

The crystal structure and crystal chemistry of mendeleevite-(Ce), $(\text{Cs}, \square)_6(\square, \text{Cs})_6(\square, \text{K})_6(\text{REE}, \text{Ca}, \square)_{30}(\text{Si}_{70}\text{O}_{175})(\text{H}_2\text{O}, \text{OH}, \text{F}, \square)_{35}$, a potential microporous material

E. SOKOLOVA^{1,2,*}, F. C. HAWTHORNE¹, L. A. PAUTOV³, A. A. AGAKHANOV³ AND V. YU. KARPENKO³

¹ Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

² Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Moscow 119017, Russia

³ Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow 117071, Russia

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ABSTRACT

The crystal structure of mendeleevite-(Ce), $(\text{Cs}, \square)_6(\square, \text{Cs})_6(\square, \text{K})_6(\text{REE}, \text{Ca}, \square)_{30}(\text{Si}_{70}\text{O}_{175})(\text{H}_2\text{O}, \text{OH}, \text{F}, \square)_{35}$, a new mineral from the moraine of the Darai-Pioz glacier, the Alai mountain ridge, Tien-Shan mountains, northern Tajikistan, was solved by direct methods and refined to $R_1 = 4.15\%$ based on 2274 observed [$F_o > 4\sigma(F)$] unique reflections measured with Mo- $K\alpha$ radiation on a Bruker P4 diffractometer equipped with a CCD detector. Mendeleevite-(Ce) is cubic, space group $Pm\bar{3}$, $a = 21.9148(4) \text{ \AA}$, $V = 10525(1) \text{ \AA}^3$, $Z = 2$, $D_{\text{calc}} = 3.066 \text{ g/cm}^3$. The empirical formula (electron microprobe) is $\text{Cs}_{5.94}\text{K}_{2.22}[(\text{Ce}_{11.35}\text{La}_{5.86}\text{Nd}_{3.23}\text{Pr}_{1.54}\text{Sm}_{0.32}\text{Gd}_{0.20})_{\Sigma 22.50}(\text{Ca}_{4.68}\text{Sr}_{1.00})_{\Sigma 5.68}]_{\Sigma 28.18}\text{Si}_{70.12}\text{O}_{203.17}\text{H}_{45.67}\text{F}_{6.83}$, $Z = 2$, calculated on the basis of 210 (O + F) a.p.f.u., with H_2O and OH calculated from structure refinement (OH + F = 17 p.f.u.; $\text{H}_2\text{O} = 17.75 \text{ p.f.u.}$).

The structural formula is $(\text{Cs}_{4.65}\square_{1.35})_{\Sigma 6}(\square_{4.71}\text{Cs}_{1.29})_{\Sigma 6}(\square_{3.78}\text{K}_{2.22})_{\Sigma 6}\{[(\text{Ce}_{11.35}\text{La}_{5.86}\text{Nd}_{3.23}\text{Pr}_{1.54}\text{Sm}_{0.32}\text{Gd}_{0.20})_{\Sigma 22.50}(\text{Ca}_{4.68}\text{Sr}_{1.00})_{\Sigma 5.68}]\square_{1.82}\}_{\Sigma 30}(\text{Si}_{70}\text{O}_{175})[(\text{OH})_{10.17}\text{F}_{6.83}]_{\Sigma 17}(\text{H}_2\text{O})_{17.75}$. Simplified and endmember formulae are as follows: $(\text{Cs}, \square)_6(\square, \text{Cs})_6(\square, \text{K})_6(\text{REE}, \text{Ca}, \square)_{30}(\text{Si}_{70}\text{O}_{175})(\text{H}_2\text{O}, \text{OH}, \text{F}, \square)_{35}$ and $\text{Cs}_6(\text{REE}_{22}\text{Ca}_6)(\text{Si}_{70}\text{O}_{175})(\text{OH}, \text{F})_{14}(\text{H}_2\text{O})_{21}$. The crystal structure of mendeleevite-(Ce) is an intercalation of two independent Si–O radicals and an M framework of (REE, Ca) polyhedra. The Si–O radicals are an $(\text{Si}_{104}\text{O}_{260})^{104-}$ framework and an $(\text{Si}_{36}\text{O}_{90})^{36-}$ cluster which do not link directly. The M framework is located between the Si–O framework and the Si–O clusters. Interstitial cations occupy two types of cages and channels. Cages I and II are 78 and 22% occupied by Cs. Channels along $[100\bar{C}]$ contain K atoms and H_2O groups. Mendeleevite-(Ce) has no natural or synthetic structural analogues. Mendeleevite-(Ce) is a framework mineral with large cavities and it has the potential to be used as a model for the synthesis of microporous materials of industrial interest.

KEYWORDS: mendeleevite-(Ce), new mineral, silicate cluster, silicate framework, electron microprobe analysis, crystal structure, microporous material, Darai-Pioz glacier, Tajikistan.

Introduction

MENDELEEVITE-(Ce) was found in the moraine of the Darai-Pioz glacier in the upper reaches of the Darai-Pioz river, the Alai mountain ridge, Tien-Shan mountains, northern Tajikistan, in associa-

tion with quartz, pectolite, baratovite, polyolithionite, aegirine, titanite, fluorite, leucosphenite, pyrochlore, neptunite and reedmergnerite (Pautov *et al.*, 2011). The endmember formula of mendeleevite-(Ce) is as follows: $\text{Cs}_6(\text{REE}_{22}\text{Ca}_6)(\text{Si}_{70}\text{O}_{175})(\text{OH}, \text{F})_{14}(\text{H}_2\text{O})_{21}$ with $Z = 2$. Mendeleevite-(Ce) is a framework mineral with large cavities and it has the potential to be used as a model for the synthesis of microporous materials of industrial interest. To

* E-mail: elena_sokolova@umanitoba.ca
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acknowledge the complexity of the structure of this mineral and its potential as a microporous material, it has been named mendeleevite in honour of Dmitrii Ivanovich Mendeleev (1834–1907), the eminent Russian chemist who created the Periodic Table of Elements and had an incredible breadth of interests in many aspects of industry and technology (Pautov *et al.*, 2011). Here, we report the crystal structure and crystal chemistry of mendeleevite-(Ce).

Experimental details

Sample description

The single crystal of mendeleevite-(Ce) that was used in this work is transparent and colourless, with dimensions 0.040 mm × 0.075 mm × 0.080 mm, which was a fragment of a larger cube.

Electron microprobe analysis

We used another crystal from the same sample for the electron-microprobe analysis. That crystal was analysed using a JXA-50A and CamScan 4D (EDS) and a Cameca SX-100 electron microprobe operating in wavelength-dispersive mode with an accelerating voltage of 15 kV, a specimen current of 10 nA, a beam size of 10 µm, and count times on peak and background of 20 and 30 s for major and minor (<1 wt.%) elements, respectively. The following standards were used for *K* or *L* X-ray lines: F: fluorophlogopite; Si, K: microcline USNM 143966, Ca: anorthite USNM 137041; Sr: SrTiO₃; Cs: CsHo(PO₃)₄; La: LaPO₄; Ce: CePO₄; Nd: NdPO₄; Pr: PrPO₄; Sm: SmPO₄; Dy: DyPO₄; Gd: GdPO₄. Data were reduced using the PAP procedure of Pouchou and Pichoir (1985). The chemical composition of mendeleevite-(Ce) is given in Table 1 and is the mean of 10 analyses. The empirical formula is Cs_{5.94}K_{2.22}[(Ce_{11.35}La_{5.86}Nd_{3.23}Pr_{1.54}Sm_{0.32}Gd_{0.20})Σ_{22.50}(Ca_{4.68}Sr_{1.00})Σ_{5.68}Σ_{28.18}Si_{70.12}O_{203.17}H_{45.67}F_{6.83}, *Z* = 2, calculated on the basis of 210 (O + F) a.p.f.u., with H₂O and OH calculated from structure refinement (OH + F = 17 p.f.u.; H₂O = 17.75 p.f.u.). Simplified and endmember formulae are as follows: (Cs, □)₆(□, Cs)₆(□, K)₆(*REE*, Ca, □)₃₀(Si₇₀O₁₇₅)(H₂O, OH, F, □)₃₅ and Cs₆(*REE*₂₂Ca₆)(Si₇₀O₁₇₅)(OH, F)₁₄(H₂O)₂₁.

