

**CERITE-(La), (La,Ce,Ca)₉(Fe,Ca,Mg)(SiO₄)₃[SiO₃(OH)]₄(OH)₃,
A NEW MINERAL SPECIES FROM THE Khibina Alkaline Massif:
Occurrence and Crystal Structure**

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ABSTRACT

Cerite-(La), ideally (La,Ce,Ca)₉(Fe,Ca,Mg)(SiO₄)₃[SiO₃(OH)]₄(OH)₃, was found in an aegirine – natrolite – microcline vein in foyaite, Mt. Yukspor, Khibina massif, Kola Peninsula, Russia. It forms porous pseudomorphs (up to 7 cm long) after an unidentified hexagonal prismatic mineral. Within the pseudomorphs, cerite-(La) occurs as a boxwork-like aggregates of equant to tabular crystals (flattened on *c*, up to 2 mm across), with dominant rhombohedral and pinacoidal faces. Associated minerals are aegirine, anatase, ancylite-(Ce), barylite, catapleiite, cerite-(Ce), chabazite-Ca, edingtonite, fluorapatite, galena, ilmenite, microcline, natrolite, sphalerite, strontianite and vanadinite. The mineral is brittle, with a conchoidal fracture. It is light yellow to pinkish brown with a white streak, and translucent with a vitreous luster. Cleavage and parting were not observed. The Mohs hardness is 5; the density is 4.7(1) g cm⁻³ (meas.) and 4.74 g cm⁻³ (calc.). It is uniaxial, optically positive, *n_o* 1.810(5), *n_e* 1.820(5) (for λ = 589 nm). An average result of seven electron-microprobe analyses for seven different crystals (each one reported as an average of 6–10 points from each crystal) gave La₂O₃ 37.57, Ce₂O₃ 23.67, Pr₂O₃ 0.61, Nd₂O₃ 1.48, Sm₂O₃ 0.10, Gd₂O₃ 0.24, SrO 1.97, CaO 5.09, Fe₂O₃ 1.40, MgO 0.51, SiO₂ 22.38, P₂O₅ 0.63, H₂O 3.20 (determined by the Penfield method), total 98.85, which corresponds to the empirical formula (La_{4.23}Ce_{2.65}Ca_{1.37}Sr_{0.35}Nd_{0.16}Pr_{0.07}Gd_{0.02}Sm_{0.01})_{Σ8.86} (Fe_{0.32}Ca_{0.30}Mg_{0.23})_{Σ0.85} [SiO₄]₃[(Si_{0.84}P_{0.16})_{Σ1.00}O₃(OH)]₄(OH)_{2.78}, calculated on the basis of (Si + P) = 7. The mineral is trigonal, *R3c*, with *a* 10.7493 (6), *c* 38.318 (3) Å, *V* 3834.36 Å³, *Z* = 6. The strongest eight lines in the X-ray powder-diffraction pattern [*d* in Å(*I*)(*hkl*)] are: 3.53(26)(10.10,211), 3.47(40)(122), 3.31(38)(214), 3.10(25)(300), 2.958(100)(02.10), 2.833(37)(128), 2.689(34)(220), 1.949(34)(238,13.13). The crystal structure has been refined on the basis of *F*² for all unique reflections collected using a CCD area detector, to an *R*1 of 0.036, calculated for the 1544 unique observed reflections (*F_o* ≥ 4σ*F_o*). Cerite-(La) is structurally related to cerite-(Ce). The mineral is named as the La-dominant analogue of cerite-(Ce). The structural formula for these minerals can be written as REE₉MCa_x[SiO₄]₃[SiO₃(OH)]_{1-x}(OH)₃[SiO₃(OH)]_{1-x}(OH)₃, where REE stands for La or Ce, and where *M* represents Fe, Mg, Ca.

Keywords: cerite-(La), new mineral species, crystal structure, alkaline hydrothermal vein, Khibina massif, Kola Peninsula, Russia.

