Mineralogical Magazine (2024), **88**, 755–765
doi:10.1180/mgm.2024.65

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Article

Hydroxylbastnäsite-(La), an 'old new' bastnäsite-group mineral

Mineralogy, petrology and geochemistry of pegmatites: Alessandro Guastoni memorial issue

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Abstract

Hydroxylbastnäsite-(La), the OH- and La-dominant member of the bastnäsite group, in fact known for many years, was studied in detail and has been approved by the IMA–CNMNC as a new mineral species with the ideal, end-member formula $La(CO_3)(OH)$. The holotype originates from the Vuoriyarvi (another spelling: Vuorijärvi) alkaline-ultrabasic complex, Northern Karelia, and the cotype from the Mochalin Log *REE* deposit, Potaniny Mts, South Urals, both in Russia. At Vuoriyarvi, hydroxylbastnäsite-(La) occurs as clusters (up to 1 mm) of light brown, honey-yellow or colourless hexagonal tabular to short-prismatic crystals up to 0.15 mm associated with fluorite and ancylite-(Ce) in cavities of calcite–dolomite carbonatites. At Mochalin Log, hydroxylbastnäsite-(La) forms light brown grains up to 0.2 mm included in massive aggregates of other *LREE* minerals: bastnäsite-(Ce), bastnäsite-(La), percleveite-(Ce), percleveite-(La), biraite-(Ce), biraite-(La), törnebohmite-(La), ferriperbøeite-(Ce), allanite-(Ce), etc. D_{meas} is 4.75(2) and D_{calc} is 4.778 g cm^{-3} (holotype). Hydroxylbastnäsite-(La) is optically uniaxial (+), $\omega = 1.76(1)$ and $\varepsilon = 1.86(1)$ (holotype). The chemical composition (wt.%, electron microprobe, CO_2 and H_2O calculated: holotype/cotype) is: CaO 0.23/0.00, SrO 0.07/0.00, La_2O_3 39.47/39.58, Ce_2O_3 33.51/31.99, Pr_2O_3 1.03/1.51, Nd_2O_3 1.95/2.38, F 0.76/3.33, CO_2 20.49/20.34, H_2O 3.77/2.58, –O=F 0.32/1.40, total 100.96/100.31. The empirical formulae, calculated based on the sum of metal cations of 1 apfu and one CO_3 group pfu, are $(La_{0.52}Ce_{0.44}Nd_{0.02}Pr_{0.01}Ca_{0.01})_{\Sigma 1.00}(CO_3)[(OH)_{0.90}F_{0.09}]_{\Sigma 0.99}$ (holotype) and $(La_{0.53}Ce_{0.42}Nd_{0.03}Pr_{0.02})_{\Sigma 1.00}(CO_3)[(OH)_{0.62}F_{0.38}]_{\Sigma 1.00}$ (cotype). Hydroxylbastnäsite-(La) is hexagonal, $P\bar{6}$, unit-cell parameters (from powder XRD data, holotype/cotype) are: $a = 12.537(3)/12.533(1)$, $c = 9.968(2)/9.908(1)$ Å, $V = 1356.8(5)/1347.9(3)$ Å^3 and $Z = 18$. Strong reflections of the powder XRD pattern [*d*,Å(*I*)(*hkl*)] are (holotype): 4.98(39)(002), 3.616(88)(300), 2.926(100)(302), 2.089(41)(330), 2.052(46)(304) and 1.927(40)(332). The crystal structure of holotype hydroxylbastnäsite-(La) was refined by the Rietveld method, $R_{wp} = 0.0071$, $R_p = 0.0050$, $R_{obs} = 0.0466$. It is isostructural to hydroxylbastnäsite-(Ce) and synthetic bastnäsite-type hydroxyl-carbonates $REE^{3+}(CO_3)(OH)$ (*REE* = La–Er), but differs from fluorine-dominant bastnäsites which adopt the space group $P\bar{6}2c$.

Keywords: hydroxylbastnäsite-(La); new mineral; bastnäsite group; rare-earth carbonate; crystal structure; Vuoriyarvi complex; Mochalin Log *REE* deposit

(Received 19 July 2024; accepted 22 August 2024; Accepted Manuscript published online: 12 November 2024)

Introduction

The minerals of the bastnäsite group (hereafter bastnäsites) are carbonates of rare-earth elements (*REE*) with the general formula $REE^{3+}(CO_3)X^-$ in which species-defining *REE* = La, Ce, Nd, or Y and *X* = F or OH. The root names of F-dominant members are based on the term 'bastnäsite' whereas OH-dominant members are based on the term 'hydroxylbastnäsite', and the Levinson's modifier indicates the prevailing *REE*. Bastnäsite-(Ce), ideally $Ce(CO_3)F$, is one of the most widespread rare-earth minerals, an important (in some deposits the major) ore mineral of *REE*. It has been known for two centuries being first described by Berzelius (1825) as *Basisk flusspatssyradt Cerium*. Other members of the

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Associate Editor: Daniel Atencio
This paper is part of a thematic set on pegmatites in memory of Alessandro Guastoni
Cite this article: Pekov IV. *et al.* (2024). Hydroxylbastnäsite-(La), an 'old new' bastnäsite-group mineral. *Mineralogical Magazine* **88**, 755–765. https://doi.org/10.1180/mgm.2024.65

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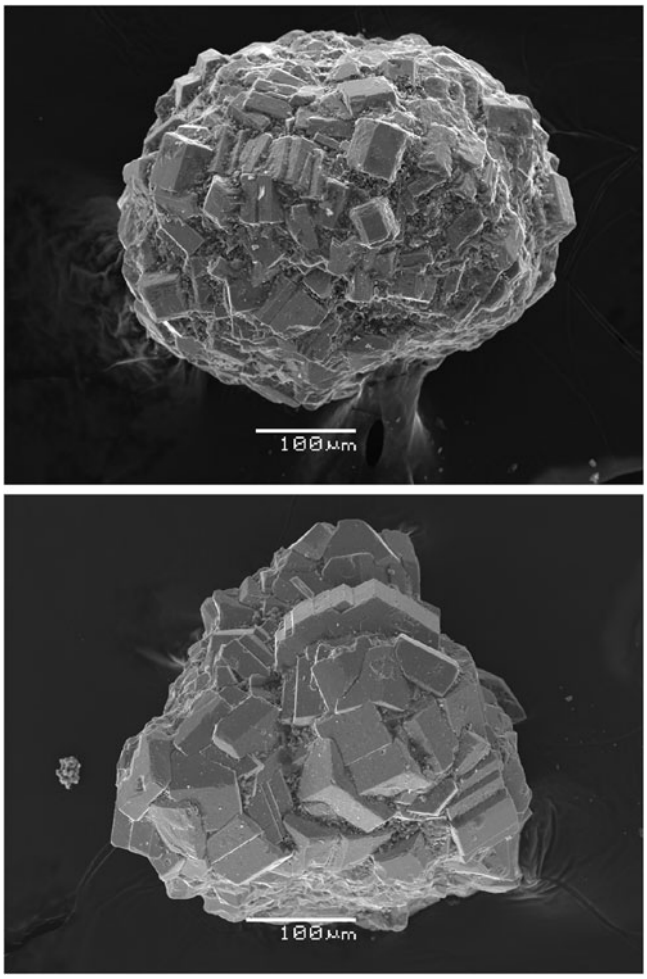


