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Article

Kalyuzhnyite-(Ce), NaKCaSrCeTi(Si$_8$O$_{21}$)OF(H$_2$O)$_3$, a new mineral from the Darai-Pioz alkaline massif, Tien-Shan mountains, Tajikistan: mineral description, crystal structure and a new double (Si$_8$O$_{21}$) sheet

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Abstract

Kalyuzhnyite-(Ce), ideally NaKCaSrCeTi(Si$_8$O$_{21}$)OF(H$_2$O)$_3$, is a new mineral from the Darai-Pioz alkaline massif, Tien-Shan mountains, Tajikistan. It occurs as equant grains up to 0.05×0.07 mm in a quartz–pectolite aggregate in a silexite-like peralkaline pegmatite. 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 3.120 g/cm^3. Kalyuzhnyite-(Ce) is monoclinic, $P2/c$, $a = 18.647(4)$, $b = 11.214(2)$, $c = 14.642(3)$ Å, $\beta = 129.55(3)°$ and $V = 2360.9(11)$ Å^3. The chemical composition of kalyuzhnyite-(Ce) is Nb$_2$O$_5$ 0.53, TiO$_2$ 0.16, SiO$_2$ 43.85, Er$_2$O$_3$ 0.13, Ho$_2$O$_3$ 0.10, Gd$_2$O$_3$ 0.09, Sm$_2$O$_3$ 0.47, Nd$_2$O$_3$ 6.22, Pr$_2$O$_3$ 1.21, Ce$_2$O$_3$ 6.34, La$_2$O$_3$ 0.82, PbO 4.90, BaO 0.85, SrO 11.39, CaO 1.86, Cs$_2$O 3.80, K$_2$O 1.59, Na$_2$O 2.99, H$_2$O 5.24, F 1.55, O = F −0.65, total 100.31 wt.%. The empirical formula calculated on 26.11 (O + F) apfu is Na$_{1.07}$K$_{0.37}$Cs$_{0.30}$Sr$_{1.21}$Ca$_{0.37}$Pb$_{0.24}$Ba$_{0.06}$(Ce$_{0.43}$Nd$_{0.41}$Pr$_{0.08}$La$_{0.06}$Sm$_{0.03}$Gd$_{0.01}$Er$_{0.01}$Ho$_{0.01}$)$_{\Sigma1.04}$(Ti$_{0.97}$Nb$_{0.04}$)$_{\Sigma1.01}$Si$_{8.06}$O$_{25.21}$F$_{0.90}$H$_{6.42}$, $Z = 4$. The simplified formula is (Na,$\square$)(K,Cs)(Ca,Pb,Sr,Na)SrLn^{3+}Ti(Si$_8$O$_{21}$)OF(H$_2$O)$_3$, where Ce is the dominant lanthanoid. The crystal structure was solved by direct methods and refined to an R_1 index of 2.74%. In kalyuzhnyite-(Ce), the main structural units are a heteropolyhedral Na–Sr–Ce–Ti sheet, ideally [NaSrCeTiOF]$^{7+}$, and a double (Si$_8$O$_{21}$)$^{10−}$ sheet parallel to (010). In the Si–O sheet, the Si tetrahedra form ten-membered rings. This is the first occurrence of such a double Si–O sheet in a mineral. The two sheets connect via common vertices of Na-, Sr-, Ce- and Ti-polyhedra and SiO$_4$ tetrahedra to form a framework. The interstitial cations and H$_2$O groups, ideally [(CaK)(H$_2$O)$_3$]$^{3+}$ occur within the Si–O sheet. The mineral is named in honour of Vasily Avksentievich Kalyuzhny (1899–1993) in recognition of his contributions to the geology of ore deposits of Komi Republic (USSR) and the mineralogy of granitic pegmatites (Tajikistan).

Introduction

This paper reports the description and the crystal structure of kalyuzhnyite-(Ce) [Russian Cyrillic: калюжныит-(Ce)], ideally NaKCaSrCeTi(Si$_8$O$_{21}$)OF(H$_2$O)$_3$, a new mineral from the well-known Darai-Pioz alkaline massif, Tien-Shan Mountains, Central Tajikistan. Kalyuzhnyite-(Ce) is a sheet-silicate mineral with large channels and can potentially be used as a model for

synthesis of microporous materials of industrial interest. Single-crystal X-ray diffraction revealed a double Si$_8$O$_{21}$ sheet of ten-membered rings of SiO$_4$ tetrahedra that has never been described in minerals (Hawthorne *et al.*, 2019). The name is in honour of Vasily Avksentievich Kalyuzhny (Russian Cyrillic: Василий Авксентьевич Калюжный) (1899–1993), a prominent Russian geologist, an authority on the geology of the Komi Republic and its ore deposits; his pioneering work resulted in the discovery of the Yaregskoe Ti-deposit in oil-bearing sandstones of the Komi Republic. Dr. Kalyuzhny was also a member of the Pamir-Tajik geological expedition (1934–1937), and he studied granite pegmatites of the Turkestan ridge around rivers of the Karavshin system and Sn-bearing pegmatites of the Kalbinsky ridge in Kazakhstan. The new mineral and its name have been approved by the

Commission on New Minerals, Nomenclature and Classification, International Mineralogical Association (IMA2022-133, Agakhanov *et al.*, 2023). The holotype material is deposited in the systematic collection of the Fersman Mineralogical Museum, Moscow, Russia, catalogue number 98144. The IMA mineral symbol is Kalu-Ce.

## Occurrence and associated minerals

Kalyuzhnyite-(Ce) occurs 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 ridges (39°30′N 70°40′E). This area is in the Rasht (formerly Garm) district, Central Tajikistan. The Darai-Pioz alkaline 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. Kalyuzhnyite-(Ce) was found in boulders (up to 2 m across) of quartz rock, i.e. silexite boulders composed of 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 minor 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 lenticular 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 present are fine-grained brown or greyish-brown aggregates of Mn-bearing pectolite, quartz, Sr-bearing fluorite and a variety of rare minerals. Kalyuzhnyite-(Ce) occurs in these pectolite-rich aggregates (Fig. 1a,b), associated with quartz, fluorite, pectolite, baratovite, aegirine, leucosphenite, neptunite, reedmergnerite, orlovite, sokolovaite, mendeleevite-(Ce), odigitriaite, pekovite, zeravshanite, kirchhoffite and garmite. The origin of the silexite boulders with pectolite aggregates, in which kalyuzhnyite-(Ce) was found, is debatable as these rocks have not been investigated *in situ*. The problem of their genesis has been discussed by Pautov *et al.* (2022).

Physical properties

Kalyuzhnyite-(Ce) occurs as equant grains with poorly developed faces in a quartz–pectolite aggregate (Fig. 1a,b). The two grains of kalyuzhnyite-(Ce) up to 70 μm were found by scanning electron microscopy in a small hand-sample. One part of grain 1 (Fig. 1a) was used for the crystal-structure work (crystal 1) and the second part of grain 1 was used for the electron-microprobe analysis (crystal 2). The microprobe mount of crystal 2 was deposited as a holotype Kalyuzhnyite-(Ce), catalogue number 98144. The second smaller grain 2 up to 50 μm (Fig. 1b) was used for Raman spectroscopy (in a thin section).

The grains are colourless and have a vitreous lustre. Kalyuzhnyite-(Ce) has an uneven fracture and does not fluoresce under cathode waves or ultraviolet light. The cleavage is {010} perfect and no parting was observed. The hardness of kalyuzhnyite-(Ce) was not measured due to the very small size of grain 2. The mineral is brittle and $D_{calc.} = 3.120$ g/cm^3.

Individual grains show no visible twinning. Kalyuzhnyite-(Ce) is nonpleochroic. In reflected light, kalyuzhnyite-(Ce) is grey. Reflectance values were measured with a UMSP-50 Opton microspectrophotometer using the Opton SiC standard 474251 (with a
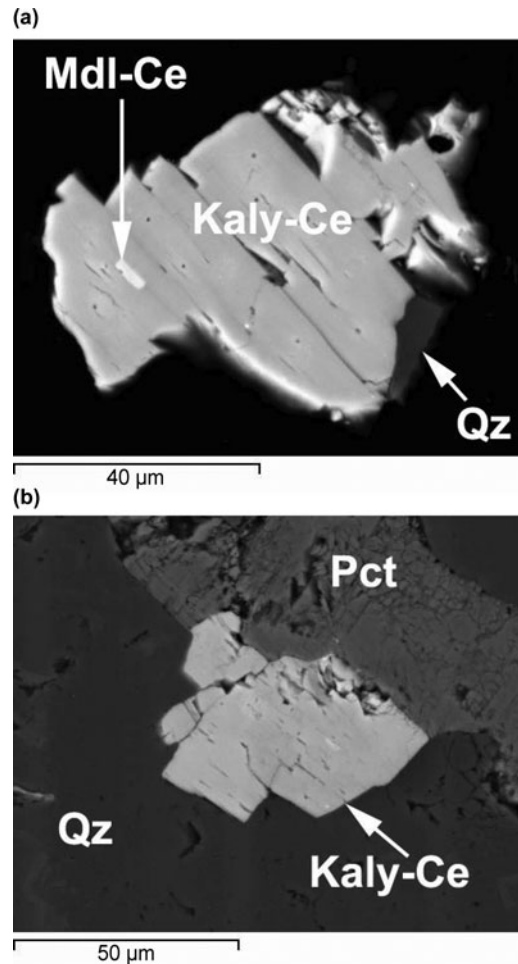
Figure 1. Back-scattered electron images of polished sections of kalyuzhnyite-(Ce) (Kaly-Ce): (a) grain 1 (holotype catalogue number 98144) in association with mendeleevite-(Ce) (Mdl-Ce) and quartz (Qz); (b) grain 2 in association with pectolite (Pct) and quartz.

spectral slot width of 10 nm) and are given in Table 1. Kalyuzhnyite-(Ce) has very weak bireflectance.

Raman spectroscopy

The Raman spectrum of kalyuzhnyite-(Ce) (Fig. 2) was obtained on a randomly oriented crystal (polished section, Fig. 1b) using Thermo DXR2xi Raman imaging confocal microscope with a green laser (532 nm) at room temperature. The output power of the laser beam was 10 mW (at 100% power), holographic

Table 1. Reflectance values (%) for kalyuzhnyite-(Ce).