Data collection and structure refinement

A single crystal of mendeleevite-(Ce) was mounted on a Bruker *P4* automated four-circle

diffractometer equipped with graphite-monochromated MoK α radiation and a Bruker 1K CCD detector. The intensities of X-ray-diffraction reflections were collected to 60.00°2 θ using 15 s per 0.2° frame. An empirical absorption correction (*SADABS*; Sheldrick, 2008) was applied. As there were very few reflections at high angles, the maximum 2 θ limit for XRD intensities was reduced to 45.00° 2 θ , corresponding to 104,500 reflections with $-23 < h, k, l < 23$. The refined unit-cell parameters for the cubic cell (Table 2) were obtained from 7440 reflections with $I > 10\sigma I$. The crystal structure of mendeleevite-(Ce) was solved by direct methods with the Bruker *SHELXTL Version 5.1* system of programs (Sheldrick, 2008) and refined in space group *Pm* $\bar{3}$ to $R_1 = 4.15\%$ based on 2274 observed [$F_o > 4\sigma(F)$] unique reflections. In mendeleevite-(Ce), the *M*(2) site is split into two sites, *M*(2A) and *M*(2B), which are occupied by ~78% and 9% (*REE* + Ca) and separated by a short distance of

TABLE 1. Chemical composition and unit formula* for mendeleevite-(Ce).

Oxide	Wt.%	Formula unit	a.p.f.u.
SiO ₂	43.52	Si	70.12
Ce ₂ O ₃	19.24		
La ₂ O ₃	9.87	Ce	11.35
Nd ₂ O ₃	5.62	La	5.86
Pr ₂ O ₃	2.63	Nd	3.23
Sm ₂ O ₃	0.58	Pr	1.54
Gd ₂ O ₃	0.38	Sm	0.32
CaO	2.71	Gd	0.20
SrO	1.07	ΣM ³⁺	22.50
Cs ₂ O	8.64		
K ₂ O	1.08	Ca	4.68
F	1.34	Sr	1.00
H ₂ O**	4.25	ΣM ²⁺	5.68
O=F	−0.56		
Total	100.37	Total M	28.18
		Cs	5.94
		K	2.22
		Σcations	106.46
		H ⁺ ***	45.67
		F	6.83

Al, Na, Y and Dy were sought but not detected;

* calculated on anion basis: O + F = 210 a.p.f.u.;

** calculated from structure solution and refinement;

*** content of H⁺ from (OH)_{10.17} and (H₂O)_{17.75}.

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TABLE 2. Miscellaneous refinement data for mendeleevite-(Ce).

Endmember formula	Cs ₆ (REE ₂₂ Ca ₆)(Si ₇₀ O ₁₇₅)(OH,F) ₁₄ (H ₂ O) ₂₁
Simplified formula	(Cs,□) ₆ (□,Cs) ₆ (□,K) ₆ (REE,Ca,□) ₃₀ (Si ₇₀ O ₁₇₅)(H ₂ O,OH,F,□) ₃₅
<i>a</i> (Å)	21.9148(4)
<i>V</i> (Å ³)	10525(1)
Space group	<i>Pm</i> $\bar{3}$
<i>Z</i>	2
Absorption coefficient (mm ⁻¹)	6.80
<i>F</i> (000)	9048.0
<i>D</i> _{calc.} (g/cm ³)	3.066
Crystal size (mm)	0.040 × 0.075 × 0.080
Radiation/filter	Mo-Kα/graphite
2θ-range for structure refinement (°)	45.00
<i>R</i> (int) (%)	5.12
Reflections collected	104500
Independent reflections	2523
<i>F</i> _o > 4σ <i>F</i>	2274
Refinement method	Full-matrix least squares on <i>F</i> ² , fixed weights proportional to 1/σ <i>F</i> _o ²
No. of refined parameters	274
Final <i>R</i> (obs) (%)	
[<i>F</i> _o > 4σ <i>F</i>]	4.15
<i>R</i> ₁	4.87
<i>wR</i> ₂	13.57
Goodness of fit on <i>F</i> ²	1.391

0.46 Å; the *B* site is split into two sites, *B*(1) and *B*(2), which are ~35% and 2% occupied by K and separated by a short distance of 0.7 Å. There is also disorder around the O(19) site where two equipoints of the O(19) site are separated by 0.78 Å and hence the O(19) site can be only partly occupied. It is 50% occupied by O atoms. Site occupancies for the O(20–27) sites, occupied by H₂O groups or (H₂O + OH + F), were first refined with fixed *U*_{iso} = 0.05 Å², then site occupancies were fixed and isotropic displacement parameters were refined. Scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson, 1992). Site-scattering values were refined for the *M* sites using the scattering curve of Ce (which is the dominant REE³⁺, Table 1), and for the *A* and *B* sites using the scattering curve of Cs. Details of the data collection and structure refinement are given in Table 2, final atom parameters, site occupancies (%) and equivalent (and isotropic) displacement parameters are given in Table 3, selected interatomic distances in Table 4, refined site-scattering values and assigned populations for selected cation and

anion sites in Table 5, and incident bond-valence values and total aggregate charges for anion sites in Table 6. Lists of observed and calculated structure factors and anisotropic displacement parameters have been deposited with the Principal Editor of *Mineralogical Magazine* and are available at www.minersoc.org/pages/e_journals/dep_mat.html.

Assignment of cation site populations

There are fifteen cation sites in the crystal structure of mendeleevite-(Ce) (Table 3). There are seven *Si* sites fully occupied by Si and tetrahedrally coordinated by O atoms, giving Si₇₀ a.p.f.u. (Tables 3 and 4). Assignment of site populations for the *M*, *A* and *B* sites (more than half of them being partly occupied) was not a trivial issue and we explain our rationale for those assignments below.

M sites

There are three *M* sites in the crystal structure of mendeleevite-(Ce); their coordination numbers vary from [8] to [10], their mean bond lengths

TABLE 3. Atom coordinates and equivalent displacement parameters for mendeleevite-(Ce).

Atom	Multiplicity (a.p.f.u.)	Occupancy (%)	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
M(1)	12	100	0.28869(2)	0.29333(2)	0.16693(2)	0.01081(16)
M(2A)	12	78	0.40430(5)	0.40992(4)	0.11371(4)	0.0182(3)
M(2B)	12	9	0.3844(4)	0.4123(4)	0.1193(4)	0.0182(9)
M(3)	6	95	0.30685(10)	0.31416(10)	0	0.0207(7)
A(1)	6	78	0.23200(7)	½	0.24858(7)	0.0448(4)
A(2)	6	22	½	0.4200(2)	0.3981(3)	0.0459(13)
B(1)	6	35	0.0892(4)	0.3728(5)	0	0.044(3)
B(2)	6	2	0.078(5)	0.404(6)	0	0.044(3)
Si(1)	6	100	0.42893(16)	½	0.24647(16)	0.0132(8)
Si(2)	12	100	0.23758(11)	0.43094(10)	0.07310(11)	0.0112(5)
Si(3)	12	100	0.06963(10)	0.26204(11)	0.16567(11)	0.0111(5)
Si(4)	12	100	0.42934(11)	0.25606(11)	0.07078(11)	0.0124(5)
Si(5)	12	100	0.14260(10)	0.37357(11)	0.15483(10)	0.0116(5)
Si(6)	12	100	0.36548(13)	0.38330(12)	0.27932(12)	0.0219(6)
Si(7)	4	100	0.16716(10)	0.16716(10)	0.16716(10)	0.0098(9)
O(1)	12	100	0.1704(3)	0.4079(3)	0.0957(3)	0.0161(14)
O(2)	6	100	0.4035(4)	½	0.1785(4)	0.020(2)
O(3)	12	100	0.1940(3)	0.3439(3)	0.1973(3)	0.0152(14)
O(4)	6	100	0	0.2518(4)	0.1432(4)	0.015(2)
O(5)	12	100	0.3861(3)	0.3043(3)	0.1037(3)	0.0178(15)
O(6)	12	100	0.4257(3)	0.1900(3)	0.1037(3)	0.0195(15)
O(7)	12	100	0.0961(3)	0.3221(3)	0.1288(3)	0.0193(15)
O(8)	12	100	0.2891(3)	0.3841(3)	0.0941(3)	0.0203(16)
O(9)	12	100	0.2706(3)	0.2376(3)	0.0762(3)	0.0192(15)
O(10)	6	100	½	0.2773(4)	0.0719(4)	0.017(2)
O(11)	12	100	0.3490(4)	0.3730(3)	0.2098(3)	0.0330(19)
O(12)	6	100	0.2342(4)	0.4333(4)	0	0.022(2)
O(13)	6	100	0.2477(4)	½	0.0992(4)	0.014(2)
O(14)	12	100	0.3992(3)	0.3238(3)	0.3079(3)	0.0304(18)
O(15)	12	100	0.4111(4)	0.4411(4)	0.2855(3)	0.050(2)
O(16)	6	100	0.4077(4)	0.2479(5)	0	0.022(2)
O(17)	12	100	0.1413(3)	0.1073(3)	0.2031(3)	0.0166(14)
O(18)	4	100	0.2095(3)	0.2095(3)	0.2095(3)	0.014(2)
O(19)	3	50	½	0.5177(7)	0.2475(9)	0.029(6)
F	4	100	0.2778(2)	0.2778(2)	0.2778(2)	0.0142(18)
O(20)	6	100	0.3779(5)	½	0.0512(5)	0.025(2)*
O(21)	6	100	½	0.4304(5)	0.0567(6)	0.060(3)*
O(22)	1.5	67	½	0	0	0.048(8)*
O(23)	6	100	½	0.3849(6)	0.1678(5)	0.054(3)*
O(24)	6	77	0.1829(7)	0.3036(7)	0	0.045(4)*
O(25)	6	100	0	0.3870(5)	0.4029(5)	0.057(3)*
O(26)	0.5	33	½	½	½	0.03(3)*
O(27)	3	33	0	0.305(2)	0	0.063(11)*

