The crystal structure of lanthanite

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Abstract

The crystal structure of lanthanite, $(La,Ce)_2(CO_3)_3 \cdot 8H_2O$, $a=9.504(4)$, $b=16.943(6)$, $c=8.937(5)$ Å; space group *Pbnb*, $Z=4$, has been determined by Patterson and Fourier methods using 1022 intensities measured with an automatic diffractometer. The hydrogen atoms belonging to three of the four independent water molecules have been located in the difference Fourier map. The least-squares refinement led to a final R index of 0.025. The principal structural feature of lanthanite consists of infinite layers of RE–O coordination polyhedra and CO_3^{2-} groups. These layers are parallel to the *ac* plane and are connected to one another only by hydrogen bonds. This feature accounts for the micaceous {010} cleavage.

Introduction

Lanthanite is a hydrated carbonate of lanthanum and cerium, originally found coating cerite at the Bastnäs mine, Västmanland, Sweden. A sample of lanthanite from this locality was kindly provided by the Smithsonian Institution, Washington, D. C. (NM NH B10530) through John S. White, Jr., of the Department of Mineral Sciences.

Experimental

The lattice parameters were determined at room temperature with a Philips PW 1100 single crystal automatic diffractometer. They are: $a=9.504(4)$, $b=16.943(6)$, $c=8.937(5)$ Å, $V=1439.1$ Å³, $Z=4$; space group *Pbnb*; specific gravity, calculated for formula $LaCe(CO_3)_3 \cdot 8H_2O$, is 2.78. The X-ray diffraction data were collected from a small fragment (dimensions: $0.13 \times 0.11 \times 0.05$ mm) using $MoK\alpha$ radiation monochromatized by a flat graphite crystal. A unique set of intensities was collected up to $2\theta = 60°$ by the $\theta-2\theta$ scan mode with a symmetrical scan range of $1.5°$ 2θ from the calculated scattering angles and a scan rate of $0.05°$/sec. Three standard reflections monitored at three-hour intervals show no variation greater than 4 percent. Processing of the data was carried out as described by Davies and Gatehouse (1973) to yield the values of F_O and σF_O. Of the 2104 measured reflections, 1022 were found to have $I > \sigma I$ and were used in the calculations; the remaining 1082 were discarded because they did not fulfil the condition $I_{pk} - 2\sqrt{I_{pk}} > I_{bkg}$. It must be noted that the reflections with $k=2n+1$ were very weak because the heavy cations and some light atoms do not contribute to their structure factors (see Table 1). Owing to the small crystal size no absorption correction was applied.

Crystal structure analysis

The coordinates of the heavy atoms RE(1) and RE(2) were obtained from a three-dimensional Patterson synthesis. A subsequent electron density map computed with the phases given by the heavy cations revealed all the remaining non-hydrogen atoms. The isotropic least-squares refinement, carried out on the structure amplitudes with the program ORFLS (Busing *et al.*, 1962), reduced the conventional R index from 0.085 to 0.047. Three successive anisotropic cycles lowered the R index to 0.026. At this stage a difference Fourier synthesis showed several maxima, six of which were assigned, on the basis of bond lengths and angles, to the hydrogen atoms belonging to the three water molecules $W(1)$, $W(2)$, and $W(3)$. It has not been possible to locate the hydrogen belonging to the water molecule $W(4)$. The positional parameters of the hydrogen atoms, refined isotropically in one least-squares cycle, were held fixed in the last cycles at the difference Fourier values as the atomic shifts were physically meaningless. The refinement was stopped when the atomic shifts were less than the estimated standard deviations. The final R index was 0.025 for the 1022 observed reflections.

