Lucasite-(Ce), CeTi$_2$(O,OH)$_6$, a new mineral from Western Australia: Its description and structure

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Abstract

Lucasite-(Ce), Ce$_{0.51}$La$_{0.27}$Nd$_{0.11}$Pr$_{0.11}$Ti$_2$(O,OH)$_6$, has been found in a heavy-mineral concentrate derived from an olivine lamproite tuff at Argyle, in the east Kimberley region of Western Australia. It occurs as brown subhedral grains, 0.5 to 1 mm in diameter, and is associated with calcite, talc, titanite, dolomite, amphibole, and manganoan ilmenite. The mineral is translucent with a resinous luster and has a white streak, prominent {001} cleavage, and a conchoidal fracture. D_{calc} is 5.00 g/cm^3. It is optically biaxial with extremely high birefringence. Reflectivity values are 16.6% at 470 nm, 15.6% at 546 nm, 15.3% at 589 nm, and 15.0% at 650 nm. VHN$_{10}$ is 761–900. The symmetry is monoclinic, space group $I2/a$, with $a = 5.178(1)$, $b = 8.756(4)$, $c = 9.768(5)$ Å, $\beta = 93.52(4)°$, $Z = 4$. The strongest eight lines in the X-ray powder pattern are 3.376 (10) ($\bar{1}$12), 3.257 (6) (022), 3.203 (8) (112, $\bar{1}$21), 2.584 (7) (200), 2.541 (4) (130), 2.225 (5) (202, 220), 2.029 (4) ($\bar{2}$13), 1.8306 (6) ($\bar{2}$04).

The structure has been determined and refined to $R = 0.054$. It is related to the PbSb$_2$O$_6$-type structure, with ordering of Ce and Ti atoms in alternate {001} cation layers in a hexagonal closest-packed anion arrangement. The Ti-centered octahedra share edges to form gibbsite-like fused hexagonal rings. The Ce atoms are sandwiched between pairs of hexagonal rings and are displaced by 0.5 Å along [010] from the centers of octahedral sites to adopt eightfold coordination.

Introduction

Some olivine lamproites, occurring as diatremes in the east Kimberley region of Western Australia, are a commercial source of diamonds. One such body, known as the Argyle AK1, is currently being mined. During the examination of concentrates produced from this lamproite by a heavy-medium separating plant, grains of an unusual mineral were observed by Mr. Hans Lucas of CRA Exploration Pty. Ltd. These grains were submitted to one of the authors (E.H.N.) for identification, and subsequent investigation showed that they were a new mineral. In all, about fifty grains of this mineral have been found at time of writing. The identities of all the grains were established by means of qualitative energy-dispersive analyses in a scanning-electron microscope (SEM), and the compositions of three of them were determined quantitatively. The crystal-structure analysis was done on a fourth grain. The crystal structure of this mineral was subsequently determined (I.E.G. and I.C.M.). The mineral was named after Mr. Lucas, who discovered the mineral, and both mineral and name have been approved by the IMA Commission on New Minerals and Mineral Names. Type specimens have been deposited with the W.A. State Mineral Collection at the Government Chemical Laboratories in Perth, Western Australia, the Museum of Victoria in Melbourne, the Smithsonian Institution in Washington, and the British Museum (Natural History) in London.

Description of the occurrence

The Argyle AK1 diatreme is probably of Precambrian age and consists of a variety of olivine lamproite tuffs, volcaniclastic sedimentary rocks, and minor olivine lamproite dikes. Five main rock types have been distinguished: lapilli ash tuff, coarse ash tuff, fine ash tuff, nonsandy tuff, and olivine lamproite dikes (Atkinson et al., 1984). Lucasite-(Ce) has been recovered from the nonsandy tuff. This is a pyroclastic rock consisting of fine-grained, commonly vesicular, altered juvenile clasts set in a matrix of broken, altered olivine crystals and fine clay or micaceous minerals, and locally veined by calcite.

Heavy-mineral concentrates from the nonsandy tuff typically contain anatase, barite, calcite, almandine, chromian pyrope, chromite, chromian diopside, orthopyroxene, manganoan ilmenite, diamond, and lucasite-(Ce). The new mineral occurs within the concentrates as discrete grains and as aggregates within calcite, talc, titanite, and manganoan ilmenite. Inclusions within grains of lucasite-(Ce) include calcite, dolomite, titanite, talc, and amphibole.

