Eur. J. Mineral.
2012, **24**, 741–747

Ferriallanite-(La), a new member of the epidote supergroup from the Eifel, Germany

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Abstract: The new mineral ferriallanite-(La) (IMA 2010-066), ideally $CaLaFe^{3+}AlFe^{2+}(SiO_4)(Si_2O_7)O(OH)$, is a member of the epidote supergroup and the La analogue of ferriallanite-(Ce). It occurs as a single, thick, tabular {100} crystal (2 mm in its longest dimension) in a void of a sanidinite xenolith found in the In den Dellen pumice quarries, Niedermendig, Mendig, Laach Lake volcanic complex, Eifel Mountains, Rhineland-Palatinate, Germany. Ferriallanite-(La) is associated with sanidine, minor ‘‘biotite’’, magnetite, nosean (grey, rounded grains) and trace amounts of dark green clinopyroxene. It is black, translucent in very thin splinters, with a brown streak, vitreous lustre, no cleavage, irregular to conchoidal fracture, Mohs hardness of *ca.* 6, $D_{calc.} = 4.208$ g cm^{-3} (for empirical formula) and $D_x = 4.099$ g cm^{-3}. Optically, it is biaxial negative, with $\alpha = 1.791(5)$, $\beta = 1.827(6)$, $\gamma = 1.845(5)$ (white light), $2V_\alpha$ (calc.) = 69°. The mineral is non-fluorescent and shows strong pleochroism, X = pale brownish, Y = greyish brown, Z = dark red-brown; absorption Z > Y >> X, orientation unknown. Dispersion is weak and the sign could not be determined. Electron microprobe analysis yielded the empirical formula (based on 12 O atoms and 1 OH group pfu): $Ca_{0.98}(La_{0.47}Ce_{0.41}Th_{0.08}Nd_{0.02}Pr_{0.02})_{\Sigma 1.00}(Fe^{3+}{}_{0.81}Al_{0.14})_{\Sigma 0.95}Al_{1.00}(Fe^{2+}{}_{0.47}Mn_{0.28}Ti_{0.16}Mg_{0.05})_{\Sigma 0.96}[(Si_{0.93}Al_{0.05})_{\Sigma 0.98}O_4](Si_2O_7)O(OH)$. Ferriallanite-(La) is monoclinic, space group $P2_1/m$, with $a = 8.938(2)$, $b = 5.789(1)$, $c = 10.153(2)$ Å, $\beta = 114.54(3)°$, $V = 477.88(6)$ Å^3 (single-crystal data) and $Z = 2$. Strongest eight lines in the X-ray powder diffraction pattern are [*d* in Å (*I*) *hkl*]: 9.22 (19) 001; 7.96 (34) $\bar{1}01$; 3.53 (38) $\bar{2}11$; 2.92 (100) $\bar{3}02$, $\bar{1}13$; 2.72 (50) 120, 013; 2.63 (36) $\bar{3}11$; 2.16 (17) 221 and 1.639 (34) $\bar{1}06$, $\bar{4}24$. A single-crystal X-ray structure refinement [$R1(F) = 0.0150$] and a derivation of the *M*3 site population from the chemical-analytical data yielded the formula $^{A1}Ca_{1.00}{}^{A2}(La_{0.49}Ce_{0.42}Ca_{0.09})^{M1}(Fe_{0.58}Al_{0.42})^{M2}(Al_{0.94}Fe_{0.06})^{M3}(Fe_{0.49}Mn_{0.29}Ti_{0.17}Mg_{0.05})_{\Sigma 1.00}(SiO_4)(Si_2O_7)O(OH)$, in reasonably good agreement with the electron microprobe data. The site refinements clearly show that there is some minor Fe at the *M*2 site, in contrast to the formula calculated using currently recommended methods for members of the epidote supergroup.

Key-words: Ferriallanite-(La), new mineral, epidote supergroup, crystal structure, Eifel, Germany.

1. Introduction

In the course of a long-term crystal-chemical study of well-developed minerals found in voids of sanidinite xenoliths in volcanic rocks of the Laach Lake volcanic complex, Eifel, Germany, samples of zirconolite, chevkinite, perrierite, aeschynite, euxenite (all non-metamict), as well as six specimens of ‘‘allanite’’, all showing the thick tabular habit and black colour characteristic of this area (vom Rath, 1861; Beyer, 1977; Hentschel, 1987, 1990), were characterised by single-crystal X-ray structure refinements. One of the ‘‘allanite’’ samples, consisting of a single black crystal, about 2 mm in maximum dimension, which was collected by the first author in June 1992 in the In den Dellen quarries, turned out to be the La-analogue of ferriallanite-(Ce) (Kartashov *et al.*, 2002, 2003), whereas the remaining five specimens were found to be either Fe^{3+} -rich allanite-(Ce) or allanite-(La). This is the first new mineral species from these famous quarries (Hentschel, 1990).