The scattering curves of the atoms RE(1) and

TABLE 1. Atomic coordinates and equivalent isotropic factors of lanthanite*

Atom	x/a	y/b	z/c	$B_H(Å^2)$
RE(1)	0.25	0.25037(2)	0.75	0.84
RE(2)	0.25	0.28122(2)	0.25	0.79
O(1)	0.25	0.0340(4)	0.25	5.44
O(2)	0.3423(4)	0.1469(2)	0.3232(4)	1.40
O(3)	0.5072(4)	0.7948(2)	0.1875(4)	1.56
O(4)	0.6164(4)	0.7620(3)	0.9791(5)	1.72
O(5)	0.3845(4)	0.7919(3)	0.9770(5)	1.66
W(1)	0.1478(6)	0.4059(3)	0.3781(5)	2.61
W(2)	0.6773(5)	0.3784(3)	0.1140(5)	2.16
W(3)	0.8837(4)	0.1209(2)	0.1844(5)	1.88
W(4)	0.6089(8)	0.4957(4)	0.3874(9)	5.31
C(1)	0.25	0.1066(4)	0.25	1.82
C(2)	0.4975(6)	0.7165(3)	0.5428(6)	1.23
H(11)	0.686(8)	0.044(5)	0.653(8)	6.49
H(12)	0.641(8)	0.096(4)	0.512(9)	6.06
H(21)	0.334(8)	0.134(4)	0.506(9)	4.04
H(22)	0.252(12)	0.081(4)	0.618(8)	8.09
H(31)	0.379(7)	0.423(4)	0.745(12)	4.55
H(32)	0.515(9)	0.134(4)	0.324(8)	5.54

*Standard deviations in parentheses; equivalent isotropic temperature factors after Hamilton (1959).

RE(2) have been computed taking into account the chemical analysis assuming that La and Ce were disordered over the two sites. The scattering curves of Hanson et al. (1964) were used. The population parameters of RE(1) and RE(2) and those of the water molecules were allowed to vary during the isotropic refinement, but they did not show any change greater than one standard deviation. The final atomic parameters are given in Tables 1 and 2; bond distances and angles are listed in Table 3. The observed and calculated structure factors are compared in Table 4.[1]

Description and discussion of the structure

The principal structural feature of lanthanite consists of infinite layers of RE–O coordination polyhedra. These layers are parallel to the *ac* plane (Fig. 1) and are connected to one another only by hydrogen bonds (Fig. 2): this fact accounts for the micaceous {010} cleavage. The two independent RE atoms have a ten-fold coordination: RE(1) is sur-

TABLE 2. Anisotropic thermal parameters for lanthanite*

Atom	r.m.s.	$U_i a$	$U_i b$	$U_i c$	Atom	r.m.s.	$U_i a$	$U_i b$	$U_i c$
RE(1)	0.079(2)	161	90	71	W(1)	0.131(8)	76	104	159
	0.099(2)	71	90	18		0.160(7)	76	17	101
	0.126(1)	90	180	90		0.237(7)	160	80	107
RE(2)	0.079(1)	173	90	84	W(2)	0.123(8)	87	93	175
	0.101(1)	83	90	6		0.173(7)	90	3	93
	0.116(1)	90	180	90		0.192(7)	177	90	93
O(1)	0.147(11)	90	180	90	W(3)	0.119(8)	166	89	76
	0.200(15)	50	90	39		0.157(7)	88	7	83
	0.381(15)	140	90	51		0.181(6)	103	83	165
O(2)	0.116(8)	112	103	153	W(4)	0.166(11)	70	149	67
	0.133(7)	32	72	115		0.227(10)	42	90	132
	0.148(7)	67	157	85		0.350(10)	125	121	129
O(3)	0.108(9)	137	104	129	C(1)	0.117(14)	90	180	90
	0.127(8)	47	108	132		0.142(24)	57	90	32
	0.177(7)	91	156	66		0.188(23)	147	90	57
O(4)	0.112(8)	154	72	72	C(2)	0.115(10)	150	78	63
	0.135(9)	68	82	22		0.123(10)	64	98	27
	0.186(7)	103	161	77		0.135(12)	104	165	92
O(5)	0.091(10)	140	96	129					
	0.146(8)	127	99	39					
	0.182(7)	79	168	94					

* Root mean square thermal vibrations along the ellipsoid axes (Å) and angles (°) between the crystallographic axes and the principal axes (U_i) of the vibration ellipsoid.