Figure 1. Clusters of hydroxylbastnäsite-(La) crystals from Vuoriyarvi. Holotype specimen number 97514. SEM (secondary electron) images.

group have been defined as individual, valid mineral species since the 1960s, i.e. after the establishment of the International Mineralogical Association (IMA) Commission on New Minerals and Mineral Names in 1959, and they are: hydroxylbastnäsite-(Ce) (Kirillov, 1964); bastnäsite-(La) (Levinson, 1966); bastnäsite-(Y) (Mineev *et al.*, 1970); hydroxylbastnäsite-(Nd) (Maksimović and Pantó, 1985); bastnäsite-(Nd) (Miyawaki *et al.*, 2013); and the mineral described in the present paper, hydroxylbastnäsite-(La) (Pekov *et al.*, 2021). It should be noted that the histories of the definition of hydroxylbastnäsite-(Ce), bastnäsite-(La), bastnäsite-(Y) and hydroxylbastnäsite-(La) as mineral species are not very simple; for the three formers, a historical overview is reported by Pekov (1998), while for hydroxylbastnäsite-(La), which is first described as a valid mineral species in the present paper, it is given in the next paragraph.

Hydroxylbastnäsite-(La) is in fact 'an old new' mineral. Probably, the first recorded locality for this mineral species is the Mochalin Log *REE* deposit in South Urals, Russia. A bastnäsite-group mineral was first described from Mochalin Log in 1861 by Fedor Korovaev as 'kyshtymoparisite', or 'Kischtim-Parisit' (Korovaev, 1861; Korovaeff, 1862); some time later this name was modified to 'kischtimite' by Brush (1863). In the 20th Century, this mineral collected from Mochalin Log was systematically studied and reported as bastnäsite by Lacroix (1912), Silberminz (1929), Alimarin (1930) and Svyazhin (1965). The bastnäsite chemically analysed by Alimarin was La-rich and contained 2.24 wt.% F and 1.83 wt.% H_2O (Alimarin, 1930) that corresponds to the OH/(OH+F) ratio equal to 0.63. Based on these data, Strunz (1962) concluded that "*kischtimite is bastnäsite with OH instead of F and relatively high La content*". Svyazhin (1965) found that bastnäsite from Mochalin Log contains comparable amounts of Ce and La and also suggested preserving the name 'kyshtymite' (modified as 'kischtimite', in accordance with common English transliteration of Russian geographical names) for a La-rich and F-depleted variety of bastnäsite. The first quantitative electron-microprobe analyses of bastnäsite-group minerals from Mochalin Log were published by us in 2002: bastnäsite-(Ce), bastnäsite-(La), hydroxylbastnäsite-(Ce) and a potential mineral species 'hydroxylbastnäsite-(La)' were identified here (Pekov *et al.*, 2002). The latter mineral was also found at several other localities. Chemical data for its supergene Ce-depleted variety from bauxite deposits of Hungary, Greece and the former Yugoslavia were reported by Maksimović and Pantó (1983) and Pantó and Maksimović (2001) (see also: Hawthorne *et al.*, 1986; Jambor and Roberts, 2002). The mineral chemically corresponding to hydroxylbastnäsite-(La) was reported from rhyolites near Tisovec-Rejkovo, Slovakia (Ondrejka *et al.*, 2005).

However, despite the use of the name 'hydroxylbastnäsite-(La)' in the literature and databases, the natural OH- and La-dominant member of the bastnäsite group was not studied in detail and had never been formally accepted by the IMA as valid mineral species. To fill this lacuna, we examined hydroxylbastnäsite-(La) on the specimens from two localities and submitted the proposal on this mineral as a new species to the IMA Commission on New Minerals, Nomenclature and Classification (CNMNC). The specimen considered as the holotype (most studied) originates from the Vuoriyarvi (another spelling: Vuorijärvi) alkaline-ultrabasic complex, Northern (Polar) Karelia (near the border with the Kola Peninsula), Murmansk Oblast, Russia. The cotype material originates from the Mochalin Log *REE* deposit located in the valley of the Mochalin Log stream, a left tributary of the Borzovka river, in Potaniny Mts, 14 km N of the city of Kyshtym, Chelyabinsk Oblast', South Urals, Russia. Note, both these localities are also the co-type localities of hydroxylbastnäsite-(Ce) (see Pekov, 1998).

Both the mineral and its name, which is obvious for OH- and the La-dominant member of the bastnäsite group, have been approved by the IMA–CNMNC, IMA2021–001 (Pekov *et al.*, 2021). The type specimens of hydroxylbastnäsite-(La) are deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia with the catalogue numbers 97514 (holotype material from Vuoriyarvi) and 97515 (cotype from Mochalin Log). The symbol for this mineral is Hbsn-La (Warr, 2021; updated March 2023 version at http://cnmnc.units.it/).

Occurrence and general appearance

At the Vuoriyarvi alkaline-ultrabasic complex (for its description see e.g.: Kukharenko *et al.*, 1965; Karchevsky and Moutte, 2004 and references therein), hydroxylbastnäsite-(La) was identified in the material collected by one of the authors (A.S.K.) in the late 1950s. This mineral forms well-shaped hexagonal tabular to short-prismatic crystals up to 0.15 mm in size. The pinacoid {001} and the hexagonal prism {100} are their main forms, the narrow faces {103} and {201} were observed on some

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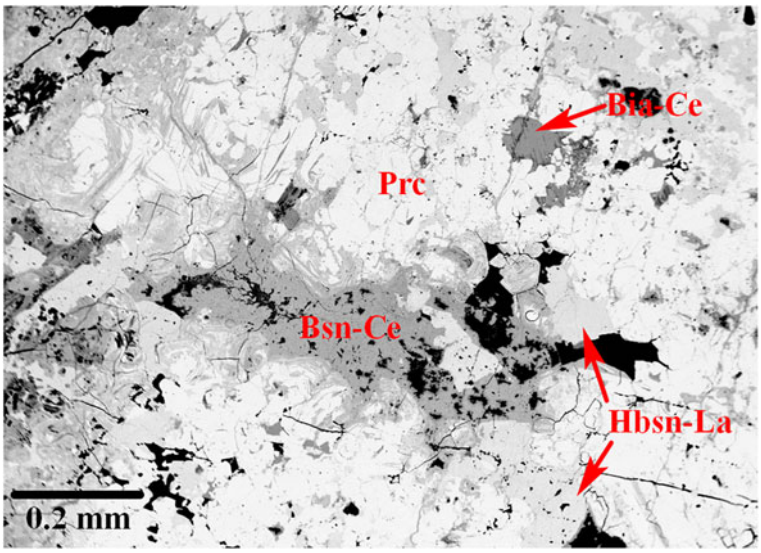


Figure 2. Hydroxylbastnäsite-(La) (Hbsn-La) grains in an aggregate of other *LREE* minerals and quartz (black areas) from Mochalin Log. Prc – percleveite-(Ce)/percleveite-(La), Bsn-Ce – Ca-enriched variety of bastnäsite-(Ce), Bia-Ce – biraite-(Ce). Cotype specimen, number 97515. Polished section, SEM (back-scattered electron) image.