The La-dominant species, described here in detail, is named for the relation to its Ce-analogue ferriallanite-(Ce) (Kartashov *et al.*, 2002, 2003) and in accordance with Levinson suffix nomenclature for REE minerals (Levinson, 1966). Ferriallanite-(La) is thus a new member of the allanite group within the epidote supergroup (Mills *et al.*, 2009). The mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification prior to publication (IMA 2010-066).

0935-1221/12/0024-2210 $ 3.15
DOI: 10.1127/0935-1221/2012/0024-2210

According to the IMA-approved nomenclature of the epidote supergroup (Armbruster *et al.*, 2006), ferriallanite-(La) is the La-dominant analogue of ferriallanite-(Ce) (Kartashov *et al.*, 2002, 2003; Holtstam *et al.*, 2003), with La dominant in the *A*2 site instead of Ce. It is also the Fe^{3+} analogue of allanite-(La) (Orlandi & Pasero, 2006). The holotype, consisting of the remainder of the studied crystal (2 × 1.7 × 0.9 mm in size) and two small crystal fragments kept in a capsule, is deposited in the Naturhistorisches Museum, Wien (Natural History Museum, Vienna), registered number N 8164, and the co-type (probe mount) is preserved in the collections of Museum Victoria, Australia, registered number M49750.

2. Occurrence and paragenesis

Ferriallanite-(La) occurs as a single, thick, tabular {100} crystal (2 mm in its longest dimension) in a void of a sanidinite xenolith found in the In den Dellen pumice quarries, Niedermendig, Mendig, Laach Lake volcanic complex, Eifel Mountains, Rhineland-Palatinate, Germany (50°23′41″N, 7°17′13″E). Ferriallanite-(La) is associated with sanidine, minor ‘‘biotite’’, magnetite (slightly rounded octahedra), nosean (pale grey, rounded grains identified by single-crystal study) and dark green clinopyroxene. The minerals formed in such subvolcanic sanidinite cumulates have crystallised at high temperatures.

3. Physical properties

Part of the crystal representing the holotype was used for all determination of physico-chemical properties. Ferriallanite-(La) is black, translucent only in very thin splinters, and has a brown streak, vitreous lustre, no cleavage and irregular to conchoidal fracture. The tenacity is brittle and the Mohs hardness is *ca.* 6. The density could not be determined experimentally, since it is larger than those of all commonly used liquids, including Clerici solution. The calculated density is 4.208 g cm^{-3} for the empirical formula; D_x is 4.099 g cm^{-3}. The single crystal is thick tabular on {100}, with additional, minor forms being small {101} or {110}, and {1*k*0} or {10*l*}; very small {010} or {001}. No twinning was observed macroscopically or during single-crystal studies.

Optically, ferriallanite-(La) is biaxial negative, with $\alpha = 1.791(5)$, $\beta = 1.827(6)$, $\gamma = 1.845(5)$ (white light) and $2V_\alpha$ (calc.) = 69° ($2V$ could not be measured because of the very dark colour even in small fragments). The mineral is non-fluorescent and shows strong pleochroism: X = pale brownish, Y = greyish brown, Z = dark red-brown; absorption $Z > Y >> X$. Dispersion is weak and the sign could not be determined. The orientation is unknown (since the optical properties were determined on tiny anhedral fragments), but is presumably similar to that observed for other Fe-rich members of the allanite group (the orientation of type ferriallanite-(Ce) could also not be determined).

The Gladstone-Dale compatibility (Mandarino, 1981) is superior (−0.018) for the empirical formula (1) (see following section) and excellent (0.034) for the empirical formula (2).

4. Chemical composition

Quantitative chemical analyses were carried out using a JEOL Superprobe JXA-8900R electron microprobe (WDS mode, 20 kV, 10 nA and 20 μm defocused beam diameter) at CSIRO Minerals, Melbourne, Australia. Due to the very small amount of material available, it was impossible to determine H_2O directly. H_2O was therefore determined by stoichiometry and the presence of the OH group confirmed by crystal-structure refinement. Chemical analysis of the holotype crystal was limited to three analyses due to its small size (~100 by 30 μm), and the fact that a defocused beam with a large diameter was needed to ensure that there was no thermal decomposition of the specimen and REE and actinide values were accurately quantified. P, Sm, Gd, U, Cl and F were analysed for but were below detection limits. Analytical data are given in Table 1. Additional SEM–EDS analyses of fragments of the holotype crystal indicated only a small variability in the chemical composition and confirmed the La-dominance throughout the crystal.

Although the electron microprobe analyses totals except H_2O attain 102.44 wt%, the chemical formula is perfectly stoichiometric. The high total is most probably due to the matrix correction program used in the JEOL software and the inability to adequately handle $L\beta$ and $M\beta$ lines, although the fact that almost no silicates were used as standards may have also played a role. Even though the holotype crystal contains some Th (3.64 wt% ThO_2), which may have led to a small metamict damage influencing the microprobe total,

Table 1. Chemical-analytical data for ferriallanite-(La).

