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# FERRIALLANITE-(Ce), $CaCeFe^{3+}AlFe^{2+}(SiO_4)(Si_2O_7)O(OH)$, A NEW MEMBER OF THE EPIDOTE GROUP: DESCRIPTION, X-RAY AND MÖSSBAUER STUDY

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## ABSTRACT

Ferriallanite-(Ce), ideally $CaCeFe^{3+}AlFe^{2+}(SiO_4)(Si_2O_7)O(OH)$, is the analogue of allanite-(Ce) with $Fe^{3+}$ dominant in the octahedral site *M*(1). It is of metasomatic origin and occurs in an alkaline granitic pegmatite of Mount Ulyn Khuren in the Altai Range (about 48°32'N, 92°55'E), Mongolian People's Republic. Ferriallanite-(Ce) is black, opaque or translucent, with a brown streak; the luster is resinous. The Mohs hardness is 6; it is brittle, without observed cleavage or parting. The fracture is conchoidal to uneven. Its density is 4.22 g/cm$^3$. It is biaxial (–), $\alpha$ 1.825(2), $\beta$ 1.855(5), $\gamma$ 1.880(5), $2V_{calc}$ 83°. The strongest five peaks in the X-ray powder-diffraction pattern [*d*(Å)(I)(*hkl*)] are: 2.93(65)($\bar{1}13$), 2.72(80)(120,013), 2.63(60)($\bar{3}11$), 2.18(100)(122,$\bar{1}23$,$\bar{4}01$), 2.14(80)(221,$\bar{4}03$,$\bar{2}23$,014). The crystal structure has been refined to $R = 0.026$ using 2296 observed reflections collected with a four-circle X-ray diffractometer [*a* 8.962(2), *b* 5.836(2), *c* 10.182(2) Å, $\beta$ 115.02(1)°, space group $P2_1/m$]. The position of the hydrogen atom has been found. On the basis of the chemical data, structure refinement, Mössbauer spectroscopy and charge-distribution calculations, the cations have been assigned to the independent crystallographic sites and the following crystal chemical formula has been obtained: $(Ca_{0.97}Ce_{0.03})(Ce_{0.89}Ca_{0.11})(Fe^{3+}{}_{0.80}Ti^{4+}{}_{0.14}Al_{0.06})(Al_{0.56}Fe^{3+}{}_{0.44})$ $(Fe^{2+}{}_{0.93}Mn_{0.07})(Si_{0.94}Al_{0.06}O_4)(Si_2O_7)O(OH)$. In the same sample, a single-point electron-microprobe analysis reveals an ideal composition $CaCeFe^{3+}{}_2Fe^{2+}(SiO_4)(Si_2O_7)O(OH)$, but not enough material is available for a full characterization of this potentially new epidote-group mineral.

*Keywords*: ferriallanite-(Ce), new mineral species, crystal structure, Mössbauer spectroscopy, allanite subgroup, epidote group, alkaline granitic pegmatite, Altai Range, Mongolia.

## SOMMAIRE

La ferriallanite-(Ce), de composition idéale $CaCeFe^{3+}AlFe^{2+}(SiO_4)(Si_2O_7)O(OH)$, est un analogue de l'allanite-(Ce) à dominance de $Fe^{3+}$ dans le site octaédrique *M*(1). Cette nouvelle espèce minérale, d'origine métasomatique, provient d'une pegmatite granitique alcaline au mont Ulyn Khuren, chaîne de montagnes Altai (environ 48°32'N, 92°55'E), en République Populaire de Mongolie. Les cristaux de ferriallanite-(Ce) sont noirs, opaques ou translucides, avec une rayure brune; l'éclat est résineux. La dureté de Mohs est 6; c'est un minéral cassant, sans clivage ou plan de séparation observé. La fracture est conchoïdale à inégale. Sa densité est 4.22 g/cm$^3$. Elle est biaxe (–), $\alpha$ 1.825(2), $\beta$ 1.855(5), $\gamma$ 1.880(5), $2V_{calc}$ 83°. Les cinq raies les plus intenses du spectre de diffraction (méthode des poudres) [*d*(Å)(I)(*hkl*)] sont: 2.93(65)($\bar{1}13$), 2.72(80)(120,013), 2.63(60)($\bar{3}11$), 2.18(100)(122,$\bar{1}23$,$\bar{4}01$) et 2.14(80)(221,$\bar{4}03$,$\bar{2}23$,014). Nous en avons affiné la structure cristalline jusqu'à un résidu *R* de 0.026 en utilisant 2296 réflexions observées prélevées avec un diffractomètre à quatre cercles [*a* 8.962(2), *b* 5.836(2), *c* 10.182(2) Å, $\beta$ 115.02(1)°, groupe spatial $P2_1/m$]. Nous précisons la position de l'atome d'hydrogène. D'après les données chimiques,

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l'affinement de la structure, la spectroscopie de Mössbauer et les calculs de la distribution des charges, nous avons pu attribuer les cations aux sites cristallographiques indépendants, et nous obtenons la formule cristallochimique suivante: $(Ca_{0.97}Ce_{0.03})(Ce_{0.89}Ca_{0.11})(Fe^{3+}_{0.80}Ti^{4+}_{0.14}Al_{0.06})(Al_{0.56}Fe^{3+}_{0.44})$ $(Fe^{2+}_{0.93}Mn_{0.07})(Si_{0.94}Al_{0.06}O_4)(Si_2O_7)O(OH)$. Dans le même échantillon, une analyse ponctuelle indique une composition idéale $CaCeFe^{3+}{}_2Fe^{2+}(SiO_4)(Si_2O_7)O(OH)$, mais dans un volume insuffisant pour permettre une caractérisation complète de ce que semble être un nouveau membre du groupe de l'épidote.

(Traduit par la Rédaction)

*Mots-clés*: ferriallanite-(Ce), nouvelle espèce minérale, structure cristalline, spectroscopie de Mössbauer, sous-groupe de l'allanite, groupe de l'épidote, pegmatite granitique alcaline, chaîne de montagnes Altai, Mongolie.