* *U*_{iso}

vary from 2.491 to 2.51 Å and they have a total refined scattering of 1371.72 e.p.f.u. (Table 5). Chemical analysis gives (Ce_{11.35}La_{5.86}Nd_{3.23}Pr_{1.54}Sm_{0.32}Gd_{0.20})Σ_{22.50}(Ca_{4.68}Sr_{1.00})Σ_{5.68}]Σ_{28.18} (Table 1), which corresponds to 1441.22 e.p.f.u. For the M cations, the

difference between the site scattering determined by structure refinement and the chemical analysis is 69.5 e.p.f.u., i.e. a 4.8% difference from the value determined by chemical analysis.

The REE content, (Ce_{11.35}La_{5.86}Nd_{3.23}Pr_{1.54}Sm_{0.32}Gd_{0.20})Σ_{22.50} a.p.f.u., has an average

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TABLE 4. Selected interatomic distances (Å) and angles (°) for mendeleevite-(Ce).

Si(1)–O(2)	1.59(1)	Si(2)–O(8)	1.593(7)	Si(3)–O(9)a	1.593(6)
Si(1)–O(15) × 2	1.596(7)	Si(2)–O(12)	1.605(2)	Si(3)–O(4)	1.619(4)
Si(1)–O(19)*	<u>1.605(4)</u>	Si(2)–O(1)	1.634(6)	Si(3)–O(17)b	1.624(6)
<Si(1)–O>	1.60	Si(2)–O(13)	<u>1.633(4)</u>	Si(3)–O(7)	<u>1.650(7)</u>
		<Si(2)–O>	1.616	<Si(3)–O>	1.622
Si(4)–O(5)	1.592(7)	Si(5)–O(3)	1.600(7)	Si(6)–O(11)	1.583(7)
Si(4)–O(10)	1.617(4)	Si(5)–O(1)	1.617(6)	Si(6)–O(15)	1.621(8)
Si(4)–O(6)	1.619(7)	Si(5)–O(6)a	1.621(7)	Si(6)–O(14)	1.624(7)
Si(4)–O(16)	<u>1.632(4)</u>	Si(5)–O(7)	<u>1.624(6)</u>	Si(6)–O(14)a	<u>1.632(8)</u>
<Si(4)–O>	1.615	<Si(5)–O>	1.616	<Si(6)–O>	1.615
Si(7)–O(18)	1.61(1)			Si(2)–O(1)–Si(5)	136.6(4)
Si(7)–O(17) × 3	<u>1.630(6)</u>			Si(3)–O(4)–Si(3)c	140.9(6)
<Si(7)–O>	1.625			Si(4)–O(6)–Si(5)b	134.0(4)
M(1)–O(9)	2.368(6)	M(2A)–O(5)	2.360(6)	Si(3)–O(7)–Si(5)	127.0(4)
M(1)–O(11)	2.382(7)	M(2A)–O(2)	2.432(5)	Si(4)–O(10)–Si(4)d	146.4(6)
M(1)–O(3)	2.444(6)	M(2A)–O(23)	2.471(6)	Si(2)–O(12)–Si(2)e	173.5(7)
M(1)–F	2.465(4)	M(2A)–O(20)	2.472(6)	Si(2)–O(13)–Si(2)f	135.8(6)
M(1)–O(3)b	2.498(6)	M(2A)–O(21)	2.482(7)	Si(6)–O(14)–Si(6)b	132.9(5)
M(1)–O(8)	2.550(6)	M(2A)–O(25)b	2.525(2)	Si(1)–O(15)–Si(6)	137.6(5)
M(1)–O(5)	2.556(6)	M(2A)–O(11)	2.560(7)	Si(4)–O(16)–Si(4)e	143.8(6)
M(1)–O(18)	<u>2.694(6)</u>	M(2A)–O(8)	<u>2.624(7)</u>	Si(3)a–O(17)–Si(7)	132.8(4)
<M(1)–φ>	2.495	<M(2A)–φ>	2.491	Si(1)–O(19)–Si(1)g	<u>151.9(1.1)</u>
				<Si–O–Si>	141.1
M(2B)–O(8)	2.25(1)	M(3)–O(9) × 2	2.497(6)	A(1)–O(14)a × 2	3.219(7)
M(2B)–O(11)	2.30(1)	M(3)–O(8) × 2	2.597(6)	A(1)–O(13)	3.291(8)
M(2B)–O(2)	2.36(1)	M(3)–O(25)b	2.62(1)	A(1)–O(23)a	3.30(1)
M(2B)–O(5)	2.39(1)	M(3)–O(16)	2.65(1)	A(1)–O(6)a × 2	3.493(6)
M(2B)–O(20)	2.44(1)	M(3)–O(24)	2.73(2)	A(1)–O(10)a	3.565(9)
M(2B)–O(25)b	2.62(1)	M(3)–O(5) × 2	2.867(6)	A(1)–O(3) × 2	<u>3.696(6)</u>
M(2B)–O(23)	2.81(1)	M(3)–O(12)	<u>3.06(1)</u>	<A(1)–φ>	3.44
M(2B)–O(21)	<u>2.91(1)</u>	<M(3)–φ>	2.70		
<M(2B)–φ>	2.51				
A(2)–O(26)	2.840(5)	B(1)–O(27)	2.46(3)	B(2)–O(22)a	2.7(1)
A(2)–O(15) × 2	3.177(9)	B(1)–O(24)	2.55(2)	B(2)–O(27)	2.8(1)
A(2)–O(15)b × 2	3.229(9)	B(1)–O(1) × 2	2.856(8)	B(2)–O(1) × 2	2.92(7)
A(2)–O(19)g*	3.57(2)	B(1)–O(7) × 2	3.037(7)	B(2)–O(24)	3.2(1)
A(2)–O(14) × 2	3.638(8)	B(1)–O(22)	3.40(1)	B(2)–O(7) × 2	<u>3.36(7)</u>
A(2)–O(19)*	<u>3.93(2)</u>	B(1)–O(12)	<u>3.44(1)</u>	<B(2)–φ>	3.04
<A(2)–φ>	3.38	<B(1)–φ>	2.95		
A(2)–A(2)a × 4	2.881(6)	B(1)–B(2)	0.7(1)	M(2A)–M(2B)	0.46(1)
A(2)–A(2)g	3.51(1)	B(2)–B(2)h	3.4(2)		

a = z, x, y; b = y, z, x; c = –x, y, z; d = –x+1, y, z; e = x, y, –z; f = x, –y+1, z; g = –x+1, –y+1, z; h = –x, y, –z; φ = O, OH, F, H₂O.

* The O(19) site is 50% occupied by O atoms [O(19)–O(19)g = 0.78(3) Å]; (1) there are two bond-lengths Si(1)–O(19) = 1.606(4) Å but only one of them is taken into account due to a partial occupancy of the O(19) site; (2) two bond lengths A(2)–O(19)g = 3.57(2) Å and A(2)–O(19) = 3.93(2) Å are taken into account in accord with their 50% occurrence.

TABLE 5. Refined site-scattering values and assigned site populations for mendelevite-(Ce).