R_{max}	R_{min}	λ (nm)	R_{max}	R_{min}	λ (nm)
7.2	6.0	400	6.0	5.0	560
7.1	5.9	420	6.0	5.0	580
6.7	5.5	440	**6.0**	**5.0**	**589**
6.6	5.4	460	6.0	5.0	600
6.4	**5.3**	**470**	6.0	5.0	620
6.1	5.1	480	6.5	5.3	640
6.0	4.9	500	**6.6**	**5.4**	**650**
5.9	4.9	520	6.8	5.4	660
6.0	4.9	540	6.8	5.6	680
6.0	**5.0**	**546**	6.8	5.6	700

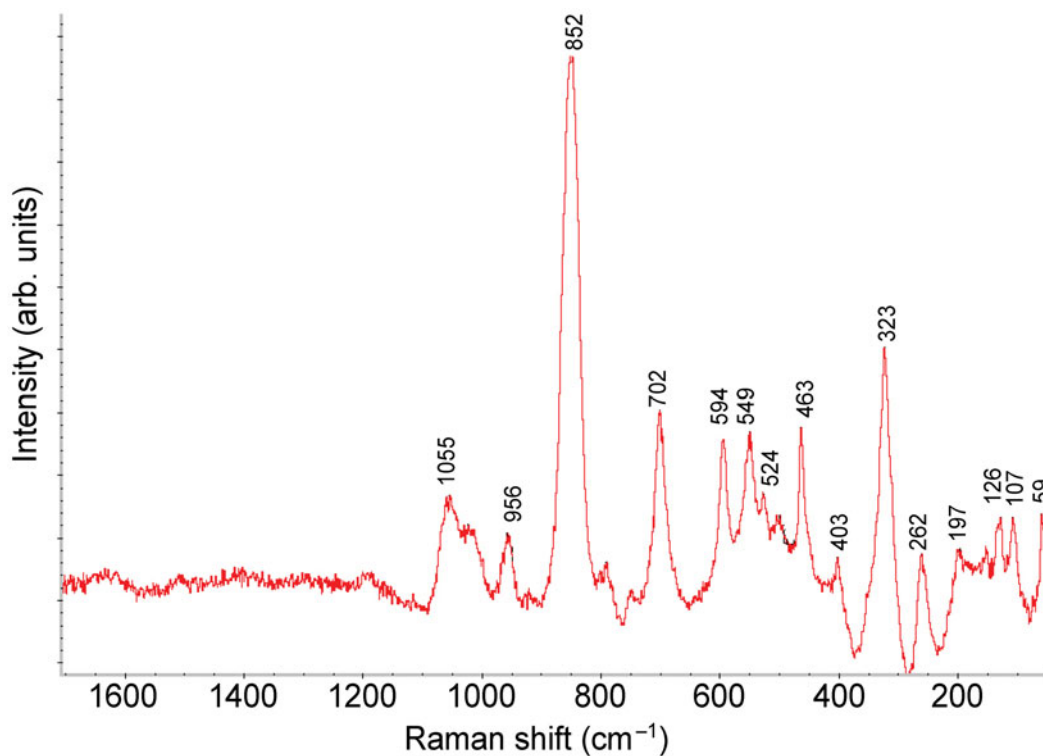The reference wavelengths required by the Commission on Ore Mineralogy (COM) are given in bold.

Figure 2. Raman spectrum of kalyuzhnyite-(Ce).

diffraction grating was used with 1800 lines cm^{-1}, spectral resolution was 2 cm^{-1}, the range was from 50 to 1800 cm^{-1}. The diameter of the focal spot on the sample was 2 μm. The back-scattered Raman signal was collected with a 100× objective; signal acquisition time for a single scan of the spectral range was 2.0 s and the signal was averaged over 20 scans. The spectrum was processed using *Omnic* software.

Lines in the Raman spectrum of kalyuzhnyite-(Ce) can be grouped into three frequency ranges by analogy with data obtained for some multi-ring silicates of Na, Sr, Ti and *REE* (Sitarz *et al.*, 1998; Frost and Xi, 2012; Tobbens *et al.*, 2008). The 800–1100 cm^{-1} range bands are due to Si–O bond-stretching modes, the 500 to 800 cm^{-1} vibrations are due to O–Si–O bending modes. The spectral region lower than 500 cm^{-1} corresponds to Me–O stretching vibrations and lattice modes, while some bonds from 300 to 500 cm^{-1} can correspond to SiO_4-unit vibrations.

Chemical composition

The chemical composition of kalyuzhnyite-(Ce) was determined using a JEOL 773 electron microprobe (energy dispersive spectroscopy mode, an accelerating voltage of 20 kV, a specimen current of 2 nA and a beam diameter of 5 μm; Fersman Mineralogical Museum). The following standards were used: microcline USNM 143966 (Si,K), albite 107 (Na), $SrTiO_3$ (Sr), $BaSO_4$ (Ba), $PbTiO_3$ (Pb), $CsTbP_4O_{12}$ (Cs), ilmenite USNM 96189 (Ti), anorthite USNM 137041 (Ca), $LiNbO_3$ (Nb), $LaPO_4$ (La), $CePO_4$ (Ce), $PrPO_4$ (Pr), $NdPO_4$ (Nd), $SmPO_4$ (Sm), $GdPO_4$ (Gd), $HoPO_4$ (Ho), $ErPO_4$ (Er), and MgF_2 (F). The data (10 analyses) were reduced and corrected by the *PAP* method of Pouchou and Pichoir (1985). The chemical composition of kalyuzhnyite-(Ce) is the mean of 10 determinations and is given in Table 2. The empirical formula calculated on 26.11 (O + F) apfu (atoms per formula unit) is $Na_{1.07}K_{0.37}Cs_{0.30}Sr_{1.21}Ca_{0.37}Pb_{0.24}Ba_{0.06}(Ce_{0.43}Nd_{0.41}Pr_{0.08}$

$La_{0.06}Sm_{0.03}Gd_{0.01}Er_{0.01}Ho_{0.01})_{\Sigma 1.04}(Ti_{0.97}Nb_{0.04})_{\Sigma 1.01}Si_{8.06}O_{25.21}F_{0.90}$ $H_{6.42}$ with $Z = 4$. The structural formula based on assigned site-populations is $(Na_{0.80}\square_{0.20})_{\Sigma 1}(K_{0.37}Cs_{0.30})_{\Sigma 0.67}[(Ca_{0.25}Pb_{0.22}$ $Sr_{0.14})Na_{0.25}Ln^{3+}_{0.08}]_{\Sigma 0.94}(Sr_{0.98}Pb_{0.02})_{\Sigma 1}(Ln^{3+}_{0.96}Ca_{0.04})_{\Sigma 1}(Ti_{0.97}Nb_{0.03})_{\Sigma 1.00}$ $(Si_8O_{21})OF_{0.50}[F_{0.40}(H_2O)_{0.10}](H_2O)_{3.11}$, where $Ln^{3+}_{1.04} = (Ce_{0.43}Nd_{0.41}$

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

	Chemical composition			Unit formula*	
	Wt.%	Range	E.s.d.		(Apfu)
Nb_2O_5	0.53	0.36–0.96	0.18	Nb	0.04
TiO_2	7.03	6.83–7.23	0.14	Ti	0.97
SiO_2	43.85	42.69–44.16	0.34	Si	8.06
Er_2O_3	0.13	0.01–0.29	0.09	Er	0.01
Ho_2O_3	0.10	0.01–0.21	0.06	Ho	0.01
Gd_2O_3	0.09	0.02–0.31	0.08	Gd	0.01
Sm_2O_3	0.47	0.07–0.68	0.16	Sm	0.03
Nd_2O_3	6.22	5.61–6.81	0.40	Nd	0.41
Pr_2O_3	1.21	0.76–1.82	0.31	Pr	0.08
Ce_2O_3	6.34	5.63–7.07	0.40	Ce	0.43
La_2O_3	0.82	0.56–1.36	0.23	La	0.06
PbO	4.90	4.37–5.38	0.45	Pb	0.24
BaO	0.85	0.44–1.11	0.19	Ba	0.06
SrO	11.39	10.47–11.73	0.34	Sr	1.21
CaO	1.86	1.49–2.09	0.16	Ca	0.37
Cs_2O	3.80	3.67–4.18	0.28	Cs	0.30
K_2O	1.59	1.11–1.88	0.20	K	0.37
Na_2O	2.99	2.49–3.35	0.32	Na	1.07
F	1.55	1.34–1.81	0.19	F	0.90
H_2O**	5.24			H	6.42
O = F	−0.65				
Total	100.31				

*The empirical formula is calculated on 26.11 (O + F) apfu.
**H_2O is calculated from structure-refinement results: $H_2O = 3.21$ pfu; E.s.d. = estimated standard deviation.

$Pr_{0.08}La_{0.06}Sm_{0.03}Gd_{0.01}Er_{0.01}Ho_{0.01})_{\Sigma1.04}$, $\square$ = vacancy and $Ba_{0.06}$ does not belong to this mineral species (see below). The simplified formula is $(Na,\square)(K,Cs)(Ca,Pb,Sr,Na)SrLn^{3+}Ti(Si_8O_{21})OF(H_2O)_3$, where Ce is the dominant lanthanoid. The ideal formula of kalyuzhnyite-(Ce), $NaKCaSrCeTi(Si_8O_{21})OF(H_2O)_3$ (see below), requires (wt.%) Na_2O 3.06, K_2O 4.58, CaO 5.46, SrO 10.08, Ce_2O_3 15.97, TiO_2 7.78, SiO_2 46.78, F 1.85, H_2O 5.26, $O \equiv F$ −0.78, 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 kalyuzhnyite-(Ce) were collected from a twinned crystal with a Bruker APEX II ULTRA three-circle diffractometer with a rotating-anode generator (MoKα), multilayer optics and an APEX II 4K CCD detector. The intensities of reflections with $-26 \leq h \leq 26$, $-15 \leq k \leq 15$ and $-20 \leq l \leq 20$ were collected with a frame width of 0.3° and a frame time of 6 s up to $2\theta \leq 60.21°$, and an empirical absorption correction (*SADABS*, Sheldrick, 2015) applied. There were few observed reflections at high 2θ, and refinement of the structure was done for $2\theta \leq 55°$, $-24 \leq h \leq 24$, $-14 \leq k \leq 15$ and $-19 \leq l \leq 19$. The crystal-structure solution by direct methods and refinement were done with the Bruker *SHELXTL* Version 2014/3 software (Sheldrick, 2015) in space group *P2/c*. 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 kalyuzhnyite-(Ce) was refined to R_1 = 2.74%, the twin ratio

Table 4. Miscellaneous refinement data for kalyuzhnyite-(Ce).