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SOMMAIRE

Nous avons découvert la cécrite-(La), dont la formule idéale serait $(\text{La,Ce,Ca})_9(\text{Fe,Ca,Mg})(\text{SiO}_4)_3[\text{SiO}_3(\text{OH})]_4(\text{OH})_3$, dans une veine à aegyrine – natrolite – microcline dans la foyaïte, au mont Yuksporr, complexe alcalin de Khibina, péninsule de Kola, en Russie. Elle s'est développée par pseudomorphose d'un minéral prismatique hexagonal non identifié, la masse poreuse atteignant 7 cm de long. La cécrite-(La) se présente sous forme d'aggrégats de cristaux équidimensionnels à tabulaires interconnectés, aplatis sur *c*, jusqu'à 2 mm de diamètre, avec des faces rhomboédriques et pinacoïdales. Lui sont associés aegyrine, anatase, ancylite-(Ce), barylite, catapléiite, cécrite-(Ce), chabazite-Ca, édingtonite, fluorapatite, galène, ilménite, microcline, natrolite, sphalérite, strontianite et vanadinite. Il s'agit d'un minéral cassant, à la fracture conchoïdale. Sa couleur est jaune pâle à brun roseâtre, avec une rayure blanche. Il est translucide avec un éclat vitreux. Aucun clivage ou plan de séparation n'a été décelé. La dureté de Mohs est 5; la densité est $4.7(1) \text{ g cm}^{-3}$ (mesurée) et 4.74 g cm^{-3} (calculée). La cécrite-(La) est uniaxe, optiquement positive, n_o 1.810(5), n_e 1.820(5) ($\lambda = 589 \text{ nm}$). Une composition moyenne a été déterminée par analyse à la microsonde électronique de sept cristaux (chacun analysé à 6 à 10 endroits): La_2O_3 37.57, Ce_2O_3 23.67, Pr_2O_3 0.61, Nd_2O_3 1.48, Sm_2O_3 0.10, Gd_2O_3 0.24, SrO 1.97, CaO 5.09, Fe_2O_3 1.40, MgO 0.51, SiO_2 22.38, P_2O_5 0.63, H_2O 3.20 (déterminé par la méthode de Penfield), pour un total de 98.85, ce qui correspond à la formule empirique $(\text{La}_{4.23}\text{Ce}_{2.65}\text{Ca}_{1.37}\text{Sr}_{0.35}\text{Nd}_{0.16}\text{Pr}_{0.07}\text{Gd}_{0.02}\text{Sm}_{0.01})_{\Sigma 8.86}(\text{Fe}_{0.32}\text{Ca}_{0.30}\text{Mg}_{0.23})_{\Sigma 0.85}[\text{SiO}_4]_3[\text{Si}_{0.84}\text{P}_{0.16}\Sigma 1.00\text{O}_3(\text{OH})]_4(\text{OH})_{2.78}$, calculée sur une base de $(\text{Si} + \text{P}) = 7$. La cécrite-(La) est trigonale, *R3c*, *a* 10.7493 (6), *c* 38.318 (3) Å, *V* 3834.36 Å³, *Z* = 6. Les huit raies les plus intenses du spectre de diffraction X (méthode des poudres) [*d* en Å(*I*)(*hkl*)] sont: 3.53(26)(10.10,211), 3.47(40)(122), 3.31(38)(214), 3.10(25)(300), 2.958(100)(02.10), 2.833(37)(128), 2.689(34)(220), et 1.949(34)(238,13.13). Nous en avons affiné la structure en utilisant les facteurs F^2 pour toutes les réflexions uniques prélevées au moyen d'un détecteur CCD, jusqu'à un résidu *R*1 de 0.036, calculé pour les 1544 réflexions observées ($F_o \geq 4\sigma F_o$). La cécrite-(La) est structurellement apparentée à la cécrite-(Ce). En fait, elle en est l'analogue à dominance de lanthane. La formule structurale de ces minéraux serait $TR_9MCa_x[\text{SiO}_4]_3[\text{SiO}_3(\text{OH})_{1-x}\text{O}_x]_3[\text{SiO}_3(\text{OH})]_{1-x}(\text{OH})_3$, dans laquelle *TR* représente La ou Ce, et *M* représente Fe, Mg, Ca.

(Traduit par la Rédaction)

Mots-clés: cécrite-(La), nouvelle espèce minérale, structure cristalline, veine hydrothermale alcaline, complexe alcalin de Khibina, péninsule de Kola, Russie.

INTRODUCTION

With an area of about 1327 km², the Khibina massif is the world's largest intrusion of nepheline syenite, melteigite–urtite and apatite–nepheline rocks. Its unique characteristics have attracted researchers for more than fifty years; over 360 minerals have been found in the intrusion, 76 of which were found first in the Khibina massif (Yakovenchuk *et al.* 1999). Up to this point, 39 minerals containing REE and yttrium have been found in the massif, of which 27 are dominated by Ce. Six minerals dominated by La are: ancylite-(La) (Yakovenchuk *et al.* 1997), belovite-(La) (Pekov *et al.* 1996, Kabalov *et al.* 1997), monazite-(La) (Yakovenchuk *et al.* 1999), nordite-(La) (Sokolova *et al.* 1992, Pekov *et al.* 1998), remondite-(La) (Pekov *et al.* 2000), and cerite-(La). All these minerals are of late hydrothermal or secondary origin, and commonly occur together with their Ce-dominant analogues or as separate zones in crystals of Ce-dominant phases.

The new mineral species described herein, cerite-(La), is a secondary mineral that forms a pseudomorph after an unidentified primary REE-bearing mineral in association with cerite-(Ce). It has been designated the La-dominant analogue of cerite-(Ce), in accordance with the Levinson system of nomenclature of REE-minerals. Both the mineral and the mineral name have been approved by the Commission on New Minerals and Mineral Names of the IMA (proposal 2001–042). Holotype material is deposited in the Mining Museum

of the St. Petersburg Mining Institute (Technical University), St. Petersburg, Russia, and also at the Mineralogical museum of the St. Petersburg State University, Russia, and the Geological and Mineralogical Museum of the Geological Institute of the Kola Science Centre, Apatity, Russia.

We note that cerite-(Ce) has been known as a mineral since 1804 (Förster 2000, and references therein).

OCCURRENCE

Cerite-(La) occurs as a late-stage, low-temperature secondary phase within an aegyrine – natrolite – microcline vein in gneissose foyaite at Mt. Yuksporr (190° strike, dip 15°). The vein, 20–60 cm wide, with sharp contacts with the host foyaite marked by 5-cm-wide zones of an aegyrine-dominant assemblage, has a well-developed symmetrical zonation.

The outer portions are composed of large, light beige, well-formed tabular crystals of microcline (up to 5 × 4 cm) with inclusions of acicular aegyrine (up to 1 cm long), plus galena and sphalerite (up to 3 mm in diameter). Small (up to 2 mm long) crystals of vanadinite occur in the interstices of the microcline crystals.

