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Letnikovite-(Ce), (Na□)Ca$_2$Ce$_2$[Si$_7$O$_{17}$(OH)]F$_4$(H$_2$O)$_4$, a new mineral from the Darai-Pioz alkaline massif, Tajikistan: mineral description, crystal structure and a new single [Si$_7$O$_{17}$(OH)] sheet

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Abstract

Letnikovite-(Ce), ideally (Na□)Ca$_2$Ce$_2$[Si$_7$O$_{17}$(OH)]F$_4$(H$_2$O)$_4$, is a new mineral with no natural or synthetic analogues (IMA2022–132). The mineral occurs at the Darai-Pioz alkaline massif, Tien-Shan mountains, Tajikistan, in a silexite-like peralkaline pegmatite. Letnikovite-(Ce) occurs as isolated prismatic grains up to 0.03×0.1 mm in a quartz–pectolite aggregate. Associated minerals are quartz, fluorite, pectolite, baratovite, aegirine, leucosphenite, neptunite, reedmergnerite, orlovite, sokolovaite, mendeleevite-(Ce), odigitriaite, pekovite, zeravshanite, kirchhoffite and garmite. The mineral is colourless with a vitreous lustre and a white streak, and $D_{calc.}$ is 2.847 g/cm^3. Letnikovite-(Ce) is monoclinic, $C2/m$, $a = 7.4726(3)$, $b = 22.9196(9)$, $c = 13.9360(6)$ Å, $\beta = 105.550(5)°$ and $V = 2299.43(17)$ Å^3. The chemical composition of letnikovite-(Ce) is SiO$_2$ 42.38, Gd$_2$O$_3$ 0.16, Eu$_2$O$_3$ 0.28, Sm$_2$O$_3$ 0.07, Nd$_2$O$_3$ 5.64, Pr$_2$O$_3$ 1.69, Ce$_2$O$_3$ 11.73, La$_2$O$_3$ 2.24, PbO 1.22, SrO 5.77, FeO 0.32, CaO 11.87, MgO 1.14, Cs$_2$O 0.57, K$_2$O 0.65, Na$_2$O 2.24, H$_2$O 7.79, F 7.29, O = F −3.07, total 99.98 wt.%. The empirical formula calculated on 7 Si apfu is Na$_{0.72}$K$_{0.14}$Cs$_{0.04}$Ca$_{2.10}$Sr$_{0.55}$Mg$_{0.28}$Pb$_{0.05}$Fe$_{0.04}$(Ce$_{0.71}$Nd$_{0.33}$La$_{0.14}$Pr$_{0.10}$Eu$_{0.02}$Gd$_{0.01}$)$_{\Sigma1.31}$Si$_7$O$_{21.84}$F$_{3.81}$H$_{8.58}$ for $Z = 4$. The structural formula is (Na$_{0.72}$Ca$_{0.16}$□$_{1.12}$)$_{\Sigma2}$(Cs$_{0.04}$□$_{0.96}$)$_{\Sigma1}$(Ca$_{1.83}$□$_{0.17}$)$_{\Sigma2}$(Mg$_{0.28}$Fe$_{0.04}$□$_{0.68}$)$_{\Sigma1}$($Ln^{3+}_{1.31}$Sr$_{0.55}$Ca$_{0.09}$Pb$_{0.05}$)$_{\Sigma2}$[Si$_7$O$_{17}$(OH)]F$_{3.81}$(H$_2$O)$_{3.79}$, where $Ln^{3+}_{1.31}$ = (Ce$_{0.71}$Nd$_{0.33}$La$_{0.14}$Pr$_{0.10}$Eu$_{0.02}$Gd$_{0.01}$)$_{\Sigma1.31}$. The simplified formula is (Na,□)$_2$Ca$_2$(Ln^{3+},Sr)$_2$[Si$_7$O$_{17}$(OH)]F$_4$(H$_2$O)$_4$, where Ce is the dominant lanthanoid. The crystal structure was solved by direct methods and refined to an R_1 index of 4.2%. In letnikovite-(Ce), the main structural unit is a layer which consists of the central heteropolyhedral Ca–Ce sheet and two adjacent single [Si$_7$O$_{17}$(OH)] sheets parallel to (001). In the Si–O–OH sheet, the Si tetrahedra form five-membered and ten-membered rings. This is the first occurrence of a single [Si$_7$O$_{17}$(OH)]$^{7-}$ sheet in a mineral. The layers connect via Na and Cs at the interstitial A(1,2) sites, H$_2$O groups and hydrogen bonding. The mineral is named in honour of Felix Artem'evich Letnikov (born October 3rd,1934) in recognition of his outstanding contributions to the field of petrology and geochemistry of Precambrian rocks.

Introduction

This paper reports the description and the crystal structure of letnikovite-(Ce) [Russian Cyrillic: летниковит-(Ce)], ideally (Na□)Ca$_2$Ce$_2$[Si$_7$O$_{17}$(OH)]F$_4$(H$_2$O)$_4$, a new mineral from the well-known Darai-Pioz alkaline massif, Tien-Shan Mountains, Central Tajikistan. Letnikovite-(Ce) is a sheet-silicate mineral with large channels and potentially can be used as a model for synthesis of microporous materials of industrial interest.

Single-crystal X-ray diffraction studies revealed a single [Si$_7$O$_{17}$(OH)]$^{7-}$ sheet of five-membered and ten-membered rings of SiO$_4$ and SiO$_3$(OH) tetrahedra that has never been described in minerals (Hawthorne *et al.*, 2019). The mineral is named for Professor Felix Artem'evich Letnikov (Russian Cyrillic: Феликс Артемьевич Летников) (born October 3rd, 1934, Polotsk, USSR), Academician of the Russian Academy of Sciences, a prominent geologist working on the petrology and geochemistry of Precambrian rocks. Professor Letnikov has had a major impact on the principal areas of his work and has made a significant contribution to the organisation of science in Siberia. The new mineral and its name (symbol Lkv-Ce) have been approved by the Commission on New Minerals, Nomenclature and Classification, International Mineralogical Association (IMA2022–132, Agakhanov *et al.*, 2023).

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The holotype material is deposited in the systematic collection of the Fersman Mineralogical Museum, Moscow, Russia, catalogue number 98145.

Occurrence and associated minerals

Letnikovite-(Ce) was found in the moraine of the Darai-Pioz glacier in the upper reaches of the Darai-Pioz River, Tien-Shan mountains, near the junction of the Turkestansky, Zeravshansky and Alaisky ranges (39°30′N 70°40′E). This area is in the Rasht (formerly Garm) district, Central Tajikistan. The alkaline Darai-Pioz massif belongs to the Upper Paleozoic Alaysky (Matchaisky) intrusive complex. Information on the geology of the Darai-Pioz massif can be found in Pautov *et al.* (2019) with reference to relevant earlier publications.

Letnikovite-(Ce) was found in boulders (up to 2 m) of quartz rock, 90–95% medium- to coarse-grained quartz of ice-like appearance (quartz grains vary from 2 mm to 2 cm) characteristic for moraine deposits of the Darai-Pioz glacier. The following subordinate and accessory minerals are present: large (up to 10 cm across) golden-brown tabular and lamellar crystals of polylithionite, pink plates of sogdianite–sugilite, pale-yellow to orange aggregates and tabular crystals of reedmergnerite, black crystals of aegirine, orange–brown semi-transparent lentil-like crystals of stillwellite-(Ce), grass-green or yellowish-green semi-transparent and transparent crystals of leucosphenite, dark-green crystals of turkestanite and aggregates of large white grains of microcline. Also common are fine-grained brown or greyish-brown aggregates of Mn-bearing pectolite, quartz, Sr-bearing fluorite, aegirine and a variety of rare minerals; letnikovite-(Ce) occurs in these pectolite-rich aggregates (Fig. 1a). Associated minerals are quartz, fluorite, pectolite, baratovite, aegirine, leucosphenite, neptunite, reedmergnerite, orlovite, sokolovaite, mendeleevite-(Ce), odigitriaite, pekovite, zeravshanite, kirchhoffite and garmite. Letnikovite-(Ce) occurs in a peralkaline pegmatite oversaturated with silica (silexite-like) and was formed at a late, probably hydrothermal, stage of the pegmatite.

Physical properties

Letnikovite-(Ce) occurs as isolated prismatic grains up to 0.1 mm long and up to 0.03 mm thick in a quartz–pectolite aggregate (Fig. 1a,b). The mineral is colourless and has a white streak and a vitreous lustre. Letnikovite-(Ce) does not fluoresce under cathode rays or ultraviolet light. The mineral is brittle, cleavage is {001} perfect, the fracture is stepped along the cleavage plane and uneven across this direction; no parting was observed. The average micro-indentation hardness is VHN50 = 239 kg/mm^2 (with a range of 193–266). Although micro-indentation and Mohs hardness are different hardness measurements (Broz *et al.*, 2006), the first representing the resistance to indentation and the second one the resistance to scratch, the present value of micro-indentation hardness corresponds roughly to a Mohs hardness of ∼4. Measurements were done on the PMT-3 instrument, calibrated on NaCl at a loading of 50 g. The calculated density, $D_{calc.}$, is 2.847 g/cm^3.