Crystal data	
a (Å)	18.647(4)
b (Å)	11.214(2)
c (Å)	14.642(3)
β (°)	129.55(3)
V (Å^3)	2360.9(11)
Space group	*P2/c*
Z	4
Absorption coefficient (mm^{-1})	8.23
F(000)	2101.0
$D_{calc.}$ (g/cm^3)	3.120
Data collection	
Crystal size (mm)	0.025 × 0.06 × 0.07
Radiation/filter	MoKα/graphite
2θ-range for structure refinement (°)	4.37–55.00
Ratio of twin components*	0.5037(9) : 0.4963(9)
R(int) (%)	2.78
Reflections collected	27630
Independent reflections	5562
$F_o > 4\sigma F$	3907
Refinement	
Refinement method	Full-matrix least squares on F^2, fixed weights proportional to $1/\sigma F_o^2$
No. of refined parameters	409
Final $R_{(obs)}$ (%) [$F_o > 4\sigma F$]	2.74
R_1	4.25
wR_2	8.09
Highest peak, deepest hole (e Å^{-3})	+1.58, −0.75
Goodness of fit on F^2	1.033

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

being 0.5037(9) : 0.4963(9) (Table 4). Details of data collection and structure refinement are given in Table 4. The occupancies of ten cation sites were refined with the following scattering curves: *M*1 site: Ti; *M*2 site: Nd; *M*3 site: Sr; *M*4 site: Na; *M*(5,6) sites: Pb; *M*(7,8) sites: Ca; *A*(1,2) and *B*(1,2) sites: K and Cs, respectively. The occupancies of the F and *X* sites were refined with the

Table 3. Simulated powder X-ray diffraction data* for kalyuzhnyite-(Ce).

$I_{est.}$	$d_{calc.}$ (Å)	*h*	*k*	*l*	$I_{est.}$	$d_{calc.}$ (Å)	*h*	*k*	*l*	$I_{est.}$	$d_{calc.}$ (Å)	*h*	*k*	*l*	$I_{est.}$	$d_{calc.}$ (Å)	*h*	*k*	*l*
12	4.407	3	1	0	10	3.172	$\bar{3}$	3	1	22	2.047	$\bar{6}$	4	2	11	1.602	0	7	0
	4.407	$\bar{3}$	1	3		3.172	$\bar{3}$	3	2		2.047	$\bar{6}$	4	4		1.601	$\overline{10}$	2	2
	4.389	1	0	2	18	3.117	0	3	2	14	1.989	0	4	4		1.601	$\overline{10}$	2	8
14	4.305	$\bar{4}$	1	2	100	3.026	4	2	0	10	1.882	0	0	6	14	1.531	6	4	2
18	4.094	$\bar{3}$	2	1		3.026	$\bar{4}$	2	4	11	1.869	0	6	0		1.531	$\bar{6}$	4	8
	4.094	$\bar{3}$	2	2	40	2.963	2	2	2		1.867	$\bar{8}$	3	2		1.529	2	2	6
	4.087	1	1	2		2.963	$\bar{2}$	2	4		1.867	$\bar{8}$	3	6		1.529	$\bar{2}$	2	8
	4.087	$\bar{1}$	1	3	24	2.895	$\bar{6}$	1	2	22	1.830	4	4	2		1.525	$\overline{10}$	3	2
24	3.978	0	2	2		2.895	$\bar{6}$	1	4		1.830	$\bar{4}$	4	6		1.525	$\overline{10}$	3	8
10	3.738	0	3	0	18	2.804	0	4	0		1.827	6	0	2	10	1.463	4	7	0
12	3.595	0	0	4	12	2.737	0	1	4		1.827	$\bar{6}$	0	8		1.463	$\bar{4}$	7	4
	3.595	$\bar{4}$	0	4	28	2.591	4	3	0	20	1.803	6	1	2		1.463	2	3	6
	3.585	$\bar{4}$	2	2		2.591	$\bar{4}$	3	4		1.803	$\bar{6}$	1	8		1.463	$\bar{2}$	3	8
11	3.490	2	0	2	17	2.396	6	0	0		1.797	8	0	0	10	1.416	6	5	2
	3.490	$\bar{2}$	0	4		2.396	$\bar{6}$	0	6		1.797	$\bar{8}$	0	8		1.416	$\bar{6}$	5	8
	3.474	3	1	1	33	2.344	6	1	0		1.796	$\bar{6}$	5	2		1.413	$\bar{6}$	7	2
	3.474	$\bar{3}$	1	4		2.343	$\bar{6}$	1	6		1.796	$\bar{6}$	5	4		1.416	$\bar{6}$	7	4
22	3.423	4	1	0		2.338	$\bar{6}$	3	2		1.792	$\bar{8}$	4	4		1.411	9	2	1
	3.423	$\bar{4}$	1	4		2.338	$\bar{6}$	3	4	14	1.756	0	5	4		1.411	$\bar{9}$	2	10
33	3.332	2	1	2		2.331	$\bar{8}$	0	4	10	1.681	0	3	6		1.411	0	0	8
	3.332	$\bar{2}$	1	4	10	2.253	0	3	4	21	1.653	$\overline{10}$	1	2					
	3.317	2	3	0		2.243	0	5	0		1.653	$\overline{10}$	1	8					
	3.317	$\bar{2}$	3	2	11	2.218	4	2	2		1.651	$\overline{10}$	3	4					
						2.218	$\bar{4}$	2	6		1.651	$\overline{10}$	3	6					
						2.211	4	4	0										
						2.211	$\bar{4}$	4	4										

*Powder data were obtained by collapsing single-crystal X-ray diffraction data into two dimensions. Intensities are listed for reflections with $I_{est.} \geq 10$.

scattering curve of F, and $W(1–9)$ sites, with the scattering curve of O. Refinement of the F, X and $W1$ 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 anisotropic displacement 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 64* software (Dowty, 2016).

Site-population assignment

Si is assigned to the eight tetrahedrally coordinated $Si(1–8)$ sites, with <Si–O> = 1.614 Å (Tables 5, 6).

The four M sites in the heteropolyhedral sheet (Table 5) are considered next. At the [6]-coordinated $M1$ site, the refined scattering is 21.97 electrons per formula unit (epfu) and the mean