rounded by six oxygen atoms belonging to the carbonate groups and by four water molecules; RE(2) is bonded to eight carbonate oxygens and two water molecules (Table 3). The corresponding coordination polyhedra are similar and cannot be described in terms of regular geometric solids. Their shape can be approximately described as that of distorted Archimedean antiprisms whose square faces are replaced by pyramids (Fig. 3). The oxygen atoms O(4) are at the apices of the pyramids. These polyhedra are linked parallel to the c axis by sharing the O(4)–O(5) edges and along the a direction by sharing the O(3) corners to form the infinite layers parallel to the ac plane. Each O(1) atom of one layer is bonded to two $W(1)$ water molecules of the adjacent layer; the $W(4)$ water molecules act as bridges between two layers being bonded to $W(3)$ and $W(2)$ water molecules. Besides the hydrogen bonds which connect adjacent layers, hydrogen bonds are also present within each layer (Table 3). The water molecule $W(4)$ has an approach of 2.891 Å to a $W(4)$ related by a center of symmetry. This could mean that there is a disordered $W(4)-\frac{1}{2}H-\frac{1}{2}H-W(4)$ bond.

The bond distances and angles within the two inde-

TABLE 3.   Interatomic distances (Å) and angle (°) in lanthanite

RE(1)–O(3)	2.495(4)	x2	RE(2)–O(4)	2.518(4)	x2
RE(1)–O(5)	2.499(4)	x2	RE(2)–O(3)	2.518(4)	x2
RE(1)–W(3)	2.591(4)	x2	RE(2)–O(2)	2.525(4)	x2
RE(1)–W(2)	2.592(5)	x2	RE(2)–W(1)	2.591(5)	x2
RE(1)–O(4)	2.742(4)	x2	RE(2)–O(5)	2.760(4)	x2
Mean value	2.584		Mean value	2.582	
C(1)–O(1)	1.232(9)		C(2)–O(5)	1.274(7)	
C(1)–O(2)	1.290(5)	x2	C(2)–O(4)	1.277(7)	
			C(2)–O(3)	1.309(6)	
Mean value	1.271		Mean value	1.287	
O(1)–C(1)–O(2)	121.9(3)	x2	O(3)–C(2)–O(4)	117.0(5)	
O(2)–C(1)–O(2)	116.1(6)		O(3)–C(2)–O(5)	118.0(5)	
			O(4)–C(2)–O(5)	125.0(5)	

Atoms		O—O	O—H	H—O
W(1)——H(11)---O(1)		2.639(7)	0.97(8)	1.69(8)
W(1)——H(12)---W(3)		2.791(7)	0.98(8)	1.83(8)
W(2)——H(21)---O(2)		2.640(6)	1.00(8)	1.65(8)
W(2)——H(22)---W(4)		2.842(8)	0.96(7)	1.89(9)
W(3)——H(31)---W(4)		2.792(8)	0.97(9)	1.82(9)
W(3)——H(32)---O(2)		2.641(6)	0.99(8)	1.66(8)