## INTRODUCTION

Minerals belonging to the epidote group are represented by the general formula $A_2M_3(SiO_4)(Si_2O_7)O(OH)$, where *A* stands for Ca, *REE*, Sr, Mn and Pb, and *M* represents Al, $Fe^{2+}$, $Fe^{3+}$, Mn, Mg and V; some F can substitute for OH. All known members are monoclinic $P2_1/m$ except for zoisite, which is orthorhombic *Pnma* and in polytypic relationship with clinozoisite (Ray *et al.* 1986). In the following minerals of the epidote group, the rare-earth elements (*REE*) are dominant in one of the two independent *A* sites, which is usually labeled *A*(2): allanite-(Ce) (Hintze 1897), androsite-(La) (Bonazzi *et al.* 1996), dissakisite-(Ce) (Grew *et al.* 1991), dollaseite-(Ce) (Peacor & Dunn 1988) and khristovite-(Ce) (Pautov *et al.* 1993); allanite-(La) and allanite-(Y) have been introduced by Levinson (1966) on the basis of data reported in the literature. A different pattern of cation occupancy at one of the three independent *M* sites (two in zoisite) generates different mineral species.

Allanite-(Ce), ideally $CaCeFe^{2+}Al_2(SiO_4)(Si_2O_7)O(OH)$, is characterized by the replacement of $Ca^{2+}$ + $Al^{3+}$ by $REE^{3+}$ + $Fe^{2+}$ and, with the minimum content of $Fe^{2+}$, becomes $Ca(Ce_{0.51}Ca_{0.49})(Al_{2.49}Fe^{2+}_{0.51})(SiO_4)(Si_2O_7)O(OH)$; some $Fe^{2+}$ can be replaced by other divalent ions (mainly $Mn^{2+}$ and $Mg^{2+}$). The dominance of $Fe^{3+}$ in the octahedral site *M*(1) leads to the new species ferriallanite-(Ce), ideally $CaCeFe^{3+}AlFe^{2+}(SiO_4)(Si_2O_7)O(OH)$, approved by IMA (2000–041) and described in this paper. The type material is labelled TsH–9026 and deposited in the Fersman Mineralogical Museum, Moscow, Russia.

## OCCURRENCE

Ferriallanite-(Ce) has been found in the "Neprimetnyi" (= Indiscernible in English) alkaline granitic pegmatite occurring in the northern slope of Mount Ulyn Khuren (approximately 48°32'N, 92°55'E), which belongs to the Khaldzan Buragtag peralkaline granite massif, exposed 55 km north–northeast of Kobdo city, Mongolian Altai range, Kobdo aimak, Mongolian People's Republic. The new mineral is of metasomatic origin and represents a major product of the pseudomorphism of *REE*-rich minerals of the eudialyte group. It occurs as an aggregate of subhedral grains from 0.3 × 0.5 to 1 × 2 mm within masses of zircon, quartz and kainosite-(Y) and is associated with aegirine, β-fergusonite-(Y), Y-rich and normal ilvaite, hingganite-(Ce), Nd-rich allanite-(Ce), magnetite, fayalite, fluorite.

## EXPERIMENTAL

### *Physical properties*

Ferriallanite-(Ce) is black and opaque, translucent (red or orange-red inner reflections), with a brown streak; the luster is resinous; fluorescence was not observed. It is brittle and shows a hardness $VHN_{100g}$ of 1250 $kg/mm^2$, corresponding to 6 on the Mohs scale. No cleavage or parting has been observed; the fracture is from conchoidal to uneven. By the microvolumetric method, a density of 4.22 $g/cm^3$ was measured; the calculated density is 4.16 and 4.21 $g/cm^3$ for the composition of the crystal used for structure refinement and that corresponding to column 2 in Table 1, respectively.

At a wavelength of 589 nm, ferriallanite-(Ce) is biaxial (–), with $\alpha$ 1.825(2), $\beta$ 1.855(5) and $\gamma$ 1.880(5); $2V$ could not be measured because of the black color; $2V_{calc}$ is equal to 83°. The dispersion is strong and shows $r < v$; pleochroism is observed: $Z > Y > X$, with *Z* dark red-brown, *Y* brown and *X* greenish gray. The compatibility index, 0.007, is superior.

The infrared absorption spectrum of ferriallanite-(Ce) shows absorption bands at the following wavelengths: 425, 465, 487, 529, 551, 569, 615, 681, 830, 864, 888, 919, 1033, and 3150 $cm^{-1}$.

### *Mössbauer spectra and chemical composition*

Substantially identical Mössbauer spectra (Fig. 1) have been collected at room temperature from the type sample (TsH–9026) and a second one (TsH–9031) with an absorber thickness of 5 mg $Fe/cm^2$. The spectra were collected in transmission mode on a constant-acceleration spectrometer using a nominal 1.85 GBq $^{57}Co$ source with a velocity scale calibrated with respect to α-iron. They could be unambiguously fitted (program NORMOS written by R.A. Brand and distributed by Wissenschaftliche Elektronik GmbH, Germany) to two Lorentzian quadrupole doublets for $Fe^{3+}$ and one

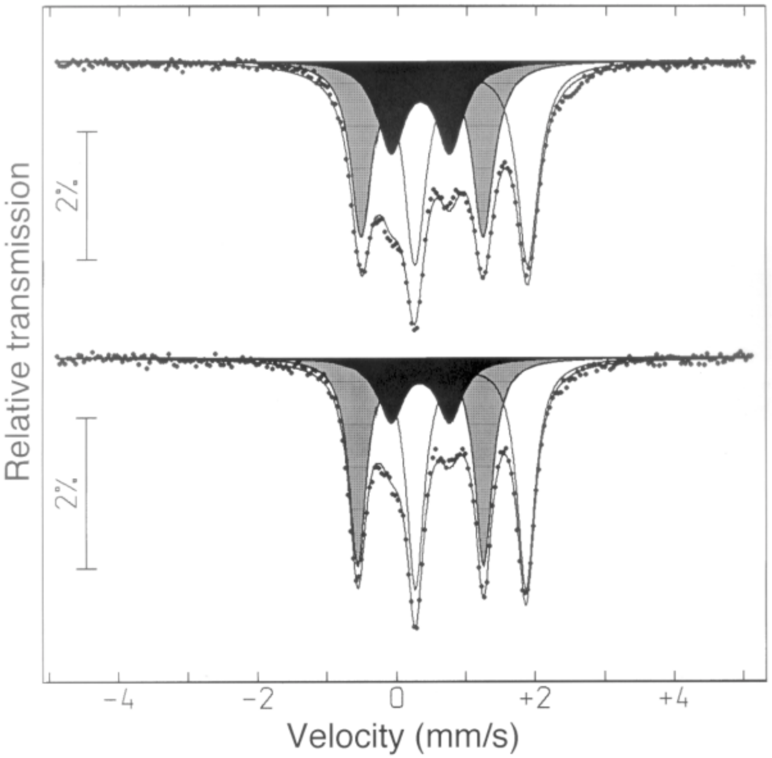

FIG. 1. Room-temperature Mössbauer spectra for two samples, TsH–9026 (top) and TsH–9031 (bottom) of ferriallanite-(Ce). The doublet corresponding to $Fe^{2+}$ is unshaded, and the two doublets corresponding to $Fe^{3+}$ are shaded black and gray.

