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Natural perovskite: $(Ca^{II}_{0.95\ (1)}Ce^{III}_{0.011\ (2)}Na^{I}_{0.010\ (4)})$-$(Fe^{III}_{0.022\ (2)}Ti^{IV}_{0.98\ (1)})O_3$

Érica G. Gravina, José D. Ayala and Nelson G. Fernandes*

Department of Chemistry, Federal University of Minas Gerais, Av. Antônio Carlos 6627, 31270-901 Belo Horizonte, Brazil
Correspondence e-mail: ngfernandes@ufmg.br

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Key indicators: single-crystal X-ray study; T = 298 K; mean σ() = 0.000 Å; some non-H atoms missing; disorder in main residue; R factor = 0.041; wR factor = 0.104; data-to-parameter ratio = 51.4.

A natural sample of perovskite (calcium caesium sodium iron titanium oxide) from the Tapira Alkaline Complex in south-eastern Brazil was found by electron microprobe analysis to have the chemical formula $(Ca^{2+}_{0.95\ (1)}Ce^{3+}_{0.011\ (2)}Na^{+}_{0.010\ (4)})$-$(Fe^{3+}_{0.022\ (2)}Ti^{4+}_{0.98\ (1)})O^{2-}_3$ and by IR spectroscopy to be an anhydrous mineral. Oxygen anions are arranged around Ti^{4+} in an almost perfect octahedron and around Ca^{2+} in a distorted 12-fold polyhedron.

Related literature

For related literature, see: Banfield & Veblen (1992); Beran *et al.* (1996); Chakhmouradian & Mitchell (1998); Haggerty & Mariano (1983); Kay & Bailey (1957); Lloyd & Bailey (1991); Mariano & Mitchell (1991); Seer & Moraes (1988); Sgarbi & Gaspar (1995); Sgarbi & Valença (1994); Soubies *et al.* (1991).

Experimental

Crystal data

$Na_{0.01}Ca_{0.96}Fe_{0.02}Ti_{0.98}Ce_{0.01}O_3$
M_r = 136.40
Orthorhombic, *Pbnm*
a = 5.3818 (4) Å
b = 5.4431 (4) Å
c = 7.6450 (5) Å
V = 223.95 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 5.94 mm^{-1}
T = 298 (2) K
0.2 × 0.15 × 0.15 mm

Data collection

Siemens P4 diffractometer
Absorption correction: refined from ΔF (*SHELXL97*; Sheldrick, 2008)
T_{min} = 0.356, T_{max} = 0.409
2383 measured reflections
1594 independent reflections
1527 reflections with $I > 2s(I)$
R_{int} = 0.033
3 standard reflections
every 197 reflections
intensity decay: 0.8%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.103
S = 1.25
1594 reflections
31 parameters
$\Delta\rho_{max}$ = 2.01 e Å^{-3}
$\Delta\rho_{min}$ = −2.88 e Å^{-3}

Table 1
Selected geometric parameters (Å ,°), where A represents the Ca^{2+}, Na^+ and Ce^{3+} cations, on a 12-coordinated site and B represents Fe^{3+} and Ti^{4+} cations on an octahedral site.

A—O_1	2.359 (2)	O_1^{iv}—A—O_1^{iv}	162.30 (6)
A—O_1^{iv}	2.481 (2)	O_2^{iv}—A—O_2^{viii}	80.97 (4)
A—O_1^{iv}	3.027 (2)	O_1—A—O_2^{vii}	118.03 (2)
A—O_1	3.052 (2)	O_2^{ii}—A—O_1^{iv}	65.08 (3)
A—O_2^{viii}	2.378 (1)		
A—O_2^{ii}	2.620 (1)		
A—O_2^{iv}	2.667 (1)		
A—O_2^{vi}	3.233 (1)		
B—O_1^{ii}	1.9513 (3)	O_1—B—O_1^{ii}	180.0
B—O_2^{vii}	1.956 (1)	O_2—B—O_2^{vii}	89.41 (1)
B—O_2^{v}	1.959 (1)	O_1—B—O_2	89.58 (6)

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

Data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *CrystalMaker* (CrystalMaker, 2007); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: MG2053).

