	0.000 (10)
O3^{v}—Nd1—Nd1^{ii}	94.99 (5)	Ca2^{viii}—Si1—Nd2^{viii}	0.000 (10)
O3^{vi}—Nd1—Nd1^{i}	110.42 (6)	Ca2^{xi}—Si1—Nd2^{viii}	65.31 (2)
O3^{i}—Nd1—Nd1^{ii}	109.12 (5)	Ca2^{xi}—Si1—Ca2^{viii}	65.31 (2)
O3^{vii}—Nd1—Nd1^{ii}	109.12 (5)	O1—Si1—Nd1	55.53 (10)

O3^{vii}—Nd1—Nd1^{i}	58.32 (5)	O1—Si1—Nd1^{ii}	130.39 (10)
O3^{vi}—Nd1—Nd1^{ii}	94.99 (5)	O1—Si1—Ca1^{ii}	130.39 (10)
O3^{vi}—Nd1—Nd2^{iii}	94.52 (6)	O1—Si1—Nd2^{xi}	136.87 (6)
O3^{i}—Nd1—Nd2^{iii}	112.89 (5)	O1—Si1—Nd2^{viii}	136.87 (6)
O3^{vii}—Nd1—Nd2^{iii}	146.38 (5)	O1—Si1—Ca2^{viii}	136.87 (6)
O3^{v}—Nd1—Nd2^{iii}	42.90 (6)	O1—Si1—Ca2^{xi}	136.87 (6)
O3^{v}—Nd1—Si1	77.25 (5)	O1—Si1—O2	113.16 (14)
O3^{vi}—Nd1—Si1^{i}	106.70 (5)	O1—Si1—O3	111.34 (9)
O3^{i}—Nd1—Si1^{i}	30.67 (4)	O1—Si1—O3^{xii}	111.34 (9)
O3^{i}—Nd1—Si1	145.64 (5)	O2—Si1—Nd1^{ii}	116.45 (10)
O3^{vii}—Nd1—Si1^{i}	30.67 (4)	O2—Si1—Nd1	168.69 (10)
O3^{v}—Nd1—Si1^{i}	106.70 (5)	O2—Si1—Ca1^{ii}	116.45 (10)
O3^{vii}—Nd1—Si1	145.64 (5)	O2—Si1—Nd2^{viii}	47.71 (6)
O3^{vi}—Nd1—Si1	77.25 (5)	O2—Si1—Nd2^{xi}	47.70 (6)
O3^{v}—Nd1—O1	70.49 (5)	O2—Si1—Ca2^{xi}	47.70 (6)
O3^{i}—Nd1—O1	146.95 (5)	O2—Si1—Ca2^{viii}	47.71 (6)
O3^{vi}—Nd1—O1	70.49 (5)	O2—Si1—O3^{xii}	107.49 (10)
O3^{vii}—Nd1—O1	146.95 (5)	O2—Si1—O3	107.49 (10)
O3^{vi}—Nd1—O2^{iv}	84.96 (5)	O3^{xii}—Si1—Nd1^{ii}	52.89 (7)
O3^{v}—Nd1—O2^{iv}	84.96 (5)	O3^{xii}—Si1—Nd1	78.94 (9)
O3^{vii}—Nd1—O3^{i}	61.28 (9)	O3—Si1—Nd1^{ii}	52.89 (7)
O3^{vi}—Nd1—O3^{vii}	77.13 (4)	O3—Si1—Nd1	78.94 (9)
O3^{vi}—Nd1—O3^{i}	136.63 (7)	O3—Si1—Ca1^{ii}	52.89 (7)
O3^{v}—Nd1—O3^{vii}	136.63 (7)	O3^{xii}—Si1—Ca1^{ii}	52.89 (7)
O3^{v}—Nd1—O3^{i}	77.13 (4)	O3^{xii}—Si1—Nd2^{xi}	60.46 (9)
O3^{v}—Nd1—O3^{vi}	137.40 (11)	O3—Si1—Nd2^{xi}	111.52 (8)
O4—Nd1—Nd1^{i}	30.0	O3^{xii}—Si1—Nd2^{viii}	111.52 (8)
O4—Nd1—Nd1^{ii}	30.0	O3—Si1—Nd2^{viii}	60.46 (9)
O4—Nd1—Nd2^{iii}	130.005 (6)	O3^{xii}—Si1—Ca2^{xi}	60.46 (9)
O4—Nd1—Si1	81.249 (17)	O3^{xii}—Si1—Ca2^{viii}	111.52 (8)
O4—Nd1—Si1^{i}	83.888 (17)	O3—Si1—Ca2^{xi}	111.52 (8)
O4—Nd1—O1	110.66 (5)	O3—Si1—Ca2^{viii}	60.46 (9)
O4—Nd1—O2^{iv}	150.15 (6)	O3^{xii}—Si1—O3	105.63 (15)
