Schlüterite-(Y), ideally (Y,*REE*)₂Al(Si₂O₇)(OH)₂F, a new mineral species from the Stetind pegmatite, Tysfjord, Nordland, Norway: description and crystal structure

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[Received 26 December 2012; Accepted 25 March 2013; Associate Editor: S. Krivovichev]

ABSTRACT

Schlüterite-(Y), ideally (Y,REE)₂Al(Si₂O₇)(OH)₂F, is a new silicate mineral species from the Stetind pegmatite, Tysfjord, Nordland, Norway. It forms dense, fibrous, radiating aggregates (up to ~2 mm) diverging to individual needle-like crystals (up to $\sim 1 \text{ mm long}$) in cavities. Crystals are acicular to bladed, flattened on {001} and elongated along [010], and the dominant form is {001}. Schlüterite-(Y) is transparent, pale pink with a white streak and a vitreous lustre, and does not fluoresce under short-wave ultraviolet light. Mohs hardness is $5\frac{1}{2}-6$, and schlüterite-(Y) is brittle with an irregular fracture, and has no cleavage. The calculated density is 4.644 g/cm³. The indices of refraction are $\alpha = 1.755$, $\beta = 1.760$, $\gamma =$ 1.770, all \pm 0.005, $2V_{obs} = 71.8$ (5)°, $2V_{calc} = 71°$, non-pleochroic, optic orientation is $X^{\land} a = 83.1°$ (β obtuse), Y // b, $Z \wedge c = 50.3^{\circ}$ (β acute). Schlüterite-(Y) is monoclinic, space group $P2_1/c$, a 7.0722(2), b 5.6198(1), c 21.4390(4) Å, β 122.7756(3)°, V 716.43(5) Å³, Z = 4. The seven strongest lines in the X-ray powder-diffraction pattern are as follows: [d(Å), I, (hkl)]: 4.769, 100, (012); 2.972, 55, (214); 3.289, 51, (112); 2.728, 49, (216); 2.810, 37, (020); 3.013, 37, ((116); 4.507, 36, (004). Chemical analysis by electron microprobe gave SiO₂ 22.64, Al₂O₃ 9.45, Y₂O₃ 15.35, La₂O₃ 3.25, Ce₂O₃ 9.69, Pr₂O₃ 2.05, Nd₂O₃ 9.50, Sm₂O₃ 3.57, Gd₂O₃ 4.65, Dy₂O₃ 4.21, Er₂O₃ 2.31, Yb₂O₃ 1.86, F 2.71, H₂O_{calc} 3.78, O = F -1.14, sum 93.88 wt%. The H₂O content was determined by crystal-structure analysis. On the basis of 10 anions with (OH) + F = 3 a.p.f.u. (atoms per formula unit), the empirical formula is $(Y_{0.73}Ce_{0.32}Nd_{0.30}Gd_{0.14}Dy_{0.12}La_{0.11}Sm_{0.11}Pr_{0.07}Er_{0.06}Yb_{0.05})_{\Sigma=2.01}Al_{0.99}Si_{2.01}O_7(OH)_{2.24}F_{0.76}.$ The crystal structure of schlüterite-(Y) was solved by direct methods and refined to an R_1 index of 1.8% based on 1422 unique observed reflections. In the structure of schlüterite-(Y), Al(OH)₄O₂ octahedra share (OH)–(OH) edges to form $[M\Phi_4]$ chains that are decorated by (Si_2O_7) groups that bridge O vertices of neighbouring octahedra in a staggered fashion on either side of the chain. These $[Al(OH)_2(Si_2O_7)]$ chains extend parallel to b, and are linked into a continuous framework via bonds to interstitial ^[8](Y,REE) (= <2.400 Å>) and ^[9](Y,REE) (= <2.548 Å>) atoms.

Keywords: Schlüterite-(Y), new mineral species, silicate, Stetind pegmatite, Tysfjord, Nordland, Norway, crystal structure, electron microprobe analysis, optical properties.

Introduction

THE Stetind pegmatite belongs to a series of quartz-microcline pegmatites of the NYF family

* E-mail: frank_hawthorne@umanitoba.ca DOI: 10.1180/minmag.2013.077.3.09 found in the Tysfjord granite, an 1800 Ma old granitic gneiss deformed during the Caledonian orogeny (Andresen and Tull, 1986). Lenticular bodies of yttrium-rich fluorite are a characteristic feature of these pegmatites, and the fluorite from the Stetind pegmatite is particularly rich in inclusions of various *REE*-minerals (Husdal,

2008), including the new species stetindite (Schlüter *et al.*, 2009), atelisite-(Y) (Malcherek *et al.*, 2012), bastnäsite-(Nd) (IMA 2011-062), cayalsite-(Y) (IMA 2011-094), perbøeite-(Ce) (IMA 2011-055) and IMA 2012-054. The recent discovery of another new species has given us the opportunity to name it in honour of Professor Jochen Schlüter (born 29 December 1955), curator and director of the Mineralogical Museum of the University of Hamburg since 1988, who has described 20 new minerals to date, including stetindite and atelisite-(Y) from the Stetind pegmatite.