References

Banfield, J. F. & Veblen, D. R. (1992). *Am. Mineral.* **77**, 545-557.
Beran, A., Libowittzky, E. & Armbruster, T. (1996). *Can. Mineral.* **34**, 803-809.
Chakhmouradian, A. R. & Mitchell, R. H. (1998). *Can. Mineral.* **36**, 953-969.
CrystalMaker (2007). *CrystalMaker for Windows*. CrystalMaker Software Ltd, Yarnton, England.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Haggerty, S. E. & Mariano, A. N. (1983). *Contrib. Mineral. Petrol.* **84**, 365-381.
Kay, H. F. & Bailey, P. C. (1957). *Acta Cryst.* **10**, 219–226.
Lloyd, F. E. & Bailey, D. K. (1991). 5th International Kimberlite Conference (Extended Abstracts), edited by O. H. Leonardos, H. O. A. Meyer & J. C. Gaspar, pp. 263–269. Araxá, Brazil, CPRM, Special Publication 3/91.
Mariano, A. N. & Mitchell, R. H. (1991). Proceedings of the 5th International Conference, Araxa, Brazil, pp. 251–253. Extended Abstracts.
Seer, H. J. & Moraes, L. C. (1988). *Rev. Bras. Geo.* **18**, 134-140.
Sgarbi, P. B. A. & Gaspar, J. C. (1995). 6th International Kimberlite Conference (Extended Abstracts), Novosibirsk, Rússia, pp. 498–499.
Sgarbi, P. B. A. & Valença, J. G. (1994). International Symposium on the Physics and Chemistry of the Upper Mantle (Extended Abstracts), pp. 27–29. São Paulo, Brazil: CPRM/FAPESP.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Siemens (1991). *XSCANS User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Soubies, F., Melfi, A. J. & Autefage, F. (1991). *Rev. Bras. Geo.* **21**, 3-16.

supporting information

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Natural perovskite: $(Ca^{II}_{0.95\ (1)}Ce^{III}_{0.011\ (2)}Na^{I}_{0.010\ (4)})(Fe^{III}_{0.022\ (2)}Ti^{IV}_{0.98\ (1)})O_3$

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S1. Comment

The term perovskite refers to both natural and synthetic compounds ABX_3 based on the mineral $CaTiO_3$. $CaTiO_3$ itself is the most commonly occurring perovskite in the Earth's crust (Chakhmouradian & Mitchell, 1998) and an important material to immobilize high-level radioactive waste. The first structure determination was reported for a synthetic material (Kay & Bailey, 1957), but structural studies of natural $CaTiO_3$ are quite rare and have been mostly limited to twinned crystals (Beran *et al.*, 1996). In central and southeastern Brazil, perovskite can be found as essential and accessory minerals of the Alto Paranaíba Igneous Province (Seer & Moraes, 1988; Sgarbi & Valença, 1994; Sgarbi & Gaspar, 1995), where they form part of five important carbonatite complexes, as in Tapira (Lloyd & Bailey, 1991). In these complexes, the conversion of perovskite in anatase (Soubies *et al.*, 1991) resulted in some of the biggest known titanium concentrations, but even so these deposits are not still economically explored for technological reasons. There are many geological studies (Haggerty & Mariano, 1983; Mariano & Mitchell, 1991; and others) describing crystals of perovskite in the Brazilian carbonatite complexes as belonging to the system lueshite ($NaNbO_3$)-loparite [$(NaCe)TiO_3$]-perovskite ($CaTiO_3$) but with the end member perovskite sensu stricto as the principal component.

In this work, a naturally occurring perovskite from the Tapira Alkaline Complex, localized at Minas Gerais State in Brazil (19°52′ south and 46°50′ west), has been investigated. The economic importance of this complex is due to the phosphates, titanium, and lanthanide and actinide elements drifts, which were formed by intemperism from primary magmatic rocks. From electron microprobe analyses (major elements: Ca - 38.9 (8) wt% CaO; Ti - 56.6 (9) wt% TiO_2; minor elements: Na - 0.224 (8) wt% Na_2O; Fe - 1.2 (1) wt% Fe_2O_3; Ce - 1.4 (3) wt% Ce_2O_3), it can be concluded that the sample is essentially the mineral $CaTiO_3$, with the calculated formula: $Ca^{2+}_{0.96\ (2)}\ Ce^{3+}_{0.011\ (2)}\ Na^{+}_{0.010\ (4)}\ Fe^{3+}_{0.022\ (2)}\ Ti^{4+}_{0.98\ (1)}\ O^{2-}_{3}$. The infrared spectra reveal characteristic bands for Ti-O and Ca-O, but importantly, the absence of bands related to OH^- and water suggests that the Tapira perovskite is indeed an anhydrous mineral. The bands at 348, 423, 528, 695 and 703 cm^{-1} observed are also present in spectra of TiO_2 polymorphs, especially anatase and TiO_2(B) as reported by Banfield & Veblen (1992). This could be due to the octahedral TiO_6 or even to the Ca^{2+} leaching from the perovskite, which has those two polymorphs as byproducts. Figure 1 shows the perovskite structure.