Toward the center, in a zone of columnar white crystals of natrolite, individual crystals are up to 20 cm long and 4 cm across. At the border between the microcline and natrolite zones, there are numerous spherulites (up to 7 mm diameter) of thin acicular strontianite. The strontianite is generally altered or even leached, and, as

a result, the relict central portions of the spherulites commonly contain only a few needles of strontianite in the middle of rounded voids within the natrolite. There are also rather large aggregates of orange catapleiite crystals (up to 1 cm in diameter) and druses of small, pale cream, short prismatic edingtonite crystals (up to 3 mm). Within the mass of columnar natrolite, there are in some cases plates of ilmenite (up to 1 mm diameter), bright dark blue pseudocubic crystals of anatase (up to 3 mm), pseudo-octahedral crystals of cerite-(Ce), and cerite-(La) pseudomorphs (up to 6×1.5 cm) after an unknown prismatic mineral.

The axial zone is mainly composed of a compact dark green spherulitic mass of aegirine, penetrated by transparent elongate prismatic crystals of natrolite (up to 15×1.5 cm).

PHYSICAL AND OPTICAL PROPERTIES

Cerite-(La) forms porous pseudomorphs after an unidentified hexagonal mineral, possibly belowite-(Ce). Individual crystals are up to 7 cm long and 2 cm across (Fig. 1a). Within the pseudomorphs, cerite-(La) occurs as framework-like aggregates of equant crystals or crystals flattened on c (up to 2 mm across), with dominant rhombohedron $\{102\}$ and pinacoid $\{001\}$ faces (Fig. 1b). Macroscopically, the crystals are light yellow to pinkish brown in color, with a vitreous luster. Cerite-(La) is translucent, and has a white streak. It is brittle, with a conchoidal fracture. Cleavage and parting were not observed. The Mohs hardness is 5. The density, measured using a pycnometer, is $4.7(1) \text{ g cm}^{-3}$, which is in good agreement with the value of 4.74 g cm^{-3} calculated for the empirical formula.

Cerite-(La) is uniaxial, optically positive, n_o 1.810(5), n_e 1.820(5) (for $\lambda = 589 \text{ nm}$), with no pleochroism. The compatibility index is 0.010, which is regarded as superior (Mandarino 1981).

CHEMICAL COMPOSITION

Chemical analyses were done by wavelength-dispersion spectroscopy on a CAMECA MS-46 electron microprobe operated at 20 kV and 20 nA. Seven different crystals were analyzed, and every composition recorded was an average of 6 to 10 points. The following standards were used: synthetic LaCeS (for La and Ce), LiPr(WO₄)₂ (Pr), LiNd(MoO₄)₂ (Nd), LiSm(MoO₄)₂ (Sm), LiGd(MoO₄)₂ (Gd), celestine (Sr), diopside (Ca and Si), hematite (Fe), pyrope (Mg), and fluorapatite (P). The H₂O content was determined using the Penfield method. The chemical composition of cerite-(La) is given in Table 1. The empirical formula, based on $(\text{Si} + \text{P}) = 7$, is $(\text{La}_{4.23}\text{Ce}_{2.65}\text{Ca}_{1.37}\text{Sr}_{0.35}\text{Nd}_{0.16}\text{Pr}_{0.07}\text{Gd}_{0.02}\text{Sm}_{0.01})_{\Sigma 8.86}(\text{Fe}_{0.32}\text{Ca}_{0.30}\text{Mg}_{0.23})_{\Sigma 0.85}[\text{SiO}_4]_3[\text{Si}_{0.84}\text{P}_{0.16}]_{\Sigma 1.00}\text{O}_3(\text{OH})_4(\text{OH})_{2.78}$, which is close to the ideal formula, $(\text{La,Ce,Ca})_9(\text{Fe,Mg,Sr})[\text{SiO}_4]_6[\text{SiO}_3(\text{OH})](\text{OH})_3$.

Cerite-(La) is insoluble in HCl, HNO₃ and H₂SO₄.

CRYSTAL STRUCTURE

Data collection

For the structure analysis, a crystal of cerite-(La) with approximate dimensions $0.28 \times 0.28 \times 0.12 \text{ mm}$ was selected. The crystal was mounted on a Bruker PLATFORM goniometer equipped with a 1K SMART

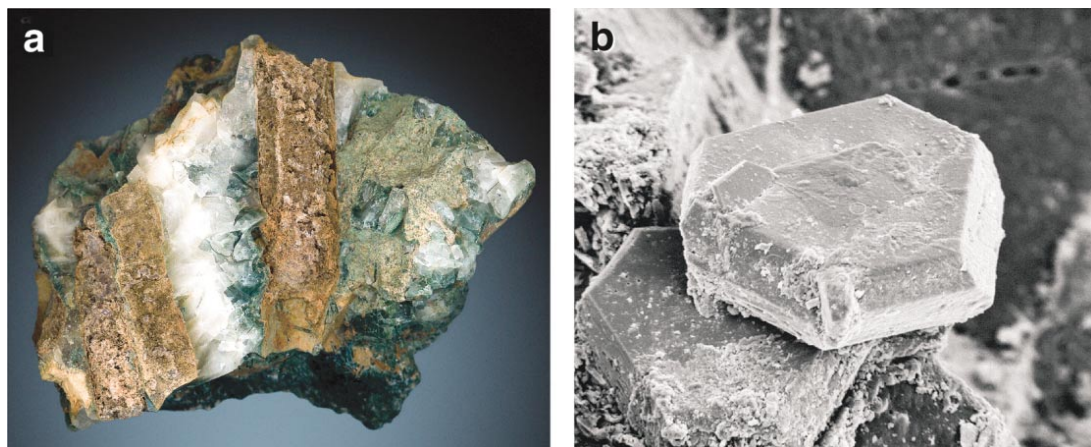


FIG. 1. a. Orange aggregates of cerite-(La) (approximately 3.5 cm across). b. SEM photomicrograph of a rhombohedral crystal of cerite-(La).