Constituent	wt%	Range	Detection limit (ppm)	Probe standard
SiO_2	30.22	30.03–30.35	341	Wollastonite
TiO_2	2.24	2.20–2.27	116	TiO_2
Al_2O_3	10.37	10.31–10.41	236	$MgAl_2O_4$
Fe_2O_3[a]	11.05	10.98–11.13	285	Fe_2O_3
FeO[a]	5.83	5.47–6.37	285	Fe_2O_3
MnO	3.43	3.40–3.75	85	Mn metal
MgO	0.36	0.05–0.50	116	$MgAl_2O_4$
CaO	9.46	9.09–9.67	119	Wollastonite
La_2O_3	13.17	12.76–13.61	1079	LaB_6
Ce_2O_3	11.58	11.15–12.76	807	CeO_2
Pr_2O_3	0.50	0.42–0.60	886	$PrSi_2$
Nd_2O_3	0.57	0.39–0.79	1061	NdF_3
Y_2O_3	0.02	0.00–0.08	276	YVO_4
ThO_2	3.64	3.36–4.03	2542	ThO_2
Total	102.44[b]			

[a] Fe measured as FeO and recalculated on the basis of $M + T = 6$ and stoichiometry.

[b] Excluding an estimated water content of ~1.55 wt% H_2O.

the observed scattering power and reflection spots of the crystal indicate perfect crystallinity. The empirical formula [based on 12 O atoms and 1 OH group per formula unit (pfu) and adopting the approach of Ercit (2002), method number 10] is: (1) $Ca_{1.01}(La_{0.49}Ce_{0.42}Th_{0.08}Nd_{0.02}Pr_{0.02})_{\Sigma 1.03}(Fe^{3+}{}_{0.83}Al_{0.17})_{\Sigma 1.00}Al_{1.00}(Fe^{2+}{}_{0.49}Mn_{0.29}Ti_{0.17}Mg_{0.05})_{\Sigma 1.00}[(Si_{0.95}Al_{0.05})_{\Sigma 1.00}O_4](Si_{2.00}O_7)O(OH)$. One OH ion pfu requires 1.55 wt% H_2O. The empirical formula (based on 12 O atoms and 1 OH group pfu alone) is: (2) $Ca_{0.98}(La_{0.47}Ce_{0.41}Th_{0.08}Nd_{0.02}Pr_{0.02})_{\Sigma 1.00}(Fe^{3+}{}_{0.81}Al_{0.14})_{\Sigma 0.95}Al_{1.00}(Fe^{2+}{}_{0.47}Mn_{0.28}Ti_{0.16}Mg_{0.05})_{\Sigma 0.96}[(Si_{0.93}Al_{0.05})_{\Sigma 0.98}O_4](Si_{2.00}O_7)O(OH)$. The simplified formula is: $Ca(La,Ce,Th)(Fe^{3+},Al)Al(Fe^{2+},Mn,Ti,Mg)(SiO_4)(Si_2O_7)O(OH)$ and the end-member formula is: $CaLaFe^{3+}AlFe^{2+}(SiO_4)(Si_2O_7)O(OH)$.

Table 2. Crystal data, data collection information and refinement details for ferriallanite-(La).

Crystal data	
Formula	$^{A1}Ca_{1.00}{}^{A2}(La_{0.49}Ce_{0.42}Ca_{0.09})_{\Sigma 1.00}$ $^{M1}(Fe_{0.58}Al_{0.42})_{\Sigma 1.00}$ $^{M2}(Al_{0.94}Fe_{0.06})_{\Sigma 1.00}$ $^{M3}(Fe_{0.49}Mn_{0.29}Ti_{0.17}Mg_{0.05})_{\Sigma 1.00}(SiO_4)$-$(Si_2O_7)O(OH)$
Formula weight	589.81
Space group, Z	$P2_1/m$ (no. 11), 2
a, b, c (Å)	8.938(2), 5.789(1), 10.153(2)
β (°)	114.54(3)
V (Å^3)	477.88(6)
F(000), ρ_{calc} ($g\cdot cm^{-3}$)	560, 4.099
μ (mm^{-1})	7.549
Absorption correction	multi-scan (Otwinowski *et al.*, 2003)
Crystal dimensions (mm)	0.07 × 0.10 × 0.17 mm
Data collection and refinement	
Diffractometer	Nonius KappaCCD system
λ (Mo–$K\alpha$) (Å), T (K)	0.71073, 293
Crystal-detector distance (mm)	30
Rotation axis, width (°)	γ, ω, 2
Total no. of frames	467
Collect. time per frame (s)	50
Collection mode, $2\theta_{max}$ (°)	Sphere, 65
h, k, l ranges	$-13 \rightarrow 13$, $-8 \rightarrow 8$, $-15 \rightarrow 15$
Total reflections measured	3462
Unique reflections	1880 ($R_{int} = 0.011$)
Refinement on	F^2
$R1(F)$, $wR2_{all}(F^2)^a$	0.0150, 0.0363
''Observed'' refls.	1870 [$F_o > 4\sigma(F_o)$]
Extinct. coefficient	0.0128(5)
No. of refined parameters	127
GooF	1.141
$(\Delta/\sigma)_{max}$	0.023
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e/Å^3)	−0.56, 0.84

Note: Unit-cell parameters were refined from 1882 recorded reflections.