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

Atom	Site occ.	x	y	z	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}	U_{eq} *
M1	100	0.40116(7)	0.4996(2)	0.55505(6)	0.0099(5)	0.0108(4)	0.0070(4)	0.0011(10)	0.0056(4)	0.0002(11)	0.0091(2)
M2	100	0.14957(2)	0.50035(8)	0.24619(3)	0.0189(2)	0.01375(13)	0.01180(13)	0.0016(4)	0.01060(16)	0.0006(4)	0.01423(9)
M3	100	0.35540(3)	0.49953(13)	0.24984(5)	0.0134(3)	0.0197(2)	0.0104(2)	0.0005(6)	0.0076(3)	−0.0009(7)	0.01449(15)
M4	80	0.1086(2)	0.5015(7)	−0.040(2)	0.0170(17)	0.0208(14)	0.0190(13)	−0.004(3)	0.0124(13)	−0.004(3)	0.0182(8)
M5	54	0	0.28485(19)	¼	0.0250(12)	0.0265(11)	0.0259(11)	0	0.0175(10)	0	0.0248(6)
M6	56	0	0.7174(5)	¼	0.0214(12)	0.028(2)	0.0210(11)	0	0.0147(10)	0	0.0226(10)
M7	25	0.006(2)	−0.005(4)	0.034(2)	0.126(15)	0.008(7)	0.13(2)	−0.00(2)	0.09(2)	−0.018(15)	0.080(7)
M8	14	0.7608(6)	0.006(4)	0.4865(9)							0.067(4)*
A1	40	½	0.2109(6)	¼	0.048(3)	0.130(5)	0.037(2)	0	0.027(2)	0	0.0715(19)
A2	20	½	0.1970(5)	¾	0.041(4)	0.040(3)	0.020(3)	0	0.011(3)	0	0.040(2)
B1	40	0	0.775(3)	¼	0.029(5)	0.030(11)	0.045(5)	0	0.020(4)	0	0.038(3)
B2	34	½	0.2887(16)	¾	0.045(12)	0.050(14)	0.061(10)	0	0.029(10)	0	0.056(6)
Si1	100	0.2580(2)	0.2877(3)	−0.0065(2)	0.0139(17)	0.0155(16)	0.0111(15)	−0.0009(12)	0.0079(14)	−0.0001(13)	0.0135(7)
Si2	100	0.1952(2)	0.7623(3)	0.1355(2)	0.0118(16)	0.0136(13)	0.0105(14)	−0.0007(12)	0.0075(13)	−0.0009(12)	0.0117(6)
Si3	100	0.4995(3)	0.30061(14)	0.5000(3)	0.0120(6)	0.0104(6)	0.0114(6)	0.0015(16)	0.0084(5)	0.0008(17)	0.0106(3)
Si4	100	0.3280(2)	0.1367(3)	0.3834(2)	0.0150(17)	0.0108(14)	0.0104(15)	−0.0011(12)	0.0094(14)	−0.0018(13)	0.0111(6)
Si5	100	0.3276(2)	0.8630(3)	0.3832(3)	0.0155(17)	0.0107(14)	0.0119(16)	0.0013(12)	0.0093(14)	0.0016(13)	0.0123(7)
Si6	100	0.19516(19)	0.2374(3)	0.1356(2)	0.0096(15)	0.0135(14)	0.0104(14)	0.0006(11)	0.0060(13)	−0.0003(12)	0.0114(6)
Si7	100	0.2578(2)	0.2880(3)	0.4929(3)	0.0177(17)	0.0147(16)	0.0132(16)	−0.0023(13)	0.0116(15)	−0.0048(13)	0.0140(7)
Si8	100	−0.0007(3)	0.29031(16)	0.0000(4)	0.0111(6)	0.0208(8)	0.0133(6)	0.0030(19)	0.0077(6)	0.0028(19)	0.0151(3)
O1	100	0.1668(6)	0.3529(8)	0.8786(8)	0.030(6)	0.027(5)	0.031(5)	0.009(4)	0.009(4)	−0.005(4)	0.037(3)
O2	100	0.2987(6)	0.8162(7)	0.4592(7)	0.041(5)	0.021(4)	0.029(5)	0.008(4)	0.030(4)	0.000(4)	0.025(2)
O3	100	0.3406(6)	0.3792(7)	0.0859(6)	0.028(4)	0.020(4)	0.014(4)	−0.003(3)	0.019(4)	−0.006(4)	0.0169(17)
O4	100	0.2318(6)	0.2080(7)	0.0619(7)	0.032(5)	0.017(5)	0.033(5)	−0.002(4)	0.029(4)	−0.003(4)	0.0215(19)
O5	100	0.2103(5)	0.6265(6)	0.1734(7)	0.018(4)	0.015(4)	0.033(5)	0.004(3)	0.018(4)	0.001(3)	0.0203(17)
O6	100	0.0869(5)	0.8010(8)	0.0498(6)	0.008(4)	0.028(5)	0.034(5)	0.009(4)	0.010(4)	0.000(4)	0.026(2)
O7	100	0.2332(5)	0.7925(7)	0.0645(6)	0.021(4)	0.018(4)	0.017(4)	0.004(3)	0.015(4)	0.003(3)	0.0163(17)
O8	100	0.2427(6)	0.8566(6)	0.2408(6)	0.027(5)	0.022(4)	0.011(4)	0.002(3)	0.006(4)	0.012(4)	0.0245(19)
O9	100	0.5086(5)	0.3802(7)	0.4151(6)	0.023(5)	0.014(4)	0.012(4)	−0.002(3)	0.007(4)	−0.010(4)	0.0192(19)
O10	100	0.4109(5)	0.2146(8)	0.4105(6)	0.030(5)	0.031(5)	0.020(4)	−0.014(4)	0.018(4)	−0.018(4)	0.026(2)
O11	100	0.4928(5)	0.3764(7)	0.5855(6)	0.013(4)	0.018(3)	0.016(4)	−0.001(3)	0.012(3)	−0.002(3)	0.0135(15)
O12	100	0.4117(5)	0.7846(8)	0.4123(6)	0.021(5)	0.026(5)	0.029(5)	0.009(4)	0.018(4)	0.012(4)	0.023(2)
O13	100	0.2446(6)	0.1419(6)	0.2460(7)	0.026(5)	0.023(4)	0.015(4)	0.009(3)	0.010(4)	0.006(4)	0.0236(19)
O14	100	0.2958(6)	0.1834(7)	0.4556(7)	0.042(6)	0.026(4)	0.039(5)	−0.009(4)	0.036(5)	−0.009(4)	0.029(2)
O15	100	0.3594(2)	0.9996(8)	0.4196(3)	0.0223(17)	0.0119(15)	0.0159(16)	0.006(4)	0.0068(15)	0.004(5)	0.0206(7)
O16	100	0.2116(5)	0.3738(7)	0.1753(6)	0.024(5)	0.018(4)	0.025(5)	−0.003(3)	0.018(4)	0.001(4)	0.0207(18)
O17	100	0.0854(5)	0.1996(8)	0.0491(6)	0.013(4)	0.025(5)	0.019(4)	−0.001(4)	0.008(4)	0.001(4)	0.0201(19)
O18	100	0.1673(6)	0.3513(7)	0.3811(6)	0.016(4)	0.031(5)	0.009(4)	0.006(3)	−0.001(4)	−0.003(4)	0.025(2)
O19	100	0.3406(5)	0.3784(7)	0.5862(6)	0.006(3)	0.019(4)	0.013(4)	−0.003(4)	0.002(3)	−0.006(3)	0.0151(16)
O20	100	−0.0218(4)	0.3684(9)	−0.1074(7)	0.020(5)	0.054(6)	0.024(5)	0.020(4)	0.010(4)	0.001(4)	0.036(2)
O21	100	0.0194(5)	0.3666(8)	0.1061(6)	0.022(4)	0.030(5)	0.021(4)	−0.001(4)	0.017(4)	0.005(4)	0.0221(19)
O22	100	0.3253(2)	0.5000(8)	0.4035(3)	0.0148(16)	0.0256(16)	0.0094(13)	−0.003(4)	0.0073(14)	−0.002(5)	0.0168(6)
F	100	½	0.4980(9)	¾	0.015(2)	0.0170(16)	0.0070(14)	0	0.006(2)	0	0.0137(7)
X	100	0	0.5024(11)	¾	0.051(4)	0.026(2)	0.030(2)	0	0.028(3)	0	0.0335(10)
W1	100	0.6256(3)	−0.0013(9)	0.3189(4)	0.062(3)	0.0077(16)	0.076(3)	0.004(6)	0.064(3)	0.002(5)	0.0340(11)
H1	100	0.571(3)	0.038(5)	0.248(4)							0.04080*
H2	100	0.603(4)	−0.081(3)	0.316(6)							0.04080*
W2	42	−0.0459(9)	0.004(3)	0.8462(12)							0.05000*
W3	28	−0.069(2)	0.098(2)	0.255(3)							0.05000*
W4	32	−0.0548(17)	−0.082(2)	0.275(2)							0.05000*
W5	40	0	−0.005(3)	¼							0.05000*
W6	14	0.8992(14)	−0.040(4)	0.635(3)							0.05000*
W7	26	0.045(2)	0.075(2)	0.356(2)							0.05000*
W8	24	0.067(2)	−0.085(3)	0.349(3)							0.05000*
W9	25	0.8778(16)	0.004(5)	0.574(2)							0.05000*

*U_{iso}

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

M1–O22	1.711(3)	M2–O(1)c	2.404(8)	M3–O16	2.578(8)	A1–O(9)g,m	2.997(9) ×2	A2–W(1)o,r	2.883(9) ×2
M1–O(9)a	1.977(8)	M2–O(20)d	2.410(9)	M3–O5	2.597(7)	A1–O(3)g,m	3.013(9) ×2	A2–O(11)g,p	3.076(8) ×2
M1–O(3)b	1.995(7)	M2–O5	2.441(7)	M3–O3	2.610(7)	A1–W(1)g,m	3.026(10) ×2	A2–O(19)g,p	3.105(8) ×2
M1–O19	1.997(8)	M2–O16	2.441(7)	M3–O(19)c	2.617(7)	A1–Fa	3.26(1)	A2–F	3.38(1)
M1–O11	2.015(7)	M2–O18	2.445(8)	M3–O22	2.644(3)	A1–O(2)c,a	3.458(9) ×2	A2–O(14)g,p	3.493(9) ×2
M1–F	2.201(1)	M2–O21	2.452(8)	M3–O9	2.646(8)	A1–O(10)a,b	3.642(7) ×2	A2–O(12)a,b	3.658(7) ×2
<M1–φ>	1.983	M2–O22	2.535(4)	M3–O(11)a	2.659(7)	<A1–φ>	3.230	<A2–φ>	3.255
		M2–X	2.8251(6)	M3–Fa	2.6949(7)				
		<M2–φ>	2.494	<M3–φ>	2.631				
M4–Xe	2.373(3)	M5–Xf	2.39(1)	M6–Xf	2.46(1)	B1–O(1)f,c	2.80(2) ×2	B2–F	2.35(2)
M4–O(21)d	2.425(10)	M5–W(3)g,h	2.49(3) ×2	M6–W(8)i,j	2.51(4) ×2	B1–O(20)d,b	2.86(2) ×2	B2–O(11)g,p	2.526(9) ×2
M4–O20	2.46(1)	M5–O(18)g,h	2.520(8) ×2	M6–O(1)g,b	2.525(9) ×2	B1–Xf	3.12(3)	B2–O(19)g,p	2.55(1) ×2
M4–O(18)c	2.62(1)	M5–O(21)g,h	2.526(7) ×2	M6–O(20)g,b	2.553(9) ×2	B1–W(2)f,c	3.22(4) ×2	B2–O(14)g,p	2.68(1) ×2
M4–O(1)e	2.65(1)	M5–W(7)g,h	2.64(3) ×2	M6–W(4)i,j	2.58(3) ×2	B1–O(17)d,b	3.593(8) ×2	B2–W(1)o,q	3.73(2) ×2
M4–O5	2.787(9)	*<M5–φ>	2.515	**<M6–φ>	2.531	<B1–φ>	3.12	B2–O(12)a,b	3.743(8) ×2
M4–O16	2.820(9)							<B2–φ>	2.983
<M4–φ>	2.591								
M7–W(2)	2.26(2)	M8–W1	2.123(2)	Si1–O(1)e	1.617(9)	Si2–O5	1.584(7)	Si3–O11	1.581(7)
M7–W(4)h	2.48(3)	M8–W6	2.124(2)	Si1–O3	1.613(8)	Si2–O8	1.594(7)	Si3–O(12)a	1.611(8)
M7–O(17)k	2.54(4)	M8–O(4)m	2.40(4)	Si1–O4	1.632(8)	Si2–O6	1.617(8)	Si3–O10	1.619(8)
M7–O(6)l	2.57(4)	M8–O(7)n	2.54(4)	Si1–O(2)c	1.635(8)	Si2–O7	1.623(7)	Si3–O9	1.624(8)
M7–O(6)d	2.65(4)	M8–O(2)a	2.64(3)	<Si1–O>	1.625	<Si2–O>	1.605	<Si3–O>	1.609
M7–O17	2.67(4)	M8–O(14)o	2.74(3)						
<M7–φ>	2.53	<M8–φ>	2.380						
Si4–O13	1.577(8)	Si5–O12	1.601(8)	Si6–O16	1.596(7)	Si7–O18	1.585(8)	Si8–O21	1.595(8)
Si4–O10	1.590(8)	Si5–O2	1.602(8)	Si6–O4	1.635(7)	Si7–O19	1.610(8)	Si8–O20	1.615(8)
Si4–O14	1.601(8)	Si5–O15	1.606(9)	Si6–O17	1.635(8)	Si7–O14	1.633(8)	Si8–O17	1.630(8)
Si4–O(15)l	1.610(9)	Si5–O8	1.629(8)	Si6–O13	1.647(7)	Si7–O(7)b	1.655(7)	Si8–O(6)d	1.635(8)
<Si4–O>	1.595	<Si5–O>	1.610	<Si6–O>	1.628	<Si7–O>	1.621	<Si8–O>	1.619
Si(1)b–O2–Si5	151.0(6)	Short distances							
Si1–O4–Si6	135.1(6)	M6–B1	0.65(3)						
Si2–O6–Si(8)d	124.5(5)	M7–M(7)k	0.88(4)						
Si2–O7–Si(7)c	134.6(5)	B2–A2	1.03(2)						
Si2–O8–Si5	139.1(5)								
Si3–O10–Si4	149.2(5)	W3–W7	1.67(4)						
Si(3)a–O12–Si5	150.8(5)	W4–W8	1.79(4)						
Si4–O13–Si6	139.2(5)	W4–W(8)h	1.68(4)						
Si4–O14–Si7	151.8(5)								
Si(4)i–O15–Si5	145.2(2)								
Si6–O17–Si8	125.1(5)								
<Si–O–Si>	140.5								

φ = O, F and H_2O; *M5–W3 and M5–W7 distances are weighted by 60 and 40%, respectively (54%-occupancy of the M5 site: 28%- and 26%-occupancies of the W3 and W7 sites); **M6–W8 and M6–W4 distances are weighted by 43 and 57%, respectively (56%-occupancy of the M6 site: 24%- and 32%-occupancies of the W8 and W4 sites).