Site	Refined site scattering reduced to one atom (el)	Site population (a.p.f.u.)	Calculated site scattering reduced to one atom (el)	<X-φ> _{obs} (Å)
[⁸]M(1)	58.58	12 REE*	58.21	2.495
[⁸]M(2A)	40.4(1)	9.17 REE + 0.21 Ca + 2.62 □	44.83	2.491
[⁸]M(2B)	4.8(1)	10.88 □ + 1.10 REE + 0.02 Ca	5.37	2.51
M(2)	45.2	10.27 REE + 0.23 Ca + 1.50 □	50.20	602.42
[¹⁰]M(3)	10.53(8)	4.45 Ca + 1.00 Sr + 0.23 REE + 0.32 □	11.70	2.70
ΣM	114.31	22.50 REE + 4.68 Ca + 1.00 Sr + 1.82 □	120.11	1441.32
[⁹]A(1)	21.31	4.65 Cs + 1.35 □	21.31	255.75
[⁸]A(2)	5.91	4.71 □ + 1.29 Cs	5.91	70.95
[⁸]B(1)	3.7(1)	3.89 □ + 2.11 K	3.35	40.09
[⁷]B(2)	0.31(9)	5.89 □ + 0.11 K	0.17	2.09
Σ(A + B)	31.23		30.74	368.88
O(20)		3.0 H ₂ O + 3.0 OH		
O(21)		3.0 H ₂ O + 3.0 OH		
O(22)		1.0 H ₂ O + 0.5 □		
O(23)		2.5 H ₂ O + (2.1 OH + 1.4 F)		
O(24)		4.62 H ₂ O + 1.38 □		
O(25)		2.5 H ₂ O + (2.07 OH + 1.43 F)		
O(26)		0.17 H ₂ O + 0.17 □		
O(27)		2.0 □ + 1.0 H ₂ O		
Total (H ₂ O,OH,F)		17.79 H ₂ O + (10.17 OH + 2.83 F)		

X-cation; φ = O, OH, F, H₂O.
* REE³⁺ = 11.35 Ce + 5.86 La + 3.23 Nd + 1.54 Pr + 0.32 Sm + 0.20 Gd (total 22.50 a.p.f.u.), average scattering factor of 58.21 el (per atom).

TABLE 6. Bond-valence* (v.u.) table for mendeleevite-(Ce).

	Si(1)	Si(2)	Si(3)	Si(4)	Si(5)	Si(6)	Si(7)	M(1)	M(2A)	M(2B)	M(3)	A(1)	A(2)	B(1)	Σ
O(1)					1.01										2.02
O(2)	1.09	0.97							$0.36 \times 2 \rightarrow$	$0.05 \times 2 \rightarrow$				$0.04 \times 2 \downarrow$	1.91
O(3)					1.06							$0.04 \times 2 \downarrow$			1.94
O(4)			$1.01 \times 2 \rightarrow$												2.02
O(5)				1.08											2.01
O(6)				1.01	1.00										2.06
O(7)			0.93		0.99							$0.05 \times 2 \downarrow$			1.95
O(8)		1.08							0.22	0.07	$0.20 \times 2 \downarrow$			$0.03 \times 2 \downarrow$	1.91
O(9)			1.08								$0.25 \times 2 \downarrow$				1.88
O(10)				$1.01 \times 2 \rightarrow$					0.26	0.06		0.05			2.07
O(11)						1.11		0.53			0.08				1.96
O(12)		$1.05 \times 2 \rightarrow$										0.08		0.01	2.19
O(13)		$0.97 \times 2 \rightarrow$													2.02
O(14)						0.99							$0.09 \times 2 \downarrow$		2.06
O(15)	$1.07 \times 2 \downarrow$					0.97							$0.01 \times 2 \downarrow$		
O(16)													$0.03 \times 2 \downarrow$		2.13
O(17)				$0.97 \times 2 \rightarrow$		1.00					0.18		$0.03 \times 2 \downarrow$		2.12
O(18)			0.99					$0.98 \times 3 \downarrow$							1.97
O(19)								1.03	$0.24 \times 3 \rightarrow$						1.75
F	$1.05 \times 2 \rightarrow$												0.01		2.11
O(20)								$0.32 \times 3 \rightarrow$							0.96
O(21)									$0.32 \times 2 \rightarrow$	$0.04 \times 2 \rightarrow$					0.72
O(22)									$0.32 \times 2 \rightarrow$	$0.01 \times 2 \rightarrow$					0.66
O(23)									$0.33 \times 2 \rightarrow$	$0.02 \times 2 \rightarrow$		0.08		$0.01 \times 4 \rightarrow$	0.04
O(24)											0.15				0.78
O(25)									$0.28 \times 2 \rightarrow$	$0.03 \times 2 \rightarrow$	0.19			0.12	0.27
O(26)**													$0.06 \times 2.64 \rightarrow$		0.81
O(27)														$0.17 \times 2 \rightarrow$	0.16
Total	4.28	4.07	4.01	4.08	4.06	4.07	3.97	3.15	2.53	0.33	1.72	0.57	0.30	0.45	
Aggr.	4.00	4.00	4.00	4.00	4.00	4.00	4.00	3.00	2.33	0.31	1.95	0.78	0.22	0.35	
charge															

* bond-valence parameters from Brown (1981);

** $0.06 \times 2.64 \rightarrow$; 2.64 corresponds to 22% occupancy by Cs ($12 \times 0.22 = 2.64$) (cf. A(2) site, Table 5).

scattering power of 58.21 el. (per atom), and we use this value to calculate the site scattering from the *REE* at the *M*(1–3) sites. To match the highest refined site scattering of 58.58 el. at the *M*(1) site, we must assign *REE*₁₂ a.p.f.u. to the *M*(1) site; the refined and calculated site scattering values, 702.96 and 698.52 e.p.f.u., are in good agreement. We are left with *REE*_{10.50}Ca_{4.68}Sr_{1.00} a.p.f.u. (742.81 e.p.f.u. from chemical analysis) to assign to two *M*(2,3) sites, with refined site scattering of 542.4 and 126.36 (= 668.76) e.p.f.u. The ionic radii of the major cations at the *M*(2,3) sites, Ce³⁺ [¹⁰]1.25, [⁸]1.14 Å, Shannon (1976)] and Ca²⁺ [¹⁰]1.23, [⁸]1.12 Å are very close and hence site-population assignment cannot be based on mean bond lengths. We assign site populations on the basis of refined site-scattering values of 542.4 [*M*(2)] and 126.36 [*M*(3)] e.p.f.u. (Table 5): 10.27 *REE* + 0.23 Ca to the *M*(2) site and 4.45 Ca + 1.00 Sr + 0.23 *REE* + 0.34 □ to the *M*(3) site (□ = vacancy). The *M*(2) site is split into two sites, *M*(2A) and *M*(2B), separated by 0.46 Å and hence these two sites can be only partly occupied. In accord with the refined site scattering for the *M*(2A) and *M*(2B) sites, we assign 9.17 *REE* + 0.21 Ca + 2.62 □ and 10.88 □ + 1.10 *REE* + 0.02 Ca p.f.u., respectively. More complicated site assignments are possible, but they cannot be justified in terms of the observed data, particularly for such a complex structure and chemistry as mendelevite-(Ce).

A and B sites

There are three sites, *A*(1), *A*(2) and *B*, in large cages and channels in the mendelevite-(Ce) structure which are occupied by large cations such as Cs and K and/or H₂O. The *B* site is split into two sites, *B*(1) and *B*(2), separated by 0.7 Å (Table 5) and hence the *B*(1) and *B*(2) sites can only be partly occupied. Together they contribute 6 a.p.f.u. (Table 3). The *A* and *B* sites have a total refined scattering of 374.76 e.p.f.u. (Table 5). The chemical analysis gives Cs_{5.94}K_{2.22} a.p.f.u. (Table 1) which is equivalent to 368.88 e.p.f.u. Longer mean bond lengths at the *A* sites, 3.44 and 3.33 Å, and shorter mean bond lengths at the *B* sites, 2.95 and 3.04 Å, correlate with larger ionic radii of Cs [⁹]1.78, [⁸]1.74 and ~[⁷]1.71 Å,

Shannon (1976)] and smaller ionic radii of K [⁹]1.55, [⁸]1.51 and [⁷]1.46 Å. The sums of the refined site-scattering values at the *A* and *B* sites, 326.64 and 48.12 e.p.f.u., match the calculated site scattering for Cs_{5.94} a.p.f.u. (326.7 e.p.f.u.) and K_{2.22} a.p.f.u. (42.18 e.p.f.u.), respectively. The *A* and *B* sites can be occupied up to {6 [*A*(1)] + 6 [*A*(2)] + 6 [*B*(1) + *B*(2)]} = 18 a.p.f.u., whereas the chemical analysis gives 8.16 a.p.f.u. (see above). So we conclude that the *A* and *B* sites are occupied by Cs and vacancy and by K and vacancy, respectively. Table 5 gives the assigned site populations for the Cs-bearing *A* and K-bearing *B* sites (see *Cation sites* for further details).