Scattering factors for neutral atoms were employed in the refinement.

[a] $w = 1/[\sigma^2(F_o{}^2) + (0.009P)^2 + 0.57P]$; $P = ([\max \text{ of } (0 \text{ or } F_o{}^2)] + 2F_c{}^2)/3$

5. X-ray crystallography

The crystal structure of ferriallanite-(La) was characterised using single-crystal X-ray intensity data collected from a high-quality crystal fragment. It was refined, using the model of Dollase (1971) as a starting point, with SHELXL-97 (Sheldrick, 2008) in space group $P2_1/m$ to $R1 = 0.0150$ and $wR2_{all} = 0.0363$. The H atom was located and freely refined. Details on data collection and refinement are given in Table 2. Fractional atom coordinates are given in Table 3 and selected bond distances and angles in Table 4. A list of observed and calculated structure factors can be obtained from the first author.

A comparison between the empirical chemical formula (1) calculated from the EPMA data and the simplified formula derived from the first structure model ($R1 = 0.0146$), $^{A1}Ca_{1.00}{}^{A2}[(La,Ce)_{0.9}Ca_{0.1}]^{M1}(Fe^{3+}{}_{0.58}Al_{0.42})_{\Sigma 1.00}{}^{M2}(Al_{0.94}Fe_{0.06})^{M3}[(Fe,Mn)_{0.90}Al_{0.10}]_{\Sigma 1.00}(SiO_4)\ (Si_2O_7)O(OH)$, obtained from a different part of the same crystal, shows that the simplified formula has a very slightly (REE+Th)- and (Fe+Mn+Ti)-poorer and Al-richer bulk composition. The refinement also clearly shows that there is some minor Fe at the $M2$ site, in contrast to the formula calculated using the currently recommended method no. 10 of Ercit (2002). In such an Fe-rich member, crystallised under high-temperature conditions, it is not unexpected, however, to find Fe partly disordered over three neighbouring sites (*cf.* also Giuli *et al.*, 1999). In both ferriallanite-(Ce) (Kartashov *et al.*, 2002, 2003) and the unnamed Mn^{2+}-analogue of ferriallanite-(Ce) (Bonazzi *et al.*, 2009), Fe^{3+} has also been observed at the $M2$ site.

Enforced use of the EPMA model/composition resulted in a considerable increase of the $R1$-factor to 0.024 (for which the $A2$ site occupancy is mainly responsible). This indicates that the large holotype crystal is slightly zoned, in agreement with the slight variations of the contents of the individual elements. The final, most plausible model was obtained after refining a La:Ce:Ca ratio for the $A2$ site (with appropriate starting values), freely refining the Al:Fe ratios on the $M1$ and $M2$ sites, and fixing the composition of the $M3$ site to that obtained by EPMA (this neglects the fact that minor amounts of divalent cations may also reside at the $M1$ site, see Bonazzi & Menchetti, 1995). Although the Ti contents in ferriallanite-(Ce) were assigned to the $M1$ site (Kartashov *et al.*, 2002), it appears more probable that Ti^{4+} ions will prefer the more distorted $M3$ site (considering their generally irregular octahedral coordination environment; Baur, 1981), and consequently we have assigned all Ti in our model to the $M3$ site. The final refinement step gave $R1 = 0.0150$, *i.e.*, a slight increase by comparison to the simplified first structure model.

Table 3. Fractional atom coordinates and displacement parameters (Å^2) for ferriallanite-(La). U_{eq} according to Fischer & Tillmanns (1988).