TABLE 1. Chemical composition of lucasite-(Ce)

	Electron-microprobe analysis (wt%)*		Atomic proportions**	
Ce₂O₃	24.99	Ce	0.508	
La₂O₃	13.12	La	0.268	1.004
Nd₂O₃	5.90	Nd	0.117	
Pr₂O₃	5.50	Pr	0.111	
CaO	0.62		—	
TiO₂	47.93	Ti	2.000	
MgO	0.03		—	
SiO₂	0.25		—	
Al₂O₃	0.04		—	
Total	98.38			

* Average of eight analyses.
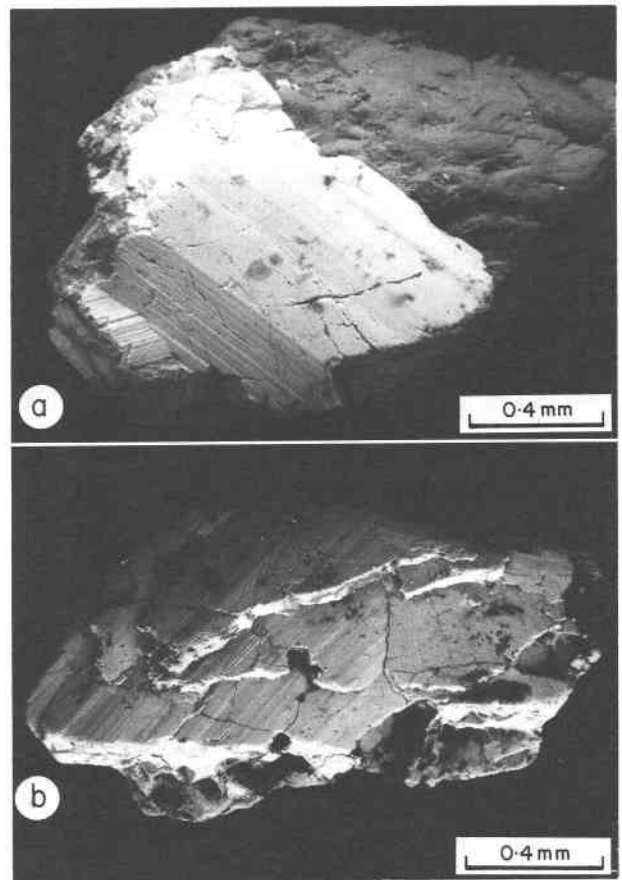** Small amounts of Al, Mg, Si, and Ca not considered.

Fig. 1. Scanning-electron micrographs of crystals of lucasite-(Ce). (a) Euhedral crystal showing {001} and {101} faces (the dark substrate is calcite); (b) subhedral crystal fragment showing cleavage or parting surfaces parallel to {001}. The striations are parallel to b.

PHYSICAL AND OPTICAL PROPERTIES

Lucasite-(Ce) recovered from the heavy-mineral concentrates occurs as grains varying from about 0.5 to 1 mm in diameter and generally consists of subhedral crystal fragments and crystal aggregates. One of the rare euhedral crystals is shown in Figure 1a; the principal crystal faces are {001} and {101} and are heavily striated parallel to b. The mineral exhibits a cleavage or parting parallel to {001}, and the cleavage or parting surfaces are also heavily striated parallel to b (Fig. 1b).

The mineral is translucent, with a resinous luster. Its color varies from light to dark brown and through shades of gray; the most common color is chocolate brown. The streak is white. In transmitted light, lucasite-(Ce) is brown and lacks pleochroism. It is optically biaxial with high 2V and has extremely high birefringence. The refractive indices of lucasite-(Ce) are substantially higher than 2.0, the liquid with highest refractive index available to us. A Gladstone-Dale calculation gave a mean refractive index of 2.321.

In reflected light, the mineral is gray with abundant brown internal reflections and is weakly anisotropic. Reflectivity values, using a Zeiss WTiC standard, are 16.6% at 470 nm, 15.6% at 546 nm, 15.3% at 589 nm, and 15.0% at 650 nm.

Lucasite-(Ce) is brittle, with a conchoidal fracture and prominent {001} cleavage or parting. Hardness determinations made with a diamond indentor and a 10-g load gave a range from VHN 761 to VHN 900, and an average of 824 kg/mm². Density could not be determined because of the fine grain size, but the density calculated from composition and unit-cell parameters is 5.00 g/cm³.

