



Article

Aluminotaipingite-(CeCa), $(\text{Ce}_6\text{Ca}_3)\text{Al}(\text{SiO}_4)_3[\text{SiO}_3(\text{OH})]_4\text{F}_3$, a new member of the cerite-super group minerals

Italo Campostrini¹, Francesco Demartin² , Giuseppe Finello³ and Pietro Vignola⁴ 

¹Università degli Studi di Milano, UNITECH COSPECT, Piattaforme Tecnologiche di Ateneo, via Golgi 19, I-20133 Milano, Italy; ²Università degli Studi di Milano, Dipartimento di Chimica, via Golgi 19, I-20133 Milano, Italy; ³Independent Researcher, Corso Casale 265, 10132 Torino, Italy; and ⁴CNR-Istituto di Geologia Ambientale e Geoingegneria, Via Mario Bianco 9-20131 Milano, Italy

Abstract

Aluminotaipingite-(CeCa), $(\text{Ce}_6\text{Ca}_3)\text{Al}(\text{SiO}_4)_3[\text{SiO}_3(\text{OH})]_4\text{F}_3$, is a new member of the cerite-super group minerals, whose general chemical formula is $A_9XM[\text{TO}_3\text{O}]_7\text{Z}_3$, ($A = \text{REE}, \text{Ca}, \text{Sr}, \text{Na}$ and \square ; $X = \square, \text{Ca}, \text{Na}$ and Fe^{2+} ; $M = \text{Mg}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Al}$ and Mn ; $T = \text{Si}$ and P ; $\text{O} = \text{O}$ and OH ; $Z = \square, \text{OH}$ and F). It was found in cavities of a leucogranitic orthogneiss at the Casette quarry, Montoso, Bagnolo Piemonte, Cuneo Province, Piedmont, Italy. Crystals of aluminotaipingite-(CeCa) are light pink to pink, transparent or semi-transparent, with a vitreous lustre. It forms pyramidal crystals up to 0.07 mm in size and observed forms are $\{0\ 0\ 1\}$, $\{1\ 0\ \bar{2}\}$. The tenacity is brittle, no distinct cleavage is observed and the fracture is uneven. The mineral does not fluoresce in long- or short-wave ultraviolet light. The streak is white. Hardness (Mohs) = 5. The calculated density is $4.476\ \text{g cm}^{-3}$.

The mineral is trigonal, space group $R3c$, with $a = 10.658(3)$, $c = 37.865(9)$ Å, $V = 3725(2)$ Å³ and $Z = 6$. The eight strongest powder X-ray diffraction lines are $[d_{\text{obs}}, \text{Å} (I, \%) (h\ k\ l)]$: $8.38(29)(0\ 1\ 2)$, $4.499(28)(2\ 0\ 2)$, $3.282(41)(2\ 1\ 4)$, $2.936(100)(0\ 2\ 10)$, $2.816(51)(1\ 2\ 8)$, $2.669(37)(2\ 2\ 0)$, $2.207(29)(3\ 0\ 12)$ and $1.935(35)(2\ 3\ 8)$. The structure was refined to $R = 0.0306$ for 2297 reflections with $I > 2\sigma(I)$. The crystal structure of aluminotaipingite-(CeCa) contains two nine-fold coordinated sites ($A1$ and $A2$), which are occupied mainly by lanthanides, and a third nine-fold coordinated $A3$ site containing almost equal amounts of lanthanides and Ca. The X site is vacant and at the octahedral M site aluminium prevails over Fe^{3+} . Among the three independent T sites, $T2$ belongs to a $(\text{SiO}_4)^{4-}$ anion, whereas $T1$ and $T3$ belong to $(\text{SiO}_3\text{OH})^{3-}$ anions. Fluorine is involved in coordination with the $A1$ and $A3$ sites.

Keywords: aluminotaipingite-(CeCa); new mineral; cerite-super group minerals; Casette quarry; Montoso

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Introduction

Aluminotaipingite-(CeCa), $(\text{Ce}_6\text{Ca}_3)\text{Al}(\text{SiO}_4)_3[\text{SiO}_3(\text{OH})]_4\text{F}_3$, is a new mineral of the cerite super group, which was found in cavities of a leucogranitic orthogneiss at the Casette quarry, Montoso, Bagnolo Piemonte, Cuneo Province, Piedmont, Italy. The cerite-super group minerals nomenclature, which includes the cerite and merrillite groups, was established by Atencio and Azzi (2020). The general chemical formula of cerite-super group minerals is $A_9XM[\text{TO}_3\text{O}]_7\text{Z}_3$, where $A = \text{REE}, \text{Ca}, \text{Sr}, \text{Na}$, and \square ; $X = \square, \text{Ca}, \text{Na}$ and Fe^{2+} ; $M = \text{Mg}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Al}$ and Mn ; $T = \text{Si}$ and P ; $\text{O} = \text{O}$ and OH ; $Z = \square, \text{OH}$ and F (Atencio and Azzi, 2020). The general structural formula of cerite-super group minerals is $A1_3A2_3A3XM[(T1O_3O)1_3(T2O_4)_3(T3O_3O)10]Z1Z2Z3$, where the structural non-equivalence of the sites is emphasised. The letter Z represents the set of anions occurring at three non-equivalent $Z1$, $Z2$ and $Z3$ sites; the root name is cerite or taipingite, if the Z sites are dominated by (OH) or F , respectively. The recent discovery of new cerite-group species, in addition to those already described, has made it necessary to change the nomenclature of this group

and divide the cerite group into two subgroups, cerite and taipingite. (Atencio *et al.*, 2023). According to the new nomenclature rules the following changes in the mineral name have been approved: cerite-(Ce) into cerite-(CeCa), aluminocerite-(Ce) into aluminocerite-(CeCa), ferricerite-(La) into ferricerite-(LaCa) and taipingite-(Ce) into taipingite-(CeCa).

