

Wakefieldite-(La), LaVO₄, a new mineral species from the Glücksstern Mine, Friedrichroda, Thuringia, Germany

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Abstract: Wakefieldite-(La), ideally LaVO₄, is a new mineral from the long abandoned Glücksstern Mine, Gottlob hill, Friedrichroda, Thuringia, Germany. The mineral occurs as light pinkish to brown prismatic crystals up to 0.5 mm in length. Wakefieldite-(La) is associated with hausmannite, baryte and gottlobite. The streak is white, the Mohs hardness 4 and the luster adamantine. The crystals are transparent to translucent. Electron microprobe analysis gave (wt.%) La₂O₃ 43.87, Ce₂O₃ 0.31, Nd₂O₃ 9.49, Pr₂O₃ 6.65, Sm₂O₃ 0.58, Y₂O₃ 0.31, CaO 0.10, UO₂ 0.01, V₂O₅ 34.91, As₂O₅ 0.06, P₂O₅ 0.02, SiO₂ 0.04, total 96.35. The empirical formula is (La_{0.71}Nd_{0.15}Pr_{0.11}Sm_{0.01}Y_{0.01})_{Σ0.99}V_{1.01}O_{4.00}, ideally LaVO₄. The new mineral (IMA 89-035a) is the La analogue of wakefieldite-(Ce) and wakefieldite-(Y) and a member of the xenotime group. Wakefieldite-(La) has a zircon-type crystal structure (tetragonal, space group *I4₁amd*), with *a* = 7.406(4), *c* = 6.504(8) Å, *V* = 356.8(6) Å³ from X-ray powder diffraction data, and *a* = 7.432(1), *c* = 6.521(1) Å, *V* = 360.18(9) Å³ from the single-crystal structure refinement (*R*₁ = 1.04 %). The La site is eight-coordinated to O atoms, with La–O distances of 2.4558(13) Å (× 4) and 2.5381(14) Å (× 4). The V–O distance equals 1.7133(13) Å (× 4). The calculated density for the measured composition is 4.703 g/cm³. Wakefieldite-(La) is uniaxial positive with ω and ε > 1.90, birefringence is medium, pleochroism E pale pinkish and O pale pinkish yellow.

Key-words: wakefieldite-(La), new mineral, crystal structure, xenotime group, zircon type, Friedrichroda, Thuringia, vanadate.

Introduction

In 2001, a few samples from the Glücksstern Mine, Friedrichroda, Thuringia, with unidentified prismatic crystals associated with hausmannite and gottlobite, were submitted for analysis by R. Schmidt (Schleusingen, Thuringia) to one of the authors (T.W.). Semi-quantitative energy-dispersive (EDX) analyses and X-ray powder diffraction studies showed the crystals to be a La-dominant REE vanadate with a zircon-type structure. Subsequent investigations, which included a single-crystal structure determination, confirmed that the mineral is a new species and the La analogue of wakefieldite-(Ce) and wakefieldite-(Y). The mineral has been named wakefieldite-(La) accordingly. Both mineral and name have been approved in November 2007 by the IMA Commission on New Minerals, Nomenclature and Classification prior to publication (vote 89-035a). Note that voting on a previous original proposal for wakefieldite-(La) (89-035) by Howard, Tschernich and Klein was suspended (Memorandum of September 29, 1989) because of doubts on the results of the chemical analysis (Ernst Burke, pers. comm., 2007). After obtaining new analyses, Howard *et al.* (1995) published their results as obtained on La-rich wakefieldite-(Ce). In spite of this, the Commission Chair-

man decided to use the same IMA number for the proposal submitted by the present authors because it concerns the same mineral name (Ernst Burke, pers. comm., 2007).

Type material is deposited in the Mineralogical Collection of the Bergakademie Freiberg, Germany, as No. 81876.