O4—Nd1—O3^{vi}	104.58 (5)	Nd2^{iii}—O1—Nd1	104.33 (7)
O4—Nd1—O3^{vii}	83.45 (5)	Nd2—O1—Nd1	104.33 (7)
O4—Nd1—O3^{i}	83.45 (5)	Nd2^{iii}—O1—Nd2	93.89 (9)
O4—Nd1—O3^{v}	104.58 (5)	Ca2^{iii}—O1—Nd1	104.33 (7)
Si1^{vi}—Nd2—Si1^{viii}	93.628 (14)	Ca2^{iii}—O1—Nd2	93.89 (9)
Si1^{ix}—Nd2—Si1^{viii}	93.628 (14)	Ca2^{iii}—O1—Nd2^{iii}	0.000 (11)
Si1^{ix}—Nd2—Si1^{vi}	93.628 (14)	Si1—O1—Nd1	95.06 (11)
O1^{iv}—Nd2—Si1^{ix}	98.07 (6)	Si1—O1—Nd2	127.73 (7)
O1^{iii}—Nd2—Si1^{vi}	165.42 (5)	Si1—O1—Nd2^{iii}	127.73 (7)
O1^{iv}—Nd2—Si1^{vi}	94.28 (5)	Si1—O1—Ca2^{iii}	127.73 (7)
O1—Nd2—Si1^{vi}	98.07 (6)	Nd1^{iii}—O2—Nd2^{viii}	115.89 (7)
O1^{iii}—Nd2—Si1^{viii}	98.07 (6)	Nd1^{iii}—O2—Nd2^{xi}	115.89 (7)
O1^{iv}—Nd2—Si1^{viii}	165.42 (5)	Nd1^{iii}—O2—Ca2^{viii}	115.89 (7)
O1^{iii}—Nd2—Si1^{ix}	94.28 (5)	Nd1^{iii}—O2—Ca2^{xi}	115.89 (7)
O1—Nd2—Si1^{ix}	165.42 (5)	Ca1^{iii}—O2—Nd1^{iii}	0.000 (9)

O1—Nd2—Si1^{viii}	94.28 (5)	Ca1^{iii}—O2—Nd2^{xi}	115.89 (7)
O1^{iii}—Nd2—O1	72.49 (7)	Ca1^{iii}—O2—Nd2^{viii}	115.89 (7)
O1^{iv}—Nd2—O1^{iii}	72.49 (7)	Ca1^{iii}—O2—Ca2^{xi}	115.89 (7)
O1^{iv}—Nd2—O1	72.49 (7)	Ca1^{iii}—O2—Ca2^{viii}	115.89 (7)
O1—Nd2—O2^{vi}	125.79 (8)	Nd2^{xi}—O2—Nd2^{viii}	90.49 (8)
O1^{iv}—Nd2—O2^{vi}	94.22 (6)	Nd2^{xi}—O2—Ca2^{viii}	90.49 (8)
O1—Nd2—O2^{ix}	153.93 (8)	Nd2^{viii}—O2—Ca2^{viii}	0.0
O1^{iv}—Nd2—O2^{viii}	153.93 (8)	Ca2^{xi}—O2—Nd2^{viii}	90.49 (8)
O1^{iii}—Nd2—O2^{ix}	94.22 (6)	Ca2^{xi}—O2—Nd2^{xi}	0.0
O1^{iii}—Nd2—O2^{vi}	153.93 (8)	Ca2^{xi}—O2—Ca2^{viii}	90.49 (8)
O1^{iv}—Nd2—O2^{ix}	125.79 (8)	Si1—O2—Nd1^{iii}	122.72 (13)
O1—Nd2—O2^{viii}	94.22 (6)	Si1—O2—Ca1^{iii}	122.72 (13)
O1^{iii}—Nd2—O2^{viii}	125.79 (8)	Si1—O2—Nd2^{xi}	103.23 (9)
O1^{iii}—Nd2—O3^{vi}	139.76 (6)	Si1—O2—Nd2^{viii}	103.23 (9)
O1—Nd2—O3^{viii}	87.87 (7)	Si1—O2—Ca2^{xi}	103.23 (9)
O1^{iv}—Nd2—O3^{x}	68.15 (7)	Si1—O2—Ca2^{viii}	103.23 (9)
O1—Nd2—O3^{vi}	68.15 (7)	Nd1^{xiii}—O3—Nd1^{ii}	116.16 (8)
O1^{iii}—Nd2—O3^{x}	87.87 (7)	Nd1^{xiii}—O3—Ca1^{ii}	116.16 (8)
O1^{iv}—Nd2—O3^{viii}	139.76 (6)	Nd1^{ii}—O3—Nd2^{viii}	101.98 (7)
O1^{iv}—Nd2—O3^{vi}	87.87 (7)	Nd1^{xiii}—O3—Nd2^{viii}	101.99 (8)