The new mineral and the mineral name aluminotaipingite-(CeCa) were approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA2022–126, Campostrini *et al.*, 2023) according to the new naming rules (with symbol Atpg-CeCa). Type material is deposited in the Reference Collection of the Museo di Storia Naturale, Milano, Italy, sample number M39041.

Aluminotaipingite-(CeCa) is therefore a member of the cerite group, classified as 9.AG in the classification of Strunz (9: SILICATES (Germanates), A: Nesosilicates, G: Nesosilicates with additional anions; cations in $> [6] \pm [6]$ coordination. Aluminotaipingite-(CeCa) does not correspond to any valid unnamed mineral (Smith and Nickel, 2007). This paper describes the complete characterisation of the new mineral.

Corresponding author: Francesco Demartin; Email: francesco.demartin@unimi.it

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Occurrence

Aluminotaipingite-(CeCa) occurs in cavities of a leucogranitic orthogneiss locally named 'Pietra di Luserna' at the Casette quarry,

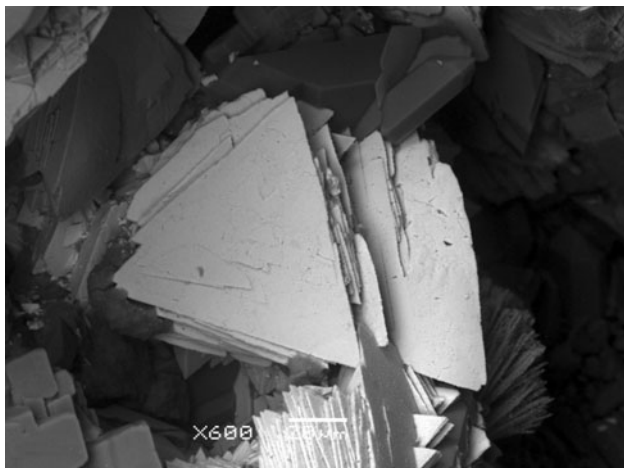


Figure 1. Aggregate of aluminotaipingite-(CeCa) crystals. Back-scatter electron image $\times 600$.



Figure 2. Aluminotaipingite-(CeCa) aggregates of pink pyramidal crystals on quartz matrix, with minor dark green clinocllore.

Montoso, Bagnolo Piemonte, Cuneo Province, Piedmont, Italy (latitude and longitude $44^{\circ}44'56''\text{N}$, $7^{\circ}13'54''\text{E}$). Associated minerals are allanite-(Ce), kainosite-(Y), laumontite, synchysite-(Ce), titanite,

Table 1. Analytical data (in wt.%) for aluminotaipingite-(CeCa) (average of 6 analyses).

Constituent	Wt.%	Range	S.D.	Probe standard
CaO	8.38	7.22–8.72	0.58	Grossular
MnO	0.42	0.36–0.49	0.04	Rhodonite
SrO	0.12	0.00–0.32	0.13	Celestine
Al ₂ O ₃	2.13	1.73–2.68	0.38	Grossular
Fe ₂ O ₃	1.05	0.70–1.23	0.18	Fayalite
Y ₂ O ₃	2.54	2.39–2.92	0.20	Synthetic phosphate**
La ₂ O ₃	7.70	6.39–8.94	0.82	Synthetic phosphate**
Ce ₂ O ₃	23.12	21.59–24.77	1.05	Synthetic phosphate**
Pr ₂ O ₃	3.14	3.00–3.25	0.09	Synthetic phosphate**
Nd ₂ O ₃	14.85	13.7–15.59	0.65	Synthetic phosphate**
Sm ₂ O ₃	4.26	3.74–4.74	0.33	Synthetic phosphate**
Gd ₂ O ₃	3.45	2.94–3.76	0.28	Synthetic phosphate**
Dy ₂ O ₃	0.74	0.62–0.83	0.07	Synthetic phosphate**
SiO ₂	25.01	24.57–25.78	0.43	Grossular
TiO ₂	0.19	0.13–0.24	0.04	Ilmenite
F	2.32	2.25–2.42	0.07	Hbl 135
H ₂ O*	1.08			
Sum	100.50			
O = F	–0.98			
Total	99.52			

*Calculated from the structure solution.

**Jarosewich and Boatner (1991)

wulfenite and clinocllore. From the geological point of view, the gneiss of the Luserna–Infernotto mining district belongs to the Dora Maira crystalline massif and represents the product of alpine metamorphic transformation of an originally magmatic rock with leucogranitic composition of late Hercynian age (Sandrone *et al.*, 1993 and 2004). Due to its strong resistance to weathering and abrasion 'Pietra di Luserna' is used primarily in north-western Italy as dimension stone for external floors and stairs.