S2. Experimental

Among crystals averaging 1-2 cm^3 in size, some have carbonate incrustations and alterations due to intemperism. The cleanest crystals were separated and the biggest were chosen for polished sections for chemical analysis. Electron microprobe analyses were performed for four crystals on a JEOL JXA-8900 RL microscope, qualitatively with wavelength-dispersive mode and quantitatively with energy-dispersive mode. Standards used included rutile (TiO_2) for Ti, anorthite ($CaAl_2Si_2O_8$) for Ca, olivine [$(Mg,Fe)_2SiO_4$] for Fe, albite ($NaAlSi_3O_8$) for Na, and synthetic glasses for the lanthanide content. Infrared spectra were recorded for ground crystals on a Perkin Elmer GX spectrophotometer. Crystals were examined by polarizing microscope.

Initial refinements were performed using scattering factors for the neutral atoms of the major elements, with site occupancies based on the microprobe analyses ($Ca_{0.96\,(2)}Ti_{0.98\,(1)}O_3$), giving R = 0.0436, wR = 0.1099, and S = 1.315. The minor elements were added next, with the cation distribution based on the loparite (Na and Ce at A site) and latrappite structures (Fe at B site), and with the constraints that the displacement parameters of atoms within each of these sites be equal. The site occupancies for Ca and Ti were refined whereas those for the Na, Ce, and Fe atoms (including their uncertainties) were taken from the chemical analysis. In the final model, scattering factors for the ions were used and electroneutrality was found to be maintained with a total cation charge of +5.89 (2), according to the chemical formula $(Ca^{2+}_{0.95\,(1)}\,Ce^{3+}_{0.011\,(2)}\,Na^{+}_{0.010\,(4)})\,(Fe^{3+}_{0.022\,(2)}Ti^{4+}_{0.98\,(1)})O^{2-}_{3}$.