Lorentzian quadrupole doublet for $Fe^{2+}$. Conventional constraints (component widths and areas constrained to be equal) were applied. Effects due to thickness and differences in the recoil-free fraction were estimated and found to be within the quoted experimental uncertainty. Average values of the center shifts [1.068(5) mm/s for $Fe^{2+}$; 0.359(5) and 0.334(5) mm/s for $Fe^{3+}$, relative to α-iron], the quadrupole splittings [1.62(1) mm/s for $Fe^{2+}$; 1.78(1) and 0.85(1) mm/s for $Fe^{3+}$], and the number of the fitted doublets show that: (*i*) $Fe^{2+}$ occupies only one octahedral site, which is distorted; (*ii*) $Fe^{3+}$ occupies two octahedral sites, one of which is more distorted than the other. From the areas of the fitted doublets, an average $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ value of 0.57(3) is obtained.

From the electron-microprobe data (Table 1), the following chemical formulae are obtained on the basis of 13 oxygen atoms per formula unit (*apfu*): $(Ca_{1.17}Ce_{0.40}La_{0.19}Nd_{0.19}Pr_{0.06})_{\Sigma 2.01}(Fe^{3+}_{1.43}Fe^{2+}_{0.71}Al_{0.61}Ti_{0.14}Mn_{0.07})_{\Sigma 2.96}[(Si_{2.89}Al_{0.11})_{\Sigma 3.00}O_{11}]O(OH)_{1.01}$ for the crystal structurally investigated (column 1, Table 1); $(Ca_{1.12}Ce_{0.43}La_{0.18}Nd_{0.17}Pr_{0.05})_{\Sigma 1.96}(Fe^{3+}_{1.44}Fe^{2+}_{0.75}Al_{0.59}Ti_{0.14}Mn_{0.12})_{\Sigma 3.04}$ $[(Si_{2.84}Al_{0.16})_{\Sigma 3.00}O_{11}]O(OH)_{1.01}$ for the mean composition of six different grains (column 2, Table 1); $(Ca_{1.01}Ce_{0.50}La_{0.21}Nd_{0.18}Pr_{0.10})_{\Sigma 2.00}(Fe^{3+}_{1.55}Fe^{2+}_{0.85}Al_{0.24}Ti_{0.20}Mn_{0.14})_{\Sigma 2.98}[(Si_{2.89}Al_{0.11})_{\Sigma 3.00}O_{11}]O(OH)_{1.00}$ for the domain poorest in Al (column 3, Table 1).

The $Fe_2O_3$ and FeO contents were calculated on the basis of the isomorphic substitution $Ca^{2+} + Fe^{3+} \leftrightarrow$ *REE*$^{3+}$ + $(Fe,Mn)^{2+}$ and are reasonably confirmed by wet-chemical analysis. Taking into account some zoning and variability in the level of the *REE*, Ca, Mn and Fe, the partitioning of $Fe_{tot}$ mentioned accumulates the analytical errors on the ratio $Fe^{3+}/Fe^{2+}$; the average amount of $Fe^{3+}/(Fe^{2+} + Fe^{3+}) = 0.65$ obtained from the electron-microprobe analysis is consistent with the value of 0.57(3) indicated by the Mössbauer spectra. A simplified formula for ferriallanite-(Ce) is $(Ca,REE)_2(Fe^{3+},Fe^{2+},Al)_3(SiO_4)(Si_2O_7)O(OH)$ or, ideally, also on the basis of the structure refinement discussed below, $CaCeFe^{3+}AlFe^{2+}(SiO_4)(Si_2O_7)O(OH)$. The order of the octahedrally coordinated cations is according to the dominance in the sites *M*(1), *M*(2) and *M*(3).

### *Single-crystal X-ray crystallography*

Single-crystal X-ray-diffraction data were collected, from the best of a few selected crystals, on a four-circle Siemens *P*4 diffractometer and anisotropically refined with the SHELX package (Sheldrick 1997) starting from the coordinates published by Comodi & Zanazzi (1997) for clinozoisite. The relevant experimental data and information on the refinement are given in Table 2. The position of the hydrogen atom was detected in a difference electron-density map and refined. As already found by neutron (Ferraris *et al.* 1989; *cf.* Kvick *et al.* 1988) and X-ray diffraction (Catti *et al.* 1988, 1989) in strontian piemontite, the hydrogen atom is covalently bonded to O(10) [O(10)–H = 0.72(7) Å] and a hydrogen bond is established with O(4) [O(10)...O(4) = 2.889(3) Å]. Table 3 reports the atom coordinates, the anisotropic displacement parameters and the number of refined electrons of the sites *A* and *M*. Table 4 shows the X-ray powder-diffraction data that have been indexed taking into account the calculated intensities of the diffraction maxima. A table with $F_o$ and $F_c$ is deposited at the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

TABLE 1. CHEMICAL COMPOSITION OF FERRIALLANITE-(Ce)

| | 1 | | 2 | | 3 |
|---|---|---|---|---|---|
| | wt.% | Range | wt.% | Range | wt.% |
| $SiO_2$ | 28.72 | 28.50-30.37 | 28.09 | 26.89-30.17 | 27.52 |
| $TiO_2$ | 1.85 | 0.93-2.00 | 1.84 | 0 73-2.53 | 2.53 |
| $Al_2O_3$ | 6.07 | 5.41-6.30 | 6.26 | 2.83-8.50 | 2.83 |
| $La_2O_3$ | 5.12 | 3.57-5.44 | 4.90 | 2.04-7.14 | 5.42 |
| $Ce_2O_3$ | 10.86 | 9.96-11.79 | 11.66 | 7.69-13.93 | 13.01 |
| $Pr_2O_3$ | 1.63 | 0.83-1.82 | 1.46 | 0.60-2.61 | 2.61 |
| $Nd_2O_3$ | 5.29 | 4.45-5.36 | 4.82 | 3.70-7.93 | 4.80 |
| CaO | 10.85 | 10.56-10.91 | 10.33 | 8.72-14.33 | 8.98 |
| FeO (total) | 25,30 | 25.02-27.57 | 25.79 | 23.29-29.44 | 27.20 |
| MnO | 0,82 | 0,59-0 94 | 1.34 | 0.28-2.13 | 1.57 |
| Total | 96.51 | | 96.49 | | 96 47 |
| $Fe_2O_3$* | 18.88 | | 18,99 | | 19.62 |
| FeO* | 8,44 | | 8.83 | | 9.68 |
| $H_2O$** | 1.48 | | 1.48 | | 1.43 |
| Total | 100.01 | | 100,00 | | 100.00 |
| $Fe_2O_3$ + FeO | 27.32 | | 27,82 | | 29.30 |