The new mineral and mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification, International Mineralogical Association (IMA 2012-015). The holotype specimen of schlüterite-(Y) has been deposited in the mineral collection of the Department of Natural History, Royal Ontario Museum, Toronto, catalogue number M56409. Additional cotype material (single-crystal structure refinement and electron-microprobe analysis) has been deposited in the collections of the Natural History Museum, Oslo, Norway, catalogue numbers 42428 and 42429.

Occurrence

Schlüterite-(Y) was discovered at the Stetind pegmatite, Tysfjord, Nordland, Norway (68°10'15.20"N 16°33'10.65"E). This pegmatite, situated at the foot of Mt Stetind, was guarried for quartz for a short period during the 1960s. Yttrian fluorite has been found in the inner parts of the quarry, forming lenticular to sheet-like white masses along a zone ~10 m long. The thickness of these masses ranges from a few cm to ~30-40 cm, only rarely exceeding 10 cm. Despite their similarity to feldspar, these masses can easily be distinguished due to a characteristic thin rim of black allanite-(Ce). More than 30 different minerals have been identified as inclusions in the fluorite, both as mm-sized grains and rounded crystals embedded in the fluorite, or as microcrystals in the numerous small cavities. The fluorite masses are typically zoned with regard to mineral content, with the richest (and youngest) paragenesis in the central cavity-rich parts. The mineral content also varies between the different fluorite masses, as well as between individual cavities in the same aggregate, a result of the high degree of differentiation. Several of the minerals from this material have been found very locally in

the fluorite (e.g. stetindite and atelisite-(Y)), but schlüterite-(Y) is relatively widespread and occurs in several different parageneses in the cavities, associated with bastnäsite-(Ce), fluorite (var. yttrian fluorite), fluorthalénite-(Y), hematite, hundholmenite-(Y), kuliokite-(Y), perbøeite-(Ce) (IMA 2011-055), törnebohmite-(Ce) and vyuntspakhkite-(Y).

Physical properties

Schlüterite-(Y) forms dense, fibrous, radiating aggregates diverging to individual needle-like crystals in cavities. The aggregates reach a size of ~2 mm; individual crystals are up to ~1 mm long and 0.025 mm thick (Fig. 1). Crystals are acicular to bladed, flattened on {001} and elongated along [010]; the dominant form is {001}. The *a:b:c* ratio calculated from the unitcell parameters is 1.258:1:3.815. Schlüterite-(Y) is transparent, pale pink with a white streak and a vitreous lustre, and does not fluoresce under shortwave ultraviolet light. No cleavage, parting or twinning was observed. Mohs hardness is $5\frac{1}{2}-6$, and schlüterite-(Y) is brittle with an irregular fracture. The density was not measured because of the fibrous nature of the crystals and the nature of their aggregation. The calculated density is 4.644 g/cm³. Optical properties were measured with the Bloss spindle stage for the wavelength 590 nm. The indices of refraction are α 1.755, β 1.760, γ 1.770, all ±0.005, $2V_{obs} = 71.8 (5)^{\circ}$ (measured with a spindle stage, data processed using Excalibr II, Bartelmehs et al., 1992), 2V_{calc} = 71°, non-pleochroic, optic orientation is $X^{\wedge} a =$ 83.1° (β obtuse), Y // b, $Z^{\land} c = 50.3^{\circ}$ (β acute).



FIG. 1. An SEM-BSE image of acicular crystals of schlüterite-(Y).

Infrared spectroscopy

The FTIR spectrum was collected in transmission mode with a Hyperion FTIR-microscope. The sample was prepared as a thin film using a Diamond Micro Compression Cell. Data over the range 4000-650 cm⁻¹ were obtained by averaging 100 scans with a resolution of 4 cm^{-1} . Base-line correction was done using OPUS spectroscopic software (Bruker Optic GmbH). The prominent peaks at 1100-800 cm⁻¹ in the spectrum (Fig. 2) are due to Si-O stretching vibrations. In the principal OH-stretching region $(3800-3100 \text{ cm}^{-1})$, peaks are observed at around 3588 cm^{-1} and 3453 cm^{-1} (Fig. 2), and are attributed to the O-H stretching vibrations of the two (OH) groups found by crystal-structure solution and refinement; there is no band at ~1630 cm⁻¹, indicating the absence of H₂O in this structure. The frequency of the O-H stretching vibration is correlated negatively to the strength of the hydrogen bond (Libowitzky, 1999), and thus the band at 3453 cm^{-1} can be assigned to H at the H(1) site (stronger hydrogen-bond) and the band at 3588 cm^{-1} can be assigned to H at the H(2) site. From the relation of Libowitsky (1999), the O(donor)-O(acceptor) distance calculated for the 3588 cm⁻¹ band is 3.31 Å, in good accord with the mean of the two observed distances for the bifurcated bond: 3.26 Å. We cannot do the same calculation for the 3453 cm^{-1} band as the acceptor anion is F rather than O, but one does expect a shorter O(donor)-O(acceptor) distance than for the 3588 cm^{-1} band, and this is the case. The intensity of the 3588 cm⁻¹ band is far weaker than the 3453 cm^{-1} band. One expects the relative intensity of the band to be related to its frequency (Skogby and Rossman, 1991; Burns and Hawthorne, 1993a,b), but the present case seems somewhat extreme. The normal intensity relations expected may be affected by the presence of the bifurcated hydrogen-bond.