Atom	Occupancy	x	y	z	U_{eq}
$A1^a$	$Ca_{1.00}$	0.76046(6)	$^3/_4$	0.15288(5)	0.01106(11)
$A2$	$La_{0.490(4)}Ce_{0.420(4)}Ca_{0.0902(18)}$	0.593880(15)	$^3/_4$	0.428249(13)	0.00776(5)
$M1$	$Fe_{0.584(4)}Al_{0.416(4)}$	0	0	0	0.00549(12)
$M2$	$Al_{0.940(4)}Fe_{0.060(4)}$	0	0	$^1/_2$	0.00508(18)
$M3^b$	$Fe_{0.49}Mn_{0.29}Ti_{0.17}Mg_{0.05}$	0.30497(4)	$^1/_4$	0.21342(4)	0.00728(9)
Si1		0.34084(7)	$^3/_4$	0.03618(6)	0.00596(12)
Si2		0.68762(7)	$^1/_4$	0.28082(6)	0.00603(12)
Si3		0.18913(7)	$^3/_4$	0.32480(6)	0.00535(12)
O1		0.23651(14)	0.9875(2)	0.02589(12)	0.0095(2)
O2		0.31313(13)	0.9707(2)	0.36550(12)	0.0088(2)
O3		0.79676(14)	0.0152(2)	0.33783(12)	0.0098(2)
O4		0.05782(19)	$^1/_4$	0.13362(18)	0.0095(3)
O5		0.05050(19)	$^3/_4$	0.15390(17)	0.0087(3)
O6		0.0688(2)	$^3/_4$	0.41141(17)	0.0085(3)
O7		0.51000(19)	$^3/_4$	0.17730(17)	0.0105(3)
O8		0.5437(2)	$^1/_4$	0.33517(19)	0.0156(4)
O9		0.6105(2)	$^1/_4$	0.10335(17)	0.0123(3)
O10		0.08640(19)	$^1/_4$	0.42927(17)	0.0080(3)
H		0.068(5)	$^1/_4$	0.342(5)	0.035(11)

[a] Occupancy of the $A1$ site was fixed to 1 since occupancy refinement gave $Ca_{0.99}$.
[b] Composition of the $M3$ site was fixed according to the EPMA-derived site occupancy.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$A1$	0.0167(2)	0.0089(2)	0.0107(2)	0	0.00868(17)	0
$A2$	0.00672(7)	0.01007(7)	0.00560(7)	0	0.00168(5)	0
$M1$	0.00505(18)	0.00505(19)	0.00593(19)	0.00025(13)	0.00185(13)	−0.00026(13)
$M2$	0.0044(3)	0.0043(3)	0.0057(3)	−0.0005(2)	0.0013(2)	0.00037(19)
$M3$	0.00510(15)	0.00764(16)	0.00694(16)	0	0.00034(12)	0
Si1	0.0065(2)	0.0057(3)	0.0054(2)	0	0.0022(2)	0
Si2	0.0060(2)	0.0060(3)	0.0060(3)	0	0.0025(2)	0
Si3	0.0052(2)	0.0058(3)	0.0055(2)	0	0.00263(19)	0
O1	0.0096(5)	0.0067(5)	0.0124(5)	0.0004(4)	0.0048(4)	0.0012(4)
O2	0.0092(5)	0.0079(5)	0.0091(5)	−0.0005(4)	0.0036(4)	−0.0019(4)
O3	0.0094(5)	0.0066(5)	0.0103(5)	−0.0004(4)	0.0012(4)	0.0006(4)
O4	0.0080(7)	0.0098(7)	0.0098(7)	0	0.0027(6)	0
O5	0.0091(7)	0.0092(7)	0.0065(7)	0	0.0020(5)	0
O6	0.0095(7)	0.0093(7)	0.0094(7)	0	0.0065(6)	0
O7	0.0090(7)	0.0126(8)	0.0072(7)	0	0.0007(6)	0
O8	0.0082(7)	0.0290(10)	0.0107(8)	0	0.0049(6)	0
O9	0.0132(7)	0.0180(8)	0.0069(7)	0	0.0053(6)	0
O10	0.0081(7)	0.0088(7)	0.0082(7)	0	0.0043(6)	0

The crystal structure (Fig. 1) is similar to that of ferriallanite-(Ce) (Kartashov *et al.*, 2002, 2003) and the unnamed Mn^{2+}-analogue of ferriallanite (Bonazzi *et al.*, 2009). For details on the topology the reader is referred to previous works on the crystal structures of epidote-type minerals. The OH group in ferriallanite-(La) is involved in a weak hydrogen bond, with O10 . . . O4 = 2.905(2) Å, very similar to the one in ferriallanite-(Ce), 2.889(3) Å. The average $M1$–O and $M2$–O bond-lengths (1.987 and 1.910 Å, respectively) reflect the lower Fe^{3+} contents on the $M1$ and $M2$ sites by comparison to type ferriallanite-(Ce) which has corresponding values of 2.010 and 1.944 Å, respectively, and a chemical formula closer to the ideal end-member composition. The relatively high Mn content at the $M3$ site (0.29 Mn pfu) appears to result in a considerably smaller bond-length distortion by comparison to the ferriallanite-(Ce) of Kartashov *et al.* (2002, 2003). Average Si–O bond lengths of the three Si sites are within 0.001 Å of the corresponding values in ferriallanite-(Ce). The well-established negative correlation between the Si1–O9–Si2 angle and the mean $M3$–O bond length in members of the epidote supergroup (Cenki-Tok *et al.*, 2006; their Fig. 2) is confirmed by the present data.

