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**ХРИСТОФСШЕФЕРИТ-(Ce),
(Ce,La,Ca)₄Mn²⁺(Ti,Fe³⁺)₃(Fe³⁺,Fe²⁺,Ti)(Si₂O₇)₂O₈ –
НОВЫЙ МИНЕРАЛ ГРУППЫ ЧЕККИНИТА ИЗ ВУЛКАНИЧЕСКОЙ
ОБЛАСТИ АЙФЕЛЬ (ГЕРМАНИЯ)**

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Новый минерал группы чевкинита христофшеферит-(Ce) найден в эруптивном обломке высокомарганцевой метасоматической породы на горе Вингертсберг (вулкан Лаахер Зее, близ г. Мендиг, горы Айфель, Рейнланд-Пфальц, Германия) в ассоциации с ортоклазом, родонитом, бустамитом, тефроитом, цирконом, фторапатитом, пирофанитом и якобитом. Христофшеферит-(Ce) образует несовершенные изометричные кристаллы до 3 мм в поперечнике. Цвет нового минерала чёрный, блеск смоляной, черта коричневая. Хрупкий, спайность не наблюдается, твёрдость по шкале Мооса 6; измеренная плотность равна 4.8(1) г/см³, вычисленная – 4.853 г/см³. Новый минерал оптически двуосный (–), $n_p = 1.945(10)$, $n_m = 2.015(10)$, $n_g = 2.050(10)$, $2V_{изм} = 70(10)^\circ$, $2V_{выч} = 68^\circ$. Дисперсия оптических осей не наблюдается. Плеохроизм сильный по схеме Z (тёмно-коричневый) > Y (коричневый) > X (светло-коричневый). В ИК-спектре отсутствуют полосы поглощения анионов CO_3^{2-} и водородсодержащих групп. Химический состав (по данным локального рентгеноспектрального анализа, валентность Mn – по данным XANES-спектроскопии, отношение Fe^{2+}/Fe^{3+} определено из структурных данных; мас.%): CaO 2.61, La₂O₃ 19.60, Ce₂O₃ 22.95, Pr₂O₃ 0.56, Nd₂O₃ 2.28, MgO 0.08, MnO 4.39, FeO 4.18, Fe₂O₃ 3.11, Al₂O₃ 0.08, TiO₂ 19.02, Nb₂O₅ 0.96, SiO₂ 19.38, сумма 99.20. Эмпирическая формула: $(Ce_{1.72}La_{1.48}Nd_{0.17}Pr_{0.04}Ca_{0.57})Mn_{0.76}^{2+}Fe_{0.72}^{2+}Mg_{0.02}Fe_{0.48}^{3+}Al_{0.02}Ti_{2.935}Nb_{0.09}Si_{3.98}O_{22}$. Кристаллическая структура изучена монокристалльным методом, R = 0.055. Христофшеферит-(Ce) моноклинный, пр. гр. $P2_1/m$; параметры элементарной ячейки: $a = 13.3722(4)$, $b = 5.7434(1)$, $c = 11.0862(2)$ Å, $\beta = 100.580(2)^\circ$, $V = 836.97(4)$ Å³, $Z = 2$. Mn^{2+} доминирует в октаэдрической позиции M1. Сильные линии порошковой рентгенограммы [d , Å (hkl)]: 4.90 (39; -111), 4.6₄(65; -202), 3.480 (78; 310), 3.169 (81; 311, -312), 3.095 (43; -113), 2.730 (100; 004), 2.169 (46; -421, -513), 1.737 (46) (603, 504, 315, 025, -622). Минерал назван в честь известного немецкого коллекционера минералов Христофа Шефера. Эталонный материал хранится в Минералогическом музее им. А.Е. Ферсмана Российской академии наук в г. Москве (регистрационный номер 4227/1). В статье 8 таблиц, 8 рисунков, список литературы из 21 наименования. Ключевые слова: христофшеферит-(Ce), группа чевкинита, новый минерал, кристаллическая структура, Айфель.

Introduction

The Eifel volcanic area situated in Germany is a unique mineralogical object. Young and almost unaltered alkaline effusive and metasomatic rocks are outcropped there by multiple operating quarries. However the mineralogy of late parageneses related to the Eifel volcanism remains insufficiently investigated. This paper contains the description of a new mineral species

christofschäferite-(Ce) discovered in the Laacher See area, Eifel mountains.

Christofschäferite-(Ce) belongs to the chevkinite mineral group. Its distinctive feature is the predominance of Mn^{2+} in the octahedral site M1.

The root name is given in honour of Christof Schäfer (b. 1961), a prominent German mineral collector. Christof Schäfer is a specialist in the mining and cement industry. His well-docu-

¹ – Christofschäferite-(Ce) is approved by the IMA Commission on New Minerals, Nomenclature and Classification on March 1, 2012, IMA no. 2011-107.

mented collection of minerals from the Eifel and from other volcanic areas repeatedly served as a source of information and specimens for scientific investigations. Christof Schäfer is the author or co-author of numerous publications (mainly popular ones) on minerals of volcanic rocks. One of these publications (Blass, Schäfer, 1993) is devoted to the description of an association with pyrophanite from the Laacher See area. Christof Schäfer provided the specimen of the new mineral for investigations. The Levinson modifier-(Ce) in the mineral name reflects the predominance of Ce among rare earth elements.

Type material is deposited in the collections of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, registration number 4227/1 (fragment of the only known specimen). Another part of this holotype specimen is present in the joint collection of Christof Schäfer and his father Helmut Schäfer.