Macroscopically, the crystals do not show twinning. However, because of the microscopic twinning, the 2V value and optic sign could not be determined. Letnikovite-(Ce) is nonpleochroic. In reflected light, letnikovite-(Ce) is grey. Bireflectance is weak, $\Delta R = 0.8\%$ (589 nm). When observed in air, internal reflections were not seen, and anisotropy is not visible. Reflectance values
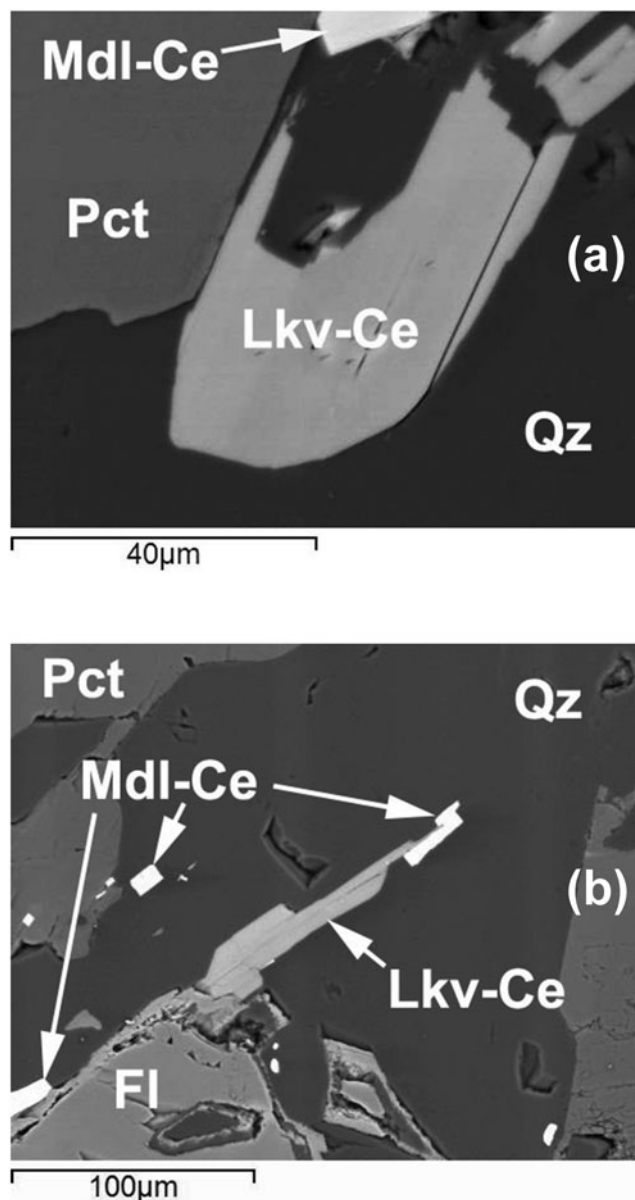
Figure 1. Back-scatter electron images of polished sections with letnikovite-(Ce) [Lkv-Ce] in association with mendeleevite-(Ce) [Mdl-Ce], pectolite [Pct], fluorite [Fl] and quartz [Qz]: (a) the grain used for Raman spectroscopy, determination of micro-indentation hardness and reflectance spectra; (b) a microprobe mount with a grain that was deposited as holotype material (#98145) at the Fersman Mineralogical Museum.

were measured with a UMSP-50 Opton microspectrophotometer using the Opton SiC standard 474251 (with a spectral slot width of 10 nm) and are given in Table 1.

Raman spectroscopy

The Raman spectrum of letnikovite-(Ce) (Fig. 2a,b) was obtained at room temperature from a randomly oriented crystal (polished section, 70 × 30 μm size) using a Thermo DXR2xi Raman imaging confocal microscope with a green laser (532 nm). The output power of the laser beam was 5 mW (at 50% power), holographic diffraction grating with 4000 lines per cm, spectral resolution was 2 cm^{-1}, and the range was from 50 to 6000 cm^{-1}. The diameter of the focal spot on the sample was 2 μm. The back-

Table 1. Reflectance values (%) for letnikovite-(Ce).*

R_{max}	R_{min}	λ (nm)	R_{max}	R_{min}	λ (nm)
5.3	4.7	400	5.1	4.3	560
5.1	4.6	420	5.0	4.2	580
4.9	4.4	440	**5.0**	**4.2**	**589**
4.7	4.2	460	4.9	4.1	600
4.7	**4.2**	**470**	4.8	4.0	620
4.7	4.1	480	4.8	4.0	640
4.9	4.2	500	**4.8**	**4.0**	**650**
5.1	4.3	520	4.8	4.1	660
5.1	4.3	540	4.9	4.3	680
5.1	**4.3**	**546**	4.9	4.4	700

*The values required by the COM are given in bold.

scattered Raman signal was collected with a 100× objective; the signal acquisition time for a single scan from 50–6000 cm⁻¹ was 0.5 s and the signal was averaged over 1000 scans. For the range 50–1800 cm⁻¹ the signal acquisition time was 2.0 s and the signal was averaged over 30 scans. The spectrum was processed using *Omnic* software (Thermo Scientific™). Letnikovite-(Ce) shows intensive luminescence from 100 to 3500 cm⁻¹, and background subtraction was applied.

On the basis of data for some ring silicates with Na, Ca and rare earth elements (REE) (Sitarz *et al.*, 1998; Frost and Xi, 2012; Tobbens *et al.*, 2008), we assign the bands at 1107 and 952 cm⁻¹ to Si–O stretching vibrations, and those at 667 and 693 cm⁻¹ are attributed to O–Si–O bending modes. Raman bands of lower frequency (500–100 cm⁻¹, Fig. 2a) are assigned to Me–O stretching vibrations and collective lattice vibrations and translational and deformation modes, including the intense band at 464 cm⁻¹ which probably corresponds to a Ca–O stretching mode (Frost and Xi, 2012).

From 3000–3700 cm⁻¹ (Fig. 2b), there are several broad peaks (3233, 3402 and 3553 cm⁻¹) corresponding to stretching modes of H_2O and OH groups.

Chemical composition

The chemical composition of letnikovite-(Ce) was determined using a JEOL 773 electron-microprobe (EDS mode, an accelerating voltage of 20 kV, a beam current of 2 nA and a beam diameter
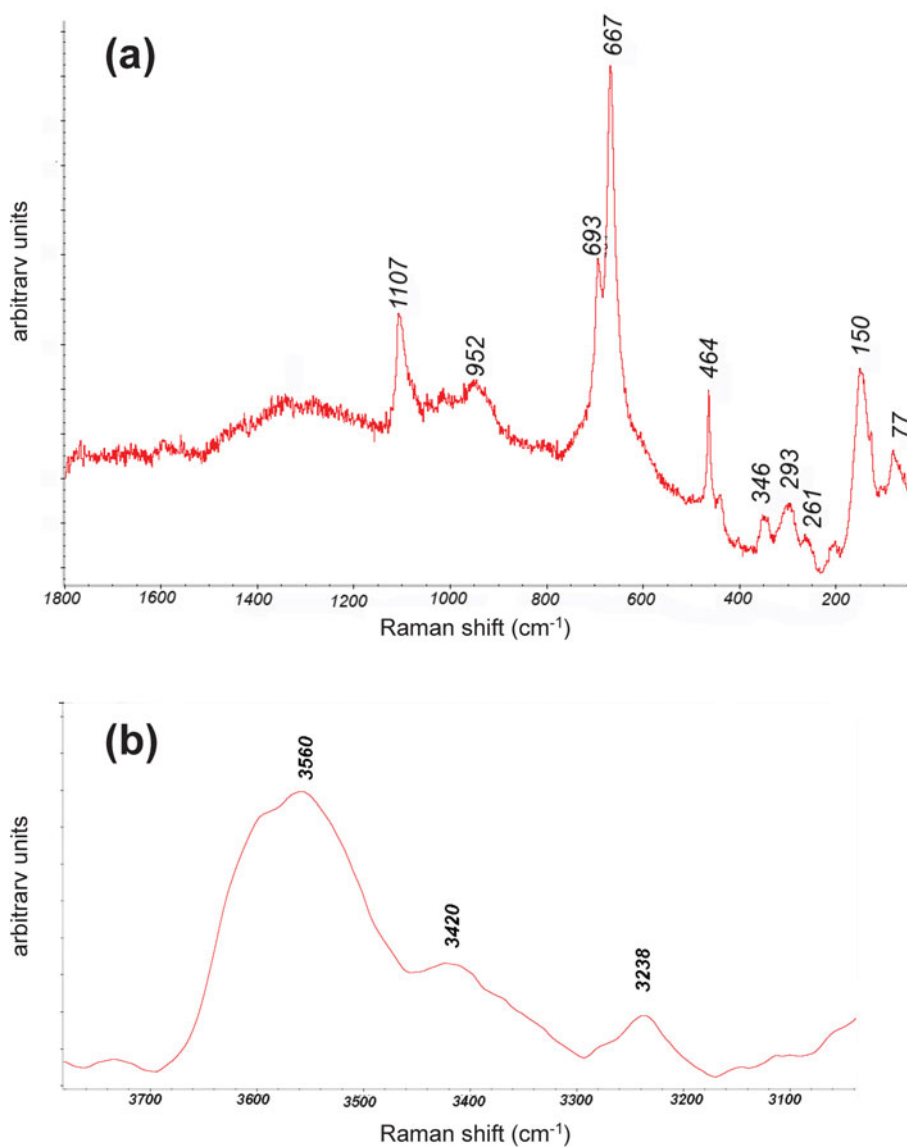

Figure 2. Background-subtracted Raman spectrum of letnikovite-(Ce): (a) the 'fingerprint' region from 50–1800 cm⁻¹; and (b) the principal O–H stretching region from 3000–3800 cm⁻¹.

of 5 μm; Fersman Mineralogical Museum). The following standards were used: microcline USNM 143966 (Si; K); albite 107 (Na); SrTiO₃ (Sr); CsTbP₄O₁₂ (Cs); ilmenite USNM 96189 (Fe); anorthite USNM 137041 (Ca); diopside USNM 11773 (Mg); LaPO₄ (La); CePO₄ (Ce); PrPO₄ (Pr); NdPO₄ (Nd); SmPO₄ (Sm); EuPO₄ (Eu); GdPO₄ (Gd); and MgF₂ (F).