Structure description

Cation sites

Si sites

The *Si*(1–7) sites are fully occupied by Si and tetrahedrally coordinated by O atoms, with <Si–O> = 1.615 Å (Table 4). The *Si*(1) and *Si*(6) tetrahedra constitute a Si–O cluster (Fig. 1¹), and *Si*(2–5,7) tetrahedra constitute a Si–O framework (Fig. 2a), with <Si–O–Si> = 141.1° (Table 4). Seven *Si*(1–7) sites give Si₇₀ a.p.f.u.

M sites

In the structure of mendelevite-(Ce), there are three *M* sites (Fig. 3a). The *M*(1) site is fully

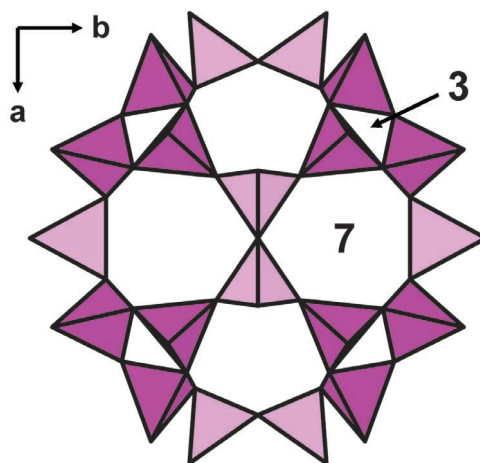


FIG. 1. General view of the (Si₃₆O₉₀)^{36–} cluster. Si tetrahedra of (Si₃O₉) groups and (Si₂O₇) groups are bright pink and pale pink, respectively. Secondary building units, three-membered and seven-membered rings, are identified by the numbers 3 and 7, respectively.

¹ For clarity, all structure diagrams are drawn with O(19)_{av} (*x* = 0.5, *y* = 0.5, *z* = 0.2475), with <Si–O–Si> = 140.8° (cf. Tables 3, 4).

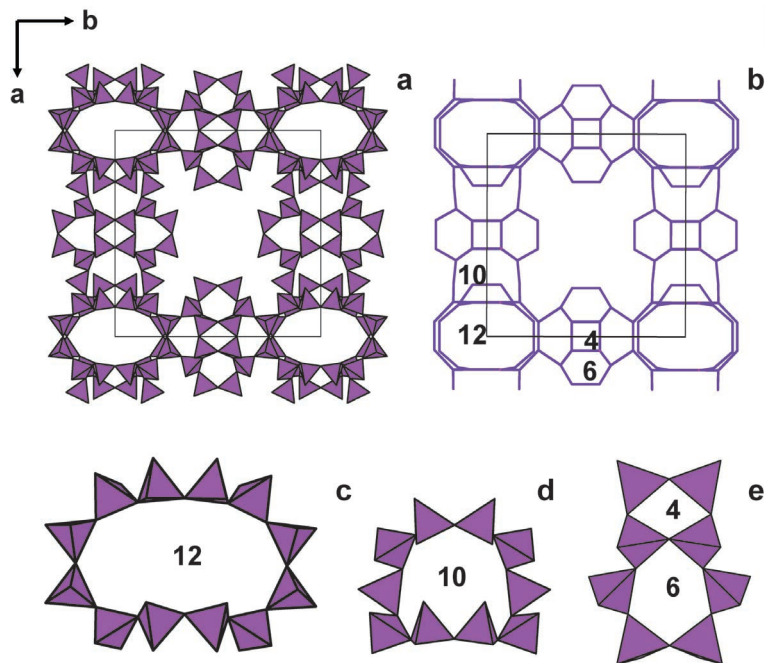


FIG. 2. The $(\text{Si}_{104}\text{O}_{260})^{104-}$ framework: (a) general view; (b) the Si framework, where twelve-, ten-, six- and four-membered rings are identified by numbers 12, 10, 6 and 4, respectively; (c) the twelve-membered Si–O ring; (d) the ten-membered Si–O ring; (e) four- and six-membered Si–O rings. SiO_4 tetrahedra of the framework are purple, next-nearest-neighbour Si–Si separations shown as purple lines in (b).

occupied by *REE*, giving REE_{12} a.p.f.u. (Table 5). The $M(1)$ site is coordinated by seven O atoms and one F atom, with $\langle M(1)-\varphi \rangle = 2.495 \text{ \AA}$, where $\varphi = \text{O}, \text{F}$ (Table 4). The $M(2)$ site is split into two [8]-coordinated sites, $M(2A)$ and $M(2B)$, separated by $0.46 \text{ \AA}$ which are 78% and 9% occupied by *REE* and minor Ca (Table 5). The $M(2A)$ and $M(2B)$ sites are each coordinated by four O atoms and four $[\text{O}(20,21,23,25)]$ sites which are occupied by H_2O , OH and F (see Table 5 and section *Anion sites* below), with mean bond lengths of 2.491 and $2.51 \text{ \AA}$, respectively (Table 4). The $M(3)$ site is 95% occupied by Ca, Sr and minor *REE* (Table 5), and the $M(3)$ site is coordinated by eight O atoms and two sites $[\text{O}(24,25)]$ which are occupied by H_2O , OH, F and $\square$ (see Table 5), with $\langle M(3)-\varphi \rangle = 2.70 \text{ \AA}$, where $\varphi = \text{O}, \text{F}$ (Table 4). The $M(1-3)$ sites give $\{[(\text{Ce}_{11.35}\text{La}_{5.86}\text{Nd}_{3.23}\text{Pr}_{1.54}\text{Sm}_{0.32}\text{Gd}_{0.20})\Sigma 22.50 (\text{Ca}_{4.68}\text{Sr}_{1.00})\Sigma 5.68]\Sigma 28.18\square_{1.82}\Sigma 30 \text{ p.f.u.}, \text{ with simplified and endmember compositions of } (\text{REE}, \text{Ca}, \square)_{30} \text{ and } (\text{REE}_{22}\text{Ca}_6) \text{ p.f.u., respectively.}$

A and B sites

There are three interstitial sites, $A(1)$, $A(2)$ and B , in the large cages and channels in the mendelevite-(Ce) structure (Figs. 4–6). The $A(1)$ site is 78% occupied by Cs (Table 5) and is coordinated by eight O atoms and $(\text{H}_2\text{O} + \text{OH} + \text{F})$ at the $\text{O}(23)$ site, with $\langle A(1)-\varphi \rangle = 3.44 \text{ \AA}$ (Fig. 4a; Table 4). The $A(2)$ site is 22% occupied by Cs. The $A(2)$ site has a multiplicity of 12 and its twelve equipoints are shown as white spheres in Fig. 5a. Each $A(2)$ equipoint has four nearest $A(2)$ neighbours at a distance of $2.881 \text{ \AA}$ (Fig. 5a, black line), one $A(2)$ neighbour at a distance of $3.51 \text{ \AA}$ (Fig. 5a, red line) and eight anions (not shown in Fig. 5a) at distances 2.84 – $3.93 \text{ \AA}$ (Table 4). Therefore, each $A(2)$ equipoint is [13]-coordinated. The ionic radius of ^{137}Cs is $>^{127}\text{Cs}$ $1.88 \text{ \AA}$ (Shannon, 1976) and thus, where Cs atom occurs at the $A(2)$ site, the Cs–Cs distances within this site must be $\geq 3.76 \text{ \AA}$. Hence for each Cs-occupied $A(2)$ equipoint, the four nearest $A(2)$ neighbours at a distance of $2.881 \text{ \AA}$ (black line in Fig. 5a) and one $A(2)$ neighbour at a distance of $3.51 \text{ \AA}$ (red line in Fig. 5a) must be vacant. This