Occurrence and paragenesis

Type locality of wakefieldite-(La) is the long abandoned Glücksstern Mine near the Gottlob quarry at the northern slope of the Gottlob hill, Friedrichroda, Thuringia (Thüringen), Germany. Until 1855, manganese and iron ores were mined at the Gottlob hill (Scheven, 1990). The mineral occurs in hydrothermal baryte veins cutting a Lower Rotliegend (Autunian) conglomerate (Seidel, 1995). Specimens of the new mineral were collected on old dumps. The Glücksstern mine is also the type locality for gottlobite (Witzke *et al.*, 2000), and the Gottlob hill, Friedrichroda (mine not specified) the type locality for crednerite, CuMnO₂ (Credner, 1847; Rammelsberg, 1847) and vésigniéite, BaCu₃(VO₄)₂(OH)₂ (Guillemin, 1955).

Wakefieldite-(La) is associated with hausmannite, baryte and gottlobite. The mineral is grown in small vugs on



Fig. 1. Prismatic crystal of wakefieldite-(La) on hausmannite. Glücksstern mine, Gottlob hill, Friedrichroda, Thuringia, Germany. Picture size 1.9 mm. Photo: Fritz Rüger.

pseudo-octahedral hausmannite as small freestanding crystals. The lanthanum vanadate has apparently crystallised from low-temperature hydrothermal solutions. It is younger than hausmannite. The very low Ce content (0.31 wt.%, see below) is explained by formation from a strongly Ce-depleted source due to oxidation of Ce^{3+} , and subsequent formation of insoluble CeO_2 , as observed for several other LREE minerals, which are not Ce-dominant. Wakefieldite-(La) is very rare, only 10 crystals on seven micromount-sized specimens have been found at present.

We note that natural $LaVO_4$ with unspecified structure type also occurs as small grains in a V-rich davidite from Mozambique (Pierre-Alain Wuelser, pers. comm. to UK, 2004). For a discussion on the polymorphism of $LaVO_4$ see further below.

Appearance and physical properties

Wakefieldite-(La) occurs as light pinkish to brown, small, freestanding prismatic crystals, elongated along [001] and 0.1–0.5 mm in length (Fig. 1). The crystals show the pinacoid {001}, the prism {100} (probably), and possibly a dipyrmaid (indistinct, observed on two crystals).

The streak of the mineral is white. The crystals are brittle, have an adamantine luster and are transparent to translucent. The Mohs hardness is around 4, the fracture is uneven. A cleavage was not observed, but according to the preferred orientation reflected by the X-ray powder diffraction pattern a cleavage on {100} is possible. Wakefieldite-(La) shows no fluorescence in long- and short-wave UV. The calculated density for $Z = 2$ for the measured composition and cell from the X-ray powder data is 4.703 g/cm^3 and for the end-member composition 4.727 g/cm^3 .

Optically, wakefieldite-(La) is uniaxial positive with ω and $\epsilon > 1.90$, birefringence is medium. The mineral shows a pleochroism E pale pinkish, O pale pinkish yellow, the absorption is $E > O$.

Chemical composition

Chemical analyses of wakefieldite-(La) were performed by means of both EDX and wavelength-dispersive X-ray spectrometry. An EDX spectrum obtained with a LEO 1525 Gemini field emission scanning electron microscope revealed La, Ce, Y, Nd, V, and O as the only elements present with atomic number > 7 , a relation of Rare Earth elements:vanadium around 1:1 and La as the dominant Rare Earth element.

Quantitative analyses were conducted with a JEOL JXA-8900R electron microprobe operated at an acceleration voltage of 15 kV, a beam current of 23 nA and a spot size of $2 \mu\text{m}$ with monazite (La, Ce, Nd, Pr, P), metallic samarium (Sm), glass with 12 % Y_2O_3 (Y), plagioclase (Ca, Si), glass with 4.3 % UO_2 (U), metallic vanadium (V) and NiAs (As) as standards. The JEOL correction method ZAF was used for data reduction.

