Lanthanite-(Ce), $(Ce,La,Nd)_2(CO_3)_3 \cdot 8H_2O$, a new mineral from Wales, U.K.

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Abstract

Lanthanite-(Ce) occurs as a secondary mineral in oxidized copper ore at the Britannia Mine, Snowdonia, North Wales, U.K. It is found as colorless transparent plates {010} covered by radiating tufts of malachite and is associated with brochantite, posnjakite and chalcoalumite. The analytical formula, based on 17 oxygens, is $(Ce_{0.78}La_{0.55}Nd_{0.55}Sm_{0.09}Gd_{0.05}Y_{0.04})_{\Sigma 2.06}C_{2.97}O_{9.03} \cdot 7.96H_2O$, and the theoretical formula is $(Ce,La,Nd)_2(CO_3)_3 \cdot 8H_2O$ with $Ce > La,Nd$. Orthorhombic, space group *Pbnb*, $a = 9.482(6)$, $b = 16.938(11)$, $c = 8.965(3)$Å, $Z = 4$, D(calc.) = 2.79 g/cm³ for the ideal formula (Ce:La:Nd = 0.83:0.59:0.58), D (meas.) = 2.76 g/cm³, $V = 1440$Å³, $a:b:c = 0.5598:1:0.5293$. Strongest lines in the X-ray powder diffraction pattern are [dÅ (I) (hkl)] 8.47(100)(020), 4.746(65)(200), 4.462(62)(002), 3.255(73)(202) and 3.028(65)(222). The mineral is biaxial negative, α 1.532(2), β 1.594(2), γ 1.616(2); orientation $X = b$, $Y = c$, $Z = a$; 2V(meas.) = 60(2)°, 2V(calc.) = 62°, no dispersion observed. The mineral is not fluorescent, and has H = 2.5, a colorless streak, a vitreous luster and is sectile. In dilute mineral acids (HCl, HNO₃), the mineral reacts with effervescence to yield a gel-like precipitate of lanthanide(III) hydroxides.

Introduction

Lanthanite, the lanthanum end-member of the series of minerals with the general stoichiometry $(RE)_2(CO_3)_3 \cdot 8H_2O$, was first described by Berzelius (1825). Its general composition was determined by Blake (1853) and Genth (1857). The presence of other lanthanides ("didymium") in the material from Bethlehem, Pennsylvania, U.S.A., was noted. It is a rare mineral species, but has been noted to occur sparingly at a number of localities (Saebø, 1961). Lanthanite-(Nd) (Roberts et al., 1980) was found recently in a silty arenaceous clay at Curitiba, Paraná, Brazil; Nd and La were the main rare earths present, together with minor Pr, Sm, Gd, Eu, Dy, Y and Ce.

In the course of our studies on the geology and mineralogy of the Britannia Mine, North Wales, U.K., (National Grid Ref. SH 615 547), we found clear platy crystals in oxidized copper ore. This material proved to be the new mineral lanthanite-(Ce), the cerium-predominant member of the lanthanite group, which is described below. The mineral and its name have been approved, prior to publication, by the Commission on New Minerals and Mineral Names, IMA. Lanthanite-(Ce) is named in accordance with the accepted rare earth minerals nomenclature (Levinson, 1966). Type material (National Museum of Wales specimen number NMW 84.6G.M1) has been deposited in the collection of the National Museum of Wales and is available for further study. Other material has been deposited with the British Museum (Natural History), the Smithsonian Institution and Musee de Mineralogie, Paris.

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Occurrence and associations

Lanthanite-(Ce) was found in the second lowest accessible level of the Britannia Mine. Well-crystallized plates (Fig. 1), up to $5 \times 5 \times 0.5$ mm, occur on the walls and back of the adit, and are coated on $\{010\}$ by spheres of acicular radiating malachite. Associated minerals are brochantite, posnjakite and rarely chalcoalumite. This whole assemblage is sometimes found coated with a glaze of ferric oxyhydroxides.

Lanthanite-(Ce), as well as its associates, is obviously of secondary origin and has crystallized due to rare earth-bearing groundwaters percolating through the old mine workings. The rare earths may have been leached from allanite which has been identified in the acid pyroclastics of the Snowdon Volcanic Group (G. Hendry, pers. comm.). In the immediate mine area, high concentrations of rare earth elements are present in the rhyolitic intrusions of the Snowdon Volcanic Group. These intrusions contain La in the range 60–100 ppm, Ce 140–200 ppm and Nd 70–120 ppm (T. K. Ball, pers. comm.).