Chemical composition

The crystal used for chemical analysis is <10 µm thick, and so could not be embedded in epoxy and polished in the usual way as it would not have survived this process. Instead it was laid flat on a plexiglass disk and the top surface was analysed unpolished with a Cameca SX-100 electron microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 10 nA, and a beam diameter of 5 µm. The following standards were used: diopside (Si); andalusite (Al); REEPO₄ (REE); topaz (F). The data were reduced and corrected by the PAP method of Pouchou and Pichoir (1985). The sum of the oxides is low (93.88 wt.%, Table 1), undoubtedly the result of analysing an unpolished surface of a very thin grain. The presence and quantity of (OH) groups were established by crystal-structure solution and refinement. In addition, the infrared spectrum (Fig. 2) shows the presence of sharp peaks assigned to O-H stretching modes. Table 1 gives the chemical composition (mean of six determinations). The empirical formula was calculated on the basis of 10 anions with (OH) + F = 3 a.p.f.u. (atoms per formula unit) as indicated by crystal-structure refinement, giving $(Y_{0.73}Ce_{0.32}Nd_{0.30}Gd_{0.14}Dy_{0.12}La_{0.11}Sm_{0.11}Pr_{0.07}$ $Er_{0.06}Yb_{0.05})_{\Sigma=2.01}Al_{0.99}Si_{2.01}O_7(OH)_{2.24}F_{0.76}.$ The general structural formula is ideally



FIG. 2. FTIR spectra of schlüterite-(Y).

Constituent	Wt.%	Range
Al ₂ O ₃	9.45(17)	9.22-9.77
SiO ₂	22.64(1.03)	22.22-23.25
Y_2O_3	15.35(72)	13.99-16.00
La ₂ O ₃	3.25(15)	2.97 - 3.43
Ce_2O_3	9.69(1.13)	8.45-11.97
Pr ₂ O ₃	2.05(15)	1.92 - 2.38
Nd ₂ O ₃	9.50(55)	8.82-10.50
Sm_2O_3	3.57(19)	3.33-3.83
Gd_2O_3	4.65(17)	4.41-4.86
Dy_2O_3	4.21(10)	4.06-4.38
Er ₂ O ₃	2.31(9)	2.20 - 2.49
Yb ₂ O ₃	1.86(11)	1.73 - 2.02
F	2.71(35)	1.95 - 2.93
H ₂ O (calc)	3.78	
O = F	-1.14	
Total	93.88	

TABLE 1. The chemical composition of schlüterite-(Y).

(Y,REE)₂Al(Si₂O₇)(OH)₂F. In our ideal formula, we use $(Y, REE)_2$ to indicate that Y is the dominant rare-earth element, and that there are significant amounts of other non-specified rareearth elements present. Three crystals were analysed by electron-microprobe analysis, and the results show that (1) Y is always dominant, (2) (neighbouring) point analyses with (Ce > Nd) and (Nd > Ce) are equally common and (3) the total lanthanides always exceeds the Y content. The *REE* occupy two general crystallographic sites, X(1) and X(2), and REE were assigned assuming that the lanthanides are disordered over both sites (see the Structure section). The X(1) site contains approximately equal amounts of Y and lanthanides, whereas the X(2) site is dominated by lanthanides and contains Y, Ce and Nd in nearequal proportions. Determining specific element dominance at both REE sites is not feasible (Hawthorne, 1983), and we have grouped the X(1)and X(2) sites together in the ideal formula. Schlüterite-(Y) is a Y-dominant species, as Y is clearly the most dominant REE constituent in all chemical analyses done.

X-ray powder diffraction

X-ray powder-diffraction data were obtained using a Gandolfi attachment mounted on a Bruker D8 rotating-anode Discover SuperSpeed micro-powder diffractometer with a multi-wire 2D detector.

The experimental X-ray diffraction (XRD) powder data (red) and a simulated trace developed from the single-crystal XRD data (black) are shown in Fig. 3. The overall similarity in the two traces is readily apparent, but the peak resolution is considerably lower in the powder data. In our laboratory, over several decades, we have collected many X-ray powder diffraction patterns using (1) automated powder diffractometers (Bragg-Brentano reflection geometry) with largesample smear mounts and (2) large-diameter (114 mm) Debye-Scherrer powder cameras (often equipped with a Gandolfi head) for small powder samples. Fairly recently, we acquired a micro-powder-diffractometer with a rotatinganode X-ray source and an area detector, and we fitted a Gandolfi head to this instrument. This arrangement has allowed us to collect and process XRD data from extremely small powder samples (or even small single crystals). There are two important attributes of the resulting data: (1) small-volume samples (sometimes consisting of only a couple of crystals) attached to tapered glass fibres and mounted on a Gandolfi head give very accurate and complete sets of diffraction data; (2) the resolution of the data is noticeably less than that from smear mounts of large samples mounted on a automated powder-diffractometer with Bragg-Brentano-geometry, and slightly less than that collected on a large-diameter Debye-Scherrer powder camera with a Gandolfi head.