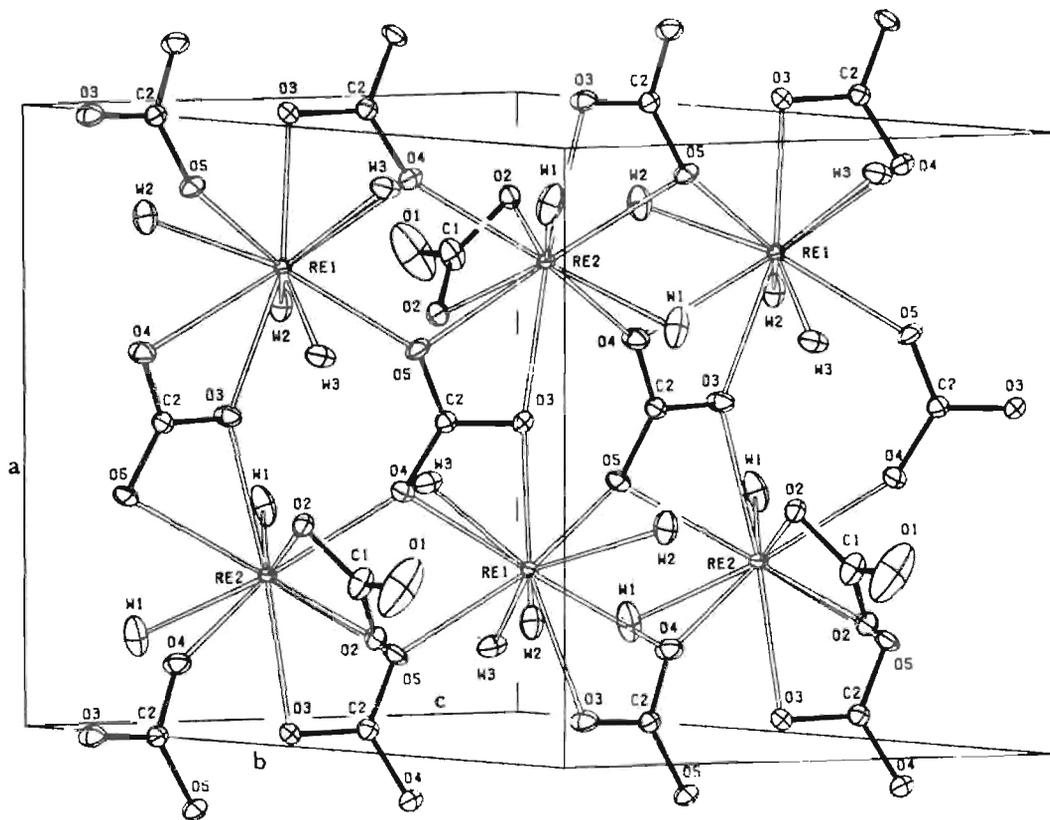| H(11)–W(1)–H(12)	109	W(1)–H(11)–O(1)	166
H(21)–W(2)–H(22)	105	W(1)–H(12)–W(3)	167
H(31)–W(3)–H(32)	106	W(2)–H(21)–O(2)	174
		W(2)–H(22)–W(4)	176
All ± 5°		W(3)–H(31)–W(4)	174
		W(3)–H(32)–O(2)	173

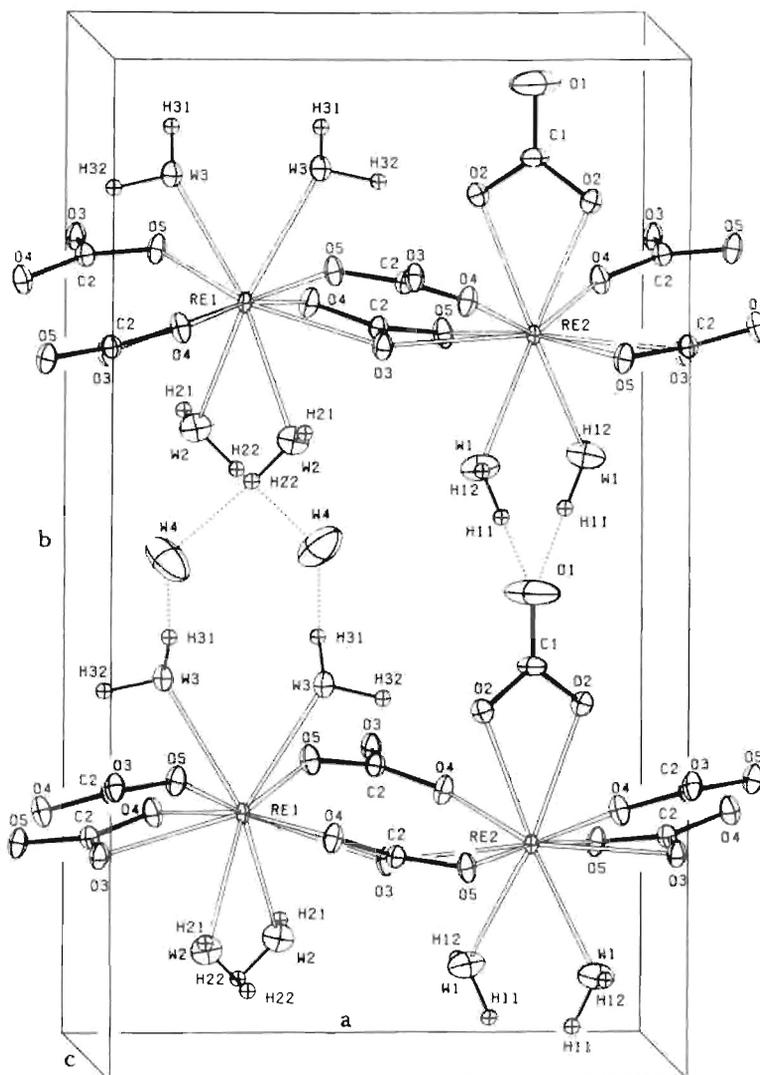FIG. 1.   ORTEP (Johnson 1965) plot of the crystal structure of lanthanite.