X-ray powder diffraction data (Ni-filtered Cu$K\alpha$ radiation) were obtained, from the crystal fragment used for the structure solution, with a 114.59 mm Debye–Scherrer camera equipped with a Gandolfi attachment, and are listed in Table 5. The unit-cell parameters refined from the powder data are: $a = 8.938(5)$, $b = 5.781(1)$, $c = 10.157(7)$ Å, $\beta = 114.54(5)°$ and $V = 477.4(4)$ Å^3. These values are very close

Table 4. Selected bond distances (Å) and angles (°) for the coordination polyhedra in ferriallanite-(La).

*A*1–O3 x2	2.3414(12)	*A*2–O7	2.3382(17)
–O7	2.3525(18)	–O2 x2	2.4990(12)
–O1 x2	2.3760(13)	–O10	2.6125(18)
–O5	2.5881(18)	–O2 x2	2.6470(13)
–O6	2.912(2)	–O3 x2	2.8055(13)
<*A*1–O>	2.469	–O8 x2	3.0200(7)
		<*A*2–O>	2.690*
*M*1–O4 x2	1.9026(11)	*M*2–O3 x2	1.8800(14)
–O1 x2	2.0203(12)	–O10 x2	1.9150(11)
–O5 x2	2.0381(11)	–O6 x2	1.9343(10)
<*M*1–O>	1.987	<*M*2–O>	1.910
*M*3–O8	1.9721(19)	Si1–O7	1.5935(18)
–O4	2.0123(17)	–O1 x2	1.6399(12)
–O2 x2	2.2161(12)	–O9	1.6456(18)
–O1 x2	2.3113(13)	<Si1–O>	1.630
<*M*3–O>	2.173		
Si2–O8	1.5966(18)	Si3–O2 x2	1.6280(12)
–O3 x2	1.6326(12)	–O6	1.6477(17)
–O9	1.6402(18)	–O5	1.6613(18)
<Si2–O>	1.626	<Si3–O>	1.641
Si2–O9–Si1	143.61(12)**	O10–H–O4	172(4)
O10–H	0.83(4)	O10. . .O4	2.905(2)

*If the two long *A*2–O8 bonds are excluded, the <*A*2–O> distance is 2.608 Å.

**In ferriallanite-(Ce) (Kartashov *et al.*, 2002; 2003), the Si–O–Si angle is 141.0(2)°.

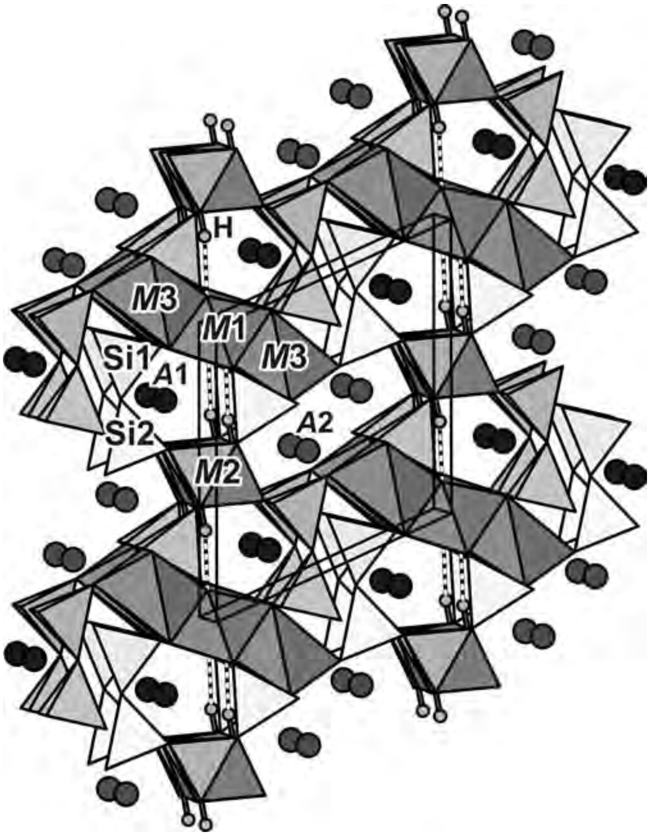

Fig. 1. View of the crystal structure of ferriallanite-(La) in a direction slightly offset from [010], in order to provide a better view of the hydrogen-bonds (dashed).