Physical and optical properties

Aluminotaipingite-(CeCa) forms trigonal pyramidal crystals up to 0.07 mm in size (Figs 1 and 2). Crystals are light pink to pink or reddish and transparent or semi-transparent, with vitreous lustre. Observed forms are $\{0\ 0\ 1\}$ and $\{1\ 0\ \bar{2}\}$. Tenacity is brittle, no

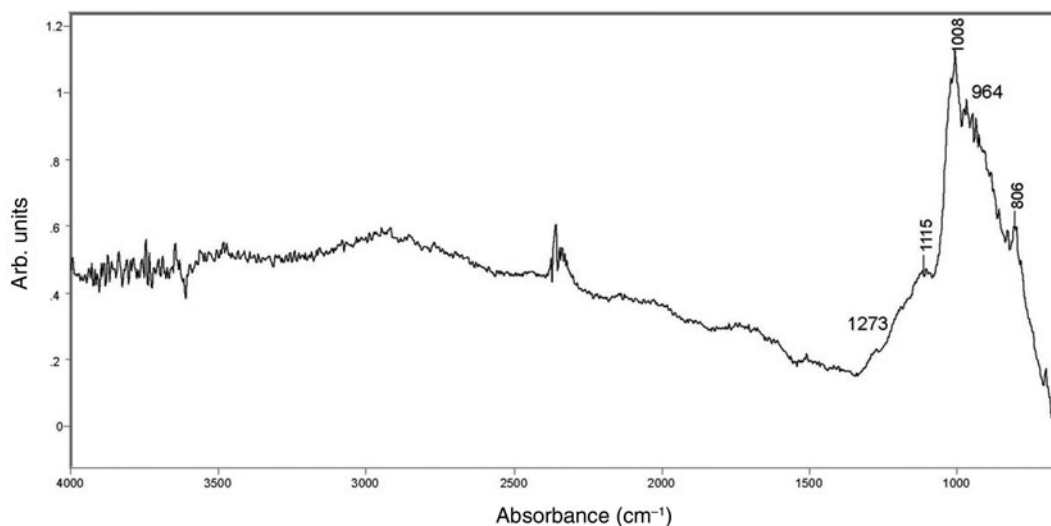


Figure 3. FTIR spectrum for aluminotaipingite-(CeCa).

Table 2. Powder X-ray diffraction data for aluminotaipingite-(CeCa).

<i>I</i> _{obs}	<i>I</i> _{calc} *	<i>d</i> _{obs} (Å)	<i>d</i> _{calc} (Å)**	<i>h k l</i>
29	30	8.38	8.306	0 1 2
8	11	6.66	6.618	1 0 4
26	21	6.36	6.322	0 0 6
14	12	5.357	5.335	1 1 0
28	21	4.499	4.489	2 0 2
22	18	4.232	4.219	0 1 8
18	6	4.168	4.153	0 2 4
20	21	3.518	3.509	1 0 10
21	24	3.431	3.435	1 2 2
14	7	3.315	3.309	2 0 8
41	49	3.282	3.277	2 1 4
12	8	3.170	3.161	0 0 12
23	28	3.082	3.080	3 0 0
100	100	2.936	2.932	0 2 10
51	47	2.816	2.812	1 2 8
31	25	2.772	2.769	3 0 6
37	42	2.669	2.667	2 2 0
20	23	2.571	2.569	2 1 10
7	9	2.541	2.540	3 1 2
4	5	2.466	2.474	1 3 4
3	4	2.341	2.337	2 0 14
11	9	2.299	2.297	1 0 16
29	25	2.207	2.206	3 0 12
13	9	2.124	2.124	1 3 10
14	5	2.107	2.107	2 3 2
18	8	2.078	2.077	4 0 8
5	5	2.069	2.069	3 2 4
10	4	2.039	2.039	2 2 12
2	6	1.972	1.973	4 0 10
35	38	1.935	1.935	2 3 8
8	6	1.921	1.921	4 1 6
7	4	1.850	1.858	1 0 20
16	16	1.838	1.839	5 0 2
5	12	1.819	1.814	0 5 4
14	22	1.777	1.778	3 3 0
19	23	1.755	1.755	2 0 20
20	15	1.740	1.739	0 3 18
8	9	1.720	1.720	5 0 8
7	7	1.669	1.670	2 3 14
11	12	1.578	1.579	3 2 16
6	7	1.548	1.550	3 3 12
4	2	1.519	1.520	5 1 10
3	2	1.499	1.496	6 0 6
2	3	1.477	1.480	5 2 0
7	4	1.456	1.457	4 1 18
6	7	1.414	1.414	2 3 20
5	2	1.406	1.406	3 0 24

Note: The strongest lines are given in bold.

*Calculated from the refined structure.

**Calculated from the unit cell *a* = 10.6695(5), *c* = 37.9364(30) Å and *V* = 3740.00(37) Å³, obtained from least-squares refinement of the above data using the program *UNITCELL* (Holland and Redfern, 1997).

distinct cleavage is observed and the fracture is uneven. The mineral does not fluoresce in long- or short-wave ultraviolet light. Observed twinning is by reflection on (001), two-fold rotation about [001] or inversion. Contact twins or complex lamellar forms are also observed. The streak is white. Hardness (Mohs) = 5. Density (meas.) was not determined because no suitable heavy liquids were available. Density (calc.) = 4.476 g cm⁻³ using the empirical formula and single-crystal cell data. The mineral is uniaxial (+) with ω = 1.750(3) and ε = 1.770(3) (white light).

The Gladstone–Dale parameters are: *K*_P = 0.1691 and *K*_C = 0.1665; compatibility (–0.015) and is rated as superior, according to Mandarino (1981).

Table 3. Details about the data collection and structure refinement for aluminotaipingite-(CeCa).