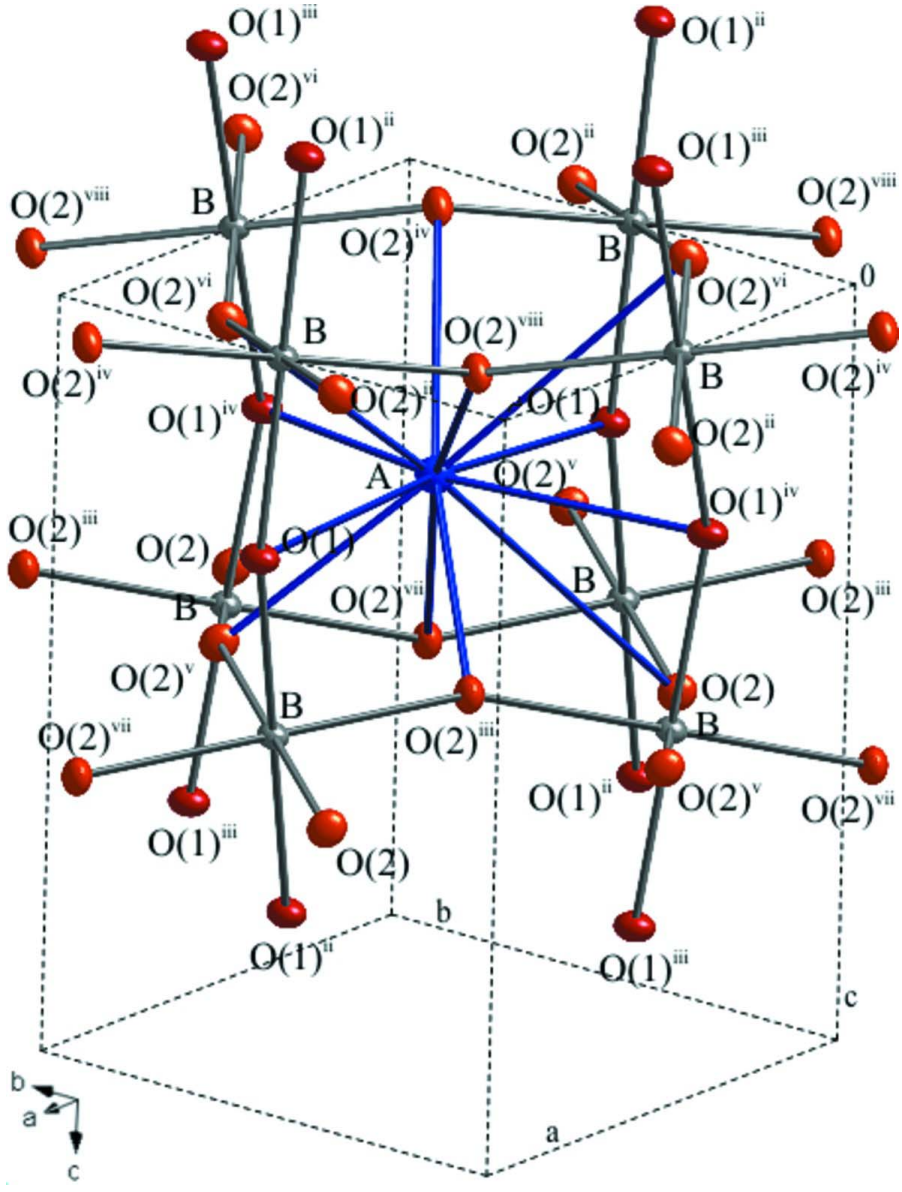

Figure 1

Part of the unit cell with the A site represented in dark blue, the B site in dark grey, and the oxygen ions in dark red. The bonds of the AO_{12} are also all represented in blue. Displacement ellipsoids are drawn at the 70% probability level [symmetry codes: (i) x, y, z; (ii) -x, -y, z+1/2; (iii) (x+1/2)-1, -y+1/2, -z; (iv) -x+1/2, (y+1/2)-1, 1-(-z+1/2); (v) -x, -y, -z; (vi) x, y, 1-(-z+1/2); (vii) -x+1/2, y+1/2, z; (viii) (x+1/2)-1, -y+1/2, z+1/2; (ix) -x, -y+1, (z+1/2)-1].

calcium caesium sodium iron titanium oxide

Crystal data

$Na_{0.01}Ca_{0.96}Fe_{0.02}Ti_{0.98}Ce_{0.01}O_3$
M_r = 136.40
Orthorhombic, *Pbnm*
Hall symbol: -P 2c 2ab
a = 5.3818 (4) Å
b = 5.4431 (4) Å
c = 7.6450 (5) Å
V = 223.95 (3) Å^3
Z = 4
F(000) = 262.9
D_x = 4.045 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å

Cell parameters from 40 reflections
θ = 4.6–56.8°
μ = 5.94 mm^{-1}
T = 298 K
Octahedral, grey
0.2 × 0.15 × 0.15 mm

Data collection

Siemens P4
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\theta/2\theta$ scans
Absorption correction: part of the refinement model (ΔF)
(*SHELXL97*; Sheldrick, 2008)
T_{min} = 0.356, T_{max} = 0.409
2383 measured reflections
1594 independent reflections
1527 reflections with $I > 2s(I)$
R_{int} = 0.033
θ_{max} = 56.8°, θ_{min} = 4.6°
h = −1→12
k = −1→12
l = −1→18
3 standard reflections every 197 reflections
intensity decay: 0.8%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.103
S = 1.25
1594 reflections
31 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0192P)^2 + 1.1174P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 2.01 e Å^{-3}
$\Delta\rho_{min}$ = −2.88 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.045 (5)

Special details

Experimental. Room temperature single-crystal X-ray diffraction standard experiment

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

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Ca	0.50660 (7)	0.53492 (7)	0.2500	0.00739 (7)	0.951 (7)
Ce	0.50660 (7)	0.53492 (7)	0.2500	0.0074 (11)	0.01
Na	0.50660 (7)	0.53492 (7)	0.2500	0.0074 (11)	0.01
Ti	0.0000	0.5000	0.5000	0.00487 (6)	0.977 (7)
Fe	0.0000	0.5000	0.5000	0.0049 (11)	0.02
O1	0.0713 (3)	0.4842 (3)	0.2500	0.00743 (19)	
O2	0.21101 (17)	0.21143 (18)	0.53714 (14)	0.00728 (15)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca	0.00587 (16)	0.00800 (13)	0.00831 (13)	0.00138 (8)	0.000	0.000
Ce	0.006 (3)	0.00800 (16)	0.00831 (13)	0.00138 (13)	0.000	0.000
Na	0.006 (3)	0.00800 (16)	0.00831 (13)	0.00138 (13)	0.000	0.000
Ti	0.00482 (11)	0.00595 (10)	0.00384 (9)	0.00000 (6)	−0.00004 (6)	−0.00027 (6)
Fe	0.005 (3)	0.00595 (11)	0.00384 (10)	0.00000 (6)	−0.00004 (6)	−0.00027 (9)
O1	0.0072 (4)	0.0104 (4)	0.0047 (4)	−0.0005 (3)	0.000	0.000
O2	0.0060 (3)	0.0072 (3)	0.0087 (3)	0.0020 (2)	0.0005 (2)	0.0010 (2)

Geometric parameters (Å, º)