CCD detector with a crystal-to-detector distance of 5 cm. The data were collected using MoK α X-radiation and frame widths of 0.3° in ω , with 10 s used to acquire each frame. A hemisphere of three-dimensional data was collected. The unit-cell dimensions were refined on the basis of 2207 reflections (Table 2). The data were reduced using the Bruker program SAINT. A semi-empirical absorption-correction based upon the intensities of equivalent reflections was applied, and the data were corrected for Lorentz, polarization, and background effects. A total of 23,586 intensities was measured; there were 1983 unique reflections ($R_{\text{INT}} = 6.9\%$), with 1544 classified as observed ($F_o > 4\sigma F_o$).

Structure refinement

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from *International Tables for X-Ray Crystallography, Vol. IV* (Ibers & Hamilton 1974). The Bruker SHELXTL Version 5.1 system of programs was used for refinement of the crystal structure on the basis of F^2 . The structure was refined on the basis of atom coordinates given for cerite-(Ce) by Moore & Shen (1983). Initially, the refinement indicated that in cerite-(La), there are no low-occupancy Ca and OH positions such as are present in cerite-(Ce). However, the Si(3)–OH(10) bond length is about 1.78 Å, which is unacceptably long for the Si–OH bond (Nyfeler & Armbruster 1998). Consequently, the OH(10) position was split into two sites: one for the OH(10) group, with a Si–OH distance of 1.69(2) Å, and another one for the Ca. In order to get reasonable bond-lengths, the isotropic parameters for the OH(10) and Ca positions were kept fixed at 0.01 Å² during the refinement. Refinement of occupancies gave 10% occupancy for the Ca position and 90% occupancies for the OH(10)

and Si(3) positions. Refinement of all atom-position parameters, allowing for anisotropic displacement of all atoms except OH(10) and Ca, and the inclusion of a refinable weighting scheme of the structure factors, resulted in a final agreement index ($R1$) of 3.6%, calculated for the 1544 unique observed reflections ($|F_o| \geq 4\sigma F_o$), and a goodness-of-fit (S) of 0.926. The final atom parameters are listed in Table 3, selected interatomic distances are in Table 4. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

Cation positions

There are three REE positions in the structure, and each is coordinated by eight O atoms and one OH group, with REE– ϕ bonds (ϕ : O, OH) in the range 2.40–2.99 Å. The REE coordination polyhedra can be described as trigonal prisms with three rectangular faces capped by additional anions. This type of coordination is common for minerals and inorganic compounds containing the REE (Bandurkin & Dzhurinskii 1997). Refinement of site-occupancy factors for these positions using the scattering curve for La (57 e^-) yields 0.956(7) (54.5 e^-), 0.875(7) (49.9 e^-) and 0.741(6) (42.2 e^-) for the REE(1), REE(2) and REE(3) sites, respectively. The lighter elements such as Ca and Sr thus occur preferentially in the REE(2) and REE(3) positions, in good agreement with the analogous observations of Moore & Shen (1983) for cerite-(Ce).

There is one octahedrally coordinated M position in the structure that is preferentially occupied by Fe³⁺, Ca²⁺ and Mg²⁺. Although Fe is a dominant element at this site, the amounts of Ca and Mg are essential, which clearly raises the possibility of a Ca- and Mg-dominant analogue of cerite. We note that Moore & Shen (1983) postulated that the occupancy of the M position in cerite-(Ce) is Mg_{0.61}Fe_{0.39}, in obvious disagreement with the results of chemical analyses reported in their paper.

The Si(1) and Si(3) atoms in the structure are tetrahedrally coordinated by three O atoms and one OH group. The Si(2) atom is coordinated by four O atoms.

TABLE 1. CHEMICAL COMPOSITION OF CERITE-(La)

Constituent	wt. %	Range	σ
La ₂ O ₃	37.57	31.14 – 39.62	2.93
Ce ₂ O ₃	23.67	21.89 – 26.58	1.63
Pr ₂ O ₃	0.61	0.35 – 1.10	0.25
Nd ₂ O ₃	1.48	0.82 – 3.62	0.98
Sm ₂ O ₃	0.10	0 – 0.51	0.20
Gd ₂ O ₃	0.24	0 – 0.42	0.14
SrO	1.97	1.66 – 2.38	0.35
CaO	5.09	4.42 – 6.48	0.68
Fe ₂ O ₃	1.40	0.94 – 1.56	0.19
MgO	0.51	0.43 – 0.61	0.06
SiO ₂	22.38	22.08 – 22.91	0.28
P ₂ O ₅	0.63	0.27 – 1.28	0.32
H ₂ O*	3.20		
Total	98.85		

* determined by the Penfield method. σ : Standard deviation.
 Empirical formula: (La_{4.25}Ce_{2.65}Ca_{1.37}Sr_{0.33}Nd_{0.14}Pr_{0.07}Gd_{0.07}Sm_{0.01})_{28.86}(Fe_{0.32}Ca_{0.30}Mg_{0.23})_{20.85}[SiO₄]₁₁([Si_{0.48}P_{0.12}])_{21.00}O₂(OH)₁(OH)_{2.78}
 Ideal formula: (La,Ce,Ca)(Fe,Ca,Mg)(SiO₄)₁₁[Si_{0.5}(OH)]₁(OH)₃