The data (5 analyses) were reduced and corrected by the *PAP* method of Pouchou and Pichoir (1985). The chemical composition of letnikovite-(Ce) is the mean of five determinations and is given in Table 2. The empirical formula calculated on 7 Si atoms per formula unit (apfu) is $Na_{0.72}K_{0.14}Cs_{0.04}Ca_{2.10}Sr_{0.55}Mg_{0.28}$ $Pb_{0.05}Fe_{0.04}(Ce_{0.71}Nd_{0.33}La_{0.14}Pr_{0.10}Eu_{0.02}Gd_{0.01})_{\Sigma1.31}Si_7O_{21.84}F_{3.81}$ $H_{8.58}$, $Z = 4$. The structural formula based on refined site-occupancies (see below) is $(Na_{0.72}Ca_{0.16}\square_{1.12})_{\Sigma2}(Cs_{0.04}\square_{0.96})_{\Sigma1}$ $(Ca_{1.83}\square_{0.17})_{\Sigma2}(Mg_{0.28}Fe_{0.04}\square_{0.68})_{\Sigma1}(Ln^{3+}_{1.31}Sr_{0.55}Ca_{0.09}Pb_{0.05})_{\Sigma2}$ $[Si_7O_{17}(OH)]F_{3.81}(H_2O)_{3.79}$, where $Ln^{3+}_{1.31} = (Ce_{0.71}Nd_{0.33}La_{0.14}$ $Pr_{0.10}Eu_{0.02}Gd_{0.01})_{\Sigma1.31}$. The simplified formula is $(Na,\square)_2Ca_2(Ln^{3+},$ $Sr)_2[Si_7O_{17}(OH)]F_4(H_2O)_4$, where Ce is the dominant lanthanoid and $(\square,Cs)$ and $(\square,Mg)$ are omitted as $\square > 70\%$. The ideal formula of letnikovite-(Ce), $(Na\square)Ca_2Ce_2[Si_7O_{17}(OH)]F_4(H_2O)_4$ (see below), requires (wt.%) Na₂O 3.04, CaO 11.03, Ce₂O₃ 32.28, SiO₂ 41.36, F 7.47, H₂O 7.97, O ≡ F −3.15, total 100.00.

Powder X-ray diffraction

Powder X-ray diffraction data were obtained by collapsing single-crystal experimental data into two dimensions. Data (in Å for MoKα) are listed in Table 3. Unit-cell parameters are therefore the same as from the single-crystal data (Table 4).

X-ray single-crystal data collection and structure solution and refinement

X-ray single-crystal data for letnikovite-(Ce) were collected from a twinned crystal with a Rigaku Oxford Diffraction diffractometer equipped with a Mo micro-source X-ray tube and a Dectris Pilatus-200 K detector, controlled by the *Crysalis-Pro*™ software (Rigaku Oxford Diffraction, 2018). The intensities of reflections with $-13 \leq h \leq 13$, $-41 \leq k \leq 41$ and $-25 \leq l \leq 25$ were collected with a frame width of 0.5° and a frame time of 40 s up to $2\theta \leq 81.34°$, and an empirical absorption correction (*SCALE3 ABSPACK*, Rigaku Oxford Diffraction, 2018) was applied. There were few observed reflections at high 2θ, and refinement of the structure was done for $2\theta \leq 54°$, $-9 \leq h \leq 9$, $-29 \leq k \leq 29$ and $-17 \leq l \leq 17$. The observed lattice is metrically orthorhombic *F* with the following cell parameters obtained from the monoclinic cell via the transformation matrix $\bar{1}00/102/010$: a = 7.473, b = 26.852 and c = 22.920 Å. However, a tentative structure solution in space group *F*222 yielded wrong coordination geometries as well as ill-defined anisotropic displacement parameters. The monoclinic cell with half-cell volume led to a much more satisfactory solution. The crystal-structure solution by direct methods and refinement were done with the Bruker *SHELXTL* Version 5.1 software (Sheldrick, 2015) in space group *C*2/*m*. We refined the structure as two components related by the TWIN matrix ($\bar{1}$ 0 0, 0 $\bar{1}$ 0, 1 0 1). The crystal structure of letnikovite-(Ce) was refined to $R_1 = 4.20\%$, the twin ratio being 0.502(5):0.498(5) (Table 4). Details of data collection and structure refinement are given in Table 4. The occupancies of six cation sites were refined with the following scattering curves: *M*1 site: Ce; *M*(2,3) sites: Ca; *M*4 site: Mg; *A*1 and *A*2 sites: Na and Cs, respectively. The occupancies of the *X*(1–4) and *W*(1–5)

anion sites were refined with the scattering curves of F and O, respectively. Refinement of the *X*2 and *W*1 site-occupancies converged to integer values (within 3 e.s.d.) and were subsequently fixed at full occupancy. Scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson, 1992). Final atom coordinates and equivalent displacement

Table 2. Chemical composition and unit formula for letnikovite-(Ce).

	Chemical composition			Unit formula*	
	wt.%	Range	Esd	(apfu)	
SiO₂	42.38	42.05–43.31	0.37	Si	7.00
Gd₂O₃	0.16	0.01–0.36	0.13	Gd	0.01
Eu₂O₃	0.28	0.09–0.47	0.14	Eu	0.02
Sm₂O₃	0.07	0.01–0.16	0.06	Sm	0.00
Nd₂O₃	5.64	5.19–6.03	0.33	Nd	0.33
Pr₂O₃	1.69	1.33–1.97	0.24	Pr	0.10
Ce₂O₃	11.73	11.18–12.06	0.35	Ce	0.71
La₂O₃	2.24	1.95–2.44	0.12	La	0.14
PbO	1.22	0.97–1.33	0.15	Pb	0.05
SrO	5.77	5.16–6.14	0.36	Sr	0.55
FeO	0.32	0.24–0.48	0.10	Fe	0.04
CaO	11.87	11.64–12.14	0.18	Ca	2.10
MgO	1.14	1.02–1.34	0.13	Mg	0.28
Cs₂O	0.57	0.45–0.70	0.12	Cs	0.04
K₂O	0.65	0.01–1.28	0.43	K	0.14
Na₂O	2.24	1.79–2.51	0.27	Na	0.72
F	7.29	6.53–7.63	0.32	F	3.81
H₂O**	7.79			H	8.58
Sum	103.05				
O = F	−3.07				
Total	99.98				

*Formula calculated on 7 Si apfu; Esd = estimated standard deviation.
**H₂O calculated from structure-refinement results: H₂O = 3.79 pfu and OH = 1.0 pfu.

Table 3. Simulated powder X-ray diffraction data (*d* in Å) * for letnikovite-(Ce).

$I_{est.}$	d_{calc}	h	k	l	$I_{est.}$	$d_{calc.}$	h	k	l	$I_{est.}$	$d_{calc.}$	h	k	l
33	5.270	0	4	1	45	2.153	$\bar{2}$	8	3	21	1.717	$\bar{4}$	4	4
23	3.820	0	6	0		2.153	2	8	1		1.717	4	4	0
47	3.581	1	5	$\bar{2}$	24	2.090	$\bar{2}$	6	5	30	1.706	$\bar{2}$	0	8
	3.581	1	5	1		2.090	2	6	3		1.706	2	0	6
67	**3.527**	0	4	3		2.084	0	4	6		1.701	$\bar{2}$	12	1
54	**3.357**	0	0	4	34	2.040	0	10	3	30	1.687	$\bar{2}$	12	2
37	3.264	2	0	1		2.038	$\bar{2}$	4	6		1.687	2	12	0
58	**3.221**	0	$\bar{2}$	4		2.038	2	4	4	28	1.651	$\bar{4}$	4	5
100	**3.140**	$\bar{2}$	2	1	23	1.920	$\bar{2}$	0	7		1.651	4	4	1
	3.130	2	4	$\bar{1}$		1.920	2	0	5		1.649	$\bar{2}$	12	3
60	**3.048**	$\bar{2}$	4	2		1.918	0	0	7		1.649	2	12	1
	3.048	2	4	0	**56**	**1.882**	$\bar{2}$	8	5	28	1.635	$\bar{2}$	4	8
65	**2.896**	0	4	4		1.882	2	8	3		1.635	2	4	6
34	2.671	$\bar{2}$	6	1	50	1.868	$\bar{4}$	0	2		1.632	$\bar{4}$	0	6
29	2.635	0	8	2	34	1.850	$\bar{4}$	0	3		1.632	4	0	2
31	2.413	0	8	3		1.850	$\bar{4}$	0	1	25	1.594	0	8	7
36	2.294	$\bar{2}$	6	4	22	1.820	$\bar{2}$	4	7		1.591	0	14	2
	2.294	2	6	2		1.820	2	4	5	20	1.570	4	4	2
	2.289	$\bar{2}$	4	5		1.819	0	4	7		1.570	$\bar{4}$	4	6
	2.289	2	4	3	22	1.764	0	8	6		1.479	$\bar{2}$	4	9
50	**2.242**	$\bar{2}$	8	2		1.761	$\bar{4}$	4	3		1.479	2	4	7
	2.242	2	8	0		1.761	$\bar{4}$	4	1		1.477	$\bar{4}$	8	5
	2.238	0	0	6		1.757	0	12	3	22	1.477	4	8	5
39	2.181	$\bar{2}$	0	6	31	1.735	$\bar{2}$	8	6					
	2.181	2	0	4		1.735	2	8	4					
	2.179	0	8	4										

*Powder data were obtained by collapsing single-crystal X-ray diffraction data into two dimensions.
Intensities are listed for reflections with $I_{est.} \geq 20$; the eight strongest peaks are marked in bold.

Table 4. Miscellaneous structure-refinement data for letnikovite-(Ce).

Crystal data
a (Å)	7.4726(3)
b (Å)	22.9196(9)
c (Å)	13.9360(6)
β (°)	105.550(5)
V (Å^3)	2299.43(17)
Space group	$C2/m$
Z	4
Absorption coefficient (mm^{-1})	5.38
$F(000)$	1894.4
$D_{calc.}$ (g/cm^3)	2.847
Data collection	
Crystal size (mm)	0.047 × 0.026 × 0.022
Radiation/filter	Mo$K\alpha$/graphite
2θ-range for structure refinement (°)	5.93–54.00
Ratio of twin components*	0.502(5) : 0.498(5)
$R(\sigma)$ (%)	3.67
Reflections collected	27160
Independent reflections	2580
$F_o > 4\sigma F$	2126
Refinement	
Refinement method	Full-matrix least squares on F^2, fixed weights proportional to $1/\sigma F_o^2$
No. of refined parameters	183
Final $R_{(obs)}$ (%) [$F_o > 4\sigma F$]	4.20
R_1	5.62
wR_2	11.64
Highest peak, deepest hole (e$^-$ Å^{-3})	+2.03, –2.24
Goodness of fit on F^2	1.124

*Twin components are related by the transformation matrix ($\bar{1}$ 0 0, 0 $\bar{1}$ 0, 1 0 1).

parameters are given in Table 5, selected interatomic distances and angles in Table 6, refined site-scattering values and assigned site-populations in Table 7, and bond-valence values

in Tables 8 and 9. A list of observed and calculated structure factors and a Crystallographic Information File (CIF) have been deposited with the Principal Editor of *Mineralogical Magazine* and are available as Supplementary Material (see below). The structure diagrams were drawn using *Atoms 6.4* software (Dowty, 2016).