Using the peaks $\overline{1}08/114$ (resolved) at ~34° 2 θ and $\overline{1}$ 1 10 / $\overline{1}$ 28 (unresolved) at ~47° 2 θ (Fig. 3), we have estimated the resolution of the micro-diffractometer powder-diffraction data for schlüterite-(Y) to be ~ 0.5° 20. Schlüterite-(Y) has relatively low symmetry (monoclinic) and a long axis (c = 21.5 Å), resulting in many closely spaced diffraction peaks of significant intensity. The "powder pattern" derived from the schlüterite-(Y) single-crystal XRD data (Table 2) is superior to the experimental powder pattern (Fig. 3) in terms of resolution and in terms of the correct indexing of the diffraction peaks. In a new mineral description, the aim should be to record an accurate and representative XRD pattern. Where high-quality single-crystal XRD data are available, the two-dimensional diffraction pattern derived from these single-crystal data should be both representative and accurate with high resolution. For mineralogical studies where there are only a few grains of the mineral available, the crushing of this (sometimes irreplaceable) material to produce an experi-



FIG. 3. Experimental XRD powder data (red) and a trace derived from the single-crystal XRD data (black); the latter trace was calculated with the *SHELXTL (PC) (Plus)* system of programs, where such a calculation is a program option within XPREP.

mental powder-diffraction record (that is likely to be inferior to that produced from single-crystal diffraction) seems both unwise and unnecessary.

To ensure that the two-dimensional diffraction pattern developed from (three-dimensional) singlecrystal XRD data is representative of the mineral, two important criteria need to be considered:

Completeness of single-crystal intensity data

When using MoK α radiation on single-crystaldiffraction instruments, reflections at very low 2 θ values can be obscured by the beam stop for minerals with one or more long cell-dimensions. Whether this occurs can be checked by comparing the two-dimensional diffraction pattern generated from three-dimensional single-crystal diffraction intensities with the analogous pattern calculated from the refined crystal-structure: low-angle reflections will not be missing from the latter.

Where larger and/or strongly diffracting crystals are mounted on single-crystal-diffraction instruments, the intensity of some reflections may exceed the dynamic range of the detector, and therefore go unrecorded. Again, this may be checked in the diagnostic output after integration of the single-crystal intensity-data, or by comparison of the two-dimensional diffraction pattern calculated from the refined crystal-structure with that derived from the single-crystal intensities.

Weak peaks in the two-dimensional pattern derived from the three-dimensional single-crystal intensities could potentially be (erroneously) missed if weak super-lattice reflections were not detected prior to integration of the raw single-crystal data-frames. This oversight is simple to avoid by carefully evaluating the observed intensities on the raw data-frames relative to an *hkl* overlay of the current cell (i.e. ensure that all observed data is integrated).

Accuracy of single-crystal intensity data

In the simplest case (which applies to schlüterite-(Y)), all intensity data observed on the detector screen images can be integrated on the single-

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TABLE 2. Simulated X-ray powder (2-dimensional) diffraction data* for schlüterite-(Y).

Ι	d (Å)	h	k	l	Ι	d (Å)	h	k	l	Ι	<i>d</i> (Å)	h	k	l
2	7.003	ī	0	2	2	2.456	2	0	2	8	1.807	ī	3	1
17	5.190	ī	0	4	4	2.439	1	2	1	5	1.803	0	0	10
100	4.769	0	1	2	10	2.384	0	2	4	4	1.798	3	2	4
36	4.507	0	0	4	5	2.356	2	1	8	3	1.794	ī	3	3
3	4.383	ī	1	2	2	2.348	1	2	5	2	1.773	3	2	3
7	4.347	ī	1	1	2	2.310	1	2	2	11	1.765	4	0	6
2	4.176	1	1	3	7	2.250	2	1	2	3	1.758	0	2	8
23	4.056	1	0	2	13	2.238	1	0	6	11	1.748	3	0	2
28	3.502	2	0	4	5	2.216	0	2	5	11	1.730	3	0	12
3	3.429	2	0	2	6	2.208	1	2	6	7	1.726	3	2	8
51	3.289	1	1	2	9	2.202	3	0	2	17	1.721	1	1	8
7	3.120	2	0	6	15	2.192	2	2	4	9	1.701	1	3	2
37	3.013	ī	1	6	16	2.187	Ī	0	8	4	1.690	1	0	12
5	2.973	2	0	0	29	2.174	2	2	2	2	1.684	4	1	6
55	2.972	2	1	4	4	2.161	3	1	4	9	1.676	4	0	10
25	2.927	2	1	2	6	2.088	2	2	6	9	1.672	4	1	8
10	2.912	1	0	4	15	2.079	1	1	6	3	1.663	ī	2	10
2	2.878	Ī	1	5	2	2.063	ī	0	10/127	5	1.659	ī	3	6
37	2.810	0	2	0	23	2.042	2	2	0	10	1.652	Ī	3	4
49	2.728	2	1	6	6	2.022	1	2	4	6	1.644	2	3	2
9	2.683	0	2	2	2	1.998	2	1	10	11	1.640	4	1	4
9	2.650	0	1	6	2	1.964	3	0	10	2	1.631	0	2	9
27	2.631	ī	0	8	3	1.950	2	2	1	5	1.614	4	0	2
13	2.628	2	1	0	20	1.936	1	1	10	5	1.610	3	2	10
4	2.608	ī	2	2	25	1.921	1	2	8	8	1.606	2	3	6
31	2.586	1	1	4	5	1.907	2	2	8	3	1.601	2	2	11
3	2.562	ī	2	3	9	1.869	3	1	0	2	1.585	2	3	0
2	2.541	1	2	0	10	1.854	3	1	10	5	1.575	1	3	4
14	2.471	ī	2	4	8	1.834	0	3	2					

 $\lambda = 1.54178$ Å; * intensities below 2% are not listed.