TABLE 2. CRYSTALLOGRAPHIC DATA FOR CERITE-(La)

a (Å)	10.7493(6)	Crystal size (mm)	0.28 × 0.28 × 0.12
c (Å)	38.318(3)	Radiation	MoK α
V (Å ³)	3834.4(4)	Total reflections	7189
Space group	$R3c$	Unique $F_o = 4\sigma F_o$	1544
F_{000}	4910	$R1$	0.036
μ (cm ⁻¹)	137.49	$wR2$	0.079
D_{calc} (g/cm ³)	4.72	s	0.926
Z	6		

Note: $R1 = \sum F_o - F_c / \sum F_o$; $wR2 = \{\sum [w(F_o^2 - F_c^2)] / \sum [w(F_o^2)]\}^{1/2}$,
 $w = 1 / [\sigma^2(F_o^2) + (0.0459P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.
 $s = \{\sum [w(F_o^2 - F_c^2)] / (n - p)\}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

TABLE 3. ATOM COORDINATES AND DISPLACEMENT PARAMETERS FOR CERITE-(La)

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
REE(1)	0.25867(7)	0.13428(8)	0.068094(12)	0.0139(3)	0.0160(4)	0.0150(5)	0.0120(4)	-0.0009(4)	0.0000(3)	0.0086(4)
REE(2)	0.14209(9)	0.26126(10)	0.43210(3)	0.0195(3)	0.0164(6)	0.0269(6)	0.0183(5)	0.0087(4)	0.0036(6)	0.0131(5)
REE(3)	0.25878(10)	0.13436(10)	0.17585(2)	0.0187(3)	0.0229(5)	0.0184(6)	0.0184(5)	-0.0048(4)	-0.0045(4)	0.0130(4)
Si(1)	0.3184(4)	0.1485(4)	0.36239(8)	0.0129(8)	0.0073(16)	0.0160(19)	0.0140(20)	0.0001(16)	-0.0002(12)	0.0051(14)
O(1)	0.2562(11)	0.0915(12)	0.3228(3)	0.0330(30)	0.0280(50)	0.0560(70)	0.0110(50)	-0.0120(40)	-0.0040(40)	0.0180(50)
O(2)	0.2781(9)	0.0026(8)	0.3850(2)	0.0160(20)	0.0120(40)	0.0160(40)	0.0190(50)	0.0020(30)	0.0040(30)	0.0060(40)
O(3)	0.2625(10)	0.2513(9)	0.3784(2)	0.0200(20)	0.0150(40)	0.0200(50)	0.0220(60)	0.0050(40)	0.0070(40)	0.0060(40)
O(4)	0.0817(10)	0.1730(9)	0.0295(2)	0.0167(20)	0.0160(50)	0.0160(40)	0.0230(50)	-0.0030(40)	0.0000(40)	0.0110(40)
Si(2)	0.1504(4)	0.3257(5)	0.13689(10)	0.0173(8)	0.0150(20)	0.0234(19)	0.0126(17)	0.0005(13)	-0.0003(18)	0.0089(18)
O(5)	0.2448(10)	0.2711(10)	0.1162(2)	0.0240(30)	0.0220(50)	0.0310(50)	0.0220(50)	-0.0100(40)	0.0010(40)	0.0150(40)
O(6)	-0.0105(11)	0.2701(9)	0.1224(3)	0.0210(20)	0.0240(50)	0.0250(50)	0.0130(50)	0.0000(40)	-0.0030(40)	0.0110(40)
O(7)	0.1668(9)	0.0742(9)	0.4664(2)	0.0168(19)	0.0140(40)	0.0160(40)	0.0200(40)	0.0010(40)	0.0010(30)	0.0080(40)
O(8)	0.1375(11)	0.2815(9)	0.1782(3)	0.0212(20)	0.0240(50)	0.0230(40)	0.0120(40)	0.0000(30)	-0.0030(30)	0.0080(40)
M(1)*	0	0	-0.00168(15)	0.0137(12)	0.0135(13)	0.0135(13)	0.0140(20)	0	0	0.0068(6)
Si(3)**	0	0	0.2520(2)	0.0125(10)	0.0111(15)	0.0111(15)	0.0150(30)	0	0	0.0055(8)
O(9)	0.1597(9)	0.0338(10)	0.2400(3)	0.0300(20)	0.0180(40)	0.0420(60)	0.0310(60)	-0.0110(40)	-0.0040(40)	0.0160(40)
OH(10)	0	0	0.2961(4)	0.0100***						
OH(11)	0	0	0.0897(4)	0.0160(30)	0.0700(40)	0.0070(40)	0.0330(90)	0	0	0.0040(20)
OH(12)	0	0	0.1600(4)	0.0210(30)	0.0120(40)	0.0120(40)	0.0390(80)	0	0	0.0060(20)
OH(13)	0	0	0.4090(6)	0.0350(50)	0.0290(70)	0.0290(70)	0.0450(120)	0	0	0.0150(30)
Ca#	0	0	0.3092(12)	0.0100***						

* $M = Fe_{0.32}Ca_{0.30}Mg_{0.23}$; ** s.o.f. = 0.90; *** fixed during refinement; # s.o.f. = 0.10.