Crystal data	
Ideal formula	(Ce ₆ Ca ₃)Al(SiO ₄) ₃ [SiO ₃ (OH)] ₄ F ₂ (OH)
<i>a</i> (Å)	10.658(3)
<i>c</i> (Å)	37.865(9)
<i>V</i> (Å ³)	3725(2)
<i>Z</i>	6
Crystal dimensions (mm)	0.04 × 0.04 × 0.03
Space group	<i>R</i> 3c
Data Collection	
Instrument	Bruker APEX II CCD diffractometer
Absorption correction	Empirical (<i>SADABS</i> , Sheldrick 2008)
Radiation, wavelength (Å)	MoKα, 0.71073
Min. θ (°)	2.455
Max. θ (°)	31.656
Measured reflections	13144
<i>R</i> _{int}	0.0482
Independent reflections	2640
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	2297
Refinement	
Parameters refined	153
Twin matrix	[$\bar{1}$ 0 0 / 0 $\bar{1}$ 0 / 0 0 $\bar{1}$]
Flack parameter	0.18(4)
Final <i>R</i> [<i>I</i> > 2σ(<i>I</i>)] and <i>wR</i> ₂ (all data)	0.0306 and 0.0670
GoF	1.124
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0277q)^2 + 35.8743q]$ where $q = [\max(0, F_o^2) + 2F_c^2]/3$
Δρ _{max} , Δρ _{min} (e ⁻ Å ⁻³)	1.91, -1.45

Notes: *R* = Σ||*F*_o|| - ||*F*_c|| / Σ||*F*_o||; *wR*₂ = { Σ[*w*(*F*_o² - *F*_c²)²] / Σ[*w*(*F*_o²)²]}^{1/2}; GoF = {Σ[*w*(*F*_o² - *F*_c²)] / (n - *p*)}^{1/2} where *n* is the number of reflections and *p* is the number of refined parameters.

Infrared spectroscopy

The FTIR (Fourier Transform Infrared Spectroscopy) spectrum obtained using a Jasco IRT-3000 shows relatively sharp bands at 806, 964, 1008 and 1115 cm⁻¹ due to Si–O fundamental modes (Fig. 3). A band at 1273 cm⁻¹ is also ascribable to Si–O fundamental modes and resembles that found in minerals having the

Table 4. Sites, site occupancies*, fractional atom coordinates and equivalent-isotropic displacement parameters (Å²) for aluminotaipingite-(CeCa).

Site	<i>x</i> / <i>a</i>	<i>y</i> / <i>b</i>	<i>z</i> / <i>c</i>	<i>U</i> _{eq}
A1*	0.74099(7)	0.86629(7)	0.93178(2)	0.01026(19)
A2*	0.85733(8)	0.74245(9)	0.56899(2)	0.0144(2)
A3*	0.74285(10)	0.86547(10)	0.82388(2)	0.0145(3)
<i>M</i> *	0.000000	0.000000	0.00162(14)	0.0097(9)
T1	0.6821(4)	0.8522(3)	0.63838(8)	0.0090(6)
T2	0.8523(3)	0.6748(4)	0.86328(9)	0.0105(6)
T3	0.000000	0.000000	0.74733(16)	0.0117(9)
OH1	0.7384(10)	0.9087(10)	0.6786(2)	0.022(2)
O2	0.5045(10)	0.7567(9)	0.6375(2)	0.0138(17)
O3	0.7399(10)	0.7499(9)	0.6230(2)	0.0151(18)
O4	1.0033(8)	0.7259(9)	0.6147(2)	0.0140(16)
O5	0.7571(9)	0.7286(10)	0.8852(2)	0.0186(18)
O6	1.0156(9)	0.7312(9)	0.8776(2)	0.0174(17)
O7	0.6133(8)	0.8053(11)	0.9882(2)	0.0129(15)
O8	0.7618(8)	0.4984(8)	0.8673(2)	0.0113(16)
O9	1.1244(9)	1.1621(9)	0.7598(2)	0.0203(17)
OH10	0.000000	0.000000	0.7025(4)	0.022(3)
F11	0.000000	0.000000	0.9115(4)	0.020(3)
F12	0.000000	0.000000	0.8388(3)	0.018(2)
OH13	0.000000	0.000000	0.5934(5)	0.021(4)

*Site occupancies for sites with <1.00 are: A1 = Ce_{0.947(7)}; A2 = Ce_{0.882(6)}; A3 = Ce_{0.683(5)}; *M* = Al_{0.56(2)} Fe_{0.44(2)}.

Table 5. Refined anisotropic displacement parameters (\AA^2) for aluminotaipingite-(CeCa).