Ca—O1	2.3586 (16)	Fe—O2^{iii}	1.9555 (9)
Ca—O2^{i}	2.3783 (11)	Fe—O2^{x}	1.9555 (9)
Ca—O2^{ii}	2.3783 (11)	Fe—O2^{ix}	1.9589 (9)
Ca—O1^{iii}	2.4814 (16)	Fe—O2	1.9589 (9)
Ca—O2^{iv}	2.6199 (11)	Fe—Ce^{xi}	3.1721 (4)
Ca—O2^{v}	2.6199 (11)	Fe—Ca^{xi}	3.1721 (4)
Ca—O2^{vi}	2.6671 (11)	Fe—Ce^{vii}	3.1721 (4)
Ca—O2^{iii}	2.6671 (11)	Fe—Ca^{vii}	3.1721 (4)
Ca—O1^{vii}	3.0266 (16)	Fe—Ca^{xii}	3.2772 (3)
Ca—O1^{viii}	3.0518 (16)	Fe—Ce^{xii}	3.2772 (3)
Ti—O1	1.9513 (3)	O1—Fe^{xiii}	1.9513 (3)
Ti—O1^{ix}	1.9513 (3)	O1—Ti^{xiii}	1.9513 (3)
Ti—O2^{iii}	1.9555 (9)	O1—Ca^{vii}	2.4814 (16)
Ti—O2^{x}	1.9555 (9)	O1—Ce^{vii}	2.4814 (16)
Ti—O2^{ix}	1.9589 (9)	O1—Ca^{iii}	3.0266 (16)
Ti—O2	1.9589 (9)	O1—Ca^{xii}	3.0518 (16)
Ti—Ce^{xi}	3.1721 (4)	O2—Fe^{ii}	1.9555 (9)
Ti—Ca^{xi}	3.1721 (4)	O2—Ti^{ii}	1.9555 (9)
Ti—Ce^{vii}	3.1721 (4)	O2—Ca^{x}	2.3783 (11)
Ti—Ca^{vii}	3.1721 (4)	O2—Ce^{x}	2.3783 (11)
Ti—Ca^{xii}	3.2772 (3)	O2—Ca^{iv}	2.6199 (11)
Ti—Ce^{xii}	3.2772 (3)	O2—Ce^{iv}	2.6199 (11)
Fe—O1	1.9513 (3)	O2—Ce^{vii}	2.6671 (11)
Fe—O1^{ix}	1.9513 (3)	O2—Ca^{vii}	2.6671 (11)
O1—Ca—O2^{i}	113.17 (4)	O2^{ix}—Fe—O2	180.0
O1—Ca—O2^{ii}	113.17 (4)	O1—Fe—Ce^{xi}	128.54 (5)
O2^{i}—Ca—O2^{ii}	86.35 (5)	O1^{ix}—Fe—Ce^{xi}	51.46 (5)
O1—Ca—O1^{iii}	86.98 (4)	O2^{iii}—Fe—Ce^{xi}	55.53 (3)
O2^{i}—Ca—O1^{iii}	129.34 (3)	O2^{x}—Fe—Ce^{xi}	124.47 (3)
O2^{ii}—Ca—O1^{iii}	129.34 (3)	O2^{ix}—Fe—Ce^{xi}	56.90 (3)
O1—Ca—O2^{iv}	129.62 (3)	O2—Fe—Ce^{xi}	123.10 (3)
O2^{i}—Ca—O2^{iv}	116.99 (3)	O1—Fe—Ca^{xi}	128.54 (5)
O2^{ii}—Ca—O2^{iv}	66.66 (2)	O1^{ix}—Fe—Ca^{xi}	51.46 (5)
O1^{iii}—Ca—O2^{iv}	65.08 (3)	O2^{iii}—Fe—Ca^{xi}	55.53 (3)