TABLE 4. SELECTED BOND-LENGTHS (Å) FOR CERITE-(La)

REE(1)-O(5)	2.408(9)	REE(3)-OH(12)	2.485(4)	Si(2)-O(5)	1.6123(9)
REE(1)-O(8)a	2.466(9)	REE(3)-O(6)b	2.517(9)	Si(2)-O(6)	1.62(1)
REE(1)-O(6)b	2.544(9)	REE(3)-O(8)	2.50(1)	Si(2)-O(8)	1.629(9)
REE(1)-OH(11)	2.547(6)	REE(3)-O(2)e	2.507(8)	Si(2)-O(7)d	1.64(1)
REE(1)-O(4)b	2.576(9)	REE(3)-O(3)a	2.518(9)	<Si(2)-O>	1.62
REE(1)-O(4)	2.603(9)	REE(3)-O(8)b	2.54(1)		
REE(1)-O(2)c	2.619(9)	REE(3)-O(9)	2.681(9)	Si(3)-O(9),f,b	1.633(9) 3×
REE(1)-O(3)d	2.771(9)	REE(3)-O(5)	2.762(9)	Si(3)-OH(10)	1.69(2)
REE(1)-O(9)e	2.813(9)	REE(3)-O(1)e	3.00(1)	<Si(3)-O>	1.65
<REE(1)-φ*>	2.59	<REE(3)-φ*>	2.61		
				Ca-O(1),f,b	2.47(1) 3×
REE(2)-O(2)f	2.437(8)	M-O(7)j,k,l	1.979(9) 3×	Ca-O(9)	3.08(4) 3×
REE(2)-O(3)	2.461(9)	M-O(4),f,b	2.006(9) 3×	<Ca-φ*>	2.78
REE(2)-O(7)f	2.491(9)	<M-O>	1.99		
REE(2)-OH(9)g	2.514(9)			a = -y + 2/3, -x + 1/3, z - 1/6;	
REE(2)-O(7)	2.524(9)	Si(1)-O(3)	1.620(9)	b = -x + y, -x, z; c = -y + 1/3,	
REE(2)-OH(13)	2.591(8)	Si(1)-O(4)h	1.63(1)	x - y - 1/3, z - 1/3; d = -x + y + 1/3,	
REE(2)-O(1)g	2.62(1)	Si(1)-O(2)	1.648(8)	-x + 2/3, z - 1/3; e = -x + y + 2/3,	
REE(2)-O(5)h	2.603(9)	Si(1)-O(1)	1.64(1)	y + 1/3, z - 1/6; f = -y, x - y, z;	
REE(2)-O(6)i	2.802(9)	<Si(1)-O>	1.64	g = -y + 1/3, -x + 2/3, z + 1/6;	
<REE(2)-φ*>	2.56			h = -y + 2/3, x - y + 1/3, z + 1/3;	
				i = -x + y - 1/3, -x + 1/3, z + 1/3;	
				j = -y, -x, z - 1/2; k = -x + y, y,	
				z - 1/2; l = x, x - y, z - 1/2	

* φ: O, OH

The Si-OH bond lengths are 1.65(1) and 1.69(2) Å for the Si(1)O₃(OH) and Si(3)O₃(OH) tetrahedra, respectively. This finding is in good agreement with the general observation that the Si-O bond in silicates is

lengthened upon protonization (Nyfeler & Armbruster 1998).

The low-occupancy Ca position is coordinated by six anions. The Caφ₆ polyhedron can be described as a distorted trigonal prism.

Bond-valence analysis

The bond-valence analysis was calculated using bond-valence parameters for $\text{La}^{3+}\text{-O}$, $\text{Mg}^{2+}\text{-O}$ and $\text{Si}^{4+}\text{-O}$ bonds, taken from Brese & O'Keeffe (1991). The bond-valence sums for the *REE*(1), *REE*(2), *REE*(3), *M*, *Si*(1), *Si*(2) and *Si*(3) positions are 3.03, 3.27, 2.96, 3.22, 3.89, 3.96 and 3.56 valence units (*vu*), respectively, which is in agreement with the expected values given that various cations occur at the same sites. The bond-valence sums for the OH(1), O(2), O(3), O(4), O(5), O(6), O(7), O(8) and O(9) positions are 1.36, 2.13, 2.06, 2.03, 2.06, 1.95, 2.26, 2.19 and 1.81 *vu*, respectively. The bond-valence sum for the OH(1) site is consistent with its assignment to a hydroxyl group. For cerite-(Ce), Moore & Shen (1983) pointed out that the O(1) site is occupied by O, although the bond-valence sum for this site in cerite-(Ce) is 1.19 *vu* (without taking into account the Ca–O(1) bond formed by the low-occupancy Ca position). Thus we suggest that cerite-(Ce) and cerite-

(La) contain four $\text{SiO}_3(\text{OH})$ and three SiO_4 groups *pfu* (per formula unit), instead of one and six as suggested by Moore & Shen (1983). The bond-valence sums for the OH(10), OH(11), OH(12) and OH(13) positions are 0.83, 1.08, 1.29 and 0.96 *vu*, which confirms the assignment of these positions to hydroxyl groups.