CHEMICAL COMPOSITION

A polished section of lucasite-(Ce) was analyzed by using a MAC model 400S electron microprobe with crystal spectrometers and the following standards: synthetic silicate glasses (La, Pr, Nd), apatite (Ca), quartz (Si), alumina (Al), magnesia (Mg), and Ti metal (Ti). The data were corrected by means of the MAGIC IV computer program (Colby, 1971). An additional correction was made to the Pr value according to the procedure recommended by Roeder (1985) because of partial overlap between the $PrL\alpha_1$ and $LaL\beta_1$ peaks. The analytical results and the atomic proportions derived therefrom are given in Table 1. The analytical total of 98.38% is somewhat low and can be ascribed to the possible presence of a minor amount of water. In support of this assumption, valence-bond calculations (see next section) indicate the likelihood of some $(OH)^-$ substituting for oxygen. The possibility of some F substitution cannot be ruled out, as this element could not be analyzed for by our microprobe system. The chemical formula, therefore, normalized to 2 Ti is $Ce_{0.51}La_{0.27}Nd_{0.11}Pr_{0.11}Ti_2(O,OH)_6$, or ideally, $CeTi_2(O,OH)_6$.

The crystals appear to be homogeneous, as no compositional zoning is evident in backscattered-electron SEM images, and microprobe analyses of different spots in each of three crystals agree with each other within the errors of measurement. Inclusions of titanite are common, and a few inclusions of what appears to be bastnäsite-(Ce) were also observed.

TABLE 2. X-ray powder-diffraction pattern of lucasite-(Ce)

I_{est}	d_{meas} (Å)	d_{calc} (Å)	hkl
3	6.49	6.514	011
3	4.449	4.450	110
10	3.376	3.378	$\overline{1}12$
6	3.257	3.257	022
8	3.203	3.201	112
		3.200	$\overline{1}21$
1	3.122	3.121	121
1	3.048	3.046	013
7	2.584	2.584	200
4	2.541	2.542	130
5	2.225	2.226	202
		2.225	220
2	2.066	2.067	$\overline{2}22$
4	2.029	2.030	$\overline{2}13$
1	1.915	1.916	213
		1.915	231
1	1.882	1.882	$\overline{2}31$
6	1.8306	1.8306	$\overline{2}04$
2	1.7320	1.7325	134
		1.7321	$\overline{1}43$
1	1.7270	1.724	051
		1.720	204
2	1.5964	1.5965	$\overline{3}21$
1	1.4839	1.4834	330

Note: Guinier camera; CuKα radiation; ThO$_2$ internal standard.

CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE

Precession and Weissenberg studies showed that lucasite-(Ce) is monoclinic, with possible space groups Cc or $C2/c$. The corresponding centrosymmetric I-centered space group, $I2/a$, was chosen because the monoclinic angle is closer to 90°. Unit-cell parameters were refined from the 2θ values of diffraction lines measured from a Guinier powder pattern (CuKα$_1$ radiation, ThO$_2$ internal standard). They are as follows: $a = 5.178(1)$, $b = 8.756(4)$, $c = 9.768(5)$ Å, $\beta = 93.52(4)°$. The powder pattern is given in Table 2.

Data collection and structure refinement

For the intensity-data collection, a platy crystal measuring $0.14 \times 0.20 \times 0.08$ mm was mounted about b (approximately perpendicular to platelet) on a Siemens AED 3-circle diffractometer. Cell dimensions were refined using the 2θ values for 11 centered reflections with $32 < 2\theta < 46°$ (MoKα radiation, $\lambda = 0.71069$). A total of 2023 intensities for reflections ($\pm h$, k, $\pm l$) was collected to a maximum 2θ value of 70°, using the θ–2θ scan mode with

scan width ($2.4° + \Delta2\theta$), where $\Delta2\theta = (180/\pi)\ [\Delta\lambda/(d\cos\theta)]$ allows for α_1/α_2 separation, and a scan speed of $0.07°$ s^{-1}. The backgrounds were counted for 20 s on each side of each reflection. A standard reflection, measured every 2 h, showed less than 1.5% variation in intensity. After correcting for absorption ($\mu_l = 138$ cm^{-1}; transmission factors between 0.15 and 0.34), reduction and averaging of the intensities gave 977 unique reflections with agreement between equivalent reflections, $R_{int} = 0.05$.