TABLE 3. Miscellaneous information for schlüterite-(Y).

a (Å)	7.0722(2)	Crystal size (um)	$7 \times 25 \times 200$
b	5.6198(1)	Radiation	ΜοΚα
с	21.4390(4)	No. of reflections	25789
β (°)	122.7756(3)	No. in Ewald sphere	7958
$V(Å^3)$	716.43(5)	No. unique reflections	2091
Space group	$P2_1/c$	No. $ F_0 > 4\sigma(F)$	2063
Z	4	$R_{\rm merge}$ %	1.1
		$R_1 \%$	1.8
		wR_2 %	4.6
		GOF	1.23
		$\Delta \rho(\min), \Delta \rho(\max)$	-0.79, 1.79
$R_1 = \Sigma(F_0 - F_c $) / $\Sigma F_{o} $		
$wR_2 = [\Sigma w (F_o^2 -$	$(F_{\rm c}^2)^2 / \Sigma w (F_{\rm o}^2)^2 $, $w = 1/[\sigma^2($	F_{o}^{2}) + (0.0176 P) ² + 3.03 P] where P =	$(\max(F_{o}^{2},0) + 2F_{c}^{2})/3$

Site	x/a	y/b	z/c	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
X(1)	0.11896(3)	0.71598(4)	0.08007(1)	0.00712(7)	0.00699(10)	0.00873(11)	0.00559(10)	-0.00035(6)	0.00337(8)	-0.00016(6)
X(2)	0.73129(3)	0.77073(3)	0.14728(1)	0.00811(6)	0.00870(9)	0.00829(9)	0.00903(9)	-0.00030(5)	0.00591(7)	-0.00030(5)
AI	0.48307(15)	0.99262(16)	0.24821(5)	0.00711(19)	0.0095(4)	0.0057(4)	0.0064(4)	0.0001(3)	0.0044(3)	0.0004(3)
Si(1)	0.60757(14)	0.74495(14)	0.39767(5)	0.00651(17)	0.0074(4)	0.0065(3)	0.0056(3)	-0.0004(3)	0.0035(3)	-0.0004(3)
Si(2)	0.24094(14)	0.73895(14)	0.44364(5)	0.00683(17)	0.0084(4)	0.0063(3)	0.0065(4)	0.0000(3)	0.0046(3)	0.0002(3)
0(1)	0.8652(4)	0.7905(4)	0.46034(12)	0.0116(4)	0.0086(10)	0.0159(11)	0.0080(10)	-0.0002(8)	0.0031(8)	-0.0013(8)
O(2)	0.5287(4)	0.9781(4)	0.34322(11)	0.0091(4)	0.0134(10)	0.0072(9)	0.0066(9)	0.0013(7)	0.0054(8)	0.0011(7)
O(3)	0.5759(4)	0.5050(4)	0.34920(11)	0.0083(4)	0.0113(9)	0.0070(9)	0.0062(9)	-0.0001(7)	0.0046(8)	-0.0001(7)
0(4)	0.4402(4)	0.7024(4)	0.42568(14)	0.0143(5)	0.0147(11)	0.0168(11)	0.0180(11)	0.0017(9)	0.0131(10)	0.0015(9)
0(5)	0.3531(4)	0.7391(4)	0.03185(12)	0.0102(4)	0.0104(10)	0.0127(10)	0.0063(9)	-0.0000(7)	0.0037(8)	-0.0009(7)
O(6)	0.9002(4)	0.9927(4)	0.09213(13)	0.0113(4)	0.0118(10)	0.0093(10)	0.0129(10)	0.0017(8)	0.0068(8)	0.0026(8)
0(7)	0.8887(4)	0.4807(4)	0.10150(12)	0.0112(4)	0.0129(10)	0.00099(10)	0.0108(10)	-0.0027(8)	0.0066(8)	-0.0032(8)
O(8) = (OH)	0.2897(4)	0.7314(4)	0.21511(12)	0.0074(4)	0.0070(9)	0.0082(9)	0.0082(9)	-0.0002(7)	0.0049(8)	-0.0015(7)
O(9) = (OH)	0.3011(4)	0.2542(4)	0.23199(12)	0.0078(4)	0.0088(9)	0.0069(9)	0.0058(9)	0.0002(7)	0.0027(8)	(7)0000(7)
Н	0.0451(3)	0.5729(4)	0.26008(12)	0.0190(4)	0.0185(10)	0.0209(11)	0.0214(10)	0.0032(8)	0.0132(9)	0.0048(8)
H(1)	0.188(7)	0.678(12)	0.230(3)	0.055(19)						
H(2)	0.148(4)	0.275(11)	0.189(2)	0.05(2)						

TABLE 4. Final atom positions and displacement parameters (\mathring{A}^2) for schlüterite-(Y).