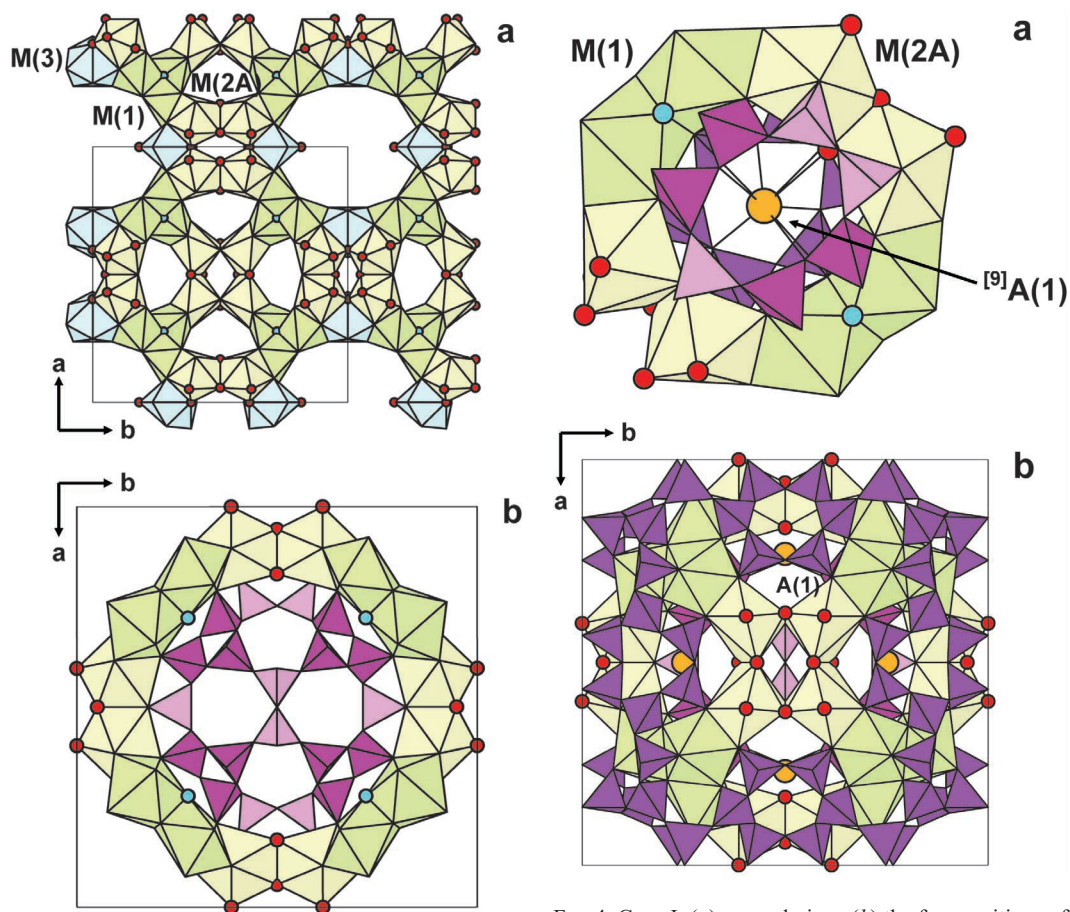


FIG. 3. The M framework: (a) general view of the M framework projected onto (001) [the M(2B) polyhedron is omitted for clarity]; (b) linkage of the $(\text{Si}_{36}\text{O}_{90})^{36-}$ cluster and M framework. The REE-dominant $^{[8]}\text{M}(1)$ and $^{[8]}\text{M}(2\text{A})$ and Ca-dominant $^{[10]}\text{M}(3)$ polyhedra are green, yellow and blue, respectively. Anion sites occupied by H_2O and $(\text{H}_2\text{O} + \text{OH} + \text{F})$ are shown as red spheres; F atoms are shown as blue spheres.

leaves two out of twelve $A(2)$ equipoints that can be occupied by Cs (Fig. 5b). Therefore a Cs atom at the $A(2)$ site is coordinated by an H_2O group [O(26)] and seven O atoms, with $\langle A(2)-\varphi \rangle = 3.33 \text{ \AA}$ (Fig. 5c; Table 4). The $A(1)$ and $A(2)$ sites contribute $(\text{Cs}_{4.65}\text{O}_{1.35})$ and $(\square_{4.71}\text{Cs}_{1.29})$ p.f.u., respectively, with a sum of $(\square_{6.06}\text{Cs}_{5.94})$ p.f.u., ideally Cs_6 a.p.f.u. The B site is split into two sites, $B(1)$ and $B(2)$, separated by $0.7 \text{ \AA}$ (Table 5) which are 35% and 2% occupied by K (Table 5). The $B(1)$ site is coordinated by five O atoms and three

FIG. 4. Cage I: (a) general view; (b) the four positions of cage I in the structure of mendelevite-(Ce). Legend as in Fig. 3; SiO_4 tetrahedra of the framework are purple; Cs atom at the [9]-coordinated $A(1)$ site is shown as an orange sphere; Cs–O and Cs– H_2O bonds are shown as black lines.

H_2O groups at the [O(22,24,27)] sites, with $\langle B(1)-\varphi \rangle = 2.95 \text{ \AA}$ (Fig. 6a, Tables 4 and 5). The $B(2)$ site is coordinated by four O atoms and three H_2O groups at the [O(22,24,27)] sites, with $\langle B(2)-\varphi \rangle = 3.04 \text{ \AA}$ (Tables 4 and 5). The $B(1)$ and $B(2)$ sites give $(\square_{3.89}\text{K}_{2.11})$ and $(\square_{5.89}\text{K}_{0.11})$ p.f.u., respectively; the $B(1)$ and $B(2)$ are partly occupied and their total must be 6 a.p.f.u. (see above), which is equal to $(\square_{3.78}\text{K}_{2.22})$ p.f.u., ideally K_2 a.p.f.u. Therefore the A and B sites give $(\text{Cs}_{4.65}\square_{1.35})\Sigma 6(\square_{4.71}\text{Cs}_{1.29})\Sigma 6(\square_{3.78}\text{K}_{2.2})\Sigma 6$ p.f.u., with simplified and endmember compositions of $(\text{Cs},\square)_6(\square,\text{Cs})_6(\square,\text{K})_6$ p.f.u. and Cs_6 a.p.f.u., respectively.

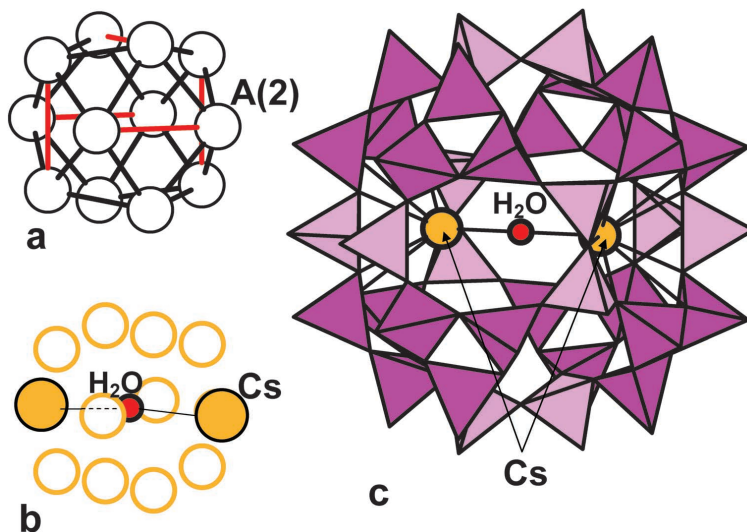


FIG. 5. Cage II: (a) the twelve equipoints of the $A(2)$ site (multiplicity = 12); (b) possible arrangement of two Cs atoms over the set of equipoints of the $A(2)$ site; (c) cage II inside the $(\text{Si}_{36}\text{O}_{90})^{36-}$ cluster. In (a), the equipoints of the $A(2)$ site are shown as white spheres with black rims, and $A(2)$ – $A(2)$ distances of 2.881 and 3.51 Å are shown as black and red lines, respectively; in (b), possible positions of Cs atoms and vacancies are shown as orange spheres with black rims and white spheres with orange rims, an H_2O group at the O(26) site is shown as a red sphere; in (c), legend as in (b), SiO_4 tetrahedra of the $(\text{Si}_{36}\text{O}_{90})^{36-}$ cluster are pink, Cs–O and Cs– H_2O bonds are shown as black lines.