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
A1	0.0118(3)	0.0099(3)	0.0105(3)	-0.0010(2)	-0.0002(2)	0.0066(3)
A2	0.0105(4)	0.0172(4)	0.0161(4)	0.0067(3)	0.0022(4)	0.0074(4)
A3	0.0161(5)	0.0147(5)	0.0168(4)	-0.0049(4)	-0.0047(3)	0.0107(4)
M	0.0083(11)	0.0083(11)	0.0125(15)	0.000	0.000	0.0041(5)
T1	0.0069(14)	0.0070(13)	0.0137(16)	-0.0008(11)	-0.0002(11)	0.0039(11)
T2	0.0101(14)	0.0104(14)	0.0107(14)	0.0007(10)	0.0009(13)	0.0050(12)
T3	0.0108(12)	0.0108(12)	0.014(2)	0.000	0.000	0.0054(6)
OH1	0.016(4)	0.029(5)	0.018(4)	-0.005(4)	-0.005(3)	0.010(4)
O2	0.013(4)	0.011(4)	0.017(4)	-0.001(3)	-0.002(3)	0.005(3)
O3	0.019(4)	0.012(4)	0.020(4)	0.002(3)	0.004(3)	0.012(3)
O4	0.009(4)	0.010(4)	0.021(4)	0.001(3)	-0.002(3)	0.003(3)
O5	0.014(4)	0.018(4)	0.021(4)	-0.008(3)	-0.001(3)	0.006(3)
O6	0.014(4)	0.016(4)	0.016(4)	-0.003(3)	-0.004(3)	0.005(3)
O7	0.012(4)	0.016(4)	0.010(3)	0.001(3)	-0.001(3)	0.006(3)
O8	0.010(4)	0.005(3)	0.018(4)	-0.002(3)	-0.002(3)	0.002(3)
O9	0.022(4)	0.016(4)	0.016(4)	0.000(3)	-0.002(3)	0.004(3)
OH10	0.019(4)	0.019(4)	0.030(9)	0.000	0.000	0.009(2)
F11	0.014(4)	0.014(4)	0.032(7)	0.000	0.000	0.007(2)
F12	0.014(3)	0.014(3)	0.026(6)	0.000	0.000	0.0068(16)
OH13	0.017(5)	0.017(5)	0.030(9)	0.000	0.000	0.009(3)

[SiO₃(OH)] tetrahedron (Chukanov, 2013; Frost et al., 2013). According to the Libowitzky's equation (Libowitzky, 1999) and to the observed hydrogen-bonds, stretching frequencies related to the OH group, should occur at $\sim 2800\text{ cm}^{-1}$. They appear as a very broad signal in this region of the infrared spectrum.

Chemical analysis

Quantitative chemical analyses (6 spots) were carried out in wavelength dispersive spectroscopy mode using a JEOL JXA-8200 WDS electron microprobe (15 kV excitation voltage, 5 nA beam current and 5 μm beam diameter). X-ray intensities were converted to wt.% by ZAF quantitative analysis software. Chemical data and the standards used in the analysis are reported in Table 1. The empirical formula, on the basis of 7 Si atoms per formula unit, is: $^A(\text{Ca}_{2.51}\text{Ce}_{2.37}\text{Nd}_{1.48}\text{La}_{0.80}\text{Sm}_{0.41}\text{Y}_{0.38}\text{Pr}_{0.32}\text{Gd}_{0.32}\text{Mn}_{0.10}\text{Dy}_{0.07}\text{Sr}_{0.02})_{\Sigma 8.77}^M(\text{Al}_{0.70}\text{Fe}_{0.22}\text{Ti}_{0.04})_{\Sigma 0.96}^T(\text{SiO}_4)_3^{T1,T3}[\text{SiO}_3(\text{OH})]_4^Z[\text{F}_{2.05}(\text{OH})_{1.02}]_{\Sigma 3.07}$. Atoms have been distributed according to the cerite general formula $A_9XM[\text{TO}_3(\emptyset)]_7Z_3$ (Atencio and Azzi, 2020), in which the X position is vacant. The simplified formula is: (Ca,Ce,Nd,La,Sm,Y,Pr,Gd,Mn,Dy)₉(Al,Fe³⁺,Ti)(SiO₄)₃[SiO₃(OH)]₄[F,(OH)]₃. The ideal formula is: (Ce₆Ca₃)Al(SiO₄)₃[SiO₃(OH)]₄F₃.

X-ray crystallography and crystal structure determination

Powder X-ray diffraction data were collected using a Rigaku Miniflex powder diffractometer with graphite monochromated CuK α radiation. Data (in \AA) are listed in Table 2 together with the pattern calculated from the crystal structure using VESTA (Momma and Izumi, 2011). Unit cell parameters refined from the powder data (Holland and Redfern, 1997) are $a = 10.6695(5)$, $c = 37.9364(30)\text{ \AA}$ and $V = 3740.00(37)\text{ \AA}^3$. Single-crystal diffraction data were collected on a crystal partly affected by merohedral twin using a Bruker Apex II diffractometer with MoK α radiation ($\lambda = 0.71073\text{ \AA}$). A total of 13144 intensities were measured up to $2\theta = 63.30^\circ$, of which 2640 were unique ($R_{\text{int}} 0.048$). A SADABS absorption correction was applied (minimum transmission factor 0.766). The structure was refined with SHELXL-2017/1

Table 6. Selected bond distances (\AA) and hydrogen bonds for aluminotaipingite-(CeCa).