The low-occupancy Ca position and a structural formula for cerite-(La) and cerite-(Ce)

The refined occupancy for the low-occupancy Ca position in cerite-(La) is 0.10(1), whereas the similar value for cerite-(Ce) (Moore & Shen 1983) is 0.169(9). The Ca–OH(10) and Ca–Si(3) distances, 0.50 and 2.19 Å, indicate that the presence of Ca in the *Ca* site is incompatible with the presence of a $\text{Si}(3)\text{O}_3(\text{OH})$ tetrahedron. The occupancy of the *Ca* site also results in formation of Ca–OH(1) bond of 2.47 Å, which adds 0.26 *vu* to the bond-valence sum for the OH(1) position. The total bond-valence sum at the OH(1) site becomes equal

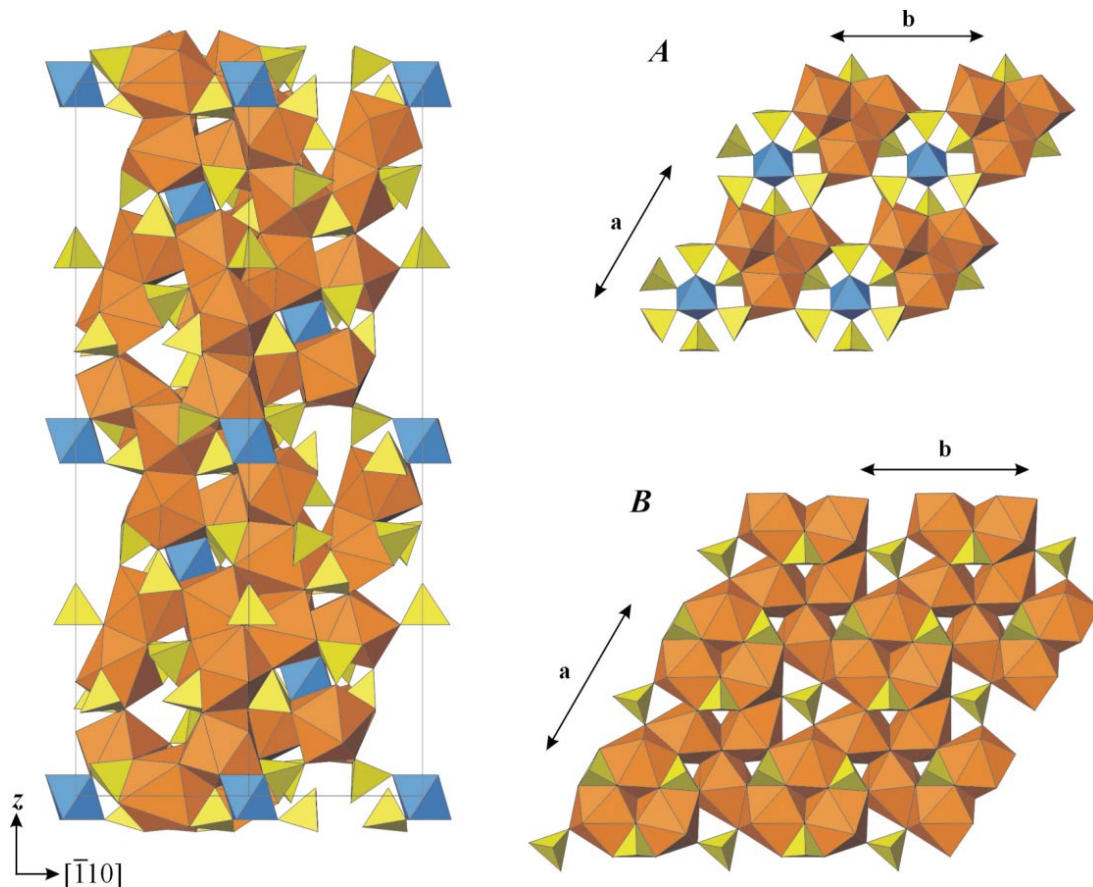
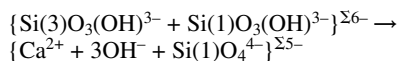


Fig. 2. Crystal structure of cerite-(La) projected along [110] (left), and the A and B sheets projected along [001] (right). Legend: *REE* polyhedra: orange, *M* octahedra: blue, Si tetrahedra: yellow.

to 1.62 *vu*, which is more characteristic of an O atom than that of an OH group. Thus, the following mechanism can be suggested for incorporation of Ca into the *Ca* site:



This mechanism can be associated with the incorporation of Ca^{2+} or Sr^{2+} into the *REE* positions to fulfill the requirement of electroneutrality.

TABLE 5. X-RAY POWDER-DIFFRACTION DATA FOR CERITE-(La)

Cerite-(La)			<i>h k l</i>	Cerite-(Ce) PDF 11-126	
<i>l</i>	<i>d</i> _{meas}	<i>d</i> _{calc}		<i>l</i>	<i>d</i> _{meas}
18	8.38	8.373	0 1 2	14	8.40
12	6.67	6.676	1 0 4	8	6.67
18	6.39	6.386	0 0 6	8	6.35
10	5.38	5.375	1 1 0	10	5.40
20	4.53	4.523	2 0 2	18	4.53
21	4.25	4.259	0 1 8	14	4.23
26	3.53	3.543	1 0 10		
		3.504	2 1 1	16	3.51
40	3.47	3.461	1 2 2	40	3.47
38	3.31	3.303	2 1 4	35	3.31
12	3.19	3.193	0 0 12	8	3.17
25	3.10	3.103	3 0 0	30	3.11
100	2.958	2.958	0 2 10	100	2.950
37	2.833	2.836	1 2 8	40	2.830
24	2.790	2.791	3 0 6	25	2.800
34	2.689	2.687	2 2 0	40	2.690
18	2.592	2.592	2 1 10	20	2.590
7	2.558	2.559	3 1 2	8	2.570
4	2.493	2.493	1 3 4	6	2.500
3	2.445	2.447	1 3 5	4	2.440
12	2.315	2.319	1 0 16		
		2.310	0 4 2	8	2.310
6	2.265	2.272	2 2 9	8	2.270
		2.262	0 4 4		
22	2.223	2.225	3 0 12	25	2.220
10	2.140	2.141	3 1 10	10	2.140
18	2.124	2.123	2 3 2	8	2.130
20	2.090	2.093	0 4 8		
		2.084	3 2 4	14	2.090
				6	2.070
9	2.056	2.056	2 2 12		
8	2.032	2.031	4 1 0	10	2.040
9	1.987	1.989	0 4 10		
34	1.949	1.951	2 3 8	50	1.954
		1.942	1 3 13	14	1.939
15	1.937	1.936	4 1 6		
15	1.876	1.877	0 1 20	25	1.863
14	1.863	1.866	2 3 10		
		1.860	0 5 1		
12	1.829	1.828	0 5 4	14	1.834
12	1.792	1.792	3 3 0	16	1.799
				6	1.791
23	1.755	1.755	3 0 18	25	1.748
				10	1.740
				6	1.717
8	1.676	1.675	2 4 7	12	1.679
6	1.652	1.651	4 2 8	8	1.655
12	1.593	1.594	3 2 16	14	1.593
				10	1.583
6	1.539	1.539	5 0 14		
7	1.530	1.530	1 1 24		