Half of a selected crystal was analyzed at 10 different points (the other half was used for the crystal structure determination, see below). The average analysis (wt.% and range) is given in Table 1. The somewhat low oxide sum obtained from the EPMA data (96.37 wt.%) may be tentatively explained by the following possible reasons: imperfect corrections for overlap of REE peaks; imperfect polishing; very minor amounts of additional REE, or the use of metallic V as standard for the measurement of the vanadium content.

Table 1. Chemical analyses of wakefieldite-(La).

Constituent	Wakefieldite-(La) wt.% (meas.)*	Range	Standard deviation	LaVO ₄ wt.% (calc.)
La ₂ O ₃	43.87	54.33–37.05	6.00	64.18
Ce ₂ O ₃	0.31	0.89–0	0.34	
Nd ₂ O ₃	9.49	13.87–2.68	4.04	
Pr ₂ O ₃	6.65	8.88–3.87	1.89	
Sm ₂ O ₃	0.58	1.11–0	0.41	
Y ₂ O ₃	0.31	0.90–0.05	0.27	
CaO	0.10	0.26–0.03	0.07	
UO ₂	0.03	0.14–0	0.04	
V ₂ O ₅	34.91	35.19–34.74	0.17	35.82
As ₂ O ₅	0.06	0.11–0	0.04	
P ₂ O ₅	0.02	0.06–0	0.02	
SiO ₂	0.04	0.08–0.01	0.02	
Total	96.37	97.25–95.43	0.65	100.00

*Average of 10 analyses.

Table 2. X-ray powder diffraction data for wakefieldite-(La).

<i>I</i> _{meas.}	<i>I</i> _{calc.}	<i>d</i> _{meas.} (Å)	<i>d</i> _{calc.} (Å)	<i>hkl</i>
2	27	4.906	4.887	101
100	100	3.707	3.703	200
5	8	2.939	2.952	211
10	67	2.759	2.763	112
7	21	2.623	2.619	220
3	3	2.447	2.444	202
5	13	2.309	2.308	301
5	8	2.088	2.081	103
–	11		1.965	321
4	54	1.902	1.901	312
19	14	1.853	1.852	400
3	4	1.811	1.814	213
3	11	1.656	1.656	420
2	2	1.626	1.629	303

Note: calculated intensities based on the refined structure model.

The empirical formula for the average composition, calculated on the basis of 4 O atoms, is (La_{0.71}Nd_{0.15}Pr_{0.11}Sm_{0.01}Y_{0.01})_{Σ0.99}V_{1.01}O_{4.00}, the ideal composition is LaVO₄. The La₂O₃ content is inversely correlated with the Nd₂O₃ + Pr₂O₃ (+ other Rare Earths) content due to solid solution. Empirical formulas for the highest and lowest measured La₂O₃ value are (La_{0.87}Pr_{0.05}Nd_{0.04}Ca_{0.01}U_{0.01})_{Σ0.98}V_{1.01}O_{4.00} and (La_{0.60}Nd_{0.21}Pr_{0.14}Ce_{0.01}Sm_{0.01}Y_{0.01}Ca_{0.01})_{Σ0.99}V_{1.00}O_{4.00}, respectively.

X-ray powder diffraction

The X-ray powder diffraction pattern (Table 2) was recorded using a Siemens D500 diffractometer with CuK α_1 radiation ($\lambda = 1.5406$ Å) and a secondary graphite monochromator. The reflections were indexed according to other members of the xenotime group. Refinement of the powder diffraction data gave the unit-cell parameters of an *I*-centred tetragonal cell with $a = 7.406(6)$, $c = 6.504(8)$ Å, $V = 356.8(6)$ Å³. The XRD pattern showed a preferred orientation on {100} due to sample preparation and/or a cleavage on {100}. The pattern was obtained from only two small prismatic

crystals, which were crushed between two glass plates and then pressed onto a zero-background silicon wafer.