Site-population assignment

Firstly, we assign Si to four tetrahedrally coordinated *Si* sites, with <Si–O> = 1.619 Å (Tables 5, 6).

Next considered are the four *M* sites in the heteropolyhedral sheet (Table 5). At the [9]-coordinated *M*1 site, the refined scattering is 104.5 electrons per formula unit (epfu), the highest value for the *M* sites; the mean bond length <M1–φ> = 2.539 Å (φ = O, F and H_2O). In accord with the grand mean bond length <[9]Ce^{3+}–O> = 2.553 Å observed in inorganic structures (Gagné, 2018), we assign heavy scatters: REE = $Ln_{1.31}^{3+}$, where Ce is the dominant lanthanoid (*Ln* = lanthanoids) and minor Pb: 0.05 apfu, plus Sr: 0.55 apfu and minor Ca: 0.09 apfu, to the *M*1 site [[9]Ce^{3+}: r = 1.196 Å, [9]Sr: r = 1.31, [9]Pb: r = 1.35 Å, [9]Ca^{2+}: r = 1.18 Å, Shannon (1976)] (Tables 5–7). There is a good agreement between refined and calculated site-scattering for the *M*1 site: 104.5 and 103.56 epfu, respectively (Table 7). On the basis of the refined site-scattering values and observed bond distances, we assign Ca$_{0.83}\square_{0.17}$ and Ca$_{1.0}$ apfu to the *M*2 and *M*3 sites, respectively (Table 7). The remaining M4 octahedron is the smallest polyhedron, and the refined scattering at the *M*4 site is 4.4 epfu, the lowest value for the *M* sites. Therefore, we allocate all the available Mg and Fe^{2+} to the *M*4 site, and the composition of the site is Mg$_{0.28}$Fe$_{0.04}^{2+}\square_{0.68}$ apfu.

Table 5. Atom coordinates, site occupancies (Site occ., %) and anisotropic displacement parameters (Å^2) for letnikovite-(Ce).

Atom	Site occ.*	x	y	z	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}	U_{eq} **
M1	100	0.24623(16)	0.36734(2)	0.49258(3)	0.0085(6)	0.0224(3)	0.0179(3)	0.00347(18)	0.0021(12)	0.0010(5)	0.01656(18)
M2	83	0.5703(9)	0	0.6398(4)	0.006(2)	0.011(2)	0.016(3)	0	0.001(2)	0	0.0114(14)
M3	100	0.9352(9)	0	0.3619(4)	0.021(2)	0.019(2)	0.028(3)	0	–0.006(2)	0	0.0249(11)
M4	32	0	0.2496(11)	½	0.007(8)	0.024(6)	0.029(6)	0	–0.001(14)	0	0.021(4)
A1	44	0.418(3)	0.5769(4)	0.8343(6)	0.028(7)	0.037(5)	0.066(6)	0.010(4)	0.022(9)	0.023(9)	0.042(3)
A2	4	0	0.7157(15)	0	0.05(4)	0.069(19)	0.07(2)	0	–0.05(6)	0	0.076(10)
Si1	100	0.1516(5)	0.31549(18)	0.7167(3)	0.0033(19)	0.015(2)	0.013(2)	–0.0017(18)	–0.0005(17)	0.0007(15)	0.0108(10)
Si2	100	0.4367(5)	0.31578(17)	0.2816(3)	0.009(2)	0.0052(18)	0.011(2)	–0.0007(17)	–0.0030(17)	0.0016(15)	0.0093(9)
Si3	100	0.1123(8)	0.39892(8)	0.22744(13)	0.0075(14)	0.0129(9)	0.0136(8)	0.0014(7)	0.002(3)	0.001(3)	0.0116(4)
Si4	100	0.6821(5)	0	0.1147(3)	0.0156(17)	0.0156(17)	0.0126(16)	0	0.0065(16)	0	0.0141(7)
O1	100	–0.0648(18)	0.5567(2)	0.8669(4)	0.008(3)	0.014(2)	0.022(3)	0.004(2)	–0.011(5)	–0.001(6)	0.0176(12)
O2	100	0.887(2)	0	0.1899(10)	0.059(10)	0.041(7)	0.012(5)	0	0.013(6)	0	0.037(4)
O3	100	0.376(2)	0.3292(2)	0.7480(4)							0.0216(11)**
O4	100	0.2851(16)	0.6415(5)	0.2127(10)	0.018(4)	0.030(5)	0.022(4)	–0.005(3)	0.005(3)	–0.021(3)	0.023(3)
O5	100	0.061(2)	0.3272(4)	0.6029(7)	0.028(7)	0.014(5)	0.019(6)	0.002(4)	0.018(6)	0.010(6)	0.018(3)
O6	100	0.457(2)	0.3256(4)	0.3976(7)	0.040(8)	0.025(6)	0.014(6)	–0.000(4)	0.018(6)	0.001(8)	0.024(3)
O7	100	0.129(3)	0.2494(5)	0.7528(4)	0.024(4)	0.009(2)	0.025(3)	–0.003(6)	–0.002(7)	–0.007(2)	0.0213(12)
O8	100	0.0700(15)	0.6418(5)	0.7881(9)							0.016(3)**
O9	100	0.164(2)	0.4308(2)	0.3335(4)	0.013(3)	0.019(3)	0.019(2)	–0.001(2)	–0.005(6)	–0.006(7)	0.0188(12)
O10	100	0.689(3)	0	–0.007(3)							0.082(5)**
X1	100	¼	¼	½							0.0246(14)**
X2	100	½	0.4391(5)	½	0.028(6)	0.022(6)	0.040(9)	0	–0.015(7)	0	0.035(3)
X3	100	0	0.4395(5)	½	0.043(8)	0.019(6)	0.029(8)	0	–0.009(7)	0	0.034(3)
X4	100	0.317(2)	0.4383(3)	0.6398(5)	0.045(6)	0.035(3)	0.068(4)	–0.001(3)	0.038(8)	–0.020(8)	0.0453(17)
W1	100	0.736(4)	0	0.815(2)							0.097(10)
W2	44	0	0.1147(11)	0							0.05**
W3	19	0.350(7)	0.5793(19)	0.005(7)							0.05**
W4	16	0.349(9)	0.636(2)	–0.010(12)							0.05**
W5	23	0.272(5)	0.6047(16)	0.012(6)							0.05**

*For composition of the *M*(1–4) and *A*(1,2) sites see Table 7; X1 = [(H$_2$O),F]; X2 = F, X(3,4) = [F,(H$_2$O)]; W(1–5) = O atoms of H$_2$O groups; **U_{iso}.

Table 6. Selected interatomic distances (Å) and angles (°) in letnikovite-(Ce).

M1–O(5)a	2.50(1)	A1–W(1)i	2.19(2)	A2–W(4)l,m	3.22(6) ×2	Si1–O5	1.57(1)		
M1–X2	2.491(7)	A1–O(2)g	2.37(2)	A2–O(8)a,n	3.56(2) ×2	Si1–O7	1.62(1)	Si(3)r–O1–Si(4)e	128.2(6)
M1–X3	2.497(8)	A1–W(2)j	2.39(1)	A2–O(4)l,m	3.58(2) ×2	Si1–O(8)k	1.63(1)	Si(2)b–O3–Si1	143.1(4)
M1–O5	2.51(1)	A1–O(3)k	2.445(9)	A2–O(7)o,p	3.88(1) ×2	Si1–O3	1.65(2)	Si(2)k–O4–Si(3)k	136.0(9)
M1–O(6)b	2.52(1)	A1–X(4)k	2.63(1)	A2–W2	3.89(4)	<Si1–O>	1.62	Si(2)e–O7–Si1	145.8(4)
M1–O6	2.50(1)	A1–O(4)b	2.89(2)	A2–O(7)q,r	3.90(1) ×2			Si(3)r–O8–Si(1)k	139.1(5)
M1–O9	2.584(5)	A1–O8	2.91(2)	<A2–φ>	3.65	Si2–O(6)	1.60(1)	<Si–O–Si>	138.4
M1–X4	2.560(6)	<A1–φ>	2.546			Si2–O(7)e	1.60(1)		
M1–X1	2.6912(4)			Si4–O2	1.61(2)	Si2–O(3)b	1.59(2)	O–O distances for possible	
<M1–φ>	2.539	M3–X(2)c,g	2.321(8) ×2	Si4–O(1)e,f	1.627(9) ×2	Si2–O(4)k	1.61(1)	hydrogen bonding	
		M3–O2	2.33(1)	Si4–O10	1.71(4)	<Si2–O>	1.60	O2–W(1)t	2.83(3)
M2–X(4)c,d	2.33(1) ×2	M3–X(4)g,h	2.33(1) ×2	<Si4–O>	1.644			O10–O(10)u	2.88(3)
M2–X(3)c,e	2.333(8) ×2	M3–O(9)c,d	2.52(1) ×2			Si3–O9	1.601(5)		
M2–W1	2.42(3)	<M3–φ>	2.382	M4–X(1)l,a	1.8682(3) ×2	Si3–O(8)r	1.62(1)	O2–W(3)c,d	3.11(8)×2
M2–O(9)e,f	2.46(1) ×2			M4–O(6)e,s	2.21(2) ×2	Si3–O(1)r	1.624(5)	O10–W(1)n	2.60(4)
<M2–φ>	2.381			M4–O(5)l,a	2.25(2) ×2	Si3–O(4)k	1.65(1)		
				<M4–φ>	2.109	<Si3–O>	1.624		

φ = O, F, H_2O and OH.
Symmetry codes: a: –x, y, –z + 1; b: –x + 1, y, –z + 1; c: x+½, y–½, z; d: x+½, –y+½, z; e: –x+½, –y+½, –z + 1; f: –x+½, y–½, –z + 1; g: –x+³/₂, –y+½, –z + 1; h: –x+³/₂, y–½, –z + 1; i: x–½, y+½, z; j: x+½, y+½, z + 1; k: x, –y + 1, z; l: x, y, z; m: –x, y, –z; n: x, y, z–1; o: x–½, y+½, z–1; p: –x+½, y+½, –z + 1; q: x, –y + 1, z–1; r: –x, –y + 1, –z + 1; s: x–½, –y–½, z; t: –x + 2, –y, –z + 1; u: –x + 1, –y, –z.