1. Crystal used for structure refinement; four point-analyses were made with wavelength-dispersion electron microprobe JXA–50A; standards: chkalovite (Si), ilmenite (Ti, Fe), microcline (Al), $LaP_5O_{14}$ (La), $CeP_5O_{14}$ (Ce), $PrP_5O_{14}$ (Pr), $NdP_5O_{14}$ (Nd) and wollastonite (Ca).
2. Average of 8 point-analyses from six different grains; ASEM JSM–5300 electron microprobe equipped with energy-dispersion micro-analyzer Link ISIS; standards: chkalovite (Si), metallic Ti, Al, Fe and Mn, nacaphite (Ca), *REE*($PO_4$) for *REE*.
3. Composition poorest in Al.

* $Fe_2O_3$ and FeO calculated according to the substitution $Ca^{2+} + Fe^{3+} = REE^{3+} + {}^{VI}(Fe,Mn)^{2+}$; a wet-microchemical determination gave 4.14% $Al_2O_3$, 20.09% $Fe_2O_3$, 8 43% FeO, 1.64% MnO.

** amount of $H_2O$ inferred on the basis of stoichiometry and charge balance; 1.5% was determined by thermal analysis in $N_2$ atmosphere. No other elements with atomic number higher than 10 were detected by electron-microprobe analysis.

## DISCUSSION

### *The structure*

The structure of ferriallanite-(Ce) (Fig. 2) shows the typical features of the monoclinic epidotes, in which two types of chains of edge-sharing octahedra run along [010]. One chain consists of *M*(2) octahedra only; in the second chain the row of *M*(1) octahedra is decorated on both sides by *M*(3) octahedra. The chains are connected both by isolated ($SiO_4$) and corner-sharing pairs ($Si_2O_7$) of tetrahedra, thus establishing a three-dimensional framework; the cations at sites *A*(1) and *A*(2) occupy two types of large cavities.

As is the case for the entire epidote group (see references), in particular for allanite-(Ce) (Dollase 1971), the coordination polyhedra for the *A* cations are characterized by a large spread of the cation-oxygen bonds. In Table 5 we report only the *A*–O distances shorter than 3 Å; the relevant effective coordination numbers ECoN (Table 5; Hoppe 1979) show how distorted the coordination polyhedra are, even for these nearest atoms of oxygen. The complete picture is as follows: *A*(1) has a coordination 6 + 1 + 3, having O(9) twice at a distance of 3.168 Å and once at 3.141 Å; *A*(2) has a coordination 6 + 2 + 3 having O(8) twice at 3.053 Å and once at 3.147 Å. The interaction of the cations occupying the two *A* sites with oxygen atoms at a distance of ~3 Å is demonstrated by the charge distribution (CD) calculation (Table 6; see below); the actual second sphere of neighbor oxygen atoms begins only at distances longer than 3.8 Å. Whereas the sites *M*(1) and *M*(2) are only moderately distorted relative to octahedral coordination, *M*(3), as already mentioned, is strongly distorted and shows a 4 + 2 coordination, as occurs also in the other structures of the epidote group, independently of the type of cations (see below).

TABLE 2. MISCELLANEOUS INFORMATION ABOUT THE CRYSTAL AND REFINEMENT DATA FOR FERRIALLANITE-(Ce)

| | | | |
|---|---|---|---|
| *a* (Å) | 8.962(2) | *b* (Å) | 5.836(2) |
| *c* (Å) | 10.182(2) | β(°) | 115.02(1) |
| V (Å$^3$) | 482.6(2) | | |
| Space group | $P2_1/m$ | *Z* | 2 |
| Absorption coefficient (mm$^{-1}$) | 8.69 | F(000) | 581.4 |
| Crystal size (mm) | 0.07 × 0.18 × 0.18 | Radiation | Mo*K*α |
| 2θ range (°) | 70.01 | *R*(int) | 0.0355 |
| Collected reflections | 4471 | Unique reflections | 2296 |
| $F_o > 4\sigma(F_o)$ | 2095 | | |
| Method of refinement: | | Full-matrix least squares on $F^2$ | |
| Weights | | $1/\sigma(F_o^2)$ | |
| Number of refined parameters | | 129 | |
| Goodness of fit on $F^2$ | | 1.124 | |
| $R_1$ [$F_o > 4\sigma(F_o)$] | | 0.026 | |
| $wR_2$ | | 0.066 | |
| $R_1$ (all data) | | 0.030 | |
| GooF | | 1.124 | |

TABLE 3. FINAL ATOMIC PARAMETERS FOR FERRIALLANITE-(Ce) AND ELECTRONS PER SITE WHERE REFINED ($el_{ref}$)