Symmetry codes: a: –x + 1, –y + 1, –z + 2; b: x, –y + 1, z+½; c: x, –y + 1, z–½; d: –x, –y + 1, –z; e: x + 1, y, z; f: –x, –y + 1, –z + 1; g: x, y, z; h: –x, y, –z+½; i: x, y + 1, z; j: –x, –y, –z + 1; k: –x, –y, –z; l: x, y–1, z; m: –x + 1, y, –z+½; n: –x + 1, y–1, –z+½; o: –x + 1, –y, –z + 1; p: –x + 1, y, –z + 3/2; q: –x, y + 1, –z+½.

bond-length <M1−φ> = 1.983 Å (φ = O, F). In accord with the grand mean bond-length <[6]Ti^{4+}–O> = 1.971 Å> observed in inorganic structures (Gagné and Hawthorne, 2020), we assign all available Ti (Table 2) and minor Nb to the M1 site: $Ti_{0.97}Nb_{0.03}$ apfu, with calculated site-scattering of 22.57 epfu (Table 7). At the [8]-coordinated M2 site, the refined scattering is 57.1 epfu and the mean bond-length <M2−φ> = 2.494 Å (φ = O, F). In accord with the grand mean bond-length <[8]Ce^{3+}–O> = 2.495 Å> observed in inorganic structures (Gagné, 2018), we assign REE = $Ln_{0.96}^{3+}$, where Ce is the dominant lanthanoid (Ln = lanthanoids), and minor Ca: 0.04 apfu, to the M2 site: $Ln_{0.96}Ca_{0.04}$ pfu [[8]Ce^{3+}: r = 1.143 Å, [8]Ca^{2+}: r = 1.12 Å, Shannon (1976)] (Tables 5–7). There is a good agreement between refined and calculated site-scattering for the M2 site: 57.1 and 57.59 epfu, respectively (Table 7). On the basis of the refined site-scattering values and observed bond-distances, we assign $Sr_{0.98}Pb_{0.02}$ and $Ca_{0.80}\square_{0.20}$ pfu to the M3 and M4 sites, respectively (Table 7).

Consider the interstitial M(5–8), A(1,2) and B(1,2) sites. The refined site-scattering value at the M5 site is slightly higher than at the M6 site: 15.3 versus 14.7 epfu; the mean bond-length values: 2.515 and 2.531 Å, are very similar. Therefore, we allocate more Pb (the heaviest scatter) to the M5 site: $Pb_{0.16}Ca_{0.11}\square_{0.23}$ pfu, and less Pb to the M6 site: $Sr_{0.14}Ln_{0.08}Pb_{0.06}Ca_{0.11}\square_{0.22}$ pfu (Table 7). Based on the refined site-scattering values and observed bond-distances, we assign $Na_{0.25}\square_{0.75}$ and $Ca_{0.14}\square_{0.86}$ pfu to the M7 and M8 sites, respectively (Table 7).

The refined site-scattering values at the [11]- and [9]- coordinated A(1,2) and B(1,2) sites sum to 21.01 epfu (Table 7). The cations to be assigned to these sites are $Cs_{0.30}$, $K_{0.37}$ and $Ba_{0.06}$, with individual calculated scattering of 16.5, 7.03 and 3.36 epfu, respectively, and a total calculated scattering 26.89 epfu (Table 2). The A(1,2) sites, with total refined site-scattering of 15.7 epfu and derived cations' radii of 1.85 and 1.88 Å, respectively [e.g. calculated as <A1–O> − r([4]O[2−]): 3.320–1.38 = 1.85 Å] must be occupied by Cs [[11]Cs: r = 1.85 Å, Shannon (1976)]. Hence, we

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

Site	Refined site-scattering (epfu)	Assigned site-population (apfu)	Calculated site-scattering (epfu)	<Cation–φ>$_{obs.}$ (Å)	Ideal composition (pfu)
		Heteropolyhedral sheet			
[6]$M1$	21.97(9)	Ti$_{0.97}$Nb$_{0.03}$	22.57	1.983	Ti
[8]$M2$*	57.1(1)	$Ln_{0.96}$Ca$_{0.04}$	57.59	2.494	Ce
[8]$M3$	38.3(1)	Sr$_{0.98}$Pb$_{0.02}$	38.88	2.631	Sr
[7]$M4$	8.3(1)	Na$_{0.80}$□$_{0.20}$	8.80	2.591	Na
ΣM(1–4)	125.67	Na$_{0.80}$Sr$_{0.98}$Ti$_{0.97}$$Ln_{0.96}Ca_{0.04}Nb_{0.03}Pb_{0.02}$	127.84		NaSrCeTi
		Interstitial cations			
[7]$M5$	15.3(1)	Pb$_{0.16}$Ca$_{0.11}$□$_{0.23}$	15.32	2.515	
[7]$M6$*	14.7(3)	Sr$_{0.14}$$Ln_{0.08}Pb_{0.06}$□$_{0.22}$	14.97	2.531	
[6]$M7$	2.5**	Na$_{0.25}$□$_{0.75}$	2.75	2.53	
[6]$M8$	2.4**	Ca$_{0.14}$□$_{0.86}$	2.80	2.38	
ΣM(5–8)	34.9	[(Ca$_{0.25}$Pb$_{0.22}$Sr$_{0.14}$)Na$_{0.25}$$Ln_{0.08}$]$_{Σ0.94}$	35.84		Ca
[11]$A1$	10.3(1)	Cs$_{0.20}$□$_{0.30}$	11.00	3.230	
[11]$A2$	5.4(1)	Cs$_{0.10}$□$_{0.40}$	5.50	3.255	
[9]$B1$	3.3(3)	K$_{0.20}$□$_{0.30}$	3.80	3.12	
[11]$B2$	2.1(1)	K$_{0.17}$□$_{0.33}$	3.23	2.983	
Σ(A,B)	21.1	(K$_{0.37}$Cs$_{0.30}$)$_{Σ0.67}$	23.53		K
Total cations	181.67		187.21		
		Si–O sheet			
[4]Si(1–8)		Si$_8$			Si$_8$
O(1–21)		O$_{21}$			O$_{21}$
Σ		Si$_8$O$_{21}$			(Si$_8$O$_{21}$)
		Anions and H$_2$O groups			
$O22$		O$_{1.00}$			O
F		F$_{0.50}$			F$_{0.50}$
X		[F$_{0.40}$(H$_2$O)$_{0.10}$]			F$_{0.50}$
$W1$		(H$_2$O)$_{1.00}$			H$_2$O
W(2–9)		(H$_2$O)$_{2.11}$			(H$_2$O)$_2$
Σ(anions, H$_2$O)		OF$_{0.90}$(H$_2$O)$_{3.21}$			OF(H$_2$O)$_3$

φ = O, F and H$_2$O.
*$Ln^{3+}_{1.04}$ = (Ce$_{0.43}$Nd$_{0.41}$Pr$_{0.08}$La$_{0.06}$Sm$_{0.03}$Gd$_{0.01}$Er$_{0.01}$Ho$_{0.01}$)$_{Σ1.04}$, with f_{av} = 59.16 *el.* (f_{av} = average scattering curve for $Ln^{3+}_{1.04}$).
**Site scattering was refined, adjusted in accord with the chemical analysis (Table 2), and then fixed at the last stages of the refinement.

Table 8. Bond-valence values* (vu) for selected anions** in kalyuzhnyite-(Ce).

Atom	M1	M2	M3	M7	B2	A1	A2	Σ
Dominant species	Ti	Ce	Sr	Na	K	Cs	Cs	
Site occ. (%)	100	100	100	25	34	40	20	
O22	1.32	0.35	0.23					1.90
F	0.24$^{→2}$		0.17$^{→2}$			0.07	0.03	0.01	0.93
W1				0.08		0.07	0.05	0.20

*Bond-valence parameters (vu) are from Brown (1981); bonds to oxygen were used for cations bonded to O22 and W1; bonds to fluorine were used for cations bonded to F; occupancies of cation sites were taken into account for all calculations.
**Anions which do not coordinate Si.

Table 9. Bond-valence values* (vu) for the X anion involved in short-range order in kalyuzhnyite-(Ce).

Atom	M2	M4	M5	M6	B1	Σ
Dominant species	Ce	Na	Pb	Sr	K	
Site occupancy (%)	100	100	54	56	40	
X = F	0.13$^{→2}$	0.15$^{→2}$	0.19	0.14	0.03	0.92
Atom	M2	M4	M5	M6	B1	Σ
Dominant species	Ce	Na	Pb	Sr	K	
Site occupancy (%)	100	0	54	0	100	
X	0.17$^{→2}$		0.19	0	0.08	0.61

*Bond-valence parameters (vu) are from Brown (1981).

refined site-scattering of 5.4 epfu and derived cation radii of 1.74 and 1.60 Å, respectively, must be occupied by K [[11]K: r = 1.62 Å, [9]K: r = 1.55 Å, Shannon (1976)]. Hence, we assign K$_{0.20}$□$_{0.30}$ and K$_{0.17}$□$_{0.33}$ pfu to the $B1$ and $B2$ sites, with calculated site-scattering values of 3.80 and 3.23 epfu, respectively, and a sum of 7.03 epfu (Table 7). There is a good agreement between refined and calculated site-scattering values for (1) the Cs-bearing A(1,2) sites: 15.7 versus 16.50 epfu; (2) the K-bearing B(1,2) sites: 5.4 versus 7.03 epfu and (3) A + B sites: 21.1 versus 23.53 epfu (Table 7). We were not able to assign Ba$_{0.06}$ apfu (calculated scattering is 3.36 epfu; [11]Ba: r = 1.57 Å, [9]Ba: r = 1.47 Å) to the A and B sites and suggest that Ba$_{0.06}$ does not occur in the crystal structure of kalyuzhnyite-(Ce).
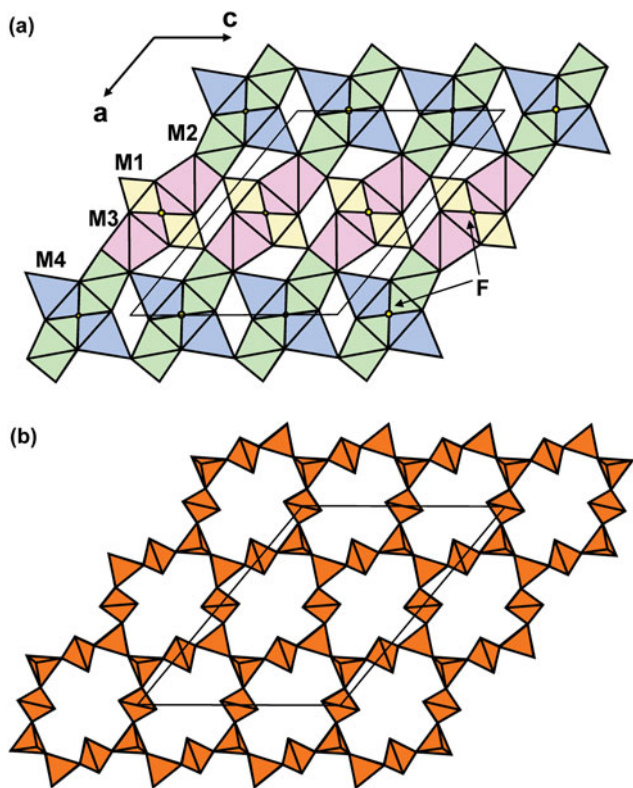
Description of the structure

Cation sites

The crystal structure of kalyuzhnyite-(Ce) contains three groups of cation sites: M sites of the heteropolyhedral sheet, Si sites of the Si–O sheet and interstitial M(5–8), A(1,2) and B(1,2) sites.