The interstitial A1 and A2 sites have refined site-scattering values of 11.0 and 2.2 epfu, respectively, with a sum of 13.2 epfu (Table 7). The cations to be assigned to these sites are Na, Ca and Cs, with a total scattering of 13.32 epfu (Table 2). The A1 polyhedron is smaller (mean bond distance of 2.546 Å), whereas the A2 polyhedron is larger, with <A2–φ> = 3.65 Å. Therefore, we assign all the available Na and Ca to the A1 site, which yields 11.12 epfu, in good agreement with the refined value of 11.0(4) epfu. Cs is the largest cation left to be assigned,

and we allocate it to the A2 site. Hence a vacancy is dominant at the A2 site (Table 7).

Description of the structure

Cation sites

The crystal structure contains three groups of cation sites: *M* sites of the heteropolyhedral sheet, *Si* sites of the Si–O–OH sheet, and interstitial A1 and A2 sites.

Table 7. Refined site-scattering and assigned site-populations for letnikovite-(Ce).

Site	Refined site-scattering (epfu)	Assigned site-population (apfu)	Calculated site-scattering (epfu)	<Cation-φ>obs. (Å)	Ideal composition (pfu)
		Cations			
		Heteropolyhedral sheet			
[9]M1*	104.5(5)	$Ln_{1.31}Sr_{0.55}Ca_{0.09}Pb_{0.05}$	103.56	2.539	Ce_2
[7]M2	16.1(3)	$Ca_{0.83}\square_{0.17}$	16.60	2.381	Ca
[7]M3	20.0	$Ca_{1.0}$	20	2.382	Ca
[6]M4	4.4(2)	$Mg_{0.28}Fe^{2+}_{0.04}\square_{0.68}$	4.40	2.109	$\square$
Total	145.0	$Ca_{1.92}Ln_{1.31}Sr_{0.55}Mg_{0.28}Pb_{0.05}Fe^{2+}_{0.04}$	144.56		Ca_2Ce_2
		Interstitial cations			
[7]A1	11.0(4)	$Na_{0.72}Ca_{0.16}\square_{1.12}$	11.12	2.546	$(Na\square)$
[11]A2**	2.2	$Cs_{0.04}\square_{0.96}$	2.2	3.65	$\square$
Total	13.2	$Na_{0.72}Ca_{0.16}Cs_{0.04}$	13.32		$(Na\square)$
		Si–O–OH sheet			
[4]Si(1–4)		Si_7			Si_7
O(1–9)		O_{17}			O_{17}
O10		OH			OH
Total		$Si_7O_{17}(OH)$			$[Si_7O_{17}(OH)]$
		Anions and H_2O groups			
X1		$(H_2O)_{0.68}F_{0.32}$			H_2O
X2		$F_{1.0}$			F
X3		$F_{0.83}(H_2O)_{0.17}$			F
X4		$F_{1.66}(H_2O)_{0.34}$			F_2
$\Sigma X(1–4)$		$F_{3.81}(H_2O)_{1.19}$			$F_4(H_2O)$
W1		$(H_2O)_{1.0}$			
W2		$(H_2O)_{0.44}$			
W3		$(H_2O)_{0.38}$			
W4		$(H_2O)_{0.32}$			
W5		$(H_2O)_{0.46}$			
$\Sigma W(1–5)$		$(H_2O)_{2.60}$			$(H_2O)_3$
Total		$F_{3.81}(H_2O)_{3.79}$			$F_4(H_2O)_4$

φ = O, F, OH and H_2O.
*$Ln_{1.31}$ = $Ce_{0.71}Nd_{0.33}La_{0.14}Pr_{0.10}Eu_{0.02}Gd_{0.01}$ [76.76 epfu]; f_{av} = 58.60 *el*. (f_{av} = average scattering curve for $Ln_{1.31}$).
**Site scattering was refined, adjusted in accord with chemical analysis (Table 2), and then fixed at the last stages of the refinement.

Table 8. Bond-valence values (vu) for anions in letnikovite-(Ce).

Atom	M1	M2	M3	M4	A1	Si1	Si2	Si3	Si4	Σ
Dominant species	Ce	Ca	Ca	Mg	Na	Si	Si	Si	Si	
Site occ. (%)	100	83	100	32	44	100	100	100	100	
O1								0.99	$0.99^{\downarrow 2}$	1.98
O2			0.34		$0.09^{\rightarrow 2}$				1.04	1.56
O3					0.07	0.93	1.09			2.09
O4					0.04		1.04	0.93		2.01
O5	0.39			$0.07^{\downarrow 2}$		1.15				1.99
	0.38									
O6	0.37			$0.08^{\downarrow 2}$			1.06			1.90
	0.39									
O7						1.01	1.06			2.07
O8					0.04	0.98		1.01		2.03
O9	0.31	$0.21^{\downarrow 2}$	$0.22^{\downarrow 2}$					1.06		1.80
O10**									0.78	0.78
X1 [O]	$0.24^{\rightarrow 2}$			$0.17^{\downarrow 2 \rightarrow 2}$						0.82
X2 [F]	$0.30^{\rightarrow 2}$		$0.29^{\downarrow 2 \rightarrow 2}$							1.18
X3 [F]	$0.29^{\rightarrow 2}$	$0.23^{\downarrow 2 \rightarrow 2}$								1.04
X4 [F]	0.25	$0.23^{\downarrow 2}$	$0.28^{\downarrow 2}$		0.04					0.80
W1		0.23			$0.12^{\rightarrow 2}$					0.47
W2					$0.08^{\rightarrow 2}$					0.16
Total	2.92	1.57	1.92	0.64	0.48	4.07	4.25	3.99	3.80	
(100%)		1.89		2.00	1.09					

*Bond-valence parameters (vu) are from Brown (1981); bonds to oxygen were used for O(1–10), X1 and W(1,2); bonds to fluorine were used for X(2–4); occupancies of cation sites were taken into account for all calculations; the last row gives bond-valence sums for M2, M4 and A1 where the corresponding sites are 100% occupied.
**See discussion in the text on the contribution of hydrogen bonding to the bond-valence sum at O10.

Heteropolyhedral sheet

There are four cation sites in the heteropolyhedral sheet: the Ce-dominant $M1$ site, the Ca-dominant $M(2,3)$ sites, and the □-dominant $M4$ site (Fig. 3a,b). The $M1$ site is occupied by $Ln_{1.31}Sr_{0.55}Ca_{0.09}Pb_{0.05}$ apfu, where Ce is the dominant lanthanoid. The $M1$ atom is coordinated by nine anions: five O atoms and four $X(1–4)$ anions where $X = F$ and H_2O (Tables 5–7) (see discussion on short-range order below). The ideal composition of the $M1$ site is Ce_2 apfu. The $M2$ site is occupied by Ca at 83%, its composition is $Ca_{0.83}□_{0.17}$ pfu, ideally $Ca_{1.0}$ apfu. The $M2$ atom is coordinated by seven anions: two O atoms, four X (3,4) anions and an H_2O group at the $W1$ site (Tables 6, 7). The $M3$ site is fully occupied by Ca, its ideal composition is $Ca_{1.0}$ apfu. The M3 atom is coordinated by seven anions: three O atoms and four $X(2,4)$ anions (Tables 6, 7). The $M4$ site is occupied by $Mg_{0.28}Fe^{2+}_{0.04}□_{0.68}$ pfu, its ideal composition is $□_{1.0}$ pfu. Ideally, cations of the heteropolyhedral sheet, $^{M2}Ca + ^{M3}Ca + ^{M1}Ce_2 + ^{M4}□$, sum to $[Ca_2Ce_2]^{10+}$ apfu (Table 7).

Si–O–OH sheet

In the Si–O–OH sheet (Fig. 4a,b), there are four $Si(1–4)$ tetrahedrally coordinated sites occupied by Si with a <Si–O> distance of 1.619 Å (Tables 5, 6). We consider the Si–O–OH sheet as a complex anion (see below).

Interstitial sites

In letnikovite-(Ce), there are two interstitial sites: $A1$ and $A2$. They occur in the large channels between two Si–O–OH sheets (Fig. 5a,b). The $A1$ site is coordinated by three basal O atoms of Si tetrahedra, two H_2O groups at the $W(1,2)$ sites and an X4 anion (Table 6, Fig. 6a,b). It is ~50% occupied by $Na_{0.72}Ca_{0.16}□_{1.12}$ pfu, and <A1–φ> = 2.546 Å (Table 7). We write the ideal composition of the $A1$ site as (Na□) pfu. The $A2$ site occurs in the centre of the channel (Fig. 5a) and is dominantly vacant. The $A2$ site is coordinated by eight basal oxygen atoms of Si tetrahedra on both sides of the channel and three H_2O groups at the $W(2,4)$ sites in the centre of the channel (Table 6, Fig. 7). It is occupied at 4% by Cs: $Cs_{0.04}□_{0.96}$ pfu, and <A2–φ> = 3.65 Å (Table 7). We write the ideal composition of the $A2$ site as □ pfu. Ideally, interstitial cations, $^{A1}(Na□) + ^{A2}□$, sum to $(Na□)^{1+}$ pfu.