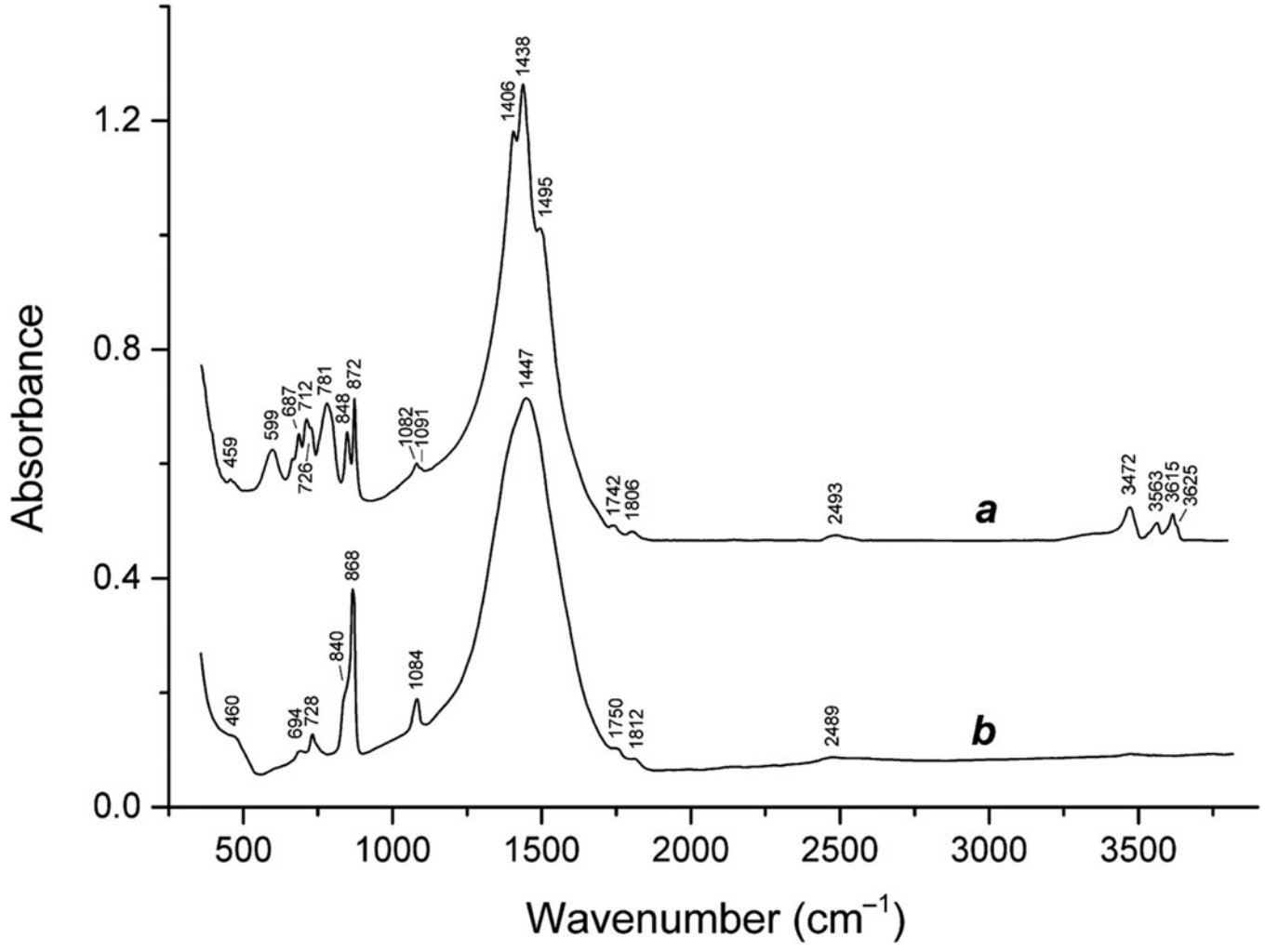


Figure 3. Powder infrared absorption spectra of (a) holotype hydroxylbastnäsite-(La) from Vuoriyarvi and (b) bastnäsite-(Ce) with the composition $(Ce_{0.54}La_{0.26}Nd_{0.12}Pr_{0.06}Sm_{0.01}Ca_{0.01})_{\Sigma 1}(CO_3)F_{0.98}(OH)_{0.01}$ from Mt. Ploskaya, Western Keivy, Kola Peninsula, Russia.

crystals. The crystals are typically combined in dense, sometimes spherical clusters (Fig. 1) up to 1 mm across. Some crystals consist completely of hydroxylbastnäsite-(La) whereas the others contain a core composed of hydroxylbastnäsite-(Ce), with Ce > La. Hydroxylbastnäsites together with fluorite and ancylite-(Ce) occur in cavities of calcite–dolomite carbonatites. We consider this mineral assemblage as formed during a late, low-temperature hydrothermal stage of the carbonatite evolution.

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Table 1. Chemical composition (in wt.%) of hydroxylbastnäsite-(La)

	Holotype (Vuoriyarvi)			Cotype (Mochalin Log)			
Constituent	Average*	Range	SD	Average**	Range	SD	Probe standard
CaO	0.23	0.08–0.28	0.08	-	-		$CaSiO_3$
SrO	0.07	0.03–0.14	0.04	-	-		$SrSO_4$
La_2O_3	39.47	36.85–42.01	2.05	39.58	39.44–39.73	0.15	$LaPO_4$
Ce_2O_3	33.51	31.75–35.17	1.34	31.99	31.75–32.12	0.21	$CePO_4$
Pr_2O_3	1.03	0.97–1.07	0.05	1.51	1.37–1.70	0.17	$PrPO_4$
Nd_2O_3	1.95	1.54–2.45	0.37	2.38	2.26–2.52	0.13	$NdPO_4$
F	0.76	0.61–0.91	0.12	3.33	3.21–3.45	0.12	MgF_2***
$CO_{2calc.}$	20.49			20.34			
$H_2O_{calc.}$	3.77			2.58			
–O=F	0.32			1.40			
Total	100.96			100.31			

*For five spot analyses; **for three spot analyses; ***for the cotype specimen, topaz was used as probe standard for F. SD – standard deviation. Dash means that the content is below detection limit.

Table 2. Powder X-ray diffraction data (*d* in Å) of holotype hydroxylbastnäsite-(La)

I_{obs}	d_{obs}	I_{calc}*	d_{calc}	*h k l*
39	**4.98**	**51**	**4.984**	**002**
88	**3.616**	**81**	**3.619**	**300**
100	**2.926**	**100**	**2.928**	**302**
5	2.650	2	2.653	222
2	2.591	1	2.582	123
1	2.577	0.5	2.577	132
9	2.490	11	2.492	004
		0.5	2.490	230
5	2.304	3	2.305	411
1	2.278	1	2.280	223
2	2.235	1	2.231	133
3	2.138	1	2.140	412
41	**2.089**	**33**	**2.090**	**330**
46	**2.052**	**50**	**2.052**	**304**
40	**1.927**	1	1.929	413
		34	**1.927**	**332**
14	1.809	12	1.810	600
24	**1.701**	**20**	**1.701**	**602**
2	1.663	0.5	1.662	135
		2	1.661	006
16	1.601	15	1.601	334
8	1.509	11	1.510	306
12	1.464	11	1.464	604
9	1.368	8	1.368	360
20	**1.319**	**17**	**1.319**	**362**
7	1.300	7	1.300	336
1	1.244	2	1.246	008
6	1.224	7	1.224	606
3	1.207	4	1.207	900
14	1.199	14	1.199	364
9	1.173	5	1.178	308
		7	1.173	902
6	1.086	6	1.086	904
4	1.070	5	1.070	338
7	1.056	11	1.056	366
4	1.045	1	1.048	357
		3	1.045	660
6	1.023	5	1.026	608
		6	1.023	662

*For the calculated pattern, only reflections with intensities ≥0.5 are given; the strongest reflections are marked in boldtype.