| Site | $el_{ref}$ | *x* | *y* | *z* | $U_{eq}$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *A*(1)* | 21,33(14) | 0.75559(8) | 3/4 | 0.484(7) | 0,129(2) | 0.0199(3) | 0,0098(3) | 0.0139(3) | 0 | 0.0120(2) | 0 |
| *A*(2)* | 53,67(17) | 0.5930(2) | 3/4 | 0.42969(2) | 0.101(1) | 0.0073(1) | 0.0141(1) | 0.0080(1) | 0 | 0.0023(1) | 0 |
| Si(1) |  | 0.3426(1) | 3/4 | 0.03835(9) | 0.069(2) | 0.0060(3) | 0.0072(3) | 0.0073(3) | 0 | 0.0027(3) | 0 |
| Si(2) |  | 0.6854(1) | 1/4 | 0.27559(9) | 0.079(2) | 0,0069(3) | 0.0083(3) | 0.0094(4) | 0 | 0.0043(3) | 0 |
| Si(3) |  | 0,1930(1) | 3/4 | 0.32639(9) | 0.066(2) | 0,0050(3) | 0.0075(3) | 0.0074(3) | 0 | 0.0027(3) | 0 |
| *M*(1)** | 24.08(5) | 0 | 0 | 0 | 0.068(1) | 0,0057(2) | 0,0063(2) | 0,0084(2) | 0.0005(1) | 0.0029(2) | -0.0001(1) |
| *M*(2)& | 18,73(3) | 0 | 0 | 1/2 | 0 077(2) | 0.0060(3) | 0,0070(3) | 0,0093(3) | -0.0007(2) | 0.0023(2) | 0.0004(2) |
| *M*(3)** | 25,52(5) | 0.30699(6) | 1/4 | 0.21701(5) | 0.095(2) | 0.0058(2) | 0.0106(2) | 0.0100(2) | 0 | 0.0012(2) | 0 |
| O(1) |  | 0.2382(2) | 0.9863(3) | 0.0256(2) | 0.100(3) | 0.0088(6) | 0.0068(6) | 0.0160(7) | 0,0002(5) | 0.0068(5) | 0.0010(5) |
| O(2) |  | 0,3169(2) | 0.9691(3) | 0.3670(2) | 0.098(3) | 0,0082(6) | 0.097(6) | 0,0106(6) | 0.0003(5) | 0.0031(5) | -0,0017(5) |
| O(3) |  | 0.7955(2) | 0.0178(3) | 0.3304(2) | 0,125(3) | 0.0103(7) | 0,0077(6) | 0,0152(7) | -0.0012(5) | 0.0013(6) | 0.0004(5) |
| O(4) |  | 0.0627(3) | 1/4 | 0.1374(2) | 0,093(4) | 0.0075(9) | 0.0107(9) | 0.0079(9) | 0 | 0.0016(7) | 0 |
| O(5) |  | 0.0525(3) | 3/4 | 0.1558(3) | 0.101(4) | 0.0098(9) | 0.0109(9) | 0.0085(9) | 0 | 0.0030(7) | 0 |
| O(6) |  | 0,0742(2) | 3/4 | 0.4132(3) | 0.104(4) | 0,0098(9) | 0.0118(9) | 0,0130(1) | 0 | 0.0075(8) | 0 |
| O(7) |  | 0.5102(3) | 3/4 | 0.1814(3) | 0,123(4) | 0.0100(1) | 0,0150(1) | 0.0099(9) | 0 | 0.0020(8) | 0 |
| O(8) |  | 0.5445(3) | 1/4 | 0.3325(3) | 0,168(5) | 0.0080(1) | 0,032() | 0.012(1) | 0 | 0,0055(8) | 0 |
| O(9) |  | 0.6041(3) | 1/4 | 0.0977(3) | 0.144(4) | 0.015(1) | 0.020(1) | 0.0098(9) | 0 | 0,0064(8) | 0 |
| O(10) |  | 0,0937(3) | 1/4 | 0.4316(3) | 0.115(4) | 0.01(1) | 0.014(1) | 0.011(1) | 0 | 0.0054(8) | 0 |
| H |  | 0,083(8) | 1/4 | 0.358(7) | 0.05 |  |  |  |  |  |  |

* The scattering curve of Ce was used. ** The scattering curve of Fe was used. & Fe *versus* Al scattering curve used.

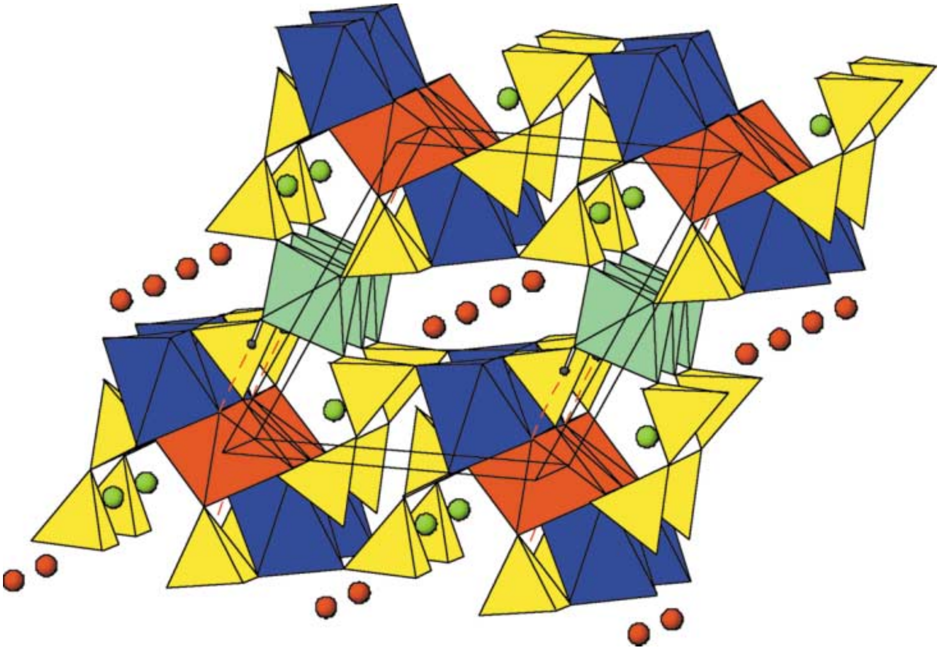

FIG. 2. Crystal structure of ferriallanite-(Ce) seen approximately along [010]. Red, green and blue octahedra represent around the *M*(1), *M*(2) and *M*(3) sites, respectively. The *A*(1), *A*(2) sites and the hydrogen atoms are represented by green, red and black circles. The $SiO_4$ tetrahedra are shown in yellow. The dashed red lines indicate the hydrogen bonds.

TABLE 4. X-RAY POWDER-DIFFRACTION DATA FOR FERRIALLANITE-(Ce)