Taking into account the previous paragraphs, the structural formula for cerites can be written as $REE_9 M\text{Ca}_x[\text{SiO}_4]_3[\text{SiO}_3((\text{OH})_{1-x}\text{O}_x)]_3[\text{SiO}_3(\text{OH})]_{1-x}(\text{OH})_3$, where *REE* = La or Ce for cerite-(La) and cerite-(Ce), respectively; *M* = Fe, Mg, Ca. The *x* parameter is 0.10(1) and 0.169(9) for cerite-(La) and cerite-(Ce), respectively.

Description of the structure

Moore & Shen (1983) described the structure of cerite-(Ce) as based on rods of corner-, edge- and face-linking SiO_4 tetrahedra, MO_6 octahedra and REEO_6OH polyhedra. Another description can be based on sheets of the above-mentioned polyhedra. The $M(\text{SiO}_4)_6$ clusters, together with $\text{REE}(3)\phi_9$ polyhedra, form the *A* layers at $z \sim 0, 1/6, 1/3, 1/2, \dots$ shown in Figure 2. The $\text{REE}(2)\phi_9$ and $\text{REE}(1)\phi_9$ polyhedra and SiO_3OH tetrahedra form the *B* layers at $z \approx 1/12, 1/4, 5/12, 7/12, \dots$. The layers are parallel to (001) and alternate as ...*ABABAB*... (Fig. 2).

X-RAY POWDER-DIFFRACTION STUDY

The X-ray powder-diffraction pattern obtained using monochromatic $\text{CuK}\alpha$ radiation (DRON-2 powder diffractometer) is given in Table 5. The powder pattern is similar to that of cerite-(Ce). The strongest eight lines in the X-ray powder-diffraction pattern are [*d* in Å (*l*)(*hkl*)]: 3.53(26)(1.0.10,211), 3.47(40)(122), 3.31(38)(214), 3.10(25)(300), 2.958(100)(02.10), 2.833(37)(128), 2.689(34)(220), and 1.949(34)(238,13.13). The unit-cell parameters of cerite-(La) were obtained by least-squares refinement of the powder-diffraction data: *a* 10.7493 (6), *c* 38.318 (3) Å, *V* 3834.36 Å³, *Z* = 6.

DISCUSSION

Table 6 gives a comparison of the main characteristics of cerite-(Ce) and cerite-(La); the unit-cell parameters are similar for each mineral. The slight expansion of the *c* unit-cell parameter in cerite-(La) (~0.7%) is compensated by the slight decrease in the *a* parameter, such that the unit-cell volumes of these two species are approximately equal.

According to Ginzburg & Kipriyanova (1966), the *REE* enter into mineral structures according to the following sequence: phosphates → tantalates and niobates → silicates. The rare-earth silicates form only after all the P is bound with Ca in apatite-like minerals or with rare earths in the form of monazite or xenotime. The rare-earth fluorocarbonates form first under conditions of high activity of CO_3^{2-} , for instance, during the postmagmatic alteration of carbonate rocks or in the last stages of hydrothermal activity. The rare-earth silicates form after the rare-earth fluorocarbonates (Ginzburg & Kipriyanova 1966). These ideas are in good agreement with the proposal of Förster (2000), that the *REE* and

TABLE 6. COMPARATIVE CHARACTERISTICS OF CERITE-(La) AND CERITE-(Ce)

	Cerite-(La)	Cerite-(Ce)
Crystal system	Trigonal	Trigonal
Space group	<i>R3c</i>	<i>R3c</i>
<i>a</i> , Å	10.7493(6)	10.779(6)
<i>c</i> , Å	38.318(3)	38.061(7)
<i>V</i> , Å ³	3834.4(4)	3829.8
Density, g/cm ³	4.7(1)	4.6
Mohs hardness	5	5½
	uniaxial (+)	uniaxial (+)
<i>n_o</i>	1.810 (5)	1.815 – 1.806
<i>n_e</i>	1.820 (5)	1.820 – 1.808

Ca in cerite-(Ce) in granites may be liberated during breakdown of earlier-formed REE fluorocarbonates. In the case of cerite-(La), its crystals probably form after belovite-(Ce) [or belovite-(La)], Sr₃NaREE(PO₄)₃ (F,OH), *i.e.*, during the alteration of a primary REE phosphate mineral by Ca²⁺-bearing solutions under low CO₂ activity.

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