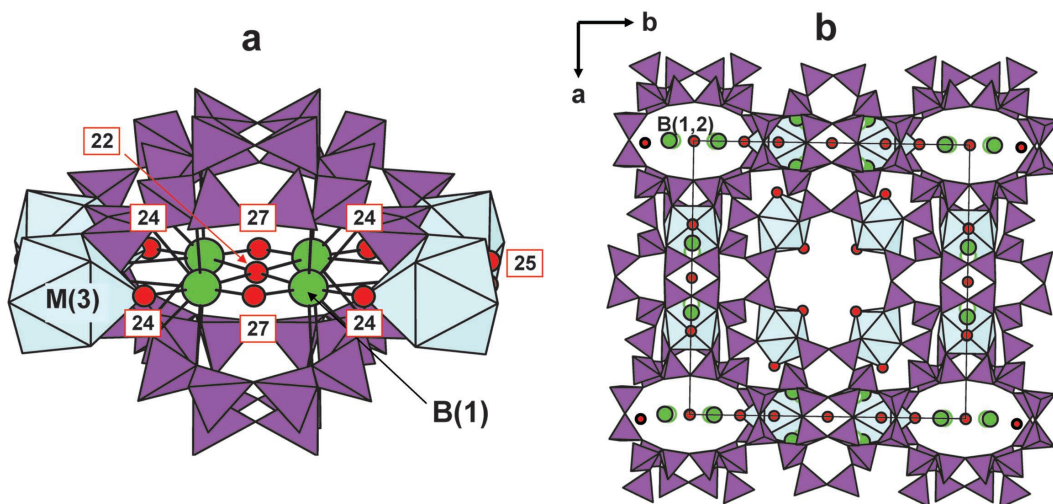


FIG. 6. The K cluster in $[100\bar{C}]$ channels: (a) a cluster of four K atoms at the $B(1)$ sites with a centre at the O(22) atom of an H_2O group at $(0 \frac{1}{2} 0)$ shown in the channel along $[010]$; (b) distribution of K atoms and H_2O groups in the $[100\bar{C}]$ channels inside the $(\text{Si}_{104}\text{O}_{260})^{104-}$ framework. K atoms at the 35% and 2% K-occupied $B(1)$ and $B(2)$ sites are shown as green spheres and white spheres with green rims, $M(3)$ polyhedra are blue, SiO_4 tetrahedra of the framework are purple, H_2O groups are shown as red spheres; in (a), O atoms of H_2O groups are labelled 22, 24, 25 and 27.

Anion sites

The 28 anion sites are listed in Table 3. The O(1–19) anions coordinate Si(1–7) sites and we conclude that the O(1–18) anion sites are fully occupied by O atoms [cf. bond-valence sums of 1.75–2.13 v.u. (valence units) in Table 6]. There is anion disorder at the O(19) site which is 50% occupied by O atoms [O(19)–O(19)' = 0.78(3) Å, Tables 3 and 4]. Therefore the O(1–19) atoms sum to O₁₇₅ a.p.f.u. The Si₇₀ and O₁₇₅ result in an aggregate complex anion of the form (Si₇₀O₁₇₅)^{70–}. There is one anion site fully occupied by F giving F₄ a.p.f.u. (Table 3). The F atom receives three bond-valence contributions of 0.32 v.u. from three M(1) atoms to satisfy its charge of 1[–] (Table 6). Except for the F site, we were not able to distinguish between OH and F at sites containing monovalent anions and H₂O groups. Consider next the O(20–26) anions. Five O(20,21,23,24,25) anions coordinate the 100–88% occupied M(1), M(2) and M(3) sites and the O(20,21,23,25) and O(24) sites are 100% and 70% occupied by anions. The three O(22, 26,27) sites coordinate partly occupied interstitial A(2) and B sites and the O(22 and 26,27) sites are 67% and 33% occupied by anions. Bond-valence sums incident at O(22,24,26,27) vary from 0.04 to 0.34 v.u., and we assign H₂O + vacancy to these four sites (Table 5), giving (H₂O)_{6.79} p.f.u. Bond-valence sums incident at O(20,21,23,25) anions vary from 0.66 to 0.81 v.u., and we assign H₂O and (OH + F) in the ratio ~1:1 to these four sites (Table 5), with a total of (H₂O)₁₁(OH)_{10.17}F_{2.83} p.f.u. The total anion content is (Si₇₀O₁₇₅)(OH)_{10.17}F_{2.83}F₄(H₂O)₁₁(H₂O)_{6.79}, which can be written (Si₇₀O₁₇₅)(OH)_{10.17}F_{6.83}(H₂O)_{17.79}, with simplified and endmember compositions of (Si₇₀O₁₇₅)(H₂O, OH, F, □)₃₅ and (Si₇₀O₁₇₅)(OH,F)₁₄(H₂O)₂₁ p.f.u., respectively.

Structure topology

Structural units

In the crystal structure of mendeleevite-(Ce), there are three main structural units: two Si–O radicals, an (Si₃₆O₉₀)^{36–} cluster and an (Si₁₀₄O₂₆₀)^{104–} framework, and an M framework of (REE,Ca)-dominant M(1–3) polyhedra. Figure 1 presents a general view of the (Si₃₆O₉₀)^{36–} cluster. For better presentation of the geometry of the cluster, we show three-membered (Si₃O₉) rings and (Si₂O₇) groups (Fig. 1).

The cage inside the thirty-six-membered cluster is ~11 Å in diameter. Although the recommended nomenclature for zeolite minerals (Coombs *et al.*, 1997) does not allow us to consider mendeleevite-(Ce) as a zeolite, we identify secondary building units in the cluster: there are three-membered rings (see above) and seven-membered rings of SiO₄ tetrahedra (Fig. 1). A general view of the second structural unit, the (Si₁₀₄O₂₆₀)^{104–} framework, is shown in Fig. 2a. The topology of the framework of Si atoms (Fig. 2b) clearly shows that the framework is built of four types of rings. The twelve-, ten- and six-membered rings are strongly convoluted and the SiO₄ tetrahedra point in different directions (Fig. 2c,d,e); the four-membered ring is less distorted (Fig. 2e). In the framework, SiO₄ tetrahedra connect to form large channels along [100 $\bar{C}$] ($\bar{C}$ indicates permutation of indices: 100, 010, 001). The maximum diameter of a channel is ~11.04 Å. The third structural unit is the M framework composed of M(1–3) polyhedra. In the M framework (Fig. 3a), three ^[8]M(1) polyhedra form a three-membered cluster with a common edge: F–O(18); in a cluster, two adjacent polyhedra share a face. The four ^[8]M(2A) [or ^[8]M(2B)] polyhedra share common edges to form a four-membered cluster (Fig. 3a). The three-membered M(1) and four-membered M(2A) clusters and isolated ^[10]M(3) polyhedra form the M framework. In the M framework, each M(1) polyhedron shares a face with an M(2A) polyhedron, and an M(3) polyhedron shares two faces and two edges with adjacent M(1) and M(2A) polyhedra, respectively. Within the M framework, M(1) and M(2A) polyhedra connect to occlude a large cavity with a diameter of ~14.1 Å, and this cavity hosts the (Si₃₆O₉₀)^{36–} cluster (Fig. 3b). The M(1) and M(2A) [or M(2B)] polyhedra share common vertices with SiO₄ tetrahedra of the cluster, whereas the M(3) polyhedra do not.

Interstitial cations

The Cs-bearing A(1) and A(2) sites and the K-bearing B site occur in large cages and channels in the mendeleevite-(Ce) structure. The M(1) and M(2A) polyhedra and SiO₄ tetrahedra of a (Si₃₆O₉₀)^{36–} cluster and the (Si₁₀₄O₂₆₀)^{104–} framework link to form cage I with a diameter of ~6.8 Å. Cage I contains [9]-coordinated Cs atoms at the A(1) site (Fig. 4a). The positions of cage I in the mendeleevite-(Ce) structure are