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Al-O(2)	1.884(2)			X(1)–O(1)d	2.566(2)
<i>Al</i> -O(3)a	1.897(2)			X(1)–O(1)e	2.196(2)
Al-O(8)	1.865(2)			X(1)–O(2)d	2.503(2)
Al-O(8)a	1.906(2)			X(1)-O(3)a	2.460(2)
<i>Al</i> -O(9)a	1.898(2)			X(1)-O(5)	2.383(2)
<i>Al</i> -O(9)b	1.858(2)			X(1)-O(6)f	2.305(2)
<al-o></al-o>	1.885			X(1) - O(7)f	2.328(2)
				X(1) - O(8)	2.462(2)
Si(1) - O(1)	1.594(2)			< X(1) - O >	2.400
Si(1) - O(2)	1.639(2)				
Si(1) - O(3)	1.642(2)			X(2)–O(2)d	2.556(2)
Si(1) - O(4)	1.609(2)			X(2) - O(3)a	2.576(2)
$\langle Si(1) - O \rangle$	1.621			X(2)–O(4)a	2.784(3)
				X(2) - O(5)	2.479(2)
Si(2) - O(4)	1.662(3)			X(2) - O(6)	2.431(2)
Si(2)–O(5)c	1.612(2)			X(2) - O(7)	2.458(2)
Si(2)–O(6)d	1.634(2)			X(2)–O(9)a	2.721(2)
<i>Si</i> (2)–O(7)a	1.632(2)			X(2)–Fa	2.435(2)
< <i>Si</i> (2)–O>	1.635			X(2)–Fg	2.490(2)
				<x(2)-φ></x(2)-φ>	2.548
O(8)–H(1)	0.980(1)	O(8)–H(1)–F O(8)–F	174(6) 2,554(3)	H(1)F	1.577(7)
O(9)–H(2)	0.980(1)	O(9)-H(2)-O(7)f	152(5)	H(2)O(7)f	2.12(3)
× / × /		O(9)-H(2)-O(6)h	130(5)	H(2)O(6)h	2.44(5)
		O(9) - O(7)f	3.020(3)	O(9)–O(6)h	3.160(3)
			~ /		(-)

TABLE 5. Selected interatomic distances (Å) and angles (°) in schlüterite-(Y).

a: -x+1, $y+\frac{1}{2}$, $-z+\frac{1}{2}$; b: x, y+1, z; c: x, $-y+\frac{3}{2}$, $z+\frac{1}{2}$; d: -x+1, $y-\frac{1}{2}$, $-z+\frac{1}{2}$; e: x-1, $-y+\frac{3}{2}$, $z-\frac{1}{2}$; f: x-1, y, z; g: x+1, y, z; h: x-1, y-1, z.

	Al	X(1)	X(2)	<i>Si</i> (1)	<i>Si</i> (2)	H(1)	H(2)	Σ
0(1)		0.25		1.08				2.01
0(1)		0.68		1.00				2.01
O(2)	0.53	0.30	0.27	0.96				2.06
O(3)	0.51	0.33	0.21	0.95				2.00
O(4)			0.22	1.04	0.90			2.16
O(5)		0.41	0.33		1.03			1.77
O(6)		0.51	0.38		0.97		0.10	1.96
O(7)		0.48	0.35		0.98		0.10	1.91
O(8)	0.56	0.33				0.60		1.99
	0.50							
O(9)	0.51		0.17				0.80	2.05
	0.57							
F			0.29			0.40		0.94
			0.25					
Σ	3.18	3.29	2.47	4.03	3.88	1.00	1.00	

TABLE 6. Bond-valence* (v.u.) table for schlüterite-(Y).

* Brown and Altermatt (1985)

Site		— As	signed of	cations	from ele	ectron-m	nicropro	be analy	ysis —		Σ	Σ	SREF
	Y	La	Ce	Pr	Nd	Sm	Gd	Dy	Er	Yb		elect.	elect.
X(1)	0.51	0.04	0.12	0.03	0.12	0.04	0.05	0.05	0.02	0.02	1.0	49.8	49.75
X(2)	0.21	0.07	0.20	0.04	0.18	0.07	0.09	0.07	0.04	0.03	1.0	56.5	56.37
Σ	0.72	0.11	0.32	0.07	0.30	0.11	0.14	0.12	0.06	0.05	2.0	106.3	106.1

TABLE 7. Site-assignment (a.p.f.u.) and refined site-scattering (e.p.f.u.) for the X sites in schlüterite-(Y).

crystal cell, and the resulting structure model refines to an acceptably low discrepancy-index (R value). Two-dimensional diffraction patterns produced from these single-crystal intensity data will always be accurate. In more difficult cases, where overlapping intensities from other crystals occur (i.e. in the presence of twins or misaligned satellite crystallites), care must be taken in assessing the validity of the resulting two-dimensional diffraction patterns.

Nomenclature

The term "powder-diffraction pattern" is somewhat misleading. Literally, it means a diffraction pattern taken from a powdered material. However, it is often taken to mean a twodimensional diffraction-pattern, i.e. a diffraction pattern represented in two dimensions. It is important to realize that these two meanings are not equivalent. For example, a diffraction pattern taken from a single crystal mounted on a Gandolfi head is often referred to as a "powder pattern", and such data are accepted as such by the CMNMN of the IMA, although it is actually a single-crystal diffraction pattern recorded in two dimensions. Similarly, a powder (consisting of, say, 3 or 4 crystals) could be attached to a glass fibre, mounted on a single-crystal diffractometer and one or more three-dimensional diffraction patterns could be collected.