Mochalin Log is a classic, historical locality of Ce- and La-dominant bastnäsites including the hydroxyl-prevailing species (Korovaev, 1861; Korovaeff, 1862; Silberminz, 1929; Alimarin, 1930; Svyazhin, 1965; Pekov *et al.*, 2002). Here they are part of a rich and diverse assemblage of light *REE* (*LREE*) minerals, which has a contact metasomatic origin. Most probably, it was formed during the fenitisation of granitic pegmatites located within granite–gneisses in the southern exocontact zone of the Vishnevogorskiy alkaline intrusive complex mainly consisting of syenites and miaskites. For the general data on the Mochalin Log deposit see recent summarising paper by Kasatkin *et al.* (2020) and references therein. At Mochalin Log, hydroxylbastnäsite-(La) occurs as anhedral grains up to 0.1 × 0.2 mm included in massive aggregates of other *LREE* minerals (Fig. 2). In different samples, it is associated with bastnäsite-(Ce), bastnäsite-(La), percleveite-(Ce), percleveite-(La), biraite-(Ce), biraite-(La), törnebohmite-(La), ferriperbøeite-(Ce), allanite-(Ce), allanite-(La), ferriallanite-(La), alexkuznetsovite-(Ce), alexkuznetsovite-(La), perrierite-(Ce), perrierite-(La), fluorbritholite-(Ce), stillwellite-(Ce), thorianite, and quartz.

Physical properties and optical data

Hydroxylbastnäsite-(La) from both type localities is transparent to translucent and typically has a light brown colour. Some crystals from Vuoriyarvi are light honey-yellow or colourless. The streak is white. The lustre is strong vitreous on crystal faces and greasy on a broken surface. The mineral is brittle, no cleavage or parting was observed. The fracture is uneven. The Mohs hardness is *ca.* 4.

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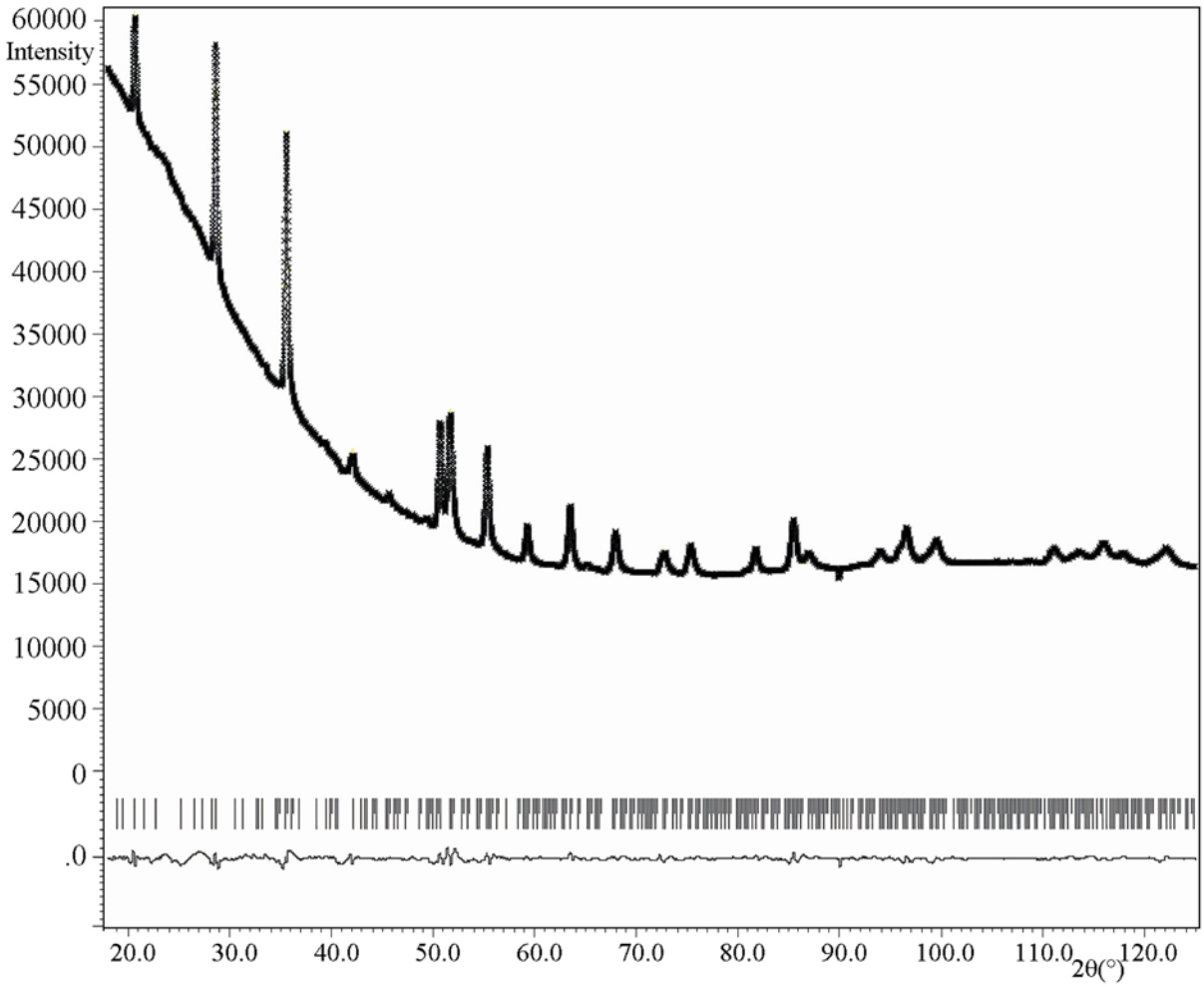


Figure 4. Observed and calculated powder X-ray diffraction patterns of hydroxylbastnäsite-(La). The solid line corresponds to calculated data, the crosses correspond to the observed pattern, vertical bars mark all possible Bragg reflections. The difference between the observed and calculated patterns is shown by curve at the bottom.

The density, measured by microvolumetric method for the holotype, is 4.75(2) g cm^{-3}. The density calculated for the holotype using the empirical formula and unit-cell volume found from powder X-ray diffraction (XRD) data is 4.778 g cm^{-3}.

Optical data were obtained for the holotype specimen. Hydroxylbastnäsite-(La) is optically uniaxial (+), $\omega = 1.76(1)$ and $\varepsilon = 1.86(1)$ (589 nm). In plane polarised transmitted light, it is colourless and non-pleochroic.

Infrared spectroscopy

In order to obtain an infrared (IR) absorption spectrum, a powdered sample of the holotype hydroxylbastnäsite-(La) (curve ***a*** in Fig. 3) was mixed with anhydrous KBr, pelletised, and analysed using an ALPHA FTIR spectrometer (Bruker Optics) at a resolution of 4 cm^{-1}. A total of 16 scans were accumulated. The IR spectrum of an analogous pellet of pure KBr was used as a reference. The typical sample of bastnäsite-(Ce) involved for comparison (curve ***b*** in Fig. 3) was prepared and studied using the same procedures.