| $I_{obs}$ | $I_{calc}$ | $d_{obs}$ | $d_{calc}$ | *hkl* | $I_{obs}$ | $I_{calc}$ | $d_{obs}$ | $d_{calc}$ | *hkl* |
|---|---|---|---|---|---|---|---|---|---|
| 20 | 22 | 9.30 | 9.23 | 001 | 15 | 12 | 2.31 | 2.301 | $\bar{3}04$ |
| 40 | 38 | 8.07 | 8,00 | $\bar{1}01$ | 100 | 13 | 2,18 | 2,224 | 122 |
| 20 | 17 | 5.15 | 5.12 | 101 |  | 9 |  | 2.212 | $\bar{1}23$ |
| 25 | 22 | 5.08 | 5.03 | $\bar{1}02$ |  | 27 |  | 2.186 | $\bar{4}01$ |
| 15 | 5 | 4.92 | 4.93 | 011 | 80 | 24 | 2.14 | 2.170 | 221 |
| 20 | 20 | 4.77 | 4.74 | 110 |  | 7 |  | 2.167 | $\bar{4}03$ |
| 15 | 18 | 4.59 | 4.61 | 002 |  | 25 |  | 2.151 | $\bar{2}23$ |
| 15 | 11 | 4.03 | 4,00 | $\bar{2}02$ |  | 7 |  | 2,145 | 014 |
| 35 | 10 | 3.58 | 3.62 | 012 | 40 | 16 | 2.10 | 2.117 | 023 |
| 55 | 60 | 3.55 | 3.55 | $\bar{2}11$ |  | 11 |  | 2.067 | 203 |
| 20 | 16 | 3.33 | 3.33 | 210 | 15 | 3 | 1.96 | 1.969 | $\bar{3}23$ |
| 35 | 14 | 3.26 | 3.24 | 201 | 20 | 21 | 1.90 | 1.904 | $\bar{2}24$ |
| 5 | 4 | 3.20 | 3.18 | $\bar{2}03$ | 10 | 8 | 1.86 | 1.888 | 312 |
| 40 | 31 | 2.94 | 2.94 | $\bar{3}02$ | 10 | 5 | 1.82 | 1.810 | 024 |
| 65 | 100 | 2.93 | 2.93 | $\bar{1}13$ | 10 | 10 | 1.75 | 1.777 | $\bar{4}22$ |
| 25 | 34 | 2,88 | 2.92 | 020 | 10 | 10 | 1.72 | 1.715 | $\bar{4}15$ |
| 20 | 14 | 2.85 | 2.84 | 211 | 10 | 5 | 1.69 | 1.695 | $\bar{2}06$ |
| 80 | 53 | 2.72 | 2.746 | 120 | 15 | 16 | 1,68 | 1,687 | $\bar{1}33$ |
|  | 40 |  | 2.721 | 013 | 10 | 28 | 1,64 | 1.650 | $\bar{4}24$ |
| 55 | 21 | 2.69 | 2.707 | 300 | 35 | 17 | 1.63 | 1.625 | $\bar{3}31$ |
| 10 | 6 | 2.65 | 2.667 | $\bar{3}03$ | 10 | 11 | 1.59 | 1.592 | $\bar{4}06$ |
| 60 | 61 | 2.63 | 2.638 | $\bar{3}11$ | 10 | 12 | 1.53 | 1.563 | 412 |
| 35 | 34 | 2,56 | 2.558 | 202 | 50 | 23 | 1,46 | 1.459 | 040 |
| 15 | 13 | 2.54 | 2.524 | $\bar{1}22$ | 15 | 8 | 1.42 | 1.419 | 215 |
| 10 | 6 | 2.51 | 2.516 | $\bar{1}04$ |  | 12 |  | 1.418 | 422 |
| 15 | 18 | 2.42 | 2.426 | $\bar{3}13$ | 10 | 3 | 1.37 | 1.362 | 502 |
| 55 | 21 | 2.34 | 2.358 | $\bar{2}22$ |  | 5 |  | 1.360 | 026 |

* Cu*K*α radiation, Guinier camera. Calculated values ($I_{calc}$ and $d_{calc}$) are taken from the single-crystal data.

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR FERRIALLANITE-(Ce)*

| | | | |
|---|---|---|---|
| *A*(1)-O(1) ×2 | 2.370(2) | *M*(3)-O(1) ×2 | 2.315(2) |
| *A*(1)-O(3) ×2 | 2.328(2) | *M*(3)-O(2) ×2 | 2.217(2) |
| *A*(1)-O(5) | 2.630(3) | *M*(3)-O(4) | 1.987(2) |
| *A*(1)-O(6) | 2.979(3) | *M*(3)-O(8) | 1.948(3) |
| *A*(1)-O(7) | 2,360(3) | < *M*(3)-O> | 2.117 |
| < *A*(1)-O> | 2.534 | | |
| | | Si(1)-O(1) ×2 | 1.641(2) |
| *A*(2)-O(2) ×2 | 2,492(2) | Si(1)-O(7) | 1.590(3) |
| *A*(2)-O(2)' ×2 | 2.613(2) | Si(1)-O(9) | 1.646(3) |
| *A*(2)-O(3) ×2 | 2.883(2) | <Si(1)-O> | 1.626 |
| *A*(2)-O(7) | 2,314(3) | | |
| *A*(2)-O(10) | 2.555(3) | Si(2)-O(3) ×2 | 1.630(2) |
| < *A*(2)-O> | 2.571 | Si(2)-O(8) | 1.597(3) |
| | | Si(2)-O(9) | 1.642(3) |
| | | <Si(2)-O> | 1.623 |
| *M*(1)-O(1) ×2 | 2.040(2) | | |
| *M*(1)-O(4) ×2 | 1.933(2)) | Si(3)-O(2) ×2 | 1.628(2) |
| *M*(1)-O(5) ×2 | 2.058(2) | Si(3)-O(5) | 1.659(3) |
| < *M*(1)-O> | 2.010 | Si(3)-O(6) | 1.646(2) |
| | | < Si(3)-O> | 1.644 |
| *M*(2)-O(3) ×2 | 1.917(2) | | |
| *M*(2)-O(6) ×2 | 1.962(2) | Si(1)-O(9)-Si(2) | 141.0(2) |
| *M*(2)-O(10) ×2 | 1.953(2) | | |
| < *M*(2)-O> | 1.964 | | |

* See text for additional distances at the sites *A*.

TABLE 6. CHARGE AT THE SITE ($C_{obs}$)[1] COMPARED WITH THE CALCULATED CHARGE-DISTRIBUTION (CD) AND BOND-VALENCE (BV) FOR FERRIALLANITE-(Ce)

| Site | $C_{obs}$ | CD | BV | ECoN* | Site | $C_{obs}$ | CD | BV |
|---|---|---|---|---|---|---|---|---|
| *A*(1) | 2.03 | 2.03 | 2.13 | 5.91 | O(1) | -2 | -1.94 | -1.94 |
| *A*(2) | 2.89 | 2.78 | 2.83 | 7.49 | O(2) | -2 | -2.07 | -1.93 |
| *M*(1) | 3.14 | 3.19 | 3.07 | 5.83 | O(3) | -2 | -2.04 | -2.04 |
| *M*(2) | 3 | 2.93 | 3.15 | 5.98 | O(4)[§] | -2 | -2.00 | -1.78[▲] |
| *M*(3) | 2 | 2.04 | 2.09 | 4.71 | O(5) | -2 | -1.96 | -1.97 |
| Si(1) | 4 | 4.06 | 3.93 | 3.97 | O(6) | -2 | -1.93 | -2.03 |
| Si(2) | 4 | 4.12 | 3.98 | 3.99 | O(7) | -2 | -2.10 | -2.02 |
| Si(3) | 3.93 | 3.93 | 3.81 | 3.99 | O(8) | -2 | -1.84 | -1.94 |
| H | 1 | 0.93 | 0.98 | 1.45 | O(9) | -2 | -1.89 | -2.09 |
| | | | | | OH** | -1 | -2,20 | -1.35[▲] |

[1] According to the assigned site-population (Table 7). * Effective coordination-number for cations (see text). ** OH = O(10), donor of the hydrogen bond; the neutron coordinates of Ferraris *et al.* (1989) were used for the calculation of CD (see text). [§] Acceptor of the hydrogen bond. [▲] Without the contribution of the H atom.