Physical and optical properties

Lanthanite-(Ce) is colorless, transparent and platy $\{010\}$. No other forms were observed, all of the plates so far seen terminating with ragged edges. It has a white streak, a
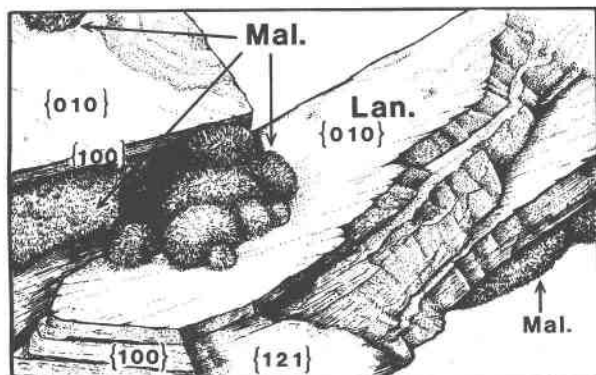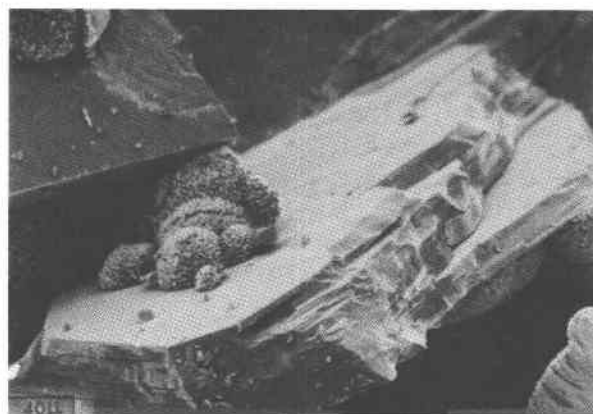

Fig. 1. (upper) Scanning electron photomicrograph of lanthanite-(Ce) encrusted with malachite and (lower) an annotated sketch of the same area. Lan = lanthanite-(Ce) and Mal = malachite.

Table 1. Analytical data for lanthanite-(Ce)

	%		%[a]
Ce	17.60	Ce_2O_3	20.61
La	12.31	La_2O_3	14.44
Nd	12.67	Nd_2O_3	14.78
Sm	2.16	Sm_2O_3	2.50
Gd	1.33	Gd_2O_3	1.53
Y	0.58	Y_2O_3	0.74
CO_2	21.0	CO_2	21.0[b]
H_2O	23.0	H_2O	23.0[b]
		Total	98.6[c]

[a] Rare-earths recalculated to oxides. Rare-earth weight percents are the average of five electron microprobe analyses.

[b] Also the average of five analyses.

[c] The empirical formula based on 17 oxygens is $(Ce_{0.78}La_{0.55}Nd_{0.55}Sm_{0.09}Gd_{0.05}Y_{0.04})_{\Sigma 2.06}C_{2.97}O_{9.03} \cdot 7.96H_2O$.

vitreous luster and is not fluorescent. The hardness is about 2.5 and the plates are sectile. Cleavage $\{010\}$ is well-developed. The mineral dissolves in dilute mineral acids (HCl, HNO_3) with effervescence to yield a gel-like precipitate of lanthanide(III) hydroxides. Density was determined by flotation of hand-picked crystals; the value of 2.76 g/cm³ compares favorably with the calculated density of 2.79 g/cm³ based on the theoretical formula with $Z = 4$.

The mineral is biaxial negative with measured refractive indices α 1.532(2), β 1.594(2), γ 1.616(2) ($\lambda = 589$ nm). $2V$(meas.) was 60(2)°, the calculated value being 62°. No dispersion was observed. The orientation is $X = b$, $Y = c$, $Z = a$. The compatibility $(1 - (K_p/K_c) = -0.010)$ is superior based on the Gladstone–Dale calculation. The physical and optical values are close to those of Larsen and Berman (1934) and Saebø (1961) for lanthanite, and those of Roberts et al. (1980) for lanthanite-(Nd).