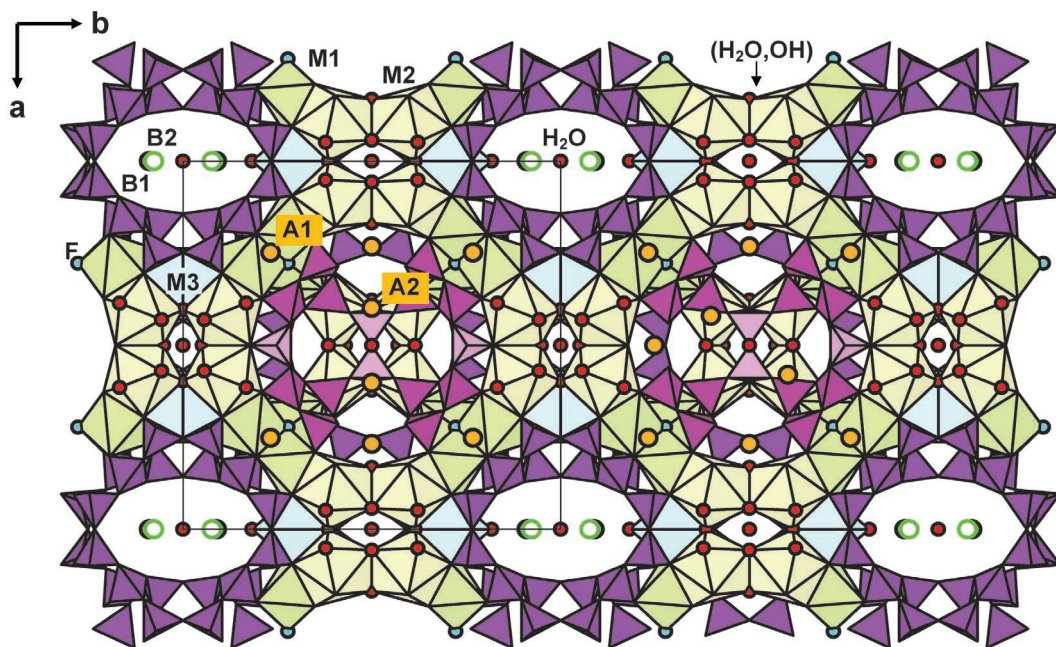


FIG. 7. General view of the crystal structure of mendeleevite-(Ce) projected onto (001). The SiO_4 tetrahedra of the cluster and framework are pink and purple; the REE-dominant $^{[8]}\text{M}(1)$ and $^{[8]}\text{M}(2\text{A})$ and Ca-dominant $^{[10]}\text{M}(3)$ polyhedra are green, yellow and blue; Cs atoms at the $A(1,2)$ sites are shown as orange spheres; K atoms at the $B(1)$ and $B(2)$ sites are shown as green spheres and white spheres with green rims; H_2O and OH groups are shown as red spheres, F atoms are shown as blue spheres.

shown in Fig. 4b. Cage II occurs inside the $(\text{Si}_{36}\text{O}_{90})^{36-}$ cluster and is $\sim 11 \text{ \AA}$ in diameter (see above). Cage II hosts [8]-coordinated Cs atoms at the $A(2)$ site and an H_2O group at the O(26) site (Fig. 5c). As these two sites are partly occupied [$A(2)$ (22%) and O(26) (33%)], three possible compositions can occur in cage II: $(\text{Cs}_2 + \text{H}_2\text{O})$ (22% occupancy); H_2O (11% occupancy) and $\square$ (67% occupancy). The K atoms at the B site occur in the $[100\bar{C}]$ channels of the $(\text{Si}_{104}\text{O}_{260})^{104-}$ framework. The B site is split into two sites, $B(1)$ and $B(2)$, which are 35% and 2% occupied by K. Figure 6a shows the cluster of four K atoms at the $B(1)$ sites. The centre of the cluster is the O(22) atom at $(0, \frac{1}{2}, 0)$. The K atoms connect through H_2O at the $[\text{O}(22,27)]$ sites and share common anions $[\text{O}(12) \text{ and } \text{O}(24) = \text{H}_2\text{O}]$ with the M(3) atoms and $\text{O}(1,7)$ with Si atoms of the $(\text{Si}_{104}\text{O}_{260})^{104-}$ framework. Four $^{[8]}\text{B}(1)$ sites are separated by distances of 5.58 and 3.91 $\text{\AA}$. The ionic radius of $^{[8]}\text{K}$ is 1.51 $\text{\AA}$ and hence all four positions in the cluster can be occupied by K (Fig. 6a). As the $B(1)$ site occupancy is 35%, the

cluster can have following compositions: K_4 , $\text{K}_3\square_1$, $\text{K}_2\square_2$ and $\text{K}_1\square_3$. The four K atoms at the $B(2)$ site form a four-membered cluster similar to that of the $B(1)$ site. These K clusters $(\frac{1}{2}, 0, 0\bar{C})$ centre edges of the unit cell of mendeleevite-(Ce), leaving the rest of the channels vacant (Fig. 6b).

A general view of the crystal structure of mendeleevite-(Ce) is shown in Fig. 7. The crystal structure of mendeleevite-(Ce) is an intercalation of two frameworks, the $(\text{Si}_{104}\text{O}_{260})^{104-}$ framework of Si tetrahedra and the M framework of (REE,Ca) polyhedra. The M framework hosts the $(\text{Si}_{36}\text{O}_{90})^{36-}$ clusters of Si tetrahedra, and the $(\text{Si}_{36}\text{O}_{90})^{36-}$ clusters and the $(\text{Si}_{104}\text{O}_{260})^{104-}$ framework do not link directly. There are two interstitial cations, Cs and K. The Cs atoms occur in (1) cage I formed at the intersection of the M framework, a $(\text{Si}_{36}\text{O}_{90})^{36-}$ cluster and the $(\text{Si}_{104}\text{O}_{260})^{104-}$ framework, and (2) cage II inside the $(\text{Si}_{36}\text{O}_{90})^{36-}$ cluster. The K atoms occur in the $[100\bar{C}]$ channels inside the $(\text{Si}_{104}\text{O}_{260})^{104-}$ framework.

Discussion: chemical formulae

We combine the cation and anion parts into the structural formula ($Z = 2$) as follows: $(\text{Cs}_{4.65}\square_{1.35})_{\Sigma 6}(\square_{4.71}\text{Cs}_{1.29})_{\Sigma 6}(\square_{3.78}\text{K}_{2.22})_{\Sigma 6}\{[(\text{Ce}_{11.35}\text{La}_{5.86}\text{Nd}_{3.23}\text{Pr}_{1.54}\text{Sm}_{0.32}\text{Gd}_{0.20})_{\Sigma 22.50}(\text{Ca}_{4.68}\text{Sr}_{1.00})_{\Sigma 5.68}]_{\Sigma 28.18}\square_{1.82}\}_{\Sigma 30}(\text{Si}_{70}\text{O}_{175})[(\text{OH})_{10.17}\text{F}_{6.83}]_{\Sigma 17}(\text{H}_2\text{O})_{17.75}$, with a simplified formula $(\text{Cs}, \square)_6(\square, \text{Cs})_6(\square, \text{K})_6(\text{REE}, \text{Ca}, \square)_{30}(\text{Si}_{70}\text{O}_{175})(\text{H}_2\text{O}, \text{OH}, \text{F}, \square)_{35}$. Note that $(\text{Cs}_{4.65}\text{O}_{1.35})_{\Sigma 6}(\square_{4.71}\text{Cs}_{1.29})_{\Sigma 6}(\square_{3.78}\text{K}_{2.22})_{\Sigma 6}$ and $[(\text{OH})_{10.17}\text{F}_{6.83}]_{\Sigma 17}(\text{H}_2\text{O})_{17.75}$ in the structural formula correspond to $(\text{Cs}, \square)_6(\square, \text{Cs})_6(\square, \text{K})_6$ and $(\text{H}_2\text{O}, \text{OH}, \text{F}, \square)_{35}$ in the simplified formula. To write an endmember formula, we have to consider the *A* and *B* interstitial sites. At the *A*(1) and *A*(2) sites, Cs and $\square$ are the dominant species and we write an endmember composition for the *A* sites as $\text{Cs}_6 + \square_6 = \text{Cs}_6$ a.p.f.u. At the *B*(1) and *B*(2) sites, $\square > \text{K}$, $\square$ is the dominant species, and we write the endmember composition for the *B* sites as $\square_6$ p.f.u. Therefore $(\text{Cs}, \square)_6(\square, \text{Cs})_6(\square, \text{K})_6$ in the simplified formula corresponds to Cs_6^{6+} in the endmember formula. The presence of Cs, K and $\square$ (vacancy) at the interstitial sites leaves us with the possibility to find other members of the Cs–K series, with endmember formulae $\text{Cs}_6\text{K}_6(\text{REE}_{22}\text{Ca}_6)(\text{Si}_{70}\text{O}_{175})(\text{OH}, \text{F})_{20}(\text{H}_2\text{O})_{15}$ and $\text{K}_6(\text{REE}_{22}\text{Ca}_6)(\text{Si}_{70}\text{O}_{175})(\text{OH}, \text{F})_{14}(\text{H}_2\text{O})_{21}$.

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