Heteropolyhedral sheet

There are four cation sites in the heteropolyhedral sheet: the Ti-dominant $M1$ site, the Ce-dominant $M2$ site, the Sr-dominant $M3$ site, and the Na-dominant $M4$ site (Fig. 3a). The $M1$ site is occupied by Ti$_{0.97}$Nb$_{0.03}$ apfu, ideally Ti apfu. The M1 atom is octahedrally coordinated by six anions: five O atoms and one F atom, <M1–φ> = 2.983 Å (φ = O and F)

assign Cs$_{0.20}$□$_{0.30}$ and Cs$_{0.10}$□$_{0.40}$ pfu to the $A1$ and $A2$ sites, with calculated site-scattering values of 11.0 and 5.50 epfu, respectively, with a sum of 16.5 epfu (Table 7). The B(1,2) sites, with total

Figure 3. Main structural units in the crystal structure of kalyuzhnyite-(Ce): (a) the heteropolyhedral sheet $(NaSrCeTiOF)^{7+}$; (b) the double $(Si_8O_{21})^{10-}$ sheet. Ti-dominant M1 octahedra are pale yellow, [8]-coordinated Ce-dominant M2 and Sr-dominant M3 polyhedra are green and pink, respectively; [7]-coordinated Na-dominant M4 polyhedra are blue, F atoms are shown as small yellow spheres and SiO_4 tetrahedra are orange.

(Tables 5–7). The $M2$ site is occupied by $Ln_{0.96}Ca_{0.04}$ apfu, ideally Ce apfu (Ce is the dominant lanthanoid). The M2 atom is coordinated by eight anions: seven O atoms and one X anion, $<M2-\varphi> = 2.494$ Å (φ = O, F and H_2O) (Tables 5–7). The $M3$ site is occupied by $Sr_{0.98}Pb_{0.02}$ pfu, ideally Sr apfu. The M3 atom is coordinated by eight anions: seven O atoms and one F atom, $<M3-\varphi> = 2.631$ Å (φ = O and F) (Tables 6, 7). The $M4$ site is occupied by Na at 80%, its ideal composition is Na apfu. The M4 atom is coordinated by seven anions: six O atoms and one X anion, $<M4-\varphi> = 2.591$ Å (φ = O, F and H_2O) (Tables 6, 7). Ideally, cations of the heteropolyhedral sheet, ^{M4}Na + ^{M3}Sr + ^{M2}Ce + ^{M1}Ti, sum to $(NaSrCeTi)^{10+}$ apfu (Table 7).

Si–O sheet

In the Si–O sheet (Fig. 3b), there are eight $Si(1-8)$ tetrahedrally coordinated sites occupied by Si with a $<Si-O>$ distance of 1.614 Å (Tables 5, 6). We consider the Si–O sheet a complex anion (see below).

Interstitial sites

Interstitial cations occur at the eight partly occupied $M(5-8)$, $A(1,2)$ and $B(1,2)$ sites within the double Si–O sheet (Fig. 4a,b; Table 5). There are short distances between cations which occur at the four interstitial sites (Table 6): M6–B1 = 0.65(3) Å and B2–A2 = 1.03(2) Å, so these sites can be only alternately occupied. There is a short distance between two points of the $M7$ site:

$M7-M7' = 0.88(4)$ Å (Table 6), hence the $M7$ site must be occupied at $\leq 50\%$. The $M5$ and $M6$ sites are 54% and 56% occupied; their compositions are $Pb_{0.16}Ca_{0.11}\square_{0.23}$ and $Sr_{0.14}Ln_{0.08}Pb_{0.06}\square_{0.22}$ pfu, respectively. The M5 and M6 sites are each coordinated by four basal O atoms of Si tetrahedra, an X ligand and H_2O groups at the partly occupied $W(3,7)$ sites [$M5$] and $W(4,8)$ sites [$M6$] (Fig. 5a; Table 6). Because of short O–O distances [W3–W7 = 1.67 Å and W4–W8 = 1.79 and 1.68 Å (Table 6)] the $W3-W7$ and $W4-W8$ sites can be only alternately occupied. The partial occupancies of the $W3$ site (28%) + $W7$ site (26%) (Table 5) sum to 54%, equivalent to the 54%-occupancy of the $M5$ site. The partial occupancies of the $W4$ site (32%) + $W8$ site (24%) (Table 5) sum to 56%, equivalent to the 56%-occupancy of the $M6$ site. Therefore, we consider [W3 + W7] and [W4 + W8] as two aggregate ligands (H_2O groups) for the M5 and M6 atoms, respectively. Hence M5 and M6 atoms are each coordinated by four O atoms of Si tetrahedra, an X ligand (see *Anion sites* below) and an H_2O group, with $<M5-\varphi> = 2.515$ Å and $<M6-\varphi> = 2.531$ Å (Tables 6, 7). The $M7$ and $M8$ sites are occupied by Na at 25% and Ca at 14%, respectively (Fig. 5b; Table 7). The M7 and M8 atoms are coordinated by four O atoms and two H_2O groups at the $W(2,4)$ sites [$M7$] and $W(1,6)$ sites [$M8$], with $<M7-\varphi> = 2.53$ Å and $<M8-\varphi> = 2.380$ Å (Tables 6, 7). The composition of the four $M(5-8)$ sites is $[(Ca_{0.25}Pb_{0.22}Sr_{0.14})Na_{0.25}Ln_{0.08})]_{\Sigma0.94}$, ideally Ca apfu (Table 7). The two [11]-coordinated $A1$ and $A2$ sites are occupied by Cs at 40% and 20%, respectively (Fig. 5c; Tables 5–7). The Cs atoms are coordinated by eight O atoms, two H_2O groups ($W1$ site) and a F atom, with $<A1-\varphi> = 3.230$ Å and $<A2-\varphi> = 3.255$ Å (Tables 6, 7). The [9]-coordinated $B1$ and [11]-coordinated $B2$ sites are occupied by K at 40% and 34%, respectively (Fig. 5d,e; Tables 5–7). The B1 atom is coordinated by six O atoms, two H_2O groups ($W2$ site) and one X ligand, with $<B1-\varphi> = 3.12$ Å and the B2 atom is coordinated by eight O atoms, two H_2O groups ($W1$ site) and a F atom, with $<B2-\varphi> = 2.983$ Å (Tables 6, 7). The $A(1,2) + B(1,2)$ sites are occupied by $(K_{0.37}Cs_{0.30})_{\Sigma0.67}$, ideally K apfu (Table 7). Ideally, interstitial cations, $^{M(5-8)}$Ca + $^{A(1,2)B(1,2)}$K, sum to $(KCa)^{3+}$ pfu.

Cations of the heteropolyhedral sheet and interstitial complex ideally sum to $(NaSrCeTi)^{10+} + (KCa)^{3+} = (NaKCaSrCeTi)^{13+}$.

Anion sites

Si–O sheet

There are 21 anion sites, $O(1-21)$, occupied by O atoms which form the tetrahedral coordination of the $Si(1-8)$ atoms (Tables 5, 6). The $Si(1-8)$ and $O(1-21)$ atoms form a distinct complex Si–O oxyanion, $(Si_8O_{21})^{10-}$ per formula unit.