A1-O5	2.357(8)	A2-O4	2.391(8)
A1-O7	2.440(8)	A2-O3	2.418(8)
A1-O6 ^a	2.491(8)	A2-O8 ^f	2.443(8)
A1-F11 ^t	2.511(5)	A2-O9 ^g	2.476(8)
A1-O2 ^b	2.559(8)	A2-O8 ^h	2.507(8)
A1-O2 ^s	2.588(8)	A2-OH13	2.554(7)
A1-O4 ^c	2.595(8)	A2-O5 ^h	2.563(9)
A1-O3 ^d	2.792(9)	A2-OH1 ⁱ	2.567(9)
A1-O9 ^e	2.813(9)	A2-O6 ^f	2.825(9)
<A1- \emptyset ,F>	2.572	<A2- \emptyset >	2.527
A3-F12 ^t	2.441(3)	M-O8 ^u	1.960(8)
A3-O7 ⁱ	2.442(10)	M-O8 ⁿ	1.960(8)
A3-O3 ^j	2.471(8)	M-O8 ^o	1.960(8)
A3-O6 ^q	2.490(9)	M-O2 ^p	1.964(9)
A3-O4 ^j	2.492(8)	M-O2 ^r	1.964(9)
A3-O7 ^k	2.533(10)	M-O2 ^f	1.964(9)
A3-O9 ^l	2.633(8)	<M-O>	1.962
A3-O5	2.785(9)		
A3-OH1 ^m	2.972(9)		
<A3- \emptyset ,F>	2.584		
T1-OH1	1.638(10)	T2-O5	1.620(9)
T1-O2	1.642(10)	T2-O6	1.624(9)
T1-O3	1.607(8)	T2-O7 ⁱ	1.642(9)
T1-O4 ^q	1.643(8)	T2-O8	1.636(9)
<T1- \emptyset >	1.633	<T2-O>	1.631
T3-O9 ^v	1.636(8)		
T3-O9 ^w	1.636(8)		
T3-O9 ^x	1.636(8)		
T3-OH10	1.698(17)		
<T3- \emptyset >	1.652		
OH1...O5 ^k	2.798(17)	OH13...O3 ^v	2.942(10)
OH1...O6 ^l	3.102(15)	OH13...O4 ^v	3.048(10)
OH1...OH10 ^t	2.613(11)	OH13...O8 ^z	2.719(18)

Symmetry operations: $a = 1-x+y, 2-x, +z$; $b = 5/3-y, 4/3+x-y, z+1/3$; $c = x-1/3, 1/3+y, 1/3+z$; $d = 2/3-x+y, 4/3-x, z+1/3$; $e = x-2/3, 2/3+x-y, 1/6+z$; $f = 4/3-x+y, 5/3-x, z-1/3$; $g = 2/3-x+y, y-2/3, z-1/6$; $h = 4/3-y, 2/3+x-y, z-1/3$; $i = 5/3-y, 4/3-x, z-1/6$; $j = 4/3-y, 5/3-x, 1/6+z$; $k = 2/3-x+y, 1/3+y, z-1/6$; $l = 2-y, 1+x-y, z$; $m = 1/3-x+y, y-1/3, 1/6+z$; $n = 1/3-x+y, y-1/3, z-5/6$; $o = x-2/3, x-y-1/3, z-5/6$; $p = x-1/3, y-2/3, z-2/3$; $q = 2/3-y, 1/3+x-y, z-2/3$; $r = -x+y-1/3, 1/3-x, z-2/3$; $s = 2/3-x+y, 4/3-x, 1/3+z$; $t = 1+x, 1+y, z$; $u = 1/3-y, 2/3-x, z-5/6$; $v = x-1, y-1, z$; $w = 1-y, x-y, z$; $x = y-x, 1-x, z$; $y = x-1/3, 1/3+x-y, z-1/6$; $z = x-2/3, y-1/3, z-1/3$.

Table 7. Bond-valence (vu) analysis for aluminotaipingite-(CeCa)*.

	OH1	O2	O3	O4	O5	O6	O7	O8	O9	OH10	F11	F12	OH13	Σ
A1		0.322, 0.297	0.171	0.292	0.558	0.386	0.444		0.162		0.268×3↓			2.900
A2	0.301		0.450	0.484	0.306	0.149		0.354, 0.422	0.386				0.312×3↓	3.173
A3	0.088		0.342	0.324	0.146	0.325	0.370, 0.290		0.221			0.269×3↓		2.375
M		0.496×3→						0.499×3→						2.985
T1	0.965	0.955	1.050	0.952										3.921
T2					1.007	0.999	0.954	0.969						3.930
T3									0.969×3→	0.820				3.727
Σ	1.354	2.070	2.013	2.052	2.017	1.859	2.058	2.244	1.738	0.820	0.804	0.807	0.936	

*Parameters used from Brese and O'Keeffe (1991) and Brown (2009). Bond-valence sums were calculated with the site occupancies of A1 (Ca_{0.08}Ce_{0.92}), A2 (Ca_{0.18}Ce_{0.82}), A3 (Ca_{0.48}Ce_{0.52}) and M (Al_{0.56}Fe_{0.44}), obtained from structure refinement.

(Sheldrick, 2017) in the space group *R3c* starting from the atomic coordinates of aluminocerite-(CeCa) (Nestola *et al.*, 2009). Crystal data and details of the structure refinement are reported in Table 3. Site scatterings for the A1, A2 and A3 sites were modelled using the scattering factors of Ce and for the M site using the scattering factors of Al and Fe. The location of the F atoms among the most probable sites was done after refinement of the occupancy of the F11, F12 and OH13 sites. In the final stages of the refinement each of these three sites were assigned full occupancies. Absolute configuration and twin refinement were carried out. The ratio of the two twin components related by inversion is 0.82/0.18. The formula of the mineral obtained from structure refinement, where only the contribution of Ce and Ca to the site scattering of the A sites was assumed is (Ce_{6.78}Ca_{2.22})Σ_{9.00}(Al_{0.56}Fe_{0.44})Σ_{1.00}(SiO₄)₃[SiO₃(OH)]₄F₂(OH).

The *c/a* ratio calculated from the unit-cell parameters is 3.5527 (single-crystal data). Fractional atom coordinates and equivalent isotropic displacement parameters are given in Table 4. Anisotropic displacement parameters are given in Table 5. Refined selected bond distances are given in Table 6. Bond-valence analysis is reported in Table 7. The crystallographic information file has been deposited with the Principal Editor of *Mineralogical Magazine* and is available as Supplementary material (see below).