Table 5. Measured and calculated X-ray powder diffraction data for ferriallanite-(La).

d_{meas} (Å)	d_{calc} (Å)	I_{meas}	I_{calc}	*h*	*k*	*l*
9.22^a	9.24	**19**	25	0	0	1
	8.13		11	1	0	0
7.96^a	7.96	**34**	34	−1	0	1
5.13	5.14	9	17	1	0	1
5.00^a	5.01	16	14	−1	0	2
4.91	4.90	4	5	0	1	1
	4.71		14	1	1	0
4.68^a	4.68	11	6	−1	1	1
4.62^a	4.62	14	13	0	0	2
3.98	3.98	7	4	−2	0	2
3.83	3.84	3	3	1	1	1
3.78	3.79	9	9	−1	1	2
3.61^a	3.61	10	12	0	1	2
3.53^a	3.54	**38**	54	−2	1	1
	3.45		1	1	0	2
3.32	3.33	4	13	2	1	0
3.27	3.28	5	4	−2	1	2
3.23	3.26	3	12	2	0	1
	3.17		4	−2	0	3
	2.96		4	1	1	2
	2.93		21	−3	0	2
2.92	2.92	**100**	100	−1	1	3
	2.89		38	0	2	0
2.84	2.84	4	12	2	1	1
2.76	2.76	5	6	0	2	1
2.72	2.72	**50**	37	1	2	0
	2.72		36	0	1	3
	2.72		1	−1	2	1
	2.71		13	3	0	0
	2.65		5	−3	0	3
2.63^a	2.63	**36**	51	−3	1	1
	2.61		3	−3	1	2
2.55	2.57	2	26	2	0	2
	2.55		2	1	0	3
	2.51		5	−1	0	4
	2.50		3	−2	0	4
2.51^a	2.50	12	7	−1	2	2
	2.45		3	3	1	0
2.45	2.45	6	6	0	2	2
2.41^a	2.41	15	14	−3	1	3
2.34^a	2.34	14	14	−2	2	2
2.30	2.30	10	5	−1	1	4
	2.30		4	−2	1	4
	2.29		8	−3	0	4
2.23	2.22	4	9	1	2	2
2.21	2.20	6	7	−1	2	3
2.19^a	2.18	13	21	−4	0	1
	2.18		3	3	1	1
2.16	2.16	**17**	21	2	2	1
	2.16		6	−4	0	3
2.14	2.14	17	7	0	1	4
	2.14		19	−2	2	3
2.11^a	2.11	10	13	0	2	3
2.06	2.07	3	9	2	0	3
	2.04		1	−4	1	1
	2.03		1	4	0	0
	2.03		2	−2	0	5
2.02	2.02	3	1	−4	1	3
1.989	1.990	2	1	−4	0	4
1.952	1.955	5	3	−3	2	3
	1.953		2	2	1	3

Table 5. Continued.

d_{meas} (Å)	d_{calc} (Å)	I_{meas}	I_{calc}	h	k	l
	1.920		14	2	2	2
	1.912		3	1	2	3
	1.901		7	1	1	4
	1.897		1	−1	2	4
1.893[a]	1.893	16	15	−2	2	4
	1.892		6	3	1	2
1.876	1.875	6	3	1	3	0
1.846	1.848	7	3	0	0	5
	1.824		1	3	2	1
1.803	1.804	5	3	0	2	4
1.781	1.783	9	6	−5	0	2
	1.779		1	0	3	2
1.769	1.769	12	8	−2	3	1
	1.768		6	−4	2	2
1.741	1.743	5	3	−4	2	1
	1.741		2	2	3	0
	1.729		2	−5	0	1
	1.724		2	2	0	4
1.704	1.706	8	7	−4	1	5
	1.704		2	−5	1	2
1.689	1.692	6	5	−2	0	6
	1.686		3	2	2	3
1.674[a]	1.674	11	13	−1	3	3
	1.663		6	4	2	0
	1.658		2	2	3	1
1.655	1.656	10	6	−5	1	1
	1.652		3	2	1	4
	1.652		5	1	2	4
1.639[b]	**1.646**	**34**[b]	8	3	2	2
	1.643		12	−1	0	6
	1.642		1	3	1	3
	1.639		18	−4	2	4
	1.639		2	−1	2	5
	1.634		4	−5	1	4
	1.634		6	0	3	3
	1.626		2	5	0	0
	1.623		2	−2	1	6
	1.616		1	−3	2	5
1.613[a]	1.614	12	12	−3	3	1
	1.610		1	−3	3	2
	1.604		3	−3	1	6
1.593	1.595	11	9	1	1	5
1.584	1.585	6	8	−4	0	6
1.561	1.567	4	8	4	1	2
	1.565		1	5	1	0
	1.559		2	−3	3	3
1.532	1.535	3	2	−5	1	5
1.528	1.528	3	1	−4	1	6
1.482	1.484	5	4	−5	2	1
	1.480		2	0	3	4
	1.468		5	−5	2	4
1.463	1.464	12	4	−6	0	4
	1.460		7	−2	2	6
	1.451		2	5	1	1
	1.446		2	−3	2	6
1.445[a]	1.445	14	17	0	4	0
	1.431		2	−6	1	2
	1.423		6	2	1	5
	1.419		2	−6	1	4
1.418[a]	1.418	13	8	4	2	2
1.403	1.403	4	2	−3	1	7

Table 5. Continued.