Crystal structure

The crystal structure of wakefieldite-(La) has been solved by direct methods from single-crystal intensity data collected with a four-circle diffractometer (MoK α radiation, CCD area detector, 293 K, crystal size $0.07 \times 0.07 \times 0.12$ mm³, full sphere, *hkl* range $-11/11$, $-8/8$ and $-10/10$, $2\theta_{\max} = 70^\circ$, multi-scan absorption correction, $R_{\text{int}} = 0.95$ %). The structure was refined with SHELXL-97 (Sheldrick, 1997) in space group *I4₁/amd* (no. 141) to $R_1 = 1.04$ % and $wR_{2\text{all}} = 2.68$ % [209 ‘observed’ reflections with $F_o > 4 \sigma(F_o)$; 12 refined parameters, extinction coefficient 0.0045(4); weighting scheme: $w = 1/[\sigma^2(F_o^2) + (0.013P)^2 + 0.34P]$, where $P = ([\max \text{ of } (0 \text{ or } F_o^2)] + 2F_c^2)/3$; GooF 1.207; $\Delta\rho_{\min}/\Delta\rho_{\max} = 0.73/-0.50$ e/Å³], with the unit-cell parameters $a = 7.432(1)$, $c = 6.521(1)$ Å, and $V = 360.18(9)$ Å³ (determined from 422 reflections). The results confirm that wakefieldite-(La) has the zircon-type structure. Coordinates and displacement parameters are given in Table 3. The occupancy of the La site was fixed according to the measured REE contents, since half of the crystal selected for the structure determination was subsequently used for EPMA. The V site was found to be fully occupied by V within error limits of the refinement, in agreement with the chemical data. Some minor variability of the chemical composition of the type material is indicated by the slight variability of the refined unit-cell parameters. The cell volume of the crystal fragment measured is slightly larger than the volume obtained from the refinement of the X-ray powder diffraction data from two different crystals, and indicated a slightly lower La content of the latter. In both cases, the unit cell is larger than all corresponding values reported for wakefieldite-(Ce) and synthetic, zircon-type CeVO₄ (Table 4). As also expected, the cell parameters of chemically pure, zircon-type LaVO₄ are slightly higher (Table 4). The La site is coordinated by eight O atoms, with La–O distances of 2.4558(13) Å ($\times 4$) and 2.5381(14) Å ($\times 4$). The V–O

Table 3. Fractional atomic coordinates and displacement parameters (in Å²) for wakefieldite-(La).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
La*	0.0	0.75	0.125	0.00758(8)	0.00875(9)	0.00875(9)	0.00524(11)	0.0	0.0	0.0
V	0.0	0.25	0.375	0.00628(12)	0.00743(17)	0.00743(17)	0.0040(2)	0.0	0.0	0.0
O	0.0	0.42758(17)	0.2075(2)	0.0134(2)	0.0203(6)	0.0101(5)	0.0098(4)	0.0009(4)	0.0	0.0

*Occupancy of La site: La_{0.71}Nd_{0.15}Pr_{0.11}Sm_{0.01}Y_{0.02} (fixed on the basis of the EPMA data).

Table 4. Comparison of relevant data for wakefieldite-(La) and related minerals and compounds.

	Wakefieldite-(La) ^a	syn. LaVO ₄	Wakefieldite-(Ce) ^b	syn. CeVO ₄	syn. CeVO ₄	Wakefieldite-(Y)
Formula	LaVO ₄	LaVO ₄	CeVO ₄	CeVO ₄	CeVO ₄	YVO ₄
Crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space group	<i>I4</i> ₁ / <i>amd</i>	<i>I4</i> ₁ / <i>amd</i>	<i>I4</i> ₁ / <i>amd</i>	<i>I4</i> ₁ / <i>amd</i>	<i>I4</i> ₁ / <i>amd</i>	<i>I4</i> ₁ / <i>amd</i>
<i>a</i> (Å)	7.406	7.458	7.354	7.383	7.400	7.105
<i>c</i> (Å)	6.504	6.542	6.488	6.485	6.497	6.29
<i>V</i> (Å ³)	356.8	363.9	350.9	354.5	355.8	317.5
<i>Z</i>	4	4	4	4	4	4
<i>D</i> _{calc.} (g/cm ³)	4.72	4.63	4.80	4.79	4.76	4.25
Optical char.	1(+)	n.d.	1(+) ^c	n.d.	n.d.	1(+)
ω	> 1.9	n.d.	1.97	n.d.	n.d.	2.00
ε	> 1.9		2.16			2.14
Reference	This work	Oka <i>et al.</i> (2000)	Deliens & Piret (1977); Baudracco-Gritti <i>et al.</i> (1987)	Range <i>et al.</i> (1990)	Chakoumakos <i>et al.</i> (1994)	Miles <i>et al.</i> (1971)