The assignment of absorption bands observed in different wavenumber ranges is as follows: 3400–3700 cm^{-1} are O–H stretching vibrations; 1400–1500 cm^{-1} are assigned to degenerate asymmetric stretching vibrations of $(CO_3)^{2-}$. 1080–1100 cm^{-1} are assigned to nondegenerate symmetric stretching vibrations of $(CO_3)^{2-}$; 840–880 cm^{-1} to out-of-plane bending vibrations of $(CO_3)^{2-}$ (a nondegenerate mode); 781 cm^{-1} to *LREE*···O–H in-plane bending vibrations (broad band, possibly, superposition of several bands); 680–730 cm^{-1} to in-plane bending vibrations of $(CO_3)^{2-}$ (a degenerate mode); and 599 cm^{-1} to *LREE*···O–H out-of-plane bending vibrations (rotation around the *LREE*···O ionic bond) – broad band, possibly, superposition of several bands. Below 500 cm^{-1} bands are assigned to lattice modes involving *LREE*···O and $(CO_3)^{2-}$ librational vibrations.

The intrinsic fundamental modes of the $(CO_3)^{2-}$ and $(OH)^{-}$ anions were assigned in accordance with Nakamoto (2008).

The remaining absorption bands with maxima at 599 and 781 cm^{-1} were assigned by analogy with numerous oxysalts with additional $(OH)^{-}$ anions in which *M*···O–H bending vibrations are usually observed in the range of 580 – 830 cm^{-1} (see the reference books Chukanov and Chervonnyi, 2016; Chukanov and Vigasina, 2020 and references therein). Note that in the IR spectra of F-dominant members of the bastnäsite group these bands are absent or are very weak.

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Table 3. Coordinates and isotropic displacement parameters (U_{iso}, in Å^2) of atoms for holotype hydroxylbastnäsite-(La)

Site	*x*	*y*	*z*	U_{iso}
*REE*1	0.112(6)	0.226(3)	0.240(3)	0.0112(10)
*REE*2	0.438(3)	0.217(4)	0.257(3)	0.0112(10)
*REE*3	0.1042(12)	0.560(3)	0.264(3)	0.0112(10)
C1	0.481 801	0.353 45	0	0.012
C2	0.200 085	0.084 242	0	0.012
C3	0.299 288	0.459 352	0	0.012
C4	0.549 888	0.422 032	½	0.012
C5	0.229 944	0.457 79	½	0.012
C6	0.198 725	0.036 634	½	0.012
O1	0.478(15)	0.244(7)	0	0.011(9)
O2	0.486(6)	0.403(4)	0.1139(14)	0.011(9)
O3	0.033(2)	0.160(15)	0	0.011(9)
O4	0.238(18)	0.15(3)	0.11(2)	0.011(9)
O5	0.081(12)	0.578(2)	0	0.011(9)
O6	0.252(5)	0.419(6)	0.1155(9)	0.011(9)
O7	0.49(4)	0.3041(8)	½	0.011(9)
O8	0.524(18)	0.100(9)	0.386(10)	0.011(9)
O9	0.3497(5)	0.52(2)	½	0.011(9)
O10	0.17(3)	0.425(17)	0.39(2)	0.011(9)
O11	0.074(5)	0.168(11)	½	0.011(9)
O12	0.250(12)	0.072(14)	0.385(4)	0.011(9)
O13 = OH	0	0	0.28(2)	0.011(9)
O14 = OH	⅔	⅓	0.24(4)	0.011(9)
O15 = OH	⅓	⅔	0.26(5)	0.011(9)
O16 = OH	0.322(4)	0.320(2)	0.332(8)	0.011(9)
O17 = OH	0.338(4)	−0.003(4)	0.189(12)	0.011(9)

Weak bands in the range of 1700–1500 cm^{-1} correspond to overtones and combination modes.

The IR spectrum of hydroxylbastnäsite-(La) differs from that of bastnäsite-(Ce) by the presence of multiple bands of O–H stretching vibrations and *LREE*···O–H bending and libration bands as well as splitting of all bands related to the $(CO_3)^{2-}$ groups. The band of nondegenerate symmetric stretching vibrations of $(CO_3)^{2-}$ (*i.e.* mode which would be inactive in the IR spectrum of a mineral with undistorted CO_3 triangles) at 1082 with the shoulder at 1091 cm^{-1} as well as splitting of the nondegenerate band of out-of-plane bending vibrations of $(CO_3)^{2-}$ indicate the presence of non-equivalent distorted CO_3 triangles in the structure of hydroxylbastnäsite-(La).

Four bands in the O–H stretching region correspond to at least four non-equivalent OH groups, but taking into account asymmetry of the bands at 3472 and 3563, one can suppose that the number of non-equivalent OH groups is > 4.

Chemical composition

The chemical composition of hydroxylbastnäsite-(La) was studied by electron microprobe in two laboratories. The holotype was investigated in the Laboratory of Analytical Techniques of High Spatial Resolution, Department of Petrology, Moscow State University, using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer, with an acceleration voltage of 20 kV and a beam current of 10 nA; the electron beam was rastered to the 5 × 5 μm area. The cotype was analysed in the Laboratory of Electron Microscopy and Microanalysis, Department of Geological Sciences, Masaryk University, Brno, using a Cameca SX-100 electron microprobe (WDS mode, acceleration voltage of 15 kV, a beam current of 10 nA, and a 5 μm beam diameter). The chemical data in wt.% are given in Table 1, as well as the probe standards. Contents of other elements with atomic numbers > 4 were below detection limits. Special attention was paid to the correctness of quantitative determination of fluorine due to an overlap of the *K* line of F with the *M* line of Ce.

Table 4. Selected interatomic distances (Å) in the structure of holotype hydroxylbastnäsite-(La)

*REE*1–O3	2.56(5)	C1–O1	1.36(11)	
*REE*1–O4	2.6(3)	C1–O2	1.28(3)	×2
*REE*1–O6	2.50(6)	<C1–O>	1.31	
*REE*1–O10	2.6(2)			
*REE*1–O11	2.66(4)	C2–O3	1.29(4)	
*REE*1–O12	2.51(13)	C2–O4	1.3(2)	×2
*REE*1–O13	2.49(5)	<C2–O>	1.30	
*REE*1–O16	2.46(8)			
*REE*1–O17	2.48(10)	C3–O5	1.35(3)	
<*REE*1–O>	2.54	C3–O6	1.28(2)	×2
		<C3–O>	1.30	
*REE*2–O1	2.60(3)			
*REE*2–O2	2.54(6)	C4–O7	1.280(10)	
*REE*2–O4	2.6(2)	C4–O8	1.26(14)	×2
*REE*2–O7	2.60(4)	<C4–O>	1.27	
*REE*2–O8	2.5(2)			
*REE*2–O12	2.50(9)	C5–O9	1.301(8)	
*REE*2–O14	2.49(4)	C5–O10	1.3(2)	×2
*REE*2–O16	2.49(7)	<C5–O>	1.30	
*REE*2–O17	2.48(7)			
<*REE*2–O>	2.53	C6–O11	1.34(7)	
		C6–O12	1.28(6)	×2
*REE*3–O2	2.59(8)	<C6–O>	1.30	
*REE*3–O5	2.67(4)			
*REE*3–O6	2.55(6)			
*REE*3–O8	2.59(10)			
*REE*3–O9	2.56(4)			
*REE*3–O10	2.6(3)			
*REE*3–O15	2.492(14)			
*REE*3–O16	2.53(7)			
*REE*3–O17	2.49(7)			
<*REE*3–O>	2.56			

The amounts of H_2O and CO_2 could not be determined directly because of the paucity of pure material. The presence of both $(CO_3)^{2-}$ and $(OH)^-$ groups as species-defining constituents in hydroxylbastnäsite-(La) is undoubtedly shown by the crystal structure data (see below) and the IR spectrum. The presence of $(CO_3)^{2-}$ (as in all other bastnäsite-group carbonates) is also confirmed by a common chemical test: the mineral dissolves in warm HCl aqueous solution or in cold dilute H_2SO_4 with effervescence (CO_2 gas bubbling release).