O1—Ca—O2^{v}	129.62 (3)	O2^{x}—Fe—Ca^{xi}	124.47 (3)
O2^{i}—Ca—O2^{v}	66.66 (2)	O2^{ix}—Fe—Ca^{xi}	56.90 (3)
O2^{ii}—Ca—O2^{v}	116.99 (3)	O2—Fe—Ca^{xi}	123.10 (3)
O1^{iii}—Ca—O2^{v}	65.08 (3)	O1—Fe—Ce^{vii}	51.46 (5)
O2^{iv}—Ca—O2^{v}	76.80 (5)	O1^{ix}—Fe—Ce^{vii}	128.54 (5)
O1—Ca—O2^{vi}	66.80 (3)	O2^{iii}—Fe—Ce^{vii}	124.47 (3)
O2^{i}—Ca—O2^{vi}	80.97 (4)	O2^{x}—Fe—Ce^{vii}	55.53 (3)
O2^{ii}—Ca—O2^{vi}	165.78 (3)	O2^{ix}—Fe—Ce^{vii}	123.10 (3)
O1^{iii}—Ca—O2^{vi}	64.58 (3)	O2—Fe—Ce^{vii}	56.90 (3)
O2^{iv}—Ca—O2^{vi}	125.177 (19)	Ce^{xi}—Fe—Ce^{vii}	180.0
O2^{v}—Ca—O2^{vi}	63.491 (11)	Ca^{xi}—Fe—Ce^{vii}	180.0
O1—Ca—O2^{iii}	66.80 (3)	O1—Fe—Ca^{vii}	51.46 (5)
O2^{i}—Ca—O2^{iii}	165.78 (3)	O1^{ix}—Fe—Ca^{vii}	128.54 (5)
O2^{ii}—Ca—O2^{iii}	80.97 (4)	O2^{iii}—Fe—Ca^{vii}	124.47 (3)
O1^{iii}—Ca—O2^{iii}	64.58 (3)	O2^{x}—Fe—Ca^{vii}	55.53 (3)
O2^{iv}—Ca—O2^{iii}	63.491 (11)	O2^{ix}—Fe—Ca^{vii}	123.10 (3)
O2^{v}—Ca—O2^{iii}	125.177 (19)	O2—Fe—Ca^{vii}	56.90 (3)
O2^{vi}—Ca—O2^{iii}	110.78 (5)	Ce^{xi}—Fe—Ca^{vii}	180.0
O1—Ca—O1^{vii}	75.32 (5)	Ca^{xi}—Fe—Ca^{vii}	180.0
O2^{i}—Ca—O1^{vii}	60.38 (3)	O1—Fe—Ca^{xii}	65.84 (4)
O2^{ii}—Ca—O1^{vii}	60.38 (3)	O1^{ix}—Fe—Ca^{xii}	114.16 (4)
O1^{iii}—Ca—O1^{vii}	162.30 (6)	O2^{iii}—Fe—Ca^{xii}	134.03 (3)
O2^{iv}—Ca—O1^{vii}	127.03 (3)	O2^{x}—Fe—Ca^{xii}	45.97 (3)
O2^{v}—Ca—O1^{vii}	127.03 (3)	O2^{ix}—Fe—Ca^{xii}	53.08 (3)
O2^{vi}—Ca—O1^{vii}	107.21 (3)	O2—Fe—Ca^{xii}	126.92 (3)
O2^{iii}—Ca—O1^{vii}	107.21 (3)	Ce^{xi}—Fe—Ca^{xii}	108.311 (8)
O1—Ca—O1^{viii}	168.10 (7)	Ca^{xi}—Fe—Ca^{xii}	108.311 (8)
O2^{i}—Ca—O1^{viii}	59.23 (3)	Ce^{vii}—Fe—Ca^{xii}	71.689 (8)
O2^{ii}—Ca—O1^{viii}	59.23 (3)	Ca^{vii}—Fe—Ca^{xii}	71.689 (8)
O1^{iii}—Ca—O1^{viii}	104.92 (5)	O1—Fe—Ce^{xii}	65.84 (4)
O2^{iv}—Ca—O1^{viii}	57.99 (3)	O1^{ix}—Fe—Ce^{xii}	114.16 (4)
O2^{v}—Ca—O1^{viii}	57.99 (3)	O2^{iii}—Fe—Ce^{xii}	134.03 (3)
O2^{vi}—Ca—O1^{viii}	118.03 (2)	O2^{x}—Fe—Ce^{xii}	45.97 (3)
O2^{iii}—Ca—O1^{viii}	118.03 (2)	O2^{ix}—Fe—Ce^{xii}	53.08 (3)
O1^{vii}—Ca—O1^{viii}	92.78 (5)	O2—Fe—Ce^{xii}	126.92 (3)
O1—Ti—O1^{ix}	180.0	Ce^{xi}—Fe—Ce^{xii}	108.311 (8)
O1—Ti—O2^{iii}	90.66 (5)	Ca^{xi}—Fe—Ce^{xii}	108.311 (8)
O1^{ix}—Ti—O2^{iii}	89.34 (5)	Ce^{vii}—Fe—Ce^{xii}	71.689 (8)
O1—Ti—O2^{x}	89.34 (5)	Ca^{vii}—Fe—Ce^{xii}	71.689 (8)
O1^{ix}—Ti—O2^{x}	90.66 (5)	Fe^{xiii}—O1—Fe	156.74 (9)
O2^{iii}—Ti—O2^{x}	180.0	Ti^{xiii}—O1—Fe	156.74 (9)
O1—Ti—O2^{ix}	90.42 (6)	Fe^{xiii}—O1—Ti	156.74 (9)
O1^{ix}—Ti—O2^{ix}	89.58 (6)	Ti^{xiii}—O1—Ti	156.74 (9)
O2^{iii}—Ti—O2^{ix}	90.586 (13)	Fe^{xiii}—O1—Ca	100.97 (4)
O2^{x}—Ti—O2^{ix}	89.414 (13)	Ti^{xiii}—O1—Ca	100.97 (4)
O1—Ti—O2	89.58 (6)	Fe—O1—Ca	100.97 (4)
O1^{ix}—Ti—O2	90.42 (6)	Ti—O1—Ca	100.97 (4)
O2^{iii}—Ti—O2	89.414 (13)	Fe^{xiii}—O1—Ca^{vii}	90.58 (5)