TABLE 7. SITE OCCUPANCY FOR FERRIALLANITE-(Ce) ON THE BASIS OF THE NUMBER OF REFINED ELECTRONS ($el_{ref}$) PER SITE

| Site | $el_{ref}$ | Site occupancy[£] | *$el_{exp}$ | Charge | [#]$L_{exp}$ | [§]$L_{obs}$ |
|---|---|---|---|---|---|---|
| *A*(1) | 21.33(14) | $Ca_{0.97}Ce_{0.03}$ | | 2.03 | 2.521 | 2.534 |
| *A*(2) | 53.67(17) | $Ce_{0.89}Ca_{0.11}$ | 71.42 | 2.89 | 2.540 | 2.571 |
| *M*(1) | 24.08(5) | $Fe^{3+}_{0.80}Ti^{4+}_{0.14}Al_{0.06}$ | | 3.14 | 1.957 | 2.010 |
| *M*(2) | 18.73(3) | $Al_{0.56}Fe^{3+}_{0.44}$ | | 3.00 | 1.942 | 1.964 |
| *M*(3) | 25.32(5) | $Fe^{2+}_{0.93}Mn_{0.07}$ | 69.32 | 2.00 | 2.014 | 2.117 |
| Si(3) | 14 (fixed) | $Si_{0.94}Al_{0.06}$ | 13.89 | 3.94 | 1.668 | 1.644 |

[£] The *REE* site is assumed to be populated by Ce only for purpose of site-occupancy refinement. * The number of electrons expected from the chemical analysis of the crystal used for the structure refinement (see text): cumulative values normalized to full occupancy are given for the sites *A* and *M*. [#] Expected site-oxygen bond lengths (Å) for the compositions shown according to the following ionic radii (Shannon 1976): O 1.40, Ca 1.12, Ce 1.143, $Fe^{3+}$ 0.55, $Fe^{2+}$ 0.61, Mn 0.67, $^{VI}Al$ 0.535, $^{IV}Al$ 0.39, Si 0.26 Å. [§] Observed average bond-lengths (Å) (Table 3).

## *Crystal chemistry*

The following features are crucial for the determination of the crystal-chemical formula of ferriallanite-(Ce).

1. The chemical composition (Table 1); in particular, the total amount of Fe must be distributed over three *M* sites.
2. For the refined number of electrons at the cation sites where mixed occupancy occurs (Tables 3, 7), most of the Al must stay in the *M*(2) site, *i.e.,* the poorest in electrons, as usually found for epidotes, in particular for allanite-(Ce) (Dollase 1971).
3. According to the results of Mössbauer spectroscopy (see also Dollase 1973), $Fe^{2+}$ occurs in only one octahedral site, which is distorted, and the amount of $Fe^{3+}$ is split between two octahedral sites. Neither of these two sites can coincide with that assigned to $Fe^{2+}$ (Table 7).
4. According to the values of the effective coordination-number (EcoN, Table 6; Hoppe 1979), *M*(3) is the most distorted octahedral site. This is a constant feature of the epidote-group structures and is related to the

absence of symmetry constraints on *M*(3), as discussed by Ferraris *et al.* (1989).

5. The small amount of tetrahedrally coordinated Al should reasonably be located in the larger (Table 5) and isolated Si(3)O$_4$ tetrahedron.

On the basis of the features listed above, the following crystal-chemical formula is assigned to the crystal of ferriallanite-(Ce) whose structure has been refined (all *REE* are ideally indicated as Ce): $(Ca_{0.97}Ce_{0.03})(Ce_{0.89}Ca_{0.11})(Fe^{3+}_{0.80}Ti^{4+}_{0.14}Al_{0.06})(Al_{0.56}Fe^{3+}_{0.44})(Fe^{2+}_{0.93}Mn_{0.07})(Si_{0.94}Al_{0.06}O_4)(Si_2O_7)O(OH)$. The ratio Ca/Ce, 1.17 in this formula, is constrained by the total number of electrons (75.00, Table 7) belonging to the two *A* sites according to the structure refinement. The value of this ratio differs from 1.39, obtained by chemical analysis. Owing to charge balance, this difference is reflected in the ratio $Fe^{3+}/(Fe^{2+} + Fe^{3+})$, which is 0.57 in the structural crystal-chemical formula, instead of 0.65 as in the analytical formula given above. However, the former value corresponds exactly to that indicated by the Mössbauer analysis. Reasonably, the difference is due to zoning and analytical errors, mainly involving *REE*, as mentioned above.

The partitioning of cations shown in the structural crystal-chemical formula has been checked by calculations of charge distribution (CD; Hoppe *et al.* 1989, Nespolo *et al.* 1999, 2001) and bond valence (BV; Brown & Wu 1976) in light of competing hypotheses, like the assignment of $Fe^{2+}$ to the site *M*(1) (Table 6). For a comparison with the values of the mean bond-lengths (Table 5), Table 7 also gives the values of the bond lengths to be expected for the mixed cations indicated according to the ionic radii published by Shannon (1976). To complete the number of positive charges in the structure, the position of the H atom obtained in the neutron-diffraction study of a sample of strontian piemontite by Ferraris *et al.* (1989) has been used for the CD calculation. In fact, the position obtained in the present study is too approximate, which is not unusual for X-ray-diffraction data. Of course, the position of H cannot be exactly the same in the two structures, and that may explain the high charge obtained for the OH group, O(10).