A model for the Ce and Ti atoms, in $I2/a$, was established from the three-dimensional Patterson map; the oxygen atoms were located in subsequent difference-Fourier maps. Refinement of all positional and anisotropic thermal parameters converged to an R value of 0.054 (all unique reflections, unit weights). The only features in the final difference-Fourier map were two peaks at ~1 e Å^{-3} near the Ce atom. The final refinement involved 42 independent parameters and the largest shift/error was 0.07. Final atomic position and thermal vibration parameters are given in Table 3. Selected interatomic distances and angles are reported in Table 4. Tables of observed and calculated structure factors have been deposited.[1]

Scattering factors for neutral atoms and anomalous dispersion coefficients were taken from *International Tables for X-ray Crystallography* (1974). The scattering curve for Ce was used for the combined rare-earth elements. All computing was performed with the SHELX-76 system of programs (Sheldrick, 1976).

Description of structure

A polyhedral representation of the structure is shown in Figure 2. It is based on a hexagonal stacking of (001) layers of closest-packed anions (hcp). Ti atoms occupy two-thirds of the octahedral sites in alternate (001) cation layers. The Ti-centered octahedra share edges to form gibbsite-like fused hexagonal rings. The Ce atoms are sandwiched between pairs of hexagonal rings. If the Ce atoms occupied the centers of the octahedral sites, the structure of lucasite-(Ce) would be isostructural with that of PbSb$_2$O$_6$ (Magneli, 1941). However, the Ce atoms are displaced by about 0.5 Å along [010] from the octahedral

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[1] To obtain copies of observed and calculated structure factors, order Document AM-87-349 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit $5.00 in advance for the microfiche.

TABLE 3. Structural parameters for lucasite-(Ce)

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12} (Å²)
Ce	4e	¼	0.1894 (1)	0	0.0111 (3)	0.0160 (3)	0.0119 (3)	0	0.0011 (2)	0
Ti	8f	0.2187 (3)	0.9154 (2)	0.2651 (2)	0.0122 (6)	0.0101 (6)	0.0163 (7)	0.0014 (5)	0.0006 (5)	0.0003 (5)
O(1)	8f	0.6007 (13)	0.2541 (8)	0.1411 (7)	0.016 (3)	0.011 (3)	0.016 (3)	0.000 (2)	0.000 (2)	0.001 (2)
O(2)	8f	0.4083 (13)	0.0799 (8)	0.3692 (8)	0.014 (3)	0.011 (3)	0.022 (3)	−0.006 (2)	0.008 (2)	−0.003 (2)
O(3)	8f	0.9976 (13)	0.0450 (8)	0.1402 (7)	0.012 (2)	0.017 (3)	0.014 (3)	0.002 (2)	0.003 (2)	0.006 (2)

Note: esd's in parentheses.

TABLE 4. Interatomic distances (Å) and angles (°) in lucasite-(Ce)

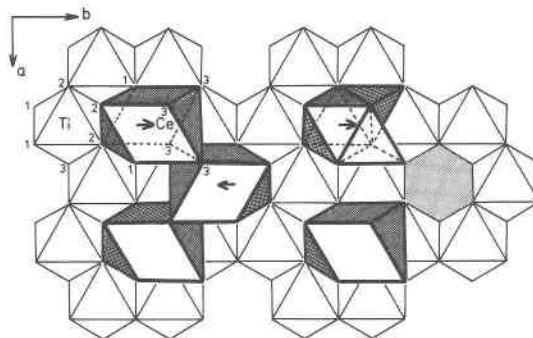|				O–M–O
Ti–O(1)	1.898 (7)	O(1)–O(2)	2.85 (1)	99.3 (3)
–O(2)	1.954 (7)	–O(3)	2.84 (1)	94.1 (3)
–O(3)	1.977 (7)	–O(2)	2.92 (1)	94.5 (3)
–O(3)	1.979 (7)	–O(1)'	2.55 (1)	82.1 (3)
–O(2)	1.987 (7)	O(2)–O(3)	2.56 (1)	81.1 (3)
–O(1)	1.988 (7)	–O(2)'	2.943 (7)	96.6 (3)
		–O(1)	2.94 (1)	95.8 (3)
		O(3)–O(3)'	2.706 (4)	86.3 (3)
		–O(2)	2.56 (7)	80.3 (3)
		–O(1)	2.67 (1)	87.9 (3)
		–O(2)	3.01 (1)	98.6 (3)
		–O(1)	2.75 (1)	84.7 (3)
Ce–O(1) × 2	2.283 (7)	Ti–Ti'	2.931 (4)	
–O(3) × 2	2.324 (7)	–Ti"	2.983 (2)	
–O(2) × 2	2.552 (7)	Ti–Ce	3.541 (2)	
–O(3) × 2	2.741 (7)	–Ce	3.559 (2)	