The empirical formulae, calculated on the basis of the sum of metal cations of one atom per formula unit (apfu) and one CO_3 group pfu, are as follows: holotype (Vuoriyarvi) is $(La_{0.52}Ce_{0.44}Nd_{0.02}Pr_{0.01}Ca_{0.01})_{\Sigma 1.00}(CO_3)[(OH)_{0.90}F_{0.09}]_{\Sigma 0.99}$; cotype (Mochalin Log) is $(La_{0.53}Ce_{0.42}Nd_{0.03}Pr_{0.02})_{\Sigma 1.00}(CO_3)[(OH)_{0.62}F_{0.38}]_{\Sigma 1.00}$.

The simplified formula is (La,Ce)(CO_3)(OH,F). The idealised, end-member formula is La(CO_3)(OH) which requires La_2O_3 75.45, CO_2 20.38, H_2O 4.17, total 100 wt.%.

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Table 5. Comparative data for hydroxylbastnäsite-(La), hydroxylbastnäsite-(Ce), bastnäsite-(La) and bastnäsite-(Ce)

Mineral	Hydroxylbastnäsite-(La)*	Hydroxylbastnäsite-(Ce)	Bastnäsite-(La)	Bastnäsite-(Ce)
Ideal formula	$La(CO_3)(OH)$	$Ce(CO_3)(OH)$	$La(CO_3)F$	$Ce(CO_3)F$
Crystal system	Hexagonal	Hexagonal	Hexagonal	Hexagonal
Space group	$P\bar{6}$	$P\bar{6}$**	$P\bar{6}2c$	$P\bar{6}2c$
Unit cell data:				
a (Å)	12.537(3)	12.41–12.47	7.12–7.16	7.08–7.12
c (Å)	9.968(2)	9.85–9.96	9.67–9.81	9.72–9.76
V (Å^3)	1357(5)	1314–1342	424–436	421–428
Z	18	18	6	6
Optical data:	Uniaxial (+)	Uniaxial (+)	Uniaxial (+)	Uniaxial (+)
ω	1.76(1)	1.760	1.714–1.717	1.717–1.722
ε	1.86(1)	1.870	1.818	1.818–1.823
Sources	This work	Kirillov (1964, 1966); Yang *et al.* (2008); Michiba *et al.* (2013)	Kupriyanova (1968); Pekov *et al.* (2002); Anthony *et al.* (2003	Aleksandrov (1965); Ni *et al.* (1993); Terada *et al.* (1993); Anthony *et al.* (2003); Miyawaki *et al.* (2013)

*Data for holotype. **Both natural samples of hydroxylbastnäsite-(Ce) with determined crystal structure possess the space group $P\bar{6}$ and unit-cell parameters a = 12.41–12.47 and c = 9.85–9.96 Å (Z = 18) (Yang *et al.*, 2008; Michiba *et al.*, 2013) [synthetic bastnäsite-like hydroxyl-carbonates $REE(CO_3)(OH)$ with REE = trivalent La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er have the same space group and unit-cell metrics: Christensen, 1973; Kutlu and Meyer, 1999; Michiba *et al.*, 2011], whereas in older publications, hydroxylbastnäsite-(Ce) and hydroxylbastnäsite-(Nd) were reported, by analogy with a fluorine-rich bastnäsites, with the hexagonal unit cell with parameters a = 7.19–7.23 and c = 9.92–9.98 Å (Z = 6) (Kirillov, 1964, 1966; Aleksandrov, 1965; Maksimović and Pantó, 1985; Minakawa *et al.*, 1992), and the space group $P\bar{6}2c$, found for the structurally studied F-rich members of the bastnäsite-(Ce) – bastnäsite-(La) series (Oftedal, 1931; Donnay and Donnay, 1953), was also suggested in this period for hydroxylbastnäsites (Anthony *et al.*, 2003).

The values of the Gladstone–Dale compatibility index 1 – (K_p/K_c) (Mandarino, 1981) for the holotype hydroxylbastnäsite-(La) calculated with D_{meas} and D_{calc} are –0.009 and –0.003, respectively (both rated as superior).

X-ray crystallography and crystal structure determination details

Single-crystal XRD studies of the holotype sample of hydroxylbastnäsite-(La) were carried out at room temperature using an Xcalibur S diffractometer equipped with a CCD detector (Mo$K\alpha$-radiation). The mineral is hexagonal, a = 12.562(2), c = 10.015(2) Å and V = 1368(1) Å^3.

Powder XRD data for both holotype and cotype samples were collected with a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with a cylindrical image plate detector (radius 127.4 mm) using Debye-Scherrer geometry, Co$K\alpha$ radiation (rotating anode with VariMAX microfocus optics), 40 kV, 15 mA and exposure 15 min. Angular resolution of the detector is 0.045° (2θ; pixel size 0.1 mm). The data were integrated using the software package *Osc2Tab* (Britvin *et al.*, 2017). Powder XRD data for the holotype are given in Table 2, the powder XRD pattern of the cotype shows no significant differences. The hexagonal unit cell parameters calculated from powder data for holotype/cotype are: a = 12.537(3)/12.533(1), c = 9.968(2)/9.908(1) Å, V = 1356.8(5)/1347.9(3) Å^3 and Z = 18.

All the single crystals of hydroxylbastnäsite-(La) tested were not very high in quality: even though they appeared to be perfect (Fig. 1), in fact they have a mosaic character in the inner structure and consist of blocks slightly disoriented with respect to each other. The crystal structure of holotype hydroxylbastnäsite-(La) was refined with the powder XRD data (for the data collecting details see above) using the Rietveld method. Data treatment and the Rietveld structure analysis were carried out using the *JANA2006* program package (Petříček *et al.*, 2006). The structure model of hydroxylbastnäsite-(Ce) (Yang *et al.*, 2008) was taken as the starting one. The scattering curve of Ce was used for the *REE* sites. The profiles were modelled using a pseudo-Voigt function. The structure was refined in isotropic approximation of atomic displacements, the values of U_{iso} for all atoms of each sort were restricted to be equal, atomic coordinates and U_{iso} of C atoms were fixed on the last stages of the refinement. The cation–anion interatomic distances were restricted nearby the values of the starting structure model. The space group is $P\bar{6}$, for the refined unit-cell parameters see above. Final agreement factors are: R_{wp} = 0.0071, R_p = 0.0050 and R_{obs} = 0.0466. The observed and calculated powder XRD diagrams demonstrate a very good agreement (Fig. 4). Coordinates and displacement parameters of atoms are given in Table 3 and selected interatomic distances in Table 4. The crystallographic information file has been deposited with the Principal Editor of *Mineralogical Magazine* and is available as Supplementary material (see below).