The assignment of $Fe^{2+}$ to *M*(3) is in accordance with the results published by Dollase (1973) for allanite-(Ce), where he also estimated a concentration of $Fe^{3+}$ higher in *M*(1) than in *M*(3), *i.e.,* the reverse of the normal distribution in epidote-group minerals. Actually, as mentioned above, in ferriallanite-(Ce) the concurrent high occurrence of $Fe^{2+}$, which occupies only one site, and $Fe^{3+}$, which partitions between two sites, excludes the presence of $Fe^{3+}$ in the same site as $Fe^{2+}$.

## CONCLUSIONS

The majority of allanite-subgroup minerals contain both $Fe^{2+}$ and $Fe^{3+}$; in general, these minerals have a composition $(Ca_{2-x}REE_x)(Al_{3-x-y}Fe^{2+}_xFe^{3+}_y)(SiO_4)(Si_2O_7)O(OH)$, where $0.50 < x \leq 1.00$ and $x + y < 2.49$. A preference of *y* around 0.3 is noted (Kepezhinskas & Khlestov 1971); the highest value of *y*, 0.84, is reported by Krivdik *et al.* (1989). The present description of ferriallanite-(Ce) shows that members with $y > 1$ and $Fe^{3+}$ dominant in the site *M*(1) occur, whereas Al still dominates in *M*(2). In an allanite-(Ce) – ferriallanite-(Ce) solid solution, ideally the end members have formula $CaCeFe^{2+}Al_2(SiO_4)(Si_2O_7)O(OH)$ [allanite-(Ce)] and $CaCeFe^{3+}AlFe^{2+}(SiO_4)(Si_2O_7)O(OH)$ [ferriallanite-(Ce)]. The composition poorest in Al reported in Table 1 corresponds to a *REE*-bearing member of the epidote group with ideal formula $CaCeFe^{2+}Fe^{3+}_2(SiO_4)(Si_2O_7)O(OH)$. However, insufficient material is available for a full characterization of this potentially new epidote.

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## REFERENCES

BONAZZI, P, MENCHETTI, S. & REINECKE, T. (1996): Solid solution between piemontite and androsite-(La), a new mineral of the epidote group from Andros Island, Greece. *Am. Mineral.* **81**, 735-742.

BROWN, I.D. & WU, KANG KUN (1976): Empirical parameters for calculating cation–oxygen bond valences. *Acta Crystallogr.* **B32**, 1957-1959.

CATTI, M., FERRARIS, G. & IVALDI, G. (1988): Thermal behavior of the crystal structure of strontian piemontite. *Am. Mineral.* **73**, 1370-1376.

________, ________ & ________ (1989): On the crystal chemistry of strontian piemontite with some remarks on the nomenclature of the epidote group. *Neues Jahrb. Mineral., Monatsh.*, 357-366.

COMODI, P. & ZANAZZI, P.F. (1997): The pressure behaviour of clinozoisite and zoisite: an X-ray diffraction study. *Am. Mineral.* **82**, 61-68.

DOLLASE, W.A. (1971): Refinement of the crystal structures of epidote, allanite and hancockite. *Am. Mineral.* **56**, 447-464.

________ (1973): Mössbauer spectra and iron distribution in the epidote-group minerals. *Z. Kristallogr.* **138**, 41-63.

FERRARIS, G., IVALDI, G., FUESS, H. & GREGSON, D. (1989): Manganese/iron distribution in a strontian piemontite by neutron diffraction. *Z. Kristallogr.* **187**, 145-151.

GREW. E.S., ESSENE, E.J., PEACOR, D.R., SU, SHU-CHUN & ASAMI, M. (1991): Dissakisite-(Ce), a new member of the epidote group and the Mg analogue of allanite-(Ce), from Antarctica. *Am. Mineral.* **76**, 1990-1997.

HINTZE, C. (1897): *Handbuch der Mineralogie* 2. Von Veit, Leipzig, Germany (259).

HOPPE, R. (1979): Effective coordination numbers (ECoN) and mean fictive ionic radii (MEFIR). *Z. Kristallogr.* **150**, 23-52.

________, VOIGT, S., GLAUM, H., KISSEL, J., MÜLLER, H.P. & BERNET, K. (1989): A new route to charge distributions in ionic solids. *J. Less-Common Metals* **156**, 105-122.

KEPEZHINSKAS, K.B. & KHLESTOV, V.V. (1971): *Statistical Analysis of Epidote Group Minerals and their Paragenetic Types*. Nauka, Moscow, Russia (in Russ., 310).

KRIVDIK, S.G., TKACHUK, V.I., MAXIMCHUK, I.G. & MICHNIK , T.L. (1989): Accessory orthite from alkaline rocks and carbonatites of the Ukrainian Shield. *Mineral. Zh.* **11**(1), 34-42 (in Russ.).

KVICK, Å., PLUTH, J.J., RICHARDSON, J.W., JR. & SMITH, J.V. (1988): The ferric ion distribution and hydrogen bonding in epidote: a neutron diffraction study at 15 K. *Acta Crystallogr.* **B44**, 351-355.

LEVINSON, A.A. (1966): A system of nomenclature for rare-earth minerals. *Am. Mineral*. **51**, 152-158.

NESPOLO, M., FERRARIS, G, IVALDI, G. & HOPPE, R. (2001): Charge distribution as a tool to investigate structural details. II. Extension to hydrogen bonds, distorted and hetero-ligand polyhedra. *Acta Crystallogr.* **B57**, 652-664.

________, ________ & OHASHI, H. (1999): Charge distribution as a tool to investigate structural details: meaning and application to pyroxenes. *Acta Crystallogr.* **B55**, 902-916.

PAUTOV, L.A., KHOROV, P.V., IGNATENKO, K.I., SOKOLOVA, E.V. & NADEZHINA, T.N. (1993): Christovite-(Ce) (Ca,*REE*)*REE*(Mg,Fe)AlMnSi$_3$O$_{11}$(OH)(F,O), a new mineral of the epidote group. *Zap. Vser. Mineral. Obshchest.* **122**(3), 103-111 (in Russ.).

PEACOR, D.R. & DUNN, P.J. (1988): Dollaseite-(Ce) (magnesium orthite redefined): structure refinement and inplications for F + M$^{2+}$ substitutions in epidote-group minerals. *Am. Mineral.* **73**, 838-842.

RAY, N.J., PUTNIS, A. & GILLET, P. (1986): Polytypic relationship between clinozoisite and zoisite. *Bull. Minéral.* **109**, 667-685.

SHANNON, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* **A32**, 751-767.

SHELDRICK, G.M. (1997): SHELX-97: program for the solution and refinement of crystal structures. Siemens Energy and Automation, Madison, Wisconsin.

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