Cations of the heteropolyhedral sheet and interstitial complex ideally sum to $(Ca_2Ce_2)^{10+} + (Na□)^+ = [(Na□)Ca_2Ce_2]^{11+}$.

Anion sites

Si–O–OH sheet

There are 10 anion sites, $O(1–10)$, occupied by O atoms which form the tetrahedral coordination of the $Si(1–4)$ atoms

Table 9. Bond-valence values (vu) for the O2 and X(1,3,4) anions involved in short-range order in letnikovite-(Ce)*.

Atom	M1	M2	M3	M4	A1	Si4	Σ
Dominant species	Ce	Ca	Ca	Mg	Na	Si	
Site occ. (%)	100	100	100	100	100	100	
O2 [O]			0.34		$0.20^{\rightarrow 2}$	1.04	1.78
X1 [F]	$0.18^{\rightarrow 2}$			$0.43^{\rightarrow 2}$			1.22
X3 [F]	$0.29^{\rightarrow 2}$	$0.28^{\rightarrow 2}$					1.14
X4 [F]	0.25	0.30	0.28		0.09		0.92

Atom	M1	M2	M3	M4	A1	Si4	Σ
Dominant species	Ce	Ca	Ca	Mg	Na	Si	
Site occ. (%)	100	0	100	0	0	100	
O2 [O]**			0.34			1.04	1.38
X1 [O]	$0.24^{\rightarrow 2}$						0.48
X3 [O]	$0.40^{\rightarrow 2}$						0.80
X4 [O]	0.33		0.33				0.66

*Bond-valence parameters (vu) are from Brown (1981); anion curves are shown in square brackets for each atom.
**There are O–O distances [O2–W1 and O2–W3, Table 6] suitable for possible hydrogen bonding which can add ~0.3 vu in total to the bond-valence sum of 1.38 vu at O2. With the bond-valence sum of 1.68 vu, O2 = O atom.
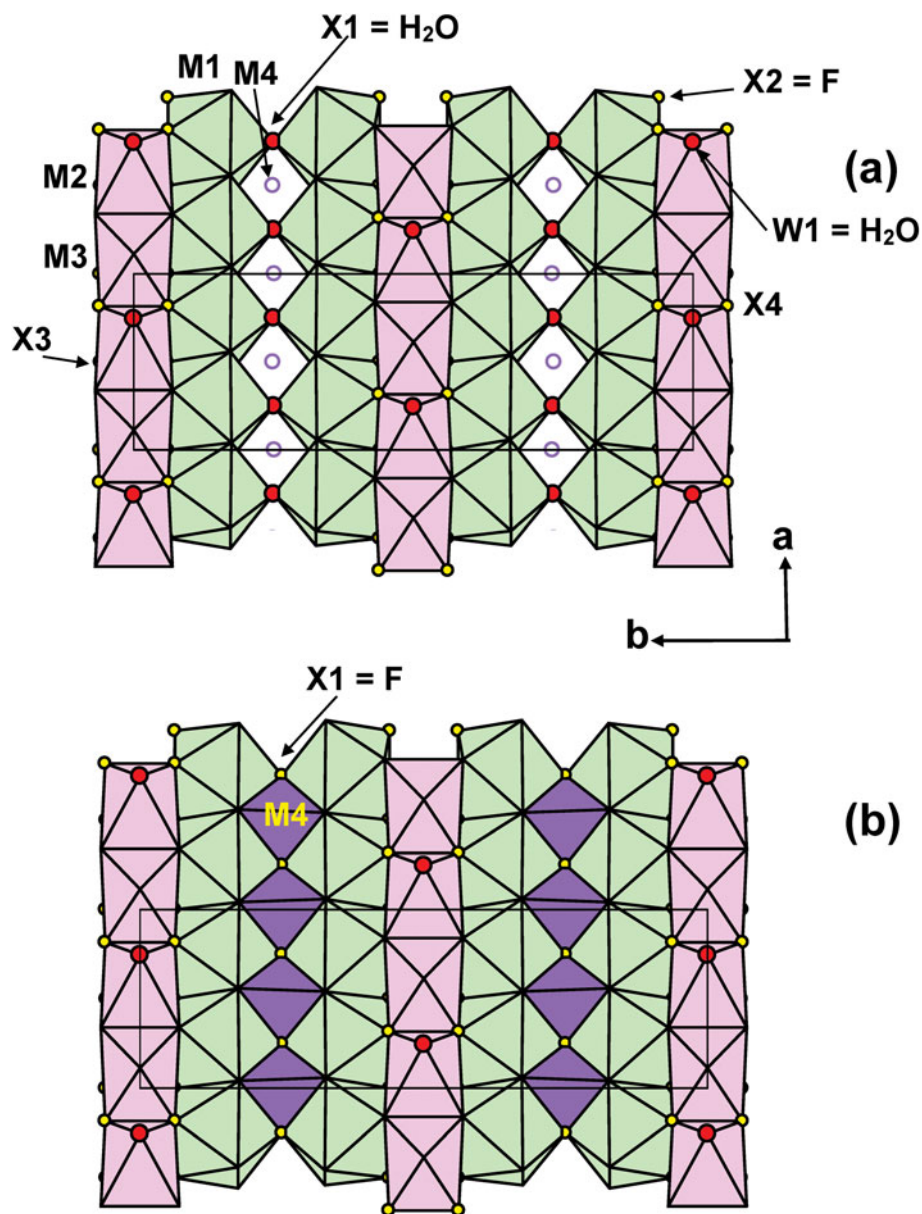
Figure 3. Short-range order (SRO) arrangements in the heteropolyhedral sheet, ideally $[Ca_2Ce_2F_4(H_2O)_2]^{7+}$: (a) SRO-68%, the *M*4 site is vacant, and the *X*1 site is occupied by an H_2O group; (b) SRO-32%, the *M*4 site is occupied by Mg plus minor Fe^{2+}, the *X*1 site is occupied by F, and M4 octahedra share edges and vertices with M1 and M2 polyhedra. The [9]-coordinated Ce-dominant M1 polyhedra are green, [7]-coordinated Ca-dominant M(1,2) polyhedra are pink, Mg-dominant M4 octahedra are purple, the vacant *M*4 site is shown as a white circle with a purple rim; H_2O groups and F atoms are shown as large red and small yellow spheres, respectively.

(Tables 5, 6). O(1, 3–9) receive bond valences of 1.80–2.09 vu (valence units) (Table 8) and hence are O atoms. The three SiO_4 tetrahedra, Si1, Si2 and Si3, are similar in size: with <Si–O> = 1.62, 1.60 and 1.624 Å, respectively. The Si4 tetrahedron, with <Si4–φ> = 1.644 Å, has one long Si4–O10 distance of 1.71 Å, and O10 receives a bond valence of 0.78 vu (Table 8), hence O10 is an oxygen atom of an OH group [φ = O and OH]. Therefore, the Si4 tetrahedron has the composition $SiO_3(OH)$.

Note that for two O atoms of Si tetrahedra, Table 8 gives significantly low bond-valence sums: 1.56 vu (instead of ∼2 vu) for O2 and 0.78 vu (instead of ∼1.2 vu) for O10, an O atom of an OH group. The O2 atom is a common vertex for the M3 [Ca] and A1 [Na, 44% occupancy] polyhedra and Si4 tetrahedron. Consider short-range order (SRO) arrangements for O2. SRO-1 (44%) occurs where the O2 atom receives bond-valence contributions from the M3 [Ca], A1 [where the A1 site is 100% occupied by Na] and Si4, with a total sum of 1.78 vu (Table 9), hence O2 is an O atom (Fig. 6a). SRO-2 (56%) occurs where the O2 atom

receives bond-valence contributions from M3 [Ca] and Si4 but does not receive a bond-valence contribution from A1 [□] [the A1 site is 56% vacant, Tables 5, 7], hence the bond-valence sum at O2 is 1.38 vu (Table 9). However, O2 can receive an additional bond-valence contribution of 0.30 vu via hydrogen bonding from O atoms of H_2O groups at the W1 and W3 sites (Fig. 6b). Distances O2–W1 = 2.83 Å and O2–W3 = 3.11 Å (Table 5) are suitable for hydrogen bonding. Hence at SRO-2 (56%), the bond-valence sum at O2 is 1.38 + 0.30 = 1.68 vu and O2 is an O atom.

The O10 atom receives 0.78 vu from Si4 (Table 8) and, possibly, bond-valence contributions from (1) O10′ related by the inversion centre [O10–O10′ = 2.88 Å, 0.15 vu] and (2) an O atom of an H_2O group at the W1 site [O10–W1 = 2.60 Å, 0.25 vu] (Table 5): 0.78 + 0.15 + 0.25 = 1.18 vu, a common value for the bond-valence sum at the O atom of an OH group.

Si(1–4) and O(1–10) atoms form a distinct complex Si–O–OH oxyanion, $[Si_7O_{17}(OH)]^{7-}$ per formula unit.