Fig. 2. Polyhedral representation of the structure of lucasite-(Ce) viewed along [001]. Oxygens are numbered as in Table 3. The representation of the Ce-centered polyhedron as the fusion of an octahedron and two tetrahedra is shown in the upper-right polyhedron. One polyhedron is omitted to show the underlying hexagonal ring of edge-shared TiO_6 octahedra. The displacement of the Ce atoms from the octahedral centers is shown by the arrows.

centers toward an octahedral edge such that they form bonds to two additional oxygens. Within the context of a hcp structure, the eightfold Ce coordination can be described as the fusion of an octahedron with two adjacent tetrahedra. This polyhedron is closely related to a bisdisphenoid, as shown by Nyman et al. (1984). The eight Ce–O distances fall into two groups, comprising four short distances, 2.28–2.32, and four longer distances, 2.55–2.74, typical of bisdisphenoid coordination. In successive (001) layers of Ce atoms, the [010] displacements are in opposite directions, resulting in a doubling of the c axis relative to that of $PbSb_2O_6$.

The mean Ce–O bond length of 2.47 Å is intermediate between mean values reported for Ce^{3+} and Ce^{4+} in a range of sulphate compounds (Gatehouse and Pring, 1981). The average Ti–O bond length of 1.96 Å compares with the mean Ti–O bond length of 1.96 Å for the TiO_2 polymorphs, rutile, brookite, and anatase. The O(1)–O(1) and O(2)–O(3) lengths, both 2.55 Å, show the shortening typical of shared edges.

Empirical bond valences have been calculated using the parameters of Brown and Wu (1976) and are listed in Table 5. The valence sum at the Ti atom site corresponds closely to Ti^{4+}, whereas that for the Ce site indicates a mixture of trivalent and tetravalent rare-earth elements. Similar results were obtained when the parameters reported by Zachariasen (1978) were used. Both Ce and Pr form tetravalent oxides, and the valence sums in Table 5 suggest that these cations are tetravalent in lucasite-(Ce). The La must be trivalent, and so some hydroxyl is required for charge balance. The valence sums at the anion

sites show that the hydroxyls occur at the undersaturated site O(2). Neither O(1) nor O(3) show low valence sums, and so the proton must also be hydrogen bonded to O(2). This is possible as three O(2) ions form a face of a tetrahedral cavity in the Ce layer, as shown in Figure 2.

DISCUSSION

Lucasite does not have any exact mineral analogues. Its composition is very similar to that of aeschynite-(Ce), which also has the chemical formula $CeTi_2(O,OH)_6$. However, the structures of the two minerals are quite different. In lucasite-(Ce), the TiO_6 octahedra share edges to form hexagonal rings. In aeschynite-(Ce), pairs of octahedra are joined by edge-sharing, and each pair is joined to six other pairs by sharing corners to form a three-dimensional network (Aleksandrov, 1962).

The structure of lucasite-(Ce) shows some similarity to that of gibbsite, $Al(OH)_3$, the unit-cell parameters of which ($a = 8.68$, $b = 5.07$, $c = 9.72$ Å, $\beta = 94.6°$) are similar to those of lucasite-(Ce). In both lucasite-(Ce) and gibbsite, the anions are in hexagonal close packing, and the octahedra share edges to form hexagonal rings. However, in lucasite-(Ce), additional structural sites are occupied by Ce.

TABLE 5. Empirical bond-valence (v.u.) table for lucasite-(Ce)

	O(1)	O(2)	O(3)	Σ
Ti	0.77 0.61	0.67 0.61	0.63 0.63	3.92
Ce*	0.70 (×2→)	0.34 (×2→)	0.62 (×2→) 0.21 (×2→)	3.74
Σ	2.08	1.62	2.09	

* Arrows indicate that two of each oxygen type contribute to the valence sums at the cation sites.

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