O1^{iii}—Nd2—O3^{viii}	68.15 (7)	Nd1^{ii}—O3—Ca2^{viii}	101.98 (7)
O1—Nd2—O3^{x}	139.76 (6)	Nd1^{xiii}—O3—Ca2^{viii}	101.99 (8)
O2^{vi}—Nd2—Si1^{ix}	64.81 (6)	Ca1^{ii}—O3—Nd1^{ii}	0.000 (14)
O2^{ix}—Nd2—Si1^{viii}	64.81 (6)	Ca1^{xiii}—O3—Nd1^{xiii}	0.0
O2^{ix}—Nd2—Si1^{vi}	98.63 (5)	Ca1^{xiii}—O3—Nd1^{ii}	116.16 (8)
O2^{ix}—Nd2—Si1^{ix}	29.07 (6)	Ca1^{xiii}—O3—Ca1^{ii}	116.16 (8)
O2^{viii}—Nd2—Si1^{viii}	29.07 (6)	Ca1^{ii}—O3—Nd2^{viii}	101.98 (7)
O2^{viii}—Nd2—Si1^{ix}	98.63 (5)	Ca1^{xiii}—O3—Nd2^{viii}	101.99 (8)
O2^{viii}—Nd2—Si1^{vi}	64.81 (6)	Ca1^{ii}—O3—Ca2^{viii}	101.98 (7)
O2^{vi}—Nd2—Si1^{vi}	29.07 (6)	Ca1^{xiii}—O3—Ca2^{viii}	101.99 (8)
O2^{vi}—Nd2—Si1^{viii}	98.63 (5)	Ca2^{viii}—O3—Nd2^{viii}	0.000 (14)
O2^{vi}—Nd2—O2^{viii}	75.14 (6)	Si1—O3—Nd1^{xiii}	141.68 (11)
O2^{vi}—Nd2—O2^{ix}	75.14 (6)	Si1—O3—Nd1^{ii}	96.43 (9)
O2^{ix}—Nd2—O2^{viii}	75.14 (6)	Si1—O3—Ca1^{xiii}	141.68 (11)
O2^{vi}—Nd2—O3^{viii}	125.24 (6)	Si1—O3—Ca1^{ii}	96.43 (9)
O2^{vi}—Nd2—O3^{x}	66.19 (7)	Si1—O3—Nd2^{viii}	89.48 (10)
O2^{viii}—Nd2—O3^{viii}	58.84 (7)	Si1—O3—Ca2^{viii}	89.48 (10)
O2^{ix}—Nd2—O3^{x}	58.84 (7)	Nd1^{i}—O4—Nd1^{ii}	120.0
O2^{vi}—Nd2—O3^{vi}	58.85 (7)	Nd1—O4—Nd1^{ii}	120.0
O2^{viii}—Nd2—O3^{x}	125.24 (6)	Nd1—O4—Nd1^{i}	120.0
O2^{ix}—Nd2—O3^{viii}	66.19 (7)	Nd1—O4—Ca1^{ii}	120.0
O2^{ix}—Nd2—O3^{vi}	125.24 (6)	Nd1^{i}—O4—Ca1^{ii}	120.0
O2^{viii}—Nd2—O3^{vi}	66.19 (7)	Nd1—O4—Ca1^{i}	120.0
O3^{vi}—Nd2—Si1^{ix}	123.63 (4)	Ca1^{i}—O4—Nd1^{i}	0.000 (16)
O3^{viii}—Nd2—Si1^{viii}	30.06 (4)	Ca1^{ii}—O4—Nd1^{ii}	0.000 (9)
O3^{x}—Nd2—Si1^{ix}	30.06 (4)	Ca1^{i}—O4—Nd1^{ii}	120.0

O3^{x}—Nd2—Si1^{vi}	92.88 (4)	Ca1^{i}—O4—Ca1^{ii}	120.0
O3^{viii}—Nd2—Si1^{vi}	123.63 (4)		

Symmetry codes: (i) −*x*+*y*, −*x*, −*z*+1/2; (ii) −*y*, *x*−*y*, *z*; (iii) −*x*+*y*+1, −*x*+1, −*z*+1/2; (iv) −*y*+1, *x*−*y*, *z*; (v) *y*, −*x*+*y*, *z*+1/2; (vi) *y*, −*x*+*y*, −*z*; (vii) −*x*+*y*, −*x*, *z*; (viii) −*x*+1, −*y*+1, −*z*; (ix) *x*−*y*+1, *x*, *z*−1/2; (x) *x*−*y*+1, *x*, −*z*; (xi) *x*−*y*, *x*, *z*+1/2; (xii) *x*, *y*, −*z*+1/2; (xiii) *x*−*y*, *x*, *z*−1/2.