d_{meas} (Å)	d_{calc} (Å)	I_{meas}	I_{calc}	h	k	l
	1.401		1	−2	1	7
1.389	1.392	4	3	1	3	4
	1.387		2	−6	1	1
1.364	1.366	5	1	−6	1	5
	1.366		2	5	0	2
	1.366		3	−4	1	7
	1.359		4	0	2	6
	1.330		2	5	1	2
	1.321		1	2	4	1
1.316	1.315	4	4	−6	2	2
	1.310		2	−4	3	5
	1.306		4	−6	2	4
1.304	1.304	8	3	−5	2	6
1.295	1.296	4	2	3	0	5
	1.296		3	−3	4	2
	1.291		3	4	2	3
1.287	1.287	5	3	−5	3	1
	1.285		1	2	3	4
	1.284		2	4	0	4
	1.281		2	−6	2	1
1.276	1.277	5	1	−5	3	4
	1.275		2	3	4	0
	1.275		1	2	0	6
	1.271		1	−2	3	6
	1.270		1	−3	0	8
	1.265		3	−6	2	5
	1.262		1	−3	3	6
1.259	1.260	8	5	2	4	2
	1.257		4	1	3	5
	1.253		1	−1	4	4
	1.244		3	4	3	2
	1.228		1	−7	1	2
1.226	1.227	5	2	6	2	0
	1.222		3	−3	4	4
	1.209		2	−6	1	7
1.205	1.205	4	3	−4	4	1
1.200	1.201	4	2	0	2	7
	1.186		2	2	4	3
	1.168		3	2	3	5
	1.166		1	−6	3	4
	1.157		1	−3	3	7
	1.148		1	−6	3	1
	1.145		1	−6	0	8
	1.139		2	7	1	0
	1.135		2	−4	3	7
	1.133		1	0	1	8
	1.123		2	−5	4	2
	1.119		1	−2	5	1
	1.116		3	−7	1	7
1.114	1.115	5	1	5	3	2
	1.114		2	−5	2	8
	1.099		1	−2	4	6
1.094	1.094	5	4	−1	5	3
	1.085		5	−1	4	6
	1.082		2	0	5	3

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[a] Reflections used for the least-squares refinement of the unit-cell parameters. These reflections have $I_{meas} \geq 10$ and can be indexed with single *hkl* values.

[b] Estimated from data without the internal Si-standard, because of overlap by the 311 reflection of Si. Indexing is based on structure refinement; only reflections with $I_{calc} \geq 1$ are listed.

Table 6. Comparison of crystal data of selected ''ferriallanites'' (space group $P2_1/m$).

Mineral	*a* (Å)	*b* (Å)	*c* (Å)	β (°)	*V* (Å^3)	Ref.
Ferriallanite-(Ce)	8.962(2)	5.836(2)	10.182(2)	115.02(1)	482.57	Kartashov *et al*. (2002)
Ferriallanite-(Ce)	8.941(4)	5.799(2)	10.151(6)	114.7(6)	478.2(5)	Holtstam *et al*. (2003)
Ferriallanite-(La)	8.938(2)	5.789(1)	10.153(2)	114.54(3)	477.88(16)	This work

to those determined by the structure solution, $a = 8.938(2)$, $b = 5.789(1)$, $c = 10.153(2)$ Å, $\beta = 114.54(3)°$ and $V = 477.88(6)$ Å^3.

6. Discussion

Ferriallanite-(La) is a new member of the epidote supergroup and allanite group. It is the La-analogue of ferriallanite-(Ce) and the Fe^{3+} analogue of allanite-(La). An unnamed Mn^{2+}-analogue of ferriallanite-(Ce) has been reported recently (Bonazzi *et al*., 2009), and a Mg-analogue of ferriallanite-(Ce) also seems to exist at the Rödberg mines, Västmanland, Sweden (Pavel Kartashov, unpublished data, http://www.mindat.org/min-39270.html). Detailed chemical and X-ray diffraction analyses will be necessary to distinguish ferriallanite-(La) from ferriallanite-(Ce), Fe-rich allanites and other dark-coloured members of the epidote supergroup. Unit-cell parameters of the two Fe^{3+}-members are very similar (Table 6). In the sanidinite xenoliths of the Laacher See area (Eifel, Germany), ferriallanite-(La) seems to be very rare. As mentioned in the introduction, five visually very similar specimens were found to be either Fe^{3+}-rich allanite-(Ce) or allanite-(La). Black allanites from Mn-rich xenoliths of the Laacher See always have $(Fe + Mg) > Mn$. It might be worthwhile to study allanites from other sanidinite-rich rocks in geologically comparable volcanic provinces such as in Italy.

Acknowledgements: Careful reviews by G.C. Capitani and an anonymous reviewer improved the paper. Colin MacRae and Nick Wilson (CSIRO) are thanked for help with the electron microprobe analyses.

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Received 11 July 2011
Modified version received 5 February 2012
Accepted 13 February 2012