^aFrom X-ray powder diffraction data (single-crystal data: *a* = 7.432, *c* = 6.521 Å, *V* = 360.2 Å³).

^bOriginally named kusuite.

^cDeliens & Piret (1977): 1(−), ω and ε > 2.0 for plumboan wakefieldite-(Ce).

Notes: n.d. = not determined.

distance equals 1.7133(13) Å (× 4). The O–V–O angles (2 × 100.77(9)° and 4 × 113.99(5)°) are similar to those in other zircon-type REE vanadates.

Polymorphism of LaVO₄

REEVO₄ compounds have been studied by a large number of authors (see Kolitsch & Holtstam, 2004, and references therein). There is general agreement that synthetic, chemically pure LaVO₄ is, under “normal” conditions (*i.e.*, if prepared by high-temperature solid-state synthesis or flux growth), the only REE vanadate crystallising in the monazite-type structure, whereas all other REE members (Ce–Lu, Sc) exhibit the zircon-type structure. However, monazite-type REEVO₄ (REE = Ce, Pr, Nd) can be prepared in metastable form. It was also reported that the structure of LaVO₄ depends on the mode of preparation; for example, it was observed that LaVO₄ precipitated from solution has the zircon-type structure, but, after heating above *ca.* 300 °C converts into the monazite-type form (*e.g.*, Ropp & Carroll, 1973). Daimon *et al.* (2002), who prepared LaVO₄ at 20 °C from aqueous solutions of LaCl₃ and ammonium vanadate (V), observed that monazite-type LaVO₄ tended to coexist with zircon-type LaVO₄ at pH 5–8. Single-phase monazite-type LaVO₄ was obtained only at pH 9. The dependency of LaVO₄ polymorph stability on pH was also observed by Fan *et al.* (2006) during

hydrothermal preparations without the presence of catalysts or templates. Jia *et al.* (2005) observed that the choice of chelating additives such as EDTA in hydrothermal preparation of LaVO₄ exerts a distinct control on which polymorph is formed.

Stabilisation of zircon-type LaVO₄ can be achieved by the partial substitution of La with other REE. Varma *et al.* (2002) synthesised mixed orthovanadates La_{1-x}Ce_xVO₄ by solid-state reaction at 600 °C, and demonstrated that a monazite-type solid-solution phase was retained for the samples with *x* ≤ 0.2, while a zircon-type solid-solution was stabilised for *x* ≥ 0.5. In the intermediate range 0.2 < *x* < 0.5, both monazite-type LaVO₄ and zircon-type La_{0.5}Ce_{0.5}VO₄ coexisted. The characterisation of crystals of La_{1-x}REE_xVO₄ (REE = Gd, Y and *x* = 0.2, 0.4, 1.0) grown by the laser-heated pedestal technique (Andreeta *et al.*, 2006) showed that zircon-type LaVO₄ solid-solution members crystallised for *x* = 0.2 and 0.4, while monazite-type LaVO₄ was found for *x* = 1.0.

The occurrence of zircon-type LaVO₄ with near end-member composition in Nature probably indicates stabilisation by the minor amounts of the smaller REE³⁺ cations detected (*i.e.*, Nd, Pr, Sm, Y) and the other impurities present (Si, P, As). Aqueous species in the hydrothermal solution may also have played a stabilising role. A monazite-type dimorph of wakefieldite-(La) could exist in assemblages that have been subjected to higher degrees of metamorphism.

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