We are of the opinion that patterns such as those in Fig. 3 should be described as twodimensional diffraction patterns, irrespective of how they are recorded. Of course, the method of recording should be described, but the similarity of the patterns shows the accuracy of both methods of recording, and indicates that the generation of two-dimensional diffraction patterns from three-dimensional diffraction data generally produces higher-resolution and more accurate data. We feel that such data should be acceptable in the formal description of new minerals.

Crystal-structure solution and refinement

A crystal was attached to a tapered glass fibre and mounted on a Bruker D8 three-circle diffractometer equipped with a rotating-anode generator (MoKa), multilayer optics and an APEX-II detector. A total of 7958 intensities (those within the Ewald sphere) was collected to $60^{\circ}2\theta$ using 3 s per 0.2° frame with a crystal-to-detector distance of 5 cm. Empirical absorption corrections (SADABS; Sheldrick, 2008) were applied and equivalent reflections were corrected for Lorentz, polarization and background effects, averaged and reduced to structure factors. The unit-cell dimensions were obtained by least-squares refinement of the positions of 9980 reflections with I > $10\sigma I$ and are given in Table 3, together with other information pertaining to data collection and structure refinement. The structure of schlüterite-(Y) was solved initially in a less-obtuse unit cell $(a = 7.0722, b = 5.6198, c = 18.2037 \text{ Å}, \beta =$ 98.0157°, V = 716.43 Å³) in the space group



FIG. 4. The [Al(OH)₂Si₂O₇] chain in schlüterite-(Y) projected onto (100); green: Al(OH)₄O₂ octahedron, blue: SiO₄ tetrahedron, black circles: H atoms.

 $P2_1/c$, and later transformed *via* [$\overline{1}00 / 0\overline{1}0 / 201$] to the current setting (Table 3) in $P2_1/c$ such that the principal features of the structure align better with the crystallographic axes.

All calculations were done with the *SHELXTL PC* (*Plus*) system of programs; *R* indices are of the form given in Table 3 and are expressed as percentages. The structure was solved in the space group $P2_1/c$ by direct methods and refined to convergence by full-matrix least-squares with anisotropic-displacement parameters on all non-H atoms. At the later stages of refinement,

difference-Fourier maps showed weak density maxima ~1 Å from the O(8) and O(9) anions that incident bond-valence sums indicate are (OH) groups. These maxima were entered into the structure model as H atoms and their parameters were refined with the soft constraint that the O–H distance be approximately 0.98 Å. The structure converged to a final R_1 index of 1.8%. Refined atom coordinates and displacement parameters are listed in Table 4, selected interatomic distances are given in Table 5, and bond valences, calculated with the parameters of Brown and



FIG. 5. Linkage of $[Al(OH)_2Si_2O_7]$ chains in schlüterite-(Y) *via* (Y,*REE*) (yellow circles), F (fuchsia circles), and hydrogen bonds (dotted lines). The structure is projected onto (010).

TABLE 8. (Y, REE)-Al-silicates containing chains of edge-sharing Al-octahedra decorated by Si tetrahedra

Altermatt (1985) are given in Table 6, for the site assignment of Table 7.

Crystal structure

Coordination of cations

In the structure of schlüterite-(Y), there are two tetrahedrally co-ordinated Si sites occupied by Si with $\langle Si-O \rangle$ distances of 1.621 and 1.635 Å, and one octahedrally co-ordinated Al site occupied by Al with an $\langle Al - O \rangle$ distance of 1.885 Å. There are two X sites that are occupied by Y and lanthanides; X(1) is co-ordinated by eight O anions, and X(2) is co-ordinated by seven O anions and two F anions, with $\langle X-O,F \rangle$ distances of 2.400 and 2.548 Å. The total refined sitescattering (Hawthorne *et al.*, 1995) at the X sites is 106.1(3) e.p.f.u. (electrons per formula unit) and the effective scattering from the large $(Y + REE)^{3+}$ cations determined by electron-microprobe analysis (Table 1) is 106.3 e.p.f.u. The individual refined site-scattering values at the X(1) and X(2)sites are 49.75(13) and 56.37(15) e.p.f.u., respectively (Table 7), indicating significant cation order over the X sites. Site-scattering refinement can determine only binary site-occupancies (Hawthorne, 1983), and hence we considered the scattering at the X sites as consisting of Y and an average lanthanide scatterer assuming disorder of the lanthanide cations over X(1) and X(2); the resulting site-populations are given in Table 7.

Anion identities and hydrogen bonding

There are ten crystallographically distinct anions, O(1)-O(9) and F (Table 4). Inspection of the bond-valence table (Table 6) shows that the bond valence incident at O(1) to O(7), omitting any contribution from H, is greater than or equal to 1.75 v.u. (valence units), indicating that these anions are O^{2-} . The incident bond-valence at the F site is 0.54 v.u. when calculated with the appropriate bond-valence curves, and the refined site-occupancy (F = 0.986(9)) suggests complete occupancy by F. The corresponding bond-valence incident at O(8) and O(9) is 1.39 and 1.25 v.u., respectively, indicating that both O(8) and O(9)are (OH) groups, and one H site was located ~1 Å from each O(8) and O(9) site in difference-Fourier maps. The resulting hydrogen-bond arrangements are given in Tables 5 and 6. The F anion is a hydrogen-bond acceptor for a strong hydrogen-bond from H(1). The H(2) atom forms a bifurcated hydrogen-bond with O(6) and O(7).