Description of the crystal structure and discussion

The crystal structure of the cerite-supergroup minerals $A_9XM [TO_3\emptyset]_7Z_3$ involves three eight-, nine- or ten-fold-coordinated A sites, one hexacoordinated X site, one octahedral M site and three [TO₃∅] tetrahedral sites. Aluminotaipingite-(CeCa) is isostructural to the other silicate minerals of the cerite supergroup: ferricerite-(LaCa), (La₆Ca₃)Fe³⁺(SiO₄)₃[SiO₃(OH)]₄(OH)₃ (Pakhomovsky *et al.*, 2002; Atencio and Azzi, 2020) and aluminocerite-(CeCa), (Ce₆Ca₃)Al(SiO₄)₃[SiO₃(OH)]₄(OH)₃ (Nestola *et al.*, 2009), where three nine-fold coordinated sites (A1 A2 and A3), with tricapped trigonal prism geometry are present (Fig. 4). In taipingite-(CeCa), (Ce₇Ca₂)Mg(SiO₄)₃[SiO₃(OH)]₄F₃ (Qu *et al.*, 2020), these sites are instead ten-fold coordinated and in cerite-(CeCa), (Ce₇Ca₂)Mg(SiO₄)₃[SiO₃(OH)]₄(OH)₃ (Moore and Shen, 1983), they are eight-fold-coordinated. Fluorine is involved in coordination with the A1 and A3 sites. In aluminotaipingite-(CeCa) the two sites A1 and A2 are mainly occupied by lanthanides and display a scattering power of ~55 and 51 electrons respectively, similar to those observed in aluminocerite-(CeCa) (53 and 48 electrons) but slightly lower than those observed in taipingite-(CeCa) (57 and 56 electrons, respectively). From structure refinement the composition of the A1 and A2 sites is therefore Ca_{0.08}Ce_{0.92} and Ca_{0.18}Ce_{0.82}, respectively. The average bond lengths A1–O,F =

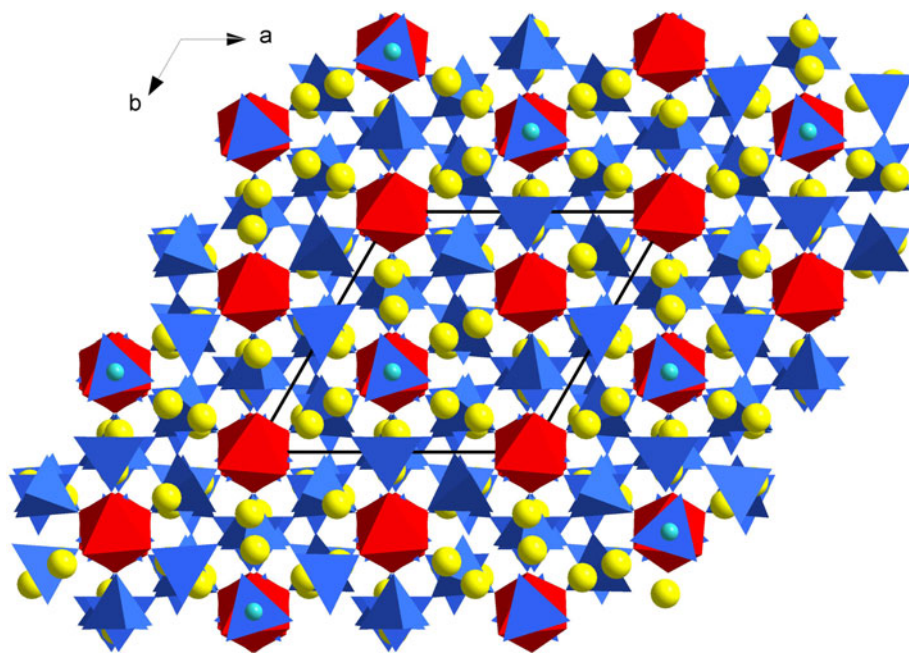


Figure 4. The crystal structure of aluminotaipingite-(CeCa) viewed along [001]. M sites = red polyhedra, T sites = blue tetrahedra, A sites = yellow balls and F = small sky-blue balls. Drawn using *Diamond* (Crystal Impact GbR, Bonn, Germany). The unit cell is outlined.

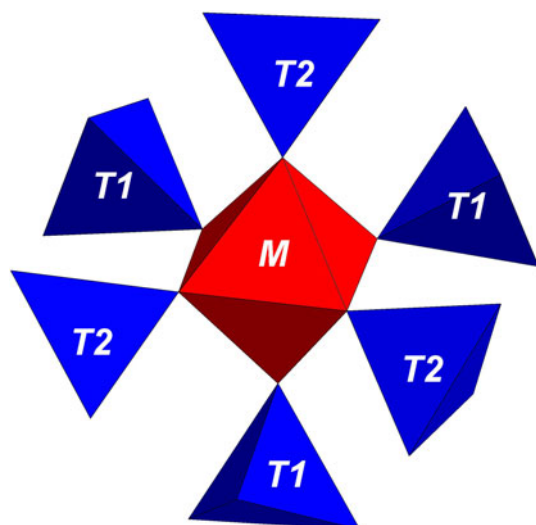


Figure 5. The $M [T1O_3\emptyset T2O_4]_3$ cluster.