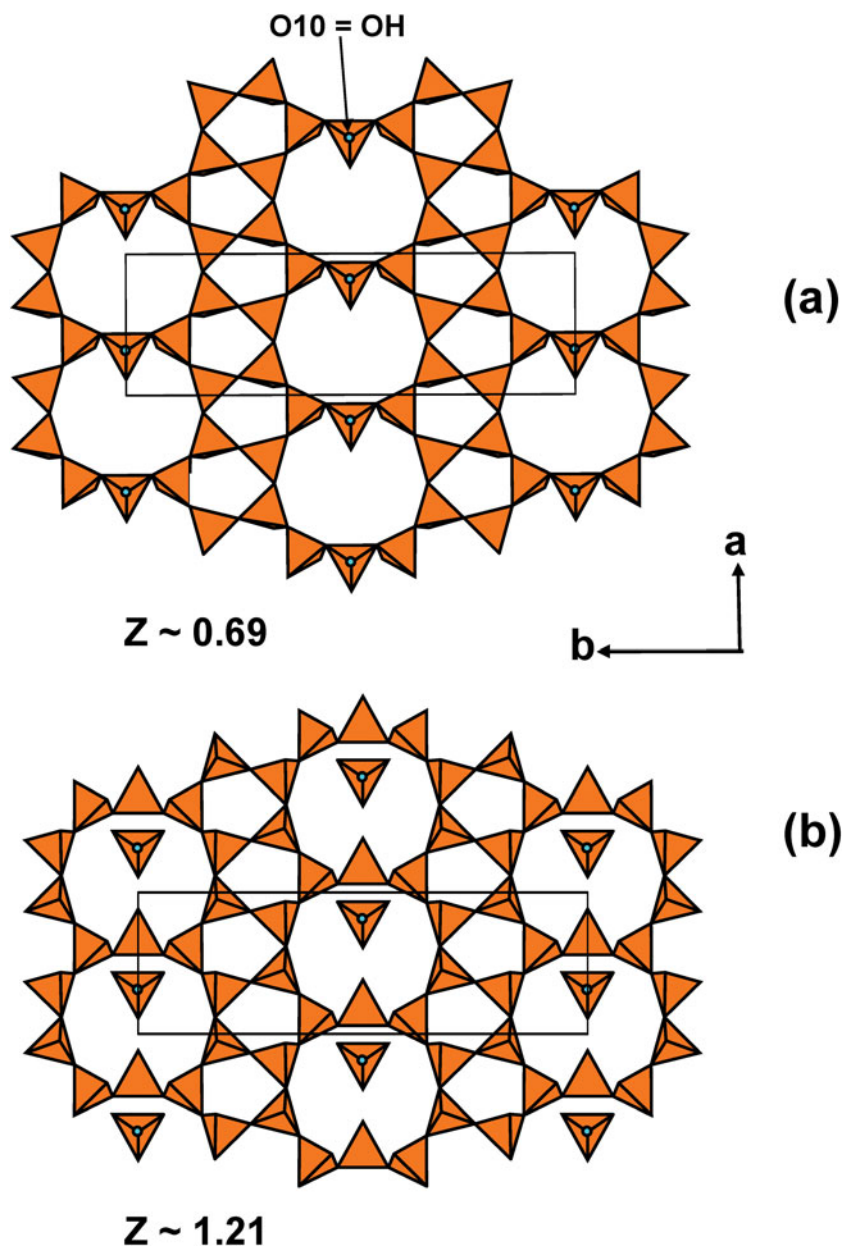**Figure 4.** A single $[Si_7O_{17}(OH)]^{7-}$ sheet of five-membered and ten-membered rings of SiO_4 and $SiO_3(OH)$ tetrahedra parallel to (001): (a) in the lower sheet at $z \approx 0.69$, $SiO_3(OH)$ tetrahedra are oriented upward along **c**; (b) in the upper sheet at $z \approx 1.21$, $SiO_3(OH)$ tetrahedra of the upper sheet are oriented downward along **c**; upward looking $SiO_3(OH)$ tetrahedra belong to the lower sheet and indicate the relative orientations of the two sheets. Si tetrahedra are orange, OH groups are shown as small turquoise spheres.

Heteropolyhedral sheet

The M(1–4) cations of the heteropolyhedral sheet are coordinated by O atoms shared with the Si–O–OH sheet, X(1–4) anions and an H_2O group at the $W1$ site (Tables 5, 6; Fig. 3a,b). The X(1–4) sites give 5 apfu, and the $W1$ site gives 1 apfu. Consider the four X(1–4) sites. The X2 anion receives four bond-valence contributions from the M1 and M3 cations which occur at fully occupied sites: these four contributions sum to 1.18 vu (Table 8) and X2 is a F atom (Fig. 3a, Table 7). The three X(1,3,4) anions are involved in short-range order, and their compositions vary (Tables 5–7). For example, the X1 anion is bonded to the M1 and M4 atoms in the polyhedral sheet. The $M1$ site is fully occupied, mainly by REE; the $M4$ site is occupied by Mg and minor Fe^{2+} at 32% (Table 7). Consider SRO-1(68%), where the $M4$ site is vacant (Fig. 3a): the X1 anion receives 0.48 vu, i.e. two bond-valence contributions from two M1 cations (Table 9), and X1 is an H_2O group. Consider SRO-2 (32%), where the $M4$ site is occupied by Mg plus minor Fe^{2+} (Fig. 3b): the X1

anion receives bond-valence contributions from the M1 and M4 atoms, summing to 1.22 vu (Table 9), and X1 is a F atom. Hence the composition of the X1 site is $(H_2O)_{0.68}F_{0.32}$ pfu (Table 7), ideally $(H_2O)_{1.0}$ pfu. Similarly, the compositions of the X3 and X4 sites are $F_{0.83}(H_2O)_{0.17}$ pfu and $F_{1.66}(H_2O)_{0.34}$ pfu (ideally F and F_2 apfu) (Table 7). Ideal compositions of the four X(1–4) sites, $^{X1}H_2O +^{X2}F +^{X3}F +^{X4}F_2$, sum to $[F_4(H_2O)]^{4-}$ pfu. The $W1$ site is 100%-occupied by H_2O groups, giving $(H_2O)_{1.0}$ pfu. Hence the ideal composition of the anions/H_2O groups of the heteropolyhedral sheet not shared with the Si–O–OH sheet is $^{X(1-4)}[F_4(H_2O)]^{4-} +^{W1}(H_2O) = [F_4(H_2O)_2]^{4-}$ pfu.

Interstitial complex

In the interstitial complex, the four W(2–5) sites are partly occupied by H_2O groups: W2 and W3 at 44 and 19%, and W4 and W5 at 16 and 23% (Table 5). The O atoms of H_2O groups at the W(2,4) sites are ligands of the A(1,2) cations: A1 [W2] and A2 [W(2,4)] (Table 6). H_2O groups at the W(3,5) sites occur in
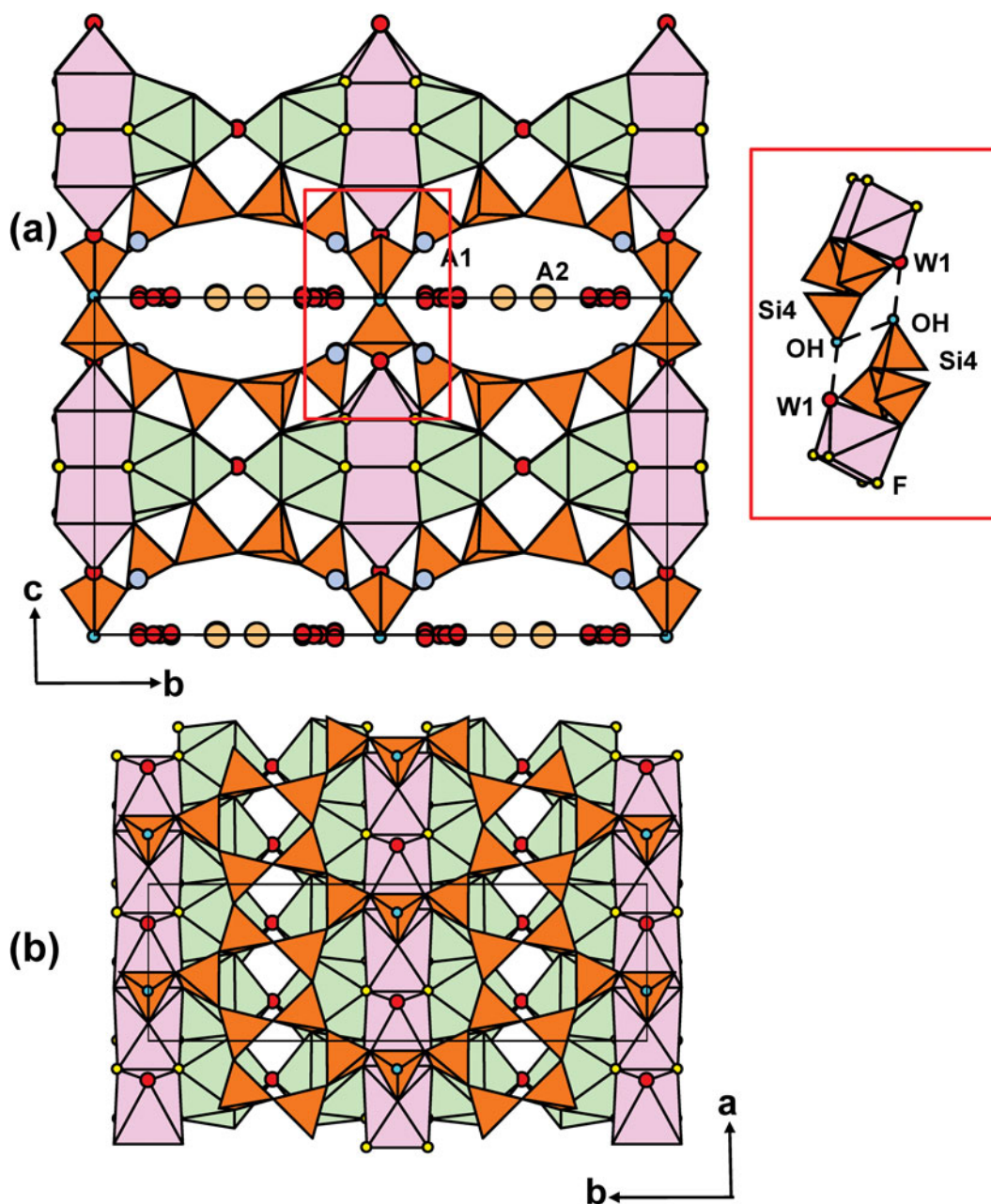
Figure 5. Letnikovite-(Ce): (a) general view of the crystal structure; (b) linkage of a heteropolyhedral sheet and a single Si–O–OH sheet. Inset on the right from (a) shows possible hydrogen bonds between OH groups of two Si4 tetrahedra in the upper and lower Si–O–OH sheets along **c**. Legend as in Fig. 3, Si tetrahedra are orange, OH groups are shown as small turquoise spheres; interstitial cations, [7]Na at the *A*1 site (44% occupancy) and [11]Cs at the *A*2 site (4% occupancy) are shown as blue and pale-orange spheres; H_2O groups at partly occupied *W*(2–5) sites in between two Si–O–OH sheets are shown as large red spheres.

the large channels of the structure (Fig. 5a). The $W(2-5)$ sites give $(H_2O)_{1.60}$ pfu, ideally $(H_2O)_2$ pfu.