Discussion

Fluorine- and hydroxyl-dominant members of the bastnäsite group are structurally close but not isostructural. Fluorine-dominant minerals of the bastnäsite-(Ce) – bastnäsite-(La) series and bastnäsite-(Nd) adopt the space group $P\bar{6}2c$ and are characterised by a unit cell with the following parameters: a = 7.1–7.2, c = 9.7–9.8 Å and V = 422–436 Å^3 (Z = 6) (Oftedal, 1931; Donnay and Donnay, 1953; Ni *et al.*, 1993; Terada *et al.*, 1993; Mi *et al.*, 1996; Miyawaki *et al.*, 2013). The crystal structure of bastnäsite-(Y) was not studied. Among hydroxyl-dominant minerals of the group, only hydroxylbastnäsite-(Ce) was structurally studied earlier, on samples from Trimouns, Luzenac, France and Kamihouri, Miyazaki Prefecture, Japan. It crystallises in the space group $P\bar{6}$ and has a unit cell with the following parameters: a = 12.41–12.47, c = 9.85–9.96 Å and V = 1314–1342 Å^3 (Z = 18) (Yang *et al.*, 2008; Michiba *et al.*, 2013): see Table 5. Synthetic bastnäsite-like hydroxyl-carbonates $REE^{3+}(CO_3)(OH)$ with REE = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho and Er demonstrate the same space group $P\bar{6}$ and unit-cell metrics as hydroxylbastnäsite-(Ce) (Christensen, 1973; Kutlu and Meyer, 1999; Michiba *et al.*,

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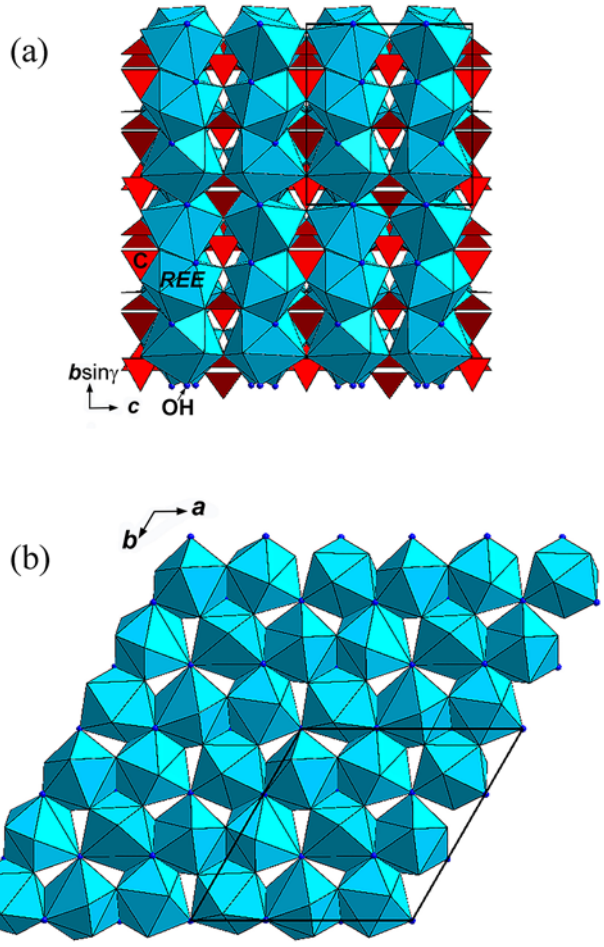


Figure 5. The crystal structure of hydroxylbastnäsite-(La) projected along the a axis (a) and the layer of *REE*-centred polyhedra in it (b). The unit cell is outlined. Drawn using *Diamond* Version 3.2k.

2011). Note, synthetic bastnäsite-like $La(CO_3)(OH)$, an analogue of the end-member hydroxylbastnäsite-(La) is known (Hsu *et al.*, 1992; Michiba *et al.*, 2011). The relationship between unit cells of F- and OH-dominant bastnäsites is as follows: $a_{\text{hydroxylbastnäsite}} \approx a_{\text{bastnäsite}}\sqrt{3}$, $c_{\text{hydroxylbastnäsite}} \approx c_{\text{bastnäsite}}$. The difference between F- and OH-dominant bastnäsites is in their atomic arrangement (Figs 5 and 6). In particular, there are 6, 3 and 5 symmetrically non-equivalent CO_3 groups, REE^{3+} cations, and X^{-} anions, respectively, in hydroxylbastnäsites as distinct to 1, 1 and 2, respectively in F-dominant bastnäsites (see references above). However, the crystal structures of the bastnäsite-like compounds crystallised in the space groups $P\bar{6}$ and $P\bar{6}2c$ exhibit many common features: they are based on the layers of *REE* and F/OH alternating with the layers of CO_3 groups (Fig. 6).

As our data show, hydroxylbastnäsite-(La) is isostructural to hydroxylbastnäsite-(Ce) (Yang *et al.*, 2008; Michiba *et al.*, 2013) and synthetic bastnäsite-like hydroxyl-carbonates $REE^{3+}(CO_3)(OH)$ with *REE* = La–Er (Michiba *et al.*, 2011 and references therein) rather than F-dominant bastnäsites. The crystal structure of hydroxylbastnäsite-(La) (Fig. 5a) is based upon the (001) layers of REE^{3+} cations and $(OH)^{-}$ anions interspersed with carbonate layers in a 1:1 ratio. Three crystallographically non-equivalent *REE* sites occupy nine-fold polyhedra $REEO_6(OH)_3$. Hydroxyl groups are located inside *REE* layers where *REE*-centred polyhedra are connected *via* common O–OH edges and OH vertices (Fig. 5b). Neighbouring *REE* layers are connected *via* CO_3 groups and one common O vertex of *REE*-centred polyhedra. As well as in hydroxylbastnäsite-(Ce), the coordination of REE^{3+} cations is formed by three $(OH)^{-}$ anions and five $(CO_3)^{2-}$ anions four of which are monodentate ligands and one is a bidentate ligand in contrast with F-dominant bastnäsites crystallising in space group $P\bar{6}2c$ where *REE* sites are coordinated by three F^{-} anions and six monodentate $(CO_3)^{2-}$ anions. The comparison of the atomic arrangements in the structures of bastnäsite-(Ce) and hydroxylbastnäsite-(La) is given in Fig. 6.

The difference in symmetry causes the difference (not too strong but distinct) in powder XRD patterns of F- and OH-dominant bastnäsites, at the first instance, due to additional systematic absences in the patterns of F-dominant bastnäsites (space group $P\bar{6}2c$) in comparison with the patterns of hydroxylbastnäsites ($P\bar{6}$). The powder XRD pattern of hydroxylbastnäsite-(La) (Table 2) shows the similarity with the calculated pattern of $REE^{3+}(CO_3)(OH)$ with the space group $P\bar{6}$. In particular, hydroxylbastnäsite-(La) demonstrates three reflections in the region 2.7–2.5 Å in which the calculated powder XRD pattern of hydroxylbastnäsites ($P\bar{6}$) also contains three reflections with $I \geq 0.5\%$, whereas the calculated pattern of F-dominant bastnäsites ($P\bar{6}2c$) contains only one reflection. A distinct reflection with $d = 2.235$ Å is present in both measured and calculated powder XRD patterns of