O2^{x}—Ti—O2	90.586 (13)	Ti^{xiii}—O1—Ca^{vii}	90.58 (5)
O2^{ix}—Ti—O2	180.0	Fe—O1—Ca^{vii}	90.58 (5)
O1—Ti—Ce^{xi}	128.54 (5)	Ti—O1—Ca^{vii}	90.58 (5)
O1^{ix}—Ti—Ce^{xi}	51.46 (5)	Ca—O1—Ca^{vii}	106.45 (6)
O2^{iii}—Ti—Ce^{xi}	55.53 (3)	Fe^{xiii}—O1—Ce^{vii}	90.58 (5)
O2^{x}—Ti—Ce^{xi}	124.47 (3)	Ti^{xiii}—O1—Ce^{vii}	90.58 (5)
O2^{ix}—Ti—Ce^{xi}	56.90 (3)	Fe—O1—Ce^{vii}	90.58 (5)
O2—Ti—Ce^{xi}	123.10 (3)	Ti—O1—Ce^{vii}	90.58 (5)
O1—Ti—Ca^{xi}	128.54 (5)	Ca—O1—Ce^{vii}	106.45 (6)
O1^{ix}—Ti—Ca^{xi}	51.46 (5)	Fe^{xiii}—O1—Ca^{iii}	85.94 (5)
O2^{iii}—Ti—Ca^{xi}	55.53 (3)	Ti^{xiii}—O1—Ca^{iii}	85.94 (5)
O2^{x}—Ti—Ca^{xi}	124.47 (3)	Fe—O1—Ca^{iii}	85.94 (5)
O2^{ix}—Ti—Ca^{xi}	56.90 (3)	Ti—O1—Ca^{iii}	85.94 (5)
O2—Ti—Ca^{xi}	123.10 (3)	Ca—O1—Ca^{iii}	91.25 (5)
O1—Ti—Ce^{vii}	51.46 (5)	Ca^{vii}—O1—Ca^{iii}	162.30 (6)
O1^{ix}—Ti—Ce^{vii}	128.54 (5)	Ce^{vii}—O1—Ca^{iii}	162.30 (6)
O2^{iii}—Ti—Ce^{vii}	124.47 (3)	Fe^{xiii}—O1—Ca^{xii}	78.47 (4)
O2^{x}—Ti—Ce^{vii}	55.53 (3)	Ti^{xiii}—O1—Ca^{xii}	78.47 (4)
O2^{ix}—Ti—Ce^{vii}	123.10 (3)	Fe—O1—Ca^{xii}	78.47 (4)
O2—Ti—Ce^{vii}	56.90 (3)	Ti—O1—Ca^{xii}	78.47 (4)
Ce^{xi}—Ti—Ce^{vii}	180.0	Ca—O1—Ca^{xii}	168.10 (7)
Ca^{xi}—Ti—Ce^{vii}	180.0	Ca^{vii}—O1—Ca^{xii}	85.45 (4)
O1—Ti—Ca^{vii}	51.46 (5)	Ce^{vii}—O1—Ca^{xii}	85.45 (4)
O1^{ix}—Ti—Ca^{vii}	128.54 (5)	Ca^{iii}—O1—Ca^{xii}	76.85 (4)
O2^{iii}—Ti—Ca^{vii}	124.47 (3)	Fe^{ii}—O2—Ti	155.77 (6)
O2^{x}—Ti—Ca^{vii}	55.53 (3)	Ti^{ii}—O2—Ti	155.77 (6)
O2^{ix}—Ti—Ca^{vii}	123.10 (3)	Fe^{ii}—O2—Fe	155.77 (6)
O2—Ti—Ca^{vii}	56.90 (3)	Ti^{ii}—O2—Fe	155.77 (6)
Ce^{xi}—Ti—Ca^{vii}	180.0	Fe^{ii}—O2—Ca^{x}	97.78 (4)
Ca^{xi}—Ti—Ca^{vii}	180.0	Ti^{ii}—O2—Ca^{x}	97.78 (4)
O1—Ti—Ca^{xii}	65.84 (4)	Ti—O2—Ca^{x}	106.45 (4)
O1^{ix}—Ti—Ca^{xii}	114.16 (4)	Fe—O2—Ca^{x}	106.45 (4)
O2^{iii}—Ti—Ca^{xii}	134.03 (3)	Fe^{ii}—O2—Ce^{x}	97.78 (4)
O2^{x}—Ti—Ca^{xii}	45.97 (3)	Ti^{ii}—O2—Ce^{x}	97.78 (4)
O2^{ix}—Ti—Ca^{xii}	53.08 (3)	Ti—O2—Ce^{x}	106.45 (4)
O2—Ti—Ca^{xii}	126.92 (3)	Fe—O2—Ce^{x}	106.45 (4)
Ce^{xi}—Ti—Ca^{xii}	108.311 (8)	Fe^{ii}—O2—Ca^{iv}	86.50 (4)
Ca^{xi}—Ti—Ca^{xii}	108.311 (8)	Ti^{ii}—O2—Ca^{iv}	86.50 (4)
Ce^{vii}—Ti—Ca^{xii}	71.689 (8)	Ti—O2—Ca^{iv}	90.22 (4)
Ca^{vii}—Ti—Ca^{xii}	71.689 (8)	Fe—O2—Ca^{iv}	90.22 (4)
O1—Ti—Ce^{xii}	65.84 (4)	Ca^{x}—O2—Ca^{iv}	98.07 (4)
O1^{ix}—Ti—Ce^{xii}	114.16 (4)	Ce^{x}—O2—Ca^{iv}	98.07 (4)
O2^{iii}—Ti—Ce^{xii}	134.03 (3)	Fe^{ii}—O2—Ce^{iv}	86.50 (4)
O2^{x}—Ti—Ce^{xii}	45.97 (3)	Ti^{ii}—O2—Ce^{iv}	86.50 (4)
O2^{ix}—Ti—Ce^{xii}	53.08 (3)	Ti—O2—Ce^{iv}	90.22 (4)
O2—Ti—Ce^{xii}	126.92 (3)	Fe—O2—Ce^{iv}	90.22 (4)
Ce^{xi}—Ti—Ce^{xii}	108.311 (8)	Ca^{x}—O2—Ce^{iv}	98.07 (4)
Ca^{xi}—Ti—Ce^{xii}	108.311 (8)	Ce^{x}—O2—Ce^{iv}	98.07 (4)