2.572 Å and $A2-\emptyset = 2.527$ Å are statistically identical to those observed in aluminocerite-(CeCa) (2.573 and 2.542 Å) and taipingite-(CeCa) (2.576 and 2.546 Å). The third A3 site exhibits a relatively lower refined site scattering (40 electrons) corresponding to the composition $Ca_{0.48}Ce_{0.52}$, indicative that Ca is more abundant here than in A1 and A2. Considering that the average scattering value for the lanthanide cations is higher than 58 electrons, probably Ca is instead slightly dominant in this site. The average $A3-\emptyset, F$ distance is 2.584 Å. The sum of the refined occupancies for the A sites is 437 electrons, to be compared to 418 electrons from the chemistry. These differences are due to the different crystal fragment used for the measurements.

In aluminotaipingite-(CeCa) the X site is vacant. In the octahedral M site aluminium prevails upon Fe^{3+} ($Al_{0.56(2)}, Fe_{0.44(2)}$ from structure refinement) and again here the refined occupancy of the M site gives 18.7 electrons in comparison to the 15.7 electrons from the chemistry for the same reason stated above. The average $M-O$ distance (1.962 Å) is larger than the corresponding mean bond length for aluminocerite-(CeCa) (1.931 Å), because a larger Al/Fe^{3+} ratio is observed in aluminocerite-(CeCa), but less than that of taipingite-(CeCa) (2.050 Å), in line with the larger ionic radius of Mg with respect to that of Al^{3+} . Considering the value of the ionic radii for $^{VI}Fe^{3+}$ is 0.645 Å, ^{VI}Al is 0.535 Å and $^{III}O^-$ is 1.36 Å, the calculated average bond length for the previous composition is 1.943 Å, a value close to the observed one, giving support for the oxidation state of Fe^{3+} .

Among the three independent T sites, from bond-valence considerations and in accordance with the structure of the other members of the group, T2 belongs to a $(SiO_4)^{4-}$ anion, whereas T1 and T3 belong to $(Si_3O_7)^{3-}$ anions.

Moore and Shen (1983) described the structure of cerite-(CeCa) as based on rods of corner-, edge- and face-sharing TO_4 tetrahedra, MO_6 octahedra and AO_8OH polyhedra. Another description of the cerite-group minerals has been suggested by Pakhomovsky *et al.* (2002) for ferricerite-(LaCa) and is based on alternating sheets made by the above-mentioned coordination polyhedra. The $M[T1O_3\emptyset T2O_4]_3$ clusters (Fig. 5), together with A(3), form the A layers at $z \approx 0, 1/6, 1/3, 1/2, \dots$ shown in Fig. 6, that should also include the X sites, whenever filled. The A1 and A2 polyhedra and the $[T3O_3\emptyset]$ tetrahedra form the B layers

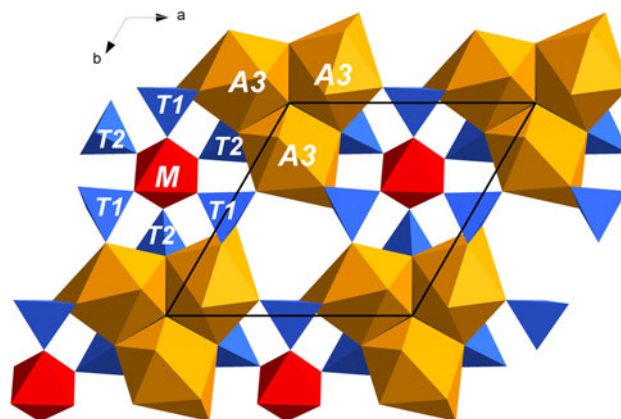


Figure 6. The A layer made by $M [T1O_3\emptyset T2O_4]_3$ clusters and A3 polyhedra.

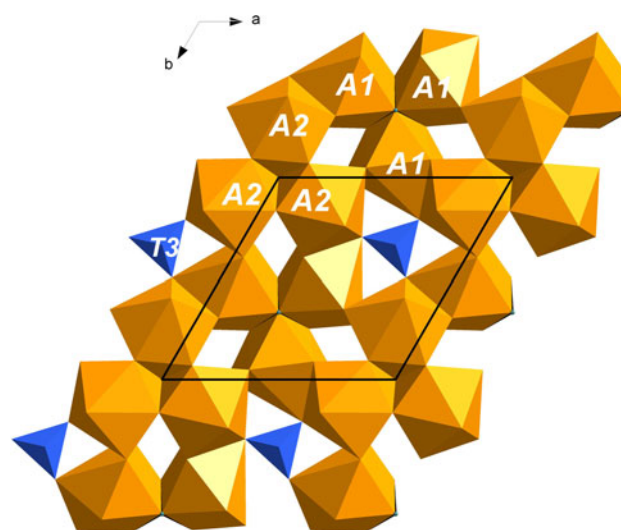


Figure 7. The B layer made by A1 and A2 polyhedra and $[T3O_3\emptyset]$ tetrahedra.

at $z \approx 1/12, 1/4, 5/12, 7/12, \dots$ (Fig. 7). The layers are parallel to (001) and alternate as **ABABAB**...

The positions of the hydrogen atoms bonded to OH1, OH10 and OH13 could not be detected in the structure determination. However, the short interatomic $O \cdots O$ distances reported in Table 6 and bond valence calculations may give some indication on the hydrogen bonds. For instance, OH1 and OH10 are at a distance of 2.613(11) Å, corresponding to a strong hydrogen bond where OH10 receives, as acceptor, bonding from three protons. This interaction contributes ~ 0.2 valence units (vu) to the low bond-valence value (0.820 vu) of OH10, (Hawthorne and Schindler, 2008), thus giving a more reasonable bond valence for a hydroxyl group. Other significant interactions of the hydroxyls involve the oxygen atoms of the silicate anions.

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Competing interests. The authors declare none

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