Chemical composition

Electron microprobe analyses were carried out at the University of Manchester using a Cameca (Camebax) instrument operating at 15 kV and with a specimen current of 3.5×10^{-8} A in the energy dispersive mode. Analytical grade rare earth oxides (Ce_2O_3, La_2O_3, Nd_2O_3, Sm_2O_3, Gd_2O_3 and Y_2O_3) were used as standards and the X-ray lines used were $L\alpha$ with corrections made for interfering $L\beta$ lines. CO_2 was determined using a Technicon CHN analyser and water of hydration analyses were performed thermogravimetrically using a Stanton Redcroft TG 750 temperature-programmed balance. Analytical data are presented in Table 1. The empirical formula based on 17 oxygen atoms is $(Ce_{0.78}La_{0.55}Nd_{0.55}Sm_{0.09}Gd_{0.05}Y_{0.04})_{\Sigma 2.06}C_{2.97}O_{9.03} \cdot 7.96H_2O$. The mass deficiency in the

Table 2. Unit cell data for lanthanite group minerals

	1	2	3
a (Å)	9.482(6)	9.504(4)	9.476(4)
b (Å)	16.938(11)	16.943(6)	16.940(8)
c (Å)	8.965(3)	8.937(5)	8.942(4)
d(meas.) (g/cm^3)	2.76		2.81
d(calc.) (g/cm^3)	2.79	2.78	2.82
Z	4	4	4
Space group	Pbnb	Pbnb	Pbnb

1. Lanthanite-(Ce); this study.

2. Lanthanite; Bastnäs, Sweden; Dal Negro et al. (1977).

3. Lanthanite-(Nd); Paraná, Brazil; Roberts et al. (1980).

analytical results may be attributed to sample deterioration during preparation and probe analysis. This was also observed during microprobe analyses of lanthanite-(Nd), but in that case sample deterioration was much more pronounced (Ansell et al., 1976). The ideal formula for

Table 3. X-ray powder data for lanthanite-(Ce)

I/I_0	d Å obs.	d Å calc.	hkl
100	8.47	8.469	020
65	4.746	4.741	200
62	4.462	4.483	002
35	4.211	4.235	040
40	4.125	4.137	220
38	3.943	3.962	022
9	3.834	3.829	041
73	3.255	3.257	202
8	3.158	3.158	240
65	3.028	3.040	222
15	3.000	3.006	151
10	2.845	2.850	103
9	2.709	2.706	160
18	2.691	2.693	061
35	2.571	2.582	242
5	2.532	2.533	340

Debye-Scherrer camera (Ni-filtered CuKα radiation) with α-Al$_2$O$_3$ added as internal standard. The pattern is indexed with a = 9.482, b = 16.938, c = 8.965 Å and intensities were estimated with a densitometer.

lanthanite-(Ce) is $(Ce,La,Nd)_2(CO_3)_3 \cdot 8H_2O$ with Ce > La,Nd, and the Ce:La:Nd ratio used to calculate the density of the mineral is 0.83:0.59:0.58.

X-ray data

Single-crystal precession studies of oriented crystals indicated orthorhombic symmetry, and measured unit cell parameters are $a = 9.482(6)$, $b = 16.938(11)$, $c = 8.965(3)$Å. Quoted errors are derived from multiple measurements of precession photographic data, using MoKα radiation. $V = 1440$Å^3 and Z = 4; $a:b:c = 0.5598:1:0.5293$. Systematic absences in the reflexion record are $0kl$ ($k = 2n + 1$), $hk0$ ($k = 2n + 1$) and $h0l$ ($h + l = 2n + 1$) which uniquely define the space group $Pbnb$ (a non-standard setting of space group $Pccn$). These data are entirely consistent with those reported by Dal Negro et al. (1977) on a natural sample of lanthanite (lanthanite-(La)) from Bastnäs, Sweden, and by Roberts et al. (1980) on lanthanite-(Nd) from Curitiba, Paraná, Brazil. Single-crystal data for all three minerals are compared in Table 2. The strongest X-ray lines in the powder diffraction pattern, listed in Table 3, are [dÅ (I)(hkl)] 8.47(100)(020), 4.746(65)(200), 4.462(62)(002), 3.255(73)(202) and 3.028(65)(222). The powder data are virtually identical to those tabulated by Roberts et al. (1980) for lanthanite-(Nd). Obviously, quantitative chemical analyses are necessary for a reliable distinction between members of the lanthanite group.

Acknowledgments

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