Ce^{vii}—Ti—Ce^{xii}	71.689 (8)	Fe^{ii}—O2—Ce^{vii}	91.02 (4)
Ca^{vii}—Ti—Ce^{xii}	71.689 (8)	Ti^{ii}—O2—Ce^{vii}	91.02 (4)
O1—Fe—$O1^{ix}$	180.0	Ti—O2—Ce^{vii}	85.12 (4)
O1—Fe—$O2^{iii}$	90.66 (5)	Fe—O2—Ce^{vii}	85.12 (4)
$O1^{ix}$—Fe—$O2^{iii}$	89.34 (5)	Ca^{x}—O2—Ce^{vii}	99.03 (4)
O1—Fe—$O2^{x}$	89.34 (5)	Ce^{x}—O2—Ce^{vii}	99.03 (4)
$O1^{ix}$—Fe—$O2^{x}$	90.66 (5)	Ca^{iv}—O2—Ce^{vii}	162.90 (4)
$O2^{iii}$—Fe—$O2^{x}$	180.0	Ce^{iv}—O2—Ce^{vii}	162.90 (4)
O1—Fe—$O2^{ix}$	90.42 (6)	Fe^{ii}—O2—Ca^{vii}	91.02 (4)
$O1^{ix}$—Fe—$O2^{ix}$	89.58 (6)	Ti^{ii}—O2—Ca^{vii}	91.02 (4)
$O2^{iii}$—Fe—$O2^{ix}$	90.586 (13)	Ti—O2—Ca^{vii}	85.12 (4)
$O2^{x}$—Fe—$O2^{ix}$	89.414 (13)	Fe—O2—Ca^{vii}	85.12 (4)
O1—Fe—O2	89.58 (6)	Ca^{x}—O2—Ca^{vii}	99.03 (4)
$O1^{ix}$—Fe—O2	90.42 (6)	Ce^{x}—O2—Ca^{vii}	99.03 (4)
$O2^{iii}$—Fe—O2	89.414 (13)	Ca^{iv}—O2—Ca^{vii}	162.90 (4)
$O2^{x}$—Fe—O2	90.586 (13)	Ce^{iv}—O2—Ca^{vii}	162.90 (4)

Symmetry codes: (i) $x+1/2, -y+1/2, z-1/2$; (ii) $x+1/2, -y+1/2, -z+1$; (iii) $-x+1/2, y+1/2, z$; (iv) $-x+1, -y+1, -z+1$; (v) $-x+1, -y+1, z-1/2$; (vi) $-x+1/2, y+1/2, -z+1/2$; (vii) $-x+1/2, y-1/2, z$; (viii) $x+1, y, z$; (ix) $-x, -y+1, -z+1$; (x) $x-1/2, -y+1/2, -z+1$; (xi) $x-1/2, -y+3/2, -z+1$; (xii) $x-1, y, z$; (xiii) $-x, -y+1, z-1/2$.