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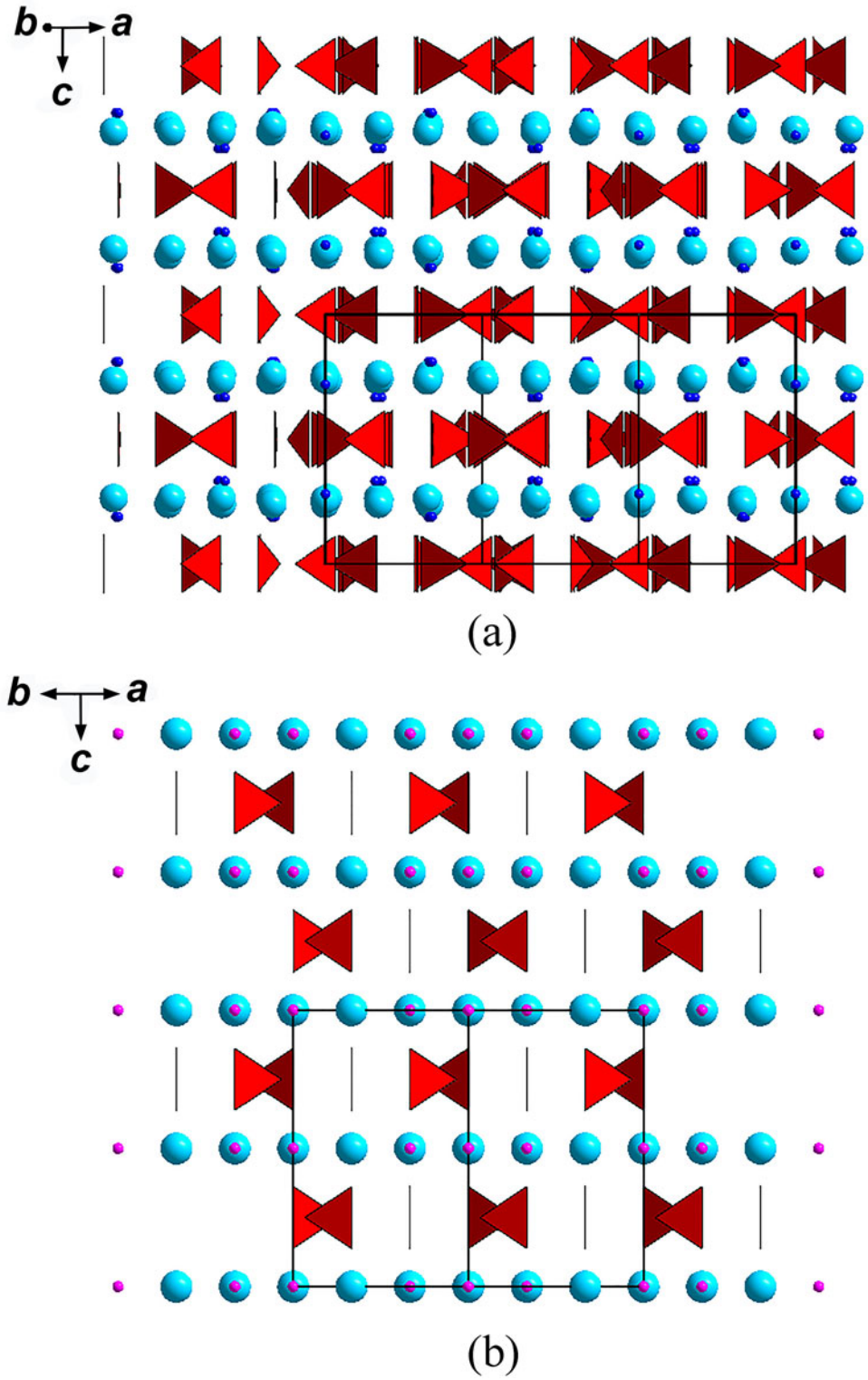


Figure 6. The crystal structures of hydroxylbastnäsite-(La) (projected along [120]; (a) and bastnäsite-(Ce) (projected along [110]; (b: drawn after Donnay and Donnay, 1953). For legend see Figure 5; fluorine atoms in bastnäsite-(Ce) are shown as small reddish-pink circles. The unit cells are outlined.

hydroxylbastnäsite-(La) but is absent in the patterns of F-dominant bastnäsites ($P\bar{6}2c$). These and some other features of the powder XRD pattern causes the choice of the space group $P\bar{6}$ and corresponding unit-cell metrics for hydroxylbastnäsite-(La).

The IR spectrum of hydroxylbastnäsite-(La) (curve ***a*** in Fig. 3), unlike the IR spectra of F-dominant bastnäsite-group minerals (see, *e.g.* curve ***b*** in Fig. 3), clearly demonstrates the presence of several non-equivalent $(CO_3)^{2-}$ and $(OH)^-$ groups (see above)

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that confirms its lower symmetry in comparison with F-dominant bastnäsites.

Hydroxylbastnäsite-(La) and hydroxylbastnäsite-(Ce) have distinctly higher values of unit-cell dimensions and volume (easily comparable in the same setting) and refractive indices in comparison with their F-dominant analogues (Table 5). The triple unit-cell volumes of bastnäsite-(Ce)–bastnäsite-(La) series minerals ($Z = 18$) varies from 1266 to 1308 Å^3 whereas minerals of the hydroxylbastnäsite-(Ce)–hydroxylbastnäsite-(La) series have a unit-cell volume from 1314 to 1357 Å^3. Unit-cell dimensions of two samples of hydroxylbastnäsite-(La), from Vuoriyarvi and Mochalin Log (see above), are in agreement with the OH:F ratio. The refractive indices of hydroxylbastnäsites are higher than corresponding values of F-dominant bastnäsites, with the significant difference of 0.04–0.05 (Table 5). The distinct increase of unit-cell dimensions with the substitution of F^- by $(OH)^-$ is typical in such pairs of isotypic or structurally close compounds [*e.g.* the fluorapatite $Ca_5(PO_4)_3F$ – hydroxylapatite $Ca_5(PO_4)_3(OH)$ (White *et al.*, 2005) or fluoborite $Mg_3(BO_3)F_3$ – hydroxylborite $Mg_3(BO_3)(OH)_3$ series (Cámara and Ottolini, 2000; Rudnev *et al.*, 2007)], as well as refractive indices. These characteristics can be used as good indicators of the prevailing of F^- or $(OH)^-$ in rare-earth minerals of the bastnäsite group. The correctness of determination of chemical and crystal data and density of hydroxylbastnäsite-(La) is confirmed by the very low (superior) value of the Gladstone–Dale compatibility index.

In terms of end-member compositions, hydroxylbastnäsite-(La) is dimorphous with kozoite-(La), ideally $La(CO_3)(OH)$, a member of the ancylite supergroup (Miyawaki *et al.*, 2003; Wang *et al.*, 2024).

Supplementary material. The supplementary material for this article can be found at https://doi.org/10.1180/mgm.2024.65.

Acknowledgements. We thank three anonymous referees for their valuable comments. The mineralogical and crystal chemical studies of hydroxylbastnäsite-(La) from Vuoriyarvi was performed in accordance with the State Task of the RF No. 121061600049-4. The IR spectra were obtained and interpreted in accordance with the State Task of the RF No. 124013100858-3. Powder XRD study was done at the Center for X-ray Diffraction Studies of the Research Park of St. Petersburg State University within the project No. AAAA-A19-119091190094-6.

Competing interests. The authors declare none.

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https://doi.org/10.1180/mgm.2024.65 Published online by Cambridge University Press