Heteropolyhedral sheet

The M(1–4) cations of the heteropolyhedral sheet are coordinated by O atoms shared with the Si–O sheet, and three other ligands. There is one O atom (O22), which is a common vertex for the M1 [Ti], M2 [Ce] and M3 [Sr] polyhedra, it receives bond-valence of 1.90 vu (valence units) (Table 8). The F atom receives bond-valence contributions from two M1 [Ti] atoms, two M3 [Sr] atoms and interstitial cations A(1,2) [Cs], and B2 [K], with a total sum of 0.93 vu (Table 8). The F site gives $F_{0.5}$ apfu (Table 7). The X anion (Tables 5, 9) is involved in short-range order (SRO). SRO-1 (80%) occurs where the X anion receives bond-valence contributions from two M4 [Na] atoms [note that the M4 site is occupied by Na at 80%, Tables 5, 7, 9],
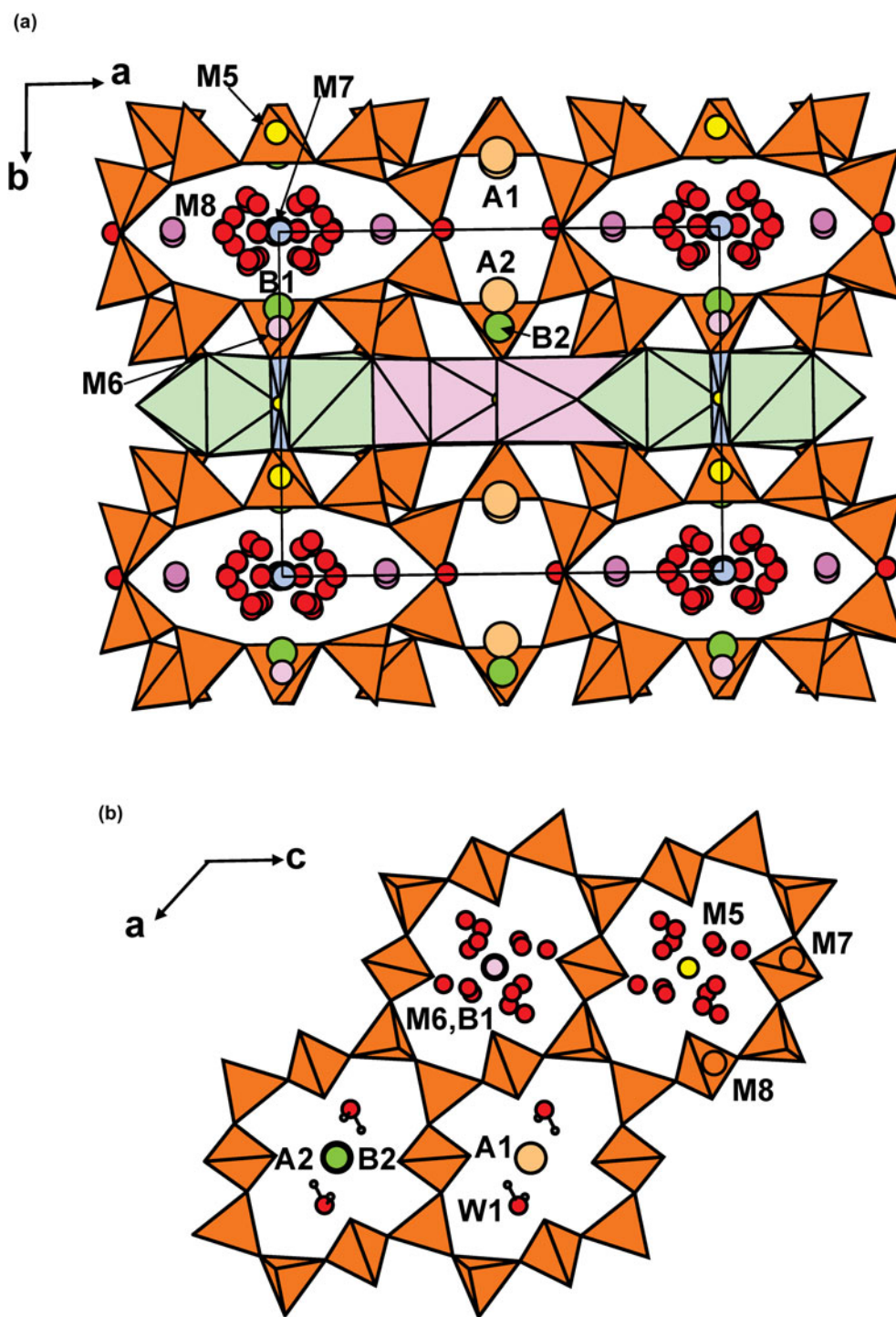
Figure 4. General view of the crystal structure of kalyuzhnyite-(Ce): (a) linkage of two double Si–O sheets and a heteropolyhedral sheet with interstitial cations at partly occupied $M(5–8)$, $A(1,2)$ and $B(1,2)$ sites and H_2O groups; (b) positions of interstitial cations and H_2O groups within the ten-membered rings of SiO_4 tetrahedra of the double Si–O sheet. Legend as in Fig. 3, dominant cations at partly occupied sites are shown as spheres: Pb (bright yellow) at the $M5$ site; Sr (pink) at the $M6$ site; Na (blue) at the $M7$ site; Ca (bright pink) at the $M8$ site; Cs (pale orange) at the $A(1,2)$ sites and K (green) at the $B(1,2)$ sites; an H_2O group at the $W1$ site is shown as a central O atom (red sphere) with two H atoms (small grey spheres), and O–H bonds are shown as black lines.

two M2 [Ce] atoms and interstitial cations: M5 [Pb], M6 [Sr] and B1 [K], with a total sum of 0.92 vu (Table 9), hence X is a F atom. SRO-2 (20%) occurs where the X anion does not receive bond-valence contributions from two M4 [Na] atoms [note that the $M4$ site is vacant at 20%, Tables 5, 7] and M(6) [Sr], but receives bond-valence contributions from two M2 [Ce] atoms and interstitial cations: M5 [Pb] and B1 [K], with a total sum of 0.61 vu (Table 9), hence X is an H_2O group. We write the composition of the X ligand as $F_{0.40}(H_2O)_{0.10}$ pfu, ideally $F_{0.5}$ apfu (Table 7). Hence ideal composition of the anions/H_2O groups of the heteropolyhedral sheet not shared with the Si–O sheet is $^{O22}O^{2-} + {^F}F_{0.5}^{0.5-} + {^X}F_{0.5}^{0.5-} = (OF)^{3-}$ pfu.
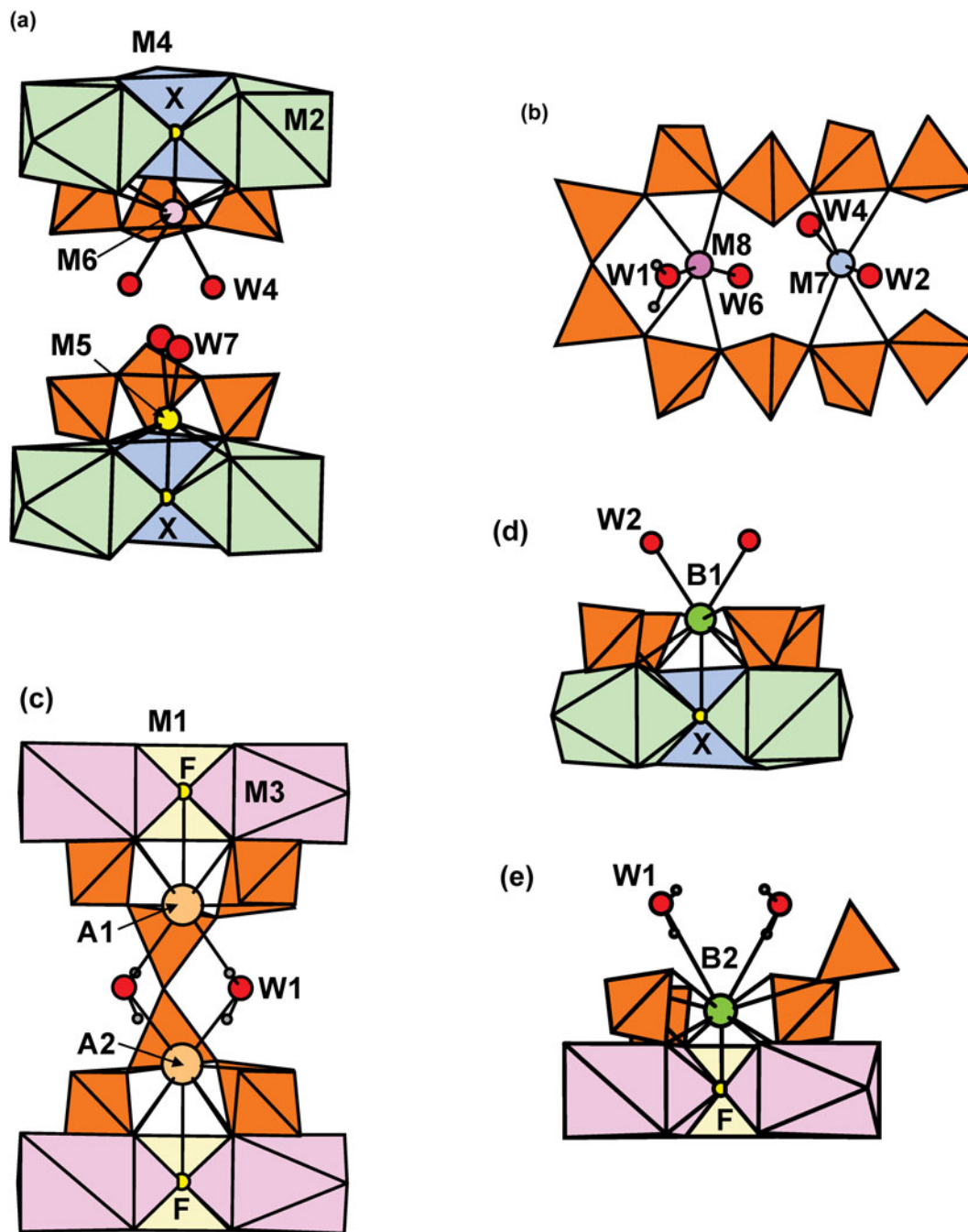
Figure 5. Details of the coordination of the interstitial cations in the crystal structure of kalyuzhnyite-(Ce): (a) [7]-coordinated Pb at the *M*5 site and Sr at the *M*6 site, respectively; (b) [6]-coordinated Na at the *M*7 site and Ca at the *M*8 site, respectively; (c) [11]-coordinated Cs at the *A*(1,2) sites; (d) [9]-coordinated K at the *B*1 site; (e) [11]-coordinated K at the *B*2 site. Legend as in Fig. 4a, W(2,4,6,7,8) are H_2O groups at partly occupied sites, the X anion has composition $[F_{0.40}(H_2O)_{0.10}]$ pfu.

Interstitial complex

The O atoms of H_2O groups at the *W*(1–9) sites occur within the Si–O sheet in the large channels at y ≈ 0 (Fig. 4a,b; Table 5). The O atom at the *W*1 site receives 0.20 vu from interstitial cations (Table 8) and it is an O atom of an H_2O group. The *W*1 site is 100%-occupied by an H_2O group, giving $(H_2O)_{1.0}$ pfu (Tables 5, 7; note positions of the two H atoms in Table 5). The eight *W*(2–9) sites are partly occupied by H_2O groups at 14–42% (Table 5), in total giving $(H_2O)_{2.11}$ pfu (Table 7). The *W*(1–9) sites give $(H_2O)_{3.11}$ pfu, ideally $(H_2O)_3$ pfu.

The complex Si–O anion, and the simple anions of the heteropolyhedral sheet and interstitial complex (charge is given in brackets), (Si_8O_{21}) (10^-) + (OF) $[O22,X,F]$ (3^-) + $(H_2O)_3$ [W(1–9)] (0), sum to $(Si_8O_{21})OF(H_2O)_3$, with a total charge of 13^-.