	Schlüterite-(Y)	Törnebohmite-(Ce)	Allanite-(Ce)	Gatelite-(Ce)
tormula	$\begin{array}{l} (Y,REE)_2Al(Si_2O_7)(OH)_2F\\ [Al_2(OH)_4(Si_2O_7)_2] \end{array}$	$Ce_2Al(SiO_4)_2(OH)$	$CaCeFe^{2+}Al_2(Si_2O_7)(SiO_4)O(OH)$	$CaCe_{3}M_{g}Al_{3}(Si_{2}O_{7})(SiO_{4})_{3}O(OH)_{2}$
Chain type		[Al ₂ (OH) ₂ (SiO ₄) ₄]	[Al_2(OH)_2(Si_2O_7)_2(SiO_4)_2]	[Al ₂ (OH) ₂ (Si ₂ O ₇)(SiO ₄) ₃]
p.group	$P2_{1/c}$ 7.07	$P2_{1/c}$ 7.38	$P2_1/m$ 8.93	P21/a 17.77
	5.62	5.67	5.76	5.65
	21.44	16.94	10.15	1746
((Å ³)	122.8	112.0	114.8	116.2
	716.4	657.5	474.0	1573.3
) gcm ⁻³ teference	4.64 (1)	4.94 (2)	4.26 (3)	4.51 (4)

Bond topology

In the crystal structure of schlüterite-(Y), (Al(OH)₄O₂) octahedra share (OH)–(OH) edges to form $[M\Phi_4]$ chains that are commensurately modulated along their length to promote linkage with the tetrahedra of the (Si₂O₇) groups that are in the eclipsed configuration. The latter decorate the chain along its length by bridging O-vertices of adjacent (Al(OH)₄O₂) octahedra in a staggered fashion on either side of the chain (Fig. 4). These [Al(OH)₂(Si₂O₇)] chains extend parallel to *b*, and are linked by (Y,*REE*)-F-(Y,*REE*) linkages, and through (H...F hydrogen bonds (Fig. 5).

Decorated *trans*-linked [^[6]M Φ_4] chains are common in a wide variety of structures (Hawthorne, 1985, 1986, 1990). Table 8 compares schlüterite-(Y) to various silicate minerals containing [Al Φ_4] chains and *REE*: allanite-(Ce) (Dollase, 1971), gatelite-(Ce) (Bonazzi et al., 2003) and törnebohmite-(Ce) (Shen and Moore, 1982). All contain interstitial REE, but this is not a requisite of this arrangement: allanite-(Ce) is a member of the epidote-group minerals, most of which do not contain essential REE. The repeat distance of the trans-linked [^[6]M Φ_4] chain is ~5.7-6.4 Å, depending on the size of the octahedrally coordinated cation, and this is frequently recognized in one of the cell dimensions of any structure with this structural unit. Schlüterite-(Y) is unusual in containing pyro-linked oxysalt tetrahedra: (Si₂O₇). In most of the $[M\Phi_4]$ containing structures, the chain is decorated by single (TO_4) groups (e.g. törnebohmite-(Ce), Fig. 6), although other $[M\Phi_4]$ -containing structures decorated by (Si₂O₇) groups are known: e.g. allanite-(Ce), gatelite-(Ce) (Fig. 6), västmanlandite-(Ce) (Holtstam et al., 2005). The octahedra of the $[M\Phi_4]$ chain may be occupied by a wide variety of divalent and trivalent cations (e.g. Mg,



FIG. 6. The aluminosilicate chains in schlüterite-(Y), törnebohmite-(Ce), allanite-(Ce) and gatelite-(Ce); legend as in Fig. 4.

Fe²⁺, Co²⁺, Cu²⁺, Zn, Mn²⁺, Al, Fe³⁺, Mn³⁺) and the chain may be decorated with various types of oxyanions: $(SiO_4)^{4-}$, $(Si_2O_7)^{6-}$, $(PO_4)^{3-}$, $(AsO_4)^{3-}$, $(VO_4)^{3-}$, $(SO_4)^{2-}$, $(CrO_4)^{2-}$, and there are many structures based on the decorated *trans* [$M\Phi_4$] chains (e.g. the minerals of the brackebuschite, fornacite and vauquelinite groups, the linarite group, the descloizite group, etc.). Those minerals with longer repeat distances tend to contain divalent ^[6]M cations and minerals with shorter repeat distances tend to contain trivalent ^[6]M cations.

Related minerals

Schlüterite-(Y) is a sorosilicate. In the classification of Strunz (Strunz and Nickel, 2001), schlüterite-(Y) is a class 9.BE sorosilicate with additional anions (OH and F) and additional cations in octahedral (Al) and greater coordinations: (Y + *REE*) in [8]- and [9]-coordination. In the classification of Dana (Gaines *et al.*, 1997), it is a class 56 sorosilicate (with isolated disilicate groups) with additional anions (OH and F). Comparative data are given in Table 8.

Acknowledgements

The authors thank Uwe Kolitsch and Giancarlo Capitani for their helpful comments on this paper. This work was supported by a Canada Research Chair in Crystallography and Mineralogy and by Natural Sciences and Engineering Research Council of Canada Discovery, Equipment and Major Installation grants of the Natural Sciences and Engineering Research Council of Canada, and by Innovation grants from the Canada Foundation for Innovation to FCH.

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