The complex Si–O–OH anion, and the simple anions of the heteropolyhedral sheet and interstitial complex (charge is given in brackets), $[Si_7O_{17}(OH)]$ (7^-) + $[F_4(H_2O)_2]$ $[X(1-4),W1]$ (4^-) + $(H_2O)_2$ $[W(2-5)]$ (0), sum to $[Si_7O_{17}(OH)]F_4(H_2O)_4$, with a total charge of 11^-. The presence of OH and H_2O groups is in accord with the Raman spectrum (Fig. 2b).

General topology of the crystal structure

In the crystal structure of letnikovite-(Ce), the main structural unit is a layer of the central heteropolyhedral Ca–Ce sheet and two

adjacent identical Si–O–OH sheets. The heteropolyhedral sheet parallel to (001) is composed of [9]-coordinated Ce-dominant M1 polyhedra, [7]-coordinated Ca-dominant M(2,3) polyhedra and vacancy-dominant M4 octahedra which share common edges and common vertices (Fig. 3a,b). We sum the cation and anion parts of the heteropolyhedral sheet to derive its ideal composition: $[Ca_2Ce_2]^{10+}$ + $[F_4(H_2O)_2]^{4-}$ = $[Ca_2Ce_2F_4(H_2O)_2]^{6+}$. The Si–O–OH sheet is composed of SiO_4 and $SiO_3(OH)$ tetrahedra in the ratio 6:1, Si tetrahedra form five-membered $[Si_5O_{15}]^{10-}$ and ten-membered $[Si_{10}O_{33}(OH)_2]^{28-}$ rings in the ratio 2:1 (Fig. 4a,b). In a sheet, ribbons of ten-membered and five-membered rings extend along [100]. Rings of tetrahedra share common vertices to form a single $[Si_7O_{17}(OH)]^{7-}$ sheet parallel to (001). This is the first
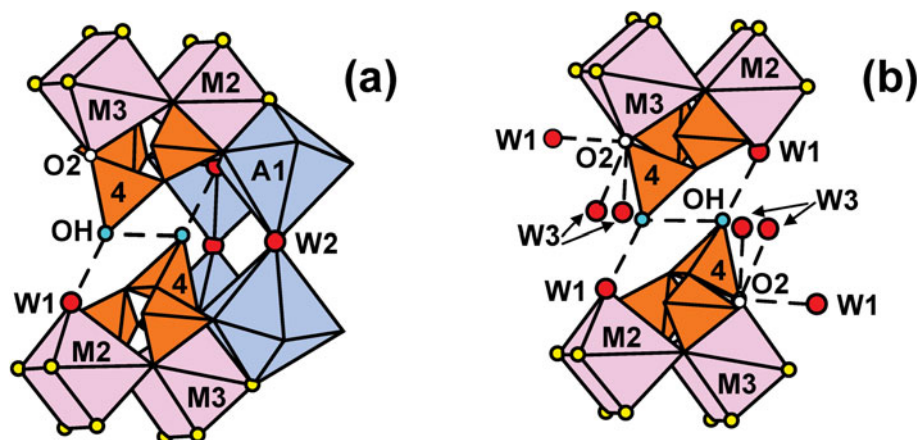
Figure 6. Short-range order arrangements related to the $A1$ site occupied by Na at 44% and $W2$ site occupied by H_2O at 44%: (a) SRO-44%, the $A1$ site is 100% occupied by Na and the [7]-coordinated $A1$ polyhedra link via vertices occupied by H_2O groups at the $W1$ and $W2$ sites; (b) SRO-56%, the $A1$ and $W2$ sites are vacant. Legend as in Fig. 5, the O atom at the $O2$ site is shown as a small white sphere.

occurrence of a single $[Si_7O_{17}(OH)]^{7-}$ sheet with a new topology that has not been found in any mineral (Hawthorne *et al.*, 2019) and we call it the 'letnikovite' sheet. Two equivalent single sheets related by a mirror plane occur at $z \approx 0.69$ and $z \approx 1.21$ and connect via hydrogen bonding between OH groups of the two $SiO_3(OH)$ tetrahedra (Fig. 5a, inset). Polyhedra of the central Ca–Ce sheet share common vertices with two adjacent Si–O–OH sheets to form a layer of composition $\{Ca_2Ce_2[Si_7O_{17}(OH)]F_4(H_2O)_2\}^{1-}$ (Fig. 5a,b). The layers are stacked along [001] and link via (1) cations at the interstitial $A(1,2)$ sites and H_2O groups, and (2) hydrogen bonding between OH groups of the Si–O–OH sheets and H_2O groups of the Ca–Ce sheets. This type of linkage yields wide channels along [100] (Fig. 5a). Along [100], the interstitial $A1$ and $A2$ sites (Figs. 6, 7) are partly occupied by Na (44%) and Cs (4%), respectively. We sum cation and anion parts of the interstitial complex to derive its ideal composition: $(Na\square)^{1+} + (H_2O)_2 = [(Na\square)(H_2O)_2]^{1+}$.

The general structural formula of letnikovite-(Ce)

On the basis of the SREF results and bond-valence calculations, we write the ideal formula of letnikovite-(Ce) as the sum of the cation and anion components: $[(Na\square)Ca_2Ce_2]^{11+} + \{[Si_7O_{17}(OH)]F_4(H_2O)_4\}^{11-} = (Na\square)Ca_2Ce_2[Si_7O_{17}(OH)]F_4(H_2O)_4$, $Z = 4$.
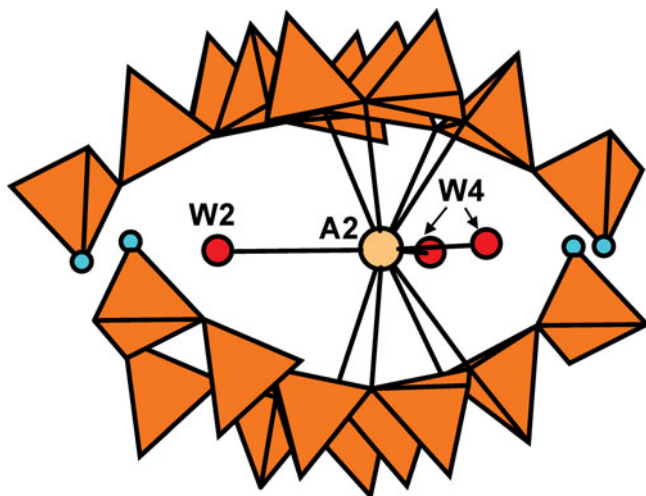
Figure 7. The $^{[11]}$Cs at the $A2$ site. Legend as in Fig. 5.

The simplified formula is $(Na,\square)_2Ca_2(Ln^{3+},Sr)_2[Si_7O_{17}(OH)]F_4(H_2O)_4$, where Ce is the dominant lanthanoid. The validity of the ideal formula is supported by the good agreement between the total charges for cations in the ideal and empirical formulae: 1^+ $(Na\square) + 10^+$ $(Ca_2Ce_2) = 11^+$ versus 1.08^+ $(\square_{2.08}Na_{0.72}Ca_{0.16}Cs_{0.04}) + 9.61^+$ $(Ca_{1.92}Ln_{1.31}Sr_{0.55}Mg_{0.28}Pb_{0.05}Fe^{2+}_{0.04}\square_{0.85}) = 10.69^+$.

Above, we wrote the ideal formulae of letnikovite-(Ce) on the basis of the sum of the cation and anion components. Here, we write the ideal structural formula and ideal formula of letnikovite-(Ce) ($Z = 4$) on the basis of ideal compositions of cation and anion sites, $^{A1}(Na\square)$, $^{A2}\square$, ^{M2}Ca, ^{M3}Ca, $^{M1}Ce_2$, $^{M4}\square$, $[Si_7O_{17}(OH)]$, ^{X2}F, ^{X3}F, $^{X4}F_2$, $^{X1}H_2O$, $^{W1}H_2O$, $^{W(2-5)}(H_2O)_2$, as $(Na\square)\square Ca_2Ce_2\square[Si_7O_{17}(OH)][F_4(H_2O)](H_2O)(H_2O)_2$ and $(Na\square)Ca_2Ce_2[Si_7O_{17}(OH)]F_4(H_2O)_4$, respectively.

Relation to other sheet silicates

We can remotely relate letnikovite-(Ce) to nekoite, $Ca_3Si_6O_{15}\cdot7H_2O$ (Alberti and Galli, 1980), okenite, $Ca_{10}Si_{18}O_{46}\cdot18H_2O$ (Merlino, 1983), and zeravshanite, $Cs_4Na_2Zr_3[Si_{18}O_{45}](H_2O)_2$ (Uvarova *et al.*, 2004; Pautov *et al.*, 2004), silicate minerals with a single sheet of five-membered rings and eight-membered rings of SiO_4 tetrahedra; the composition of this sheet is $(Si_6O_{15})^{6-}$. In zeravshanite, the Si–O sheet is folded, hence Uvarova *et al.* (2004) wrote its composition as $(Si_{18}O_{45})^{18-}$. In a Si–O–OH sheet in letnikovite-(Ce), ribbons of ten-membered rings and five-membered rings are parallel to [100], $a = 7.4726(3)$ Å. In nekoite, okenite and zeravshanite, ribbons of eight-membered rings and five-membered rings are parallel to: [001], $c = 7.339$ Å (nekoite); [010], $b = 7.28$ Å (okenite) and [010], $b = 7.5464$ Å (zeravshanite).

Competing interests. The authors declare none.

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