General topology of the crystal structure

There are two main structural units in the crystal structure of kalyuzhnyite-(Ce): a heteropolyhedral sheet and a double Si–O sheet (Fig. 3a,b). The heteropolyhedral sheet parallel to (010) is composed of Ti-dominant M1 octahedra, Ce-dominant M2

polyhedra, and Sr-dominant M3 polyhedra and Na-dominant M4 polyhedra which share edges and vertices (Fig. 3a, Tables 5–7). We sum the cation and anion parts of the heteropolyhedral sheet to derive its ideal composition: $(NaSrCeTi)^{10+} + (OF)^{3-} = [NaSrCeTi(OF)]^{7+}$. The double Si–O sheet parallel to (010) is composed of ten-membered rings of SiO_4 tetrahedra (Figs 3b, 4b). The ten-membered rings occur at $y \approx +0.265$ and $y \approx -0.265$ and connect via two SiO_4 tetrahedra which form an Si4–O15–Si5 bridge oriented along **b** (Fig. 4a; Table 6). The composition of this double Si–O sheet is $(Si_8O_{21})^{10-}$. Such a double Si–O sheet is new – a sheet with this topology and composition has never been described in minerals before (Hawthorne *et al.*, 2019); we call this the *kalyuzhnyite* sheet. The heteropolyhedral and Si–O sheets alternate along **b**; there is one heteropolyhedral sheet and one Si–O sheet per *b* unit-cell parameter (Fig. 4a). The sheets connect via common vertices of M(1–4) polyhedra and SiO_4 tetrahedra to form a framework. Summation of the ideal compositions of the heteropolyhedral sheet and double Si–O sheet, gives ideal composition of the framework: $[NaSrCeTiOF]^{7+} + (Si_8O_{21})^{10-} = NaSrCeTi(Si_8O_{21})OF]^{3-}$. The interstitial complex is composed of M(5–8), A(1,2) and B(1,2) cations and H_2O groups at the W(1–9) sites. The interstitial complex is located within the double Si–O sheet (Figs 4, 5). The larger cations, Pb and Sr at the M(5,6) sites, Cs at the A(1,2) sites and K at the B(1,2) sites occupy centres of ten membered rings of SiO_4 tetrahedra (Fig. 4b). Smaller cations, Na and Ca at the M7 and M8 sites and H_2O groups at the W(1–9) sites occur in the large channels along *c* (Figs 4a, 5b). The ideal composition is derived by a sum of cation and anion/H_2O parts of the interstitial complex to give: $(KCa)^{3+} + (H_2O)_3 = [(KCa) (H_2O)_3]^{3+}$.

The general structural formula of kalyuzhnyite-(Ce)

The structural formula on the basis of assigned site-populations (Table 7) is $(Na_{0.80}\square_{0.20})_{\Sigma1}(K_{0.37}Cs_{0.30})_{\Sigma0.67}[(Ca_{0.25}Pb_{0.22}Sr_{0.14})Na_{0.25}Ln^{3+}_{0.08}]_{\Sigma0.94}(Sr_{0.98}Pb_{0.02})_{\Sigma1}(Ln^{3+}_{0.96}Ca_{0.04})_{\Sigma1}(Ti_{0.97}Nb_{0.03})_{\Sigma1.00}(Si_8O_{21})OF_{0.50}[F_{0.40}(H_2O)_{0.10}](H_2O)_{3.11}$, where $Ln^{3+}_{1.04} = (Ce_{0.43}Nd_{0.41}Pr_{0.08}La_{0.06}Sm_{0.03}Gd_{0.01}Er_{0.01}Ho_{0.01})_{\Sigma1.04}$ and Ce is the dominant lanthanoid. The simplified formula is $Na(K,Cs,\square)(Ca,Na,Pb,Sr)SrLn^{3+}Ti(Si_8O_{21})OF(H_2O)_3$. On the basis of the structure refinement results and bond-valence calculations, the ideal formula of kalyuzhnyite-(Ce) can be written as the sum of the cation and anion components: $(NaKCaSrCeTi)^{13+} + [(Si_8O_{21})OF(H_2O)_3]^{13-} = NaKCaSrCeTi(Si_8O_{21})OF(H_2O)_3$, $Z = 4$. 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) $+ 1^+$ (K) $+ 2^+$ (Ca) $+ 2^+$ (Sr) $+ 3^+$ (Ce) $+ 4^+$ (Ti) $= 13^+$ *versus* 1.07^+ $(Na_{1.07}) + 0.67^+$ $(K_{0.37}Cs_{0.30}) + 1.64^+$ $(Ca_{0.37}Pb_{0.24}Sr_{0.21}) + 2^+$ $(Sr_{1.00}) + 3.12^+$ $(Ln_{1.04}) + 4.08^+$ $(Ti_{0.97}Nb_{0.04}) = 12.58^+$.

The ideal formulae of kalyuzhnyite-(Ce), above, was based on the sum of the cation and anion components. The ideal formula of kalyuzhnyite-(Ce) ($Z = 4$) based on ideal compositions of cation and anion sites ^{M4}Na, $^{A(1,2)B(1,2)}K$, $^{M(5–8)}Ca$, ^{M3}Sr, ^{M2}Ce, $^{Si(1–8)}Si_8$, $^{O(1–21)}O_{21}$, ^{O22}O, ^{F+X}F and $^{W(1–9)}(H_2O)_3$, can be written as $NaKCaSrCeTi(Si_8O_{21})OF(H_2O)_3$.

Relation to other sheet silicates

Kalyuzhnyite-(Ce) has no analogues. The double $(Si_8O_{21})^{10-}$ sheet consists of ten-membered rings of SiO_4 tetrahedra. It has unique topology and composition, and its Si–O double sheet has not previously been described in minerals (Hawthorne *et al.*, 2019). We can relate kalyuzhnyite-(Ce) to penkvilksite, $Na_2TiSi_4O_{11}\cdot2H_2O$ (Bussen *et al.*, 1974; Merlino *et al.*, 1994; Cadoni and Ferraris, 2008) and tumchaite, $Na_2(Zr,Sn)Si_4O_{11}\cdot2H_2O$ (Subbotin *et al.*, 2000), two silicate minerals with a single corrugated sheet of ten-membered rings of SiO_4 tetrahedra; the composition of this single sheet is $(Si_4O_{11})^{6-}$.

References

Agakhanov A.A., Sokolova E., Karpenko V.Y., Hawthorne F.C., Pautov L.A., Kasatkin A.V., Pekov I.V., Agakhanova V.A. (2023) Kalyuzhnyite-(Ce), IMA 2022-133. CNMNC Newsletter 72. *Mineralogical Magazine*, **87**, https://doi.org/10.1180/mgm.2023.21

Brown I.D. (1981) The bond-valence method: an empirical approach to chemical structure and bonding. Pp. 1–30 in: *Structure and Bonding in Crystals II* (M. O'Keeffe and A. Navrotsky, editors). Academic Press, New York.

Bussen I.V., Men'shikov Yu.P., Merkov A.M., Nedorezova A.P., Uspenskaya E.I. and Khomyakov A.P. (1974) Penkvilksite, a new hydrous silicate of titanium and sodium. *Doklady Earth Sciences*, **217**, 126–129.

Cadoni M. and Ferraris G. (2008) Penkvilksite-2*O*: $Na_2TiSi_4O_{11}\cdot2H_2O$. *Acta Crystallographica*, **C64**, 187–190.

Dowty E. (2016) *ATOMS (Version 6.5.0)*. Shape Software, Kingsport, Tennessee, USA.

Frost R. and Xi Y. (2012) Vibrational spectroscopic study of the minerals nekoite $Ca_3Si_6O_{15}\cdot7H_2O$ and okenite $Ca_{10}Si_{18}O_{46}\cdot18H_2O$ – Implications for the molecular structure. *Journal of Molecular Structure*, **1020**, 96–104.

Gagné O.C. (2018) Bond-length distributions for ions bonded to oxygen: results for the lanthanides and actinides and discussion of the f-block contraction. *Acta Crystallographica*, **B74**, 49–62.

Gagné O.C. and Hawthorne F.C. (2020) Bond-length distributions for ions bonded to oxygen: Results for the transition metals and quantification of the factors underlying bond-length variation in inorganic solids. *IUCrJ*, **7**, 581–629.

Hawthorne F.C., Uvarova Yu.A. and Sokolova E. (2019) A structure hierarchy for silicate minerals: sheet silicates. *Mineralogical Magazine*, **83**, 3–55.

Merlino S., Pasero M., Artioli G. and Khomyakov A.P. (1994) Penkvilksite, a new kind of silicate structure: OD character, X-ray single-crystal (1M), and powder Rietveld (2O) refinements of two MDO polytypes. *American Mineralogist*, **79**, 1185–1193.

Pautov L.A., Agakhanov A.A., Karpenko V.Yu., Uvarova Yu.A., Sokolova E. and Hawthorne F.C. (2019) Rinkite-(Y), $Na_2Ca_4YTi(Si_2O_7)_2OF_3$, a seidozerite-supergroup TS-block mineral from the Darai-Pioz alkaline massif, the Tien-Shan mountains, Tajikistan: Description and crystal structure. *Mineralogical Magazine*, **83**, 373–380.

Pautov L.A., Agakhanov, A.A., Pekov, I.V. and Karpenko, V.Yu. (2022) "Quartz Lumps" in the Darai-Pioz alkaline massif (Tajikistan): on problems of their genesis and the cesium accumulation. *Zapiski Rossiiskogo Mineralogicheskogo Obshchestva* (*Proceedings of the Russian Mineralogical Society*), **151**, 102–122 [in Russian].

Pouchou J.L. and Pichoir F. (1985) 'PAP' φ(ρZ) procedure for improved quantitative microanalysis. Pp. 104–106 in: *Microbeam Analysis* (J.T. Armstrong, editor). San Francisco Press, California.

Shannon R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica*, **A32**, 751–767.

Sheldrick G.M. (2015) Crystal structure refinement with *SHELX*. *Acta Crystallographica*, **C71**, 3–8.

Sitarz M., Mozgawa W. and Handke M. (1998) Vibrational spectroscopy of ring silicates. *AIP Conference Proceedings*, **430**, 685.

Subbotin V.V., Merlino S., Pushcharovsky D.Yu., Pakhomovsky Ya.A., Ferro O., Bogdanova A.N., Voloshin A.V., Sorokhtina N.V. and Zubkova N.V. (2000) Tumchaite $Na_2(Zr,Sn)Si_4O_{11}\cdot2H_2O$ – a new mineral from carbonatites of the Vuoriyarvi alkali-ultrabasic massif, Murmansk region, Russia. *American Mineralogist*, **85**, 1516–1520.

Tobbens D.M., Kahlenberg V., Kaindl R., Sartory B. and Konzett J. (2008) $Na_{8.25}Y_{1.25}Si_6O_{18}$ and its family of zwölfer ring silicates. *Zeitschrift für Kristallographie*, **223**, 389–398.

Wilson A.J.C. (editor) (1992) *International Tables for Crystallography. Volume C: Mathematical, Physical and Chemical.* Kluwer Academic Publishers, Dordrecht, The Netherlands.