FIG. 2. ORTEP plot of the crystal structure of lanthanite showing the connection among adjacent layers of RE-O polyhedra.

pendent carbonate groups deserve some comment. In the C(1)-O_3 triangle the C(1)-O(1) bond length (1.23 Å) is remarkably shorter than the average C-O distance (1.28 Å). It must be pointed out that O(1) is not bonded to RE, but it is only involved in hydrogen bonds with W(1). The C(1)-O bond lengths calculated following the method suggested by Baur (1970), C(1)-O(1)=1.237 Å and C(1)-O(2)=1.288 Å, are in good agreement with those given in Table 4. The distortions in C(2)-O_3 groups are smaller and, also in this case, correlated with the environment of the oxygen atoms. The long C(2)-O(3) distance (1.309 Å) is possibly related to the fact that O(3) is the only

oxygen atom in that carbonate groups which has two short contacts to RE. The O(4)-C(2)-O(5) angle (125°) is notably larger than the expected value of 120°: O(4) and O(5), which form one side of the C(2)-O_3 triangle, are bonded to two different RE atoms. On the other hand, the sides of the triangle formed by the oxygen atoms bonded to the same RE cation subtend O-C-O angles smaller than 120°.

The deviation of the C(2) atom from the plane passing through the oxygens O(3), O(4), and O(5) is −0.017 Å (e.s.d. 0.007 Å). No deviation can be observed in the C(1)-O_3 triangle because C(1) and O(1) occur on a diad axis.
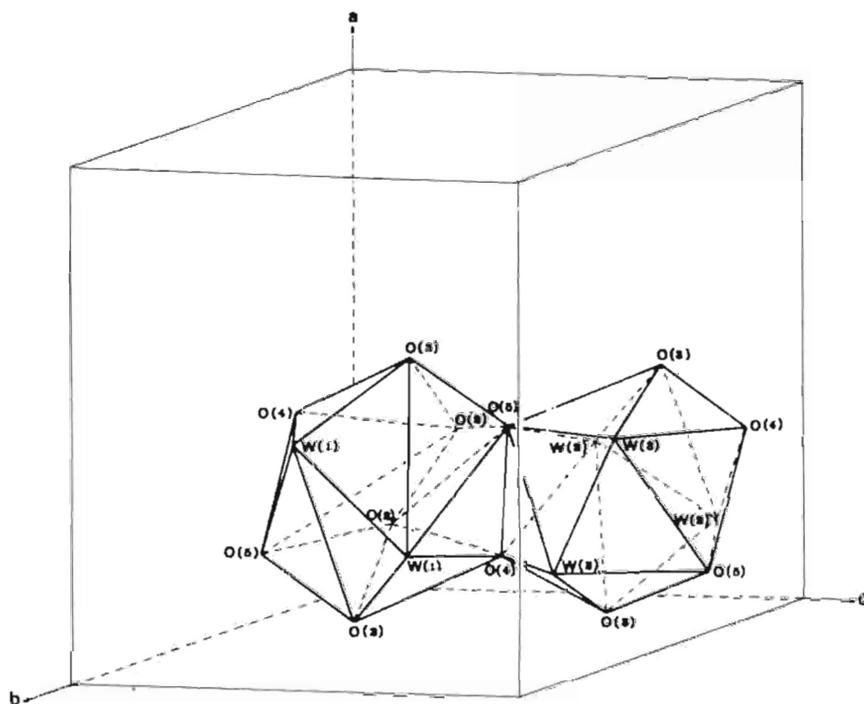
FIG. 3.   The coordination polyhedra of RE(1) and RE(2) atoms.

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