Occurrence, general appearance and physical properties

Christofschäferite-(Ce) was discovered in a volcanic ejected block collected in 1982 at the famous outcrop of the Laacher See volcano Wingertsbergwand (Wingertsberg Mt.) located near Mendig, Eifel Mountains, Rhineland-Palatinate (Rheinland-Pfalz), Germany. This deposit was formed as a result of a powerful eruption about 13000 years ago. This specimen is the only find of christofschäferite-(Ce). The block consists mainly of orthoclase with subordinate amounts of manganese silicates (rhodonite, bustamite, tephroite). Other (accessory) minerals, zircon, fluorapatite, pyrophanite and jacobsonite, form isolated grains and their intergrowths in grained aggregate of orthoclase. Occasionally euhedral crystals of these minerals are observed in cavities (Fig. 1).

The new mineral forms coarse crystals and isolated anhedral grains up to 3 mm in size in an aggregate of associated minerals. Idiomorphic crystals are rare (Fig. 2).

Christofschäferite-(Ce) has a metasomatic origin. It is an accessory mineral of a metasomate formed at the contact of differentiated phonolitic magma and a Mn-rich rock. The material containing christofschäferite-(Ce) has signs of relict layering. Note that metamorphosed Mn-rich sediments of Silurian and Cambrian age, containing carpholite, braunite, spessartine, ardenite and accessory rutile and monazite, are known from 70 km to the west of Wingertsberg.

Christofschäferite-(Ce) is black, translucent in thin fragments, with resinous lustre and brown streak. It is brittle, with conchoidal fracture. Mohs' hardness is 6. Cleavage is not observed. Density measured by the microvolumetric method is $D_{\text{meas}} = 4.8(1) \text{ g/cm}^3$, calculated density is $D_{\text{calc}} = 4.85 \text{ g/cm}^3$.

The new mineral is optically biaxial (-), $\alpha = 1.945(10)$, $\beta = 2.015(10)$, $\gamma = 2.050(10)$, $2V_{\text{meas}} = 70(10)^\circ$, $2V_{\text{calc}} = 68^\circ$. Dispersion is none observed. Pleochroism is strong, $Z > Y > X$ (light brown to very dark brown).

In order to obtain IR spectra, mineral samples have been mixed with anhydrous KBr, pelletized, and analysed using ALPHA FTIR spectrometer (for christofschäferite-(Ce)) and Specord 75 IR spectrophotometer (for other minerals). IR spectrum of pure KBr-disk was subtracted from the overall spectrum. Polystyrene and gaseous NH_3 were used as frequency standards; the precision of frequency measurement is $\pm 1 \text{ cm}^{-1}$; the mean resolution for the region $400 - 1600 \text{ cm}^{-1}$ is 0.8 cm^{-1} .

The IR spectrum of christofschäferite-(Ce) (Fig. 3a) is similar to those of other chevkinite group minerals (Fig. 3b, c). Absorption bands in the IR spectrum and their assignments are (cm^{-1} ; s – strong band, sh – shoulder): 1119, 1035s, 1010sh, 904s, 849s (Si-O stretching vibrations), 671, 609, 562 (Ti-O stretching vibrations and mixed vibrations of Si_2O_7 groups), 511s, 469s, 410sh, 390sh, 374s (combination of Si-O-Si bending vibrations and stretching vibrations of the MnO_6 and FeO_6 octahedra). Bands of H-, B- or C-bearing groups are absent in the spectrum.



Fig. 1. Christofschäferite-(Ce) (black) with orthoclase and rhodonite. Field width: 1 cm.

Fig. 2. Tephroite (orange-brown) and pyrophanite (black) in aggregate of orthoclase, from the association with christofschäferite-(Ce). Field width: 3 mm.

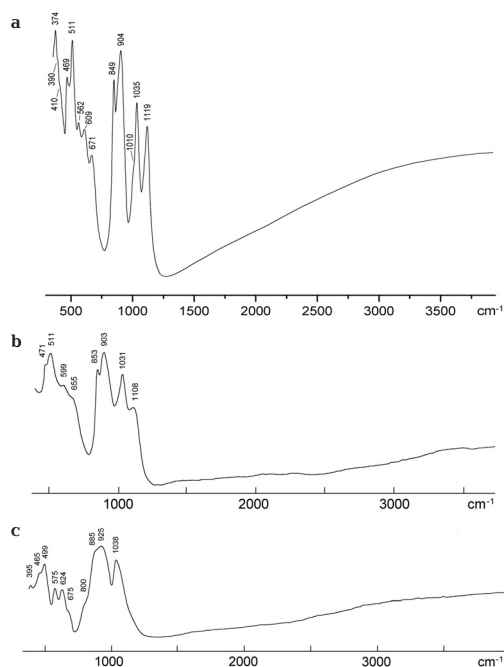


Fig. 3. IR spectra of christofschäferite-(Ce) (a), chevkinite-(Ce) from the Ilmeny Mountains, Urals, Russia (b) and perrierite-(La) from Mendig, Laacher See area, Eifel Mountains (c).

Chemical composition

Five chemical analyses of christofschäferite-(Ce) were carried out using an Oxford INCA Wave 700 electron microprobe (wave length dispersive = WDS mode, 20 kV, 20 nA, 300 nm beam diameter, analyst A.A. Virus). H₂O and CO₂ were not analysed because of the absence of absorption bands corresponding to vibrations of O-H and C-O bonds in the IR spectrum. F, Na, P, S, Cl, K, Cr, Zr, REE heavier than Nd, Th and U contents are below detection limits. Analytical data are given in Table 1. Individuals of christofschäferite-(Ce) are uniform in composition and do not show any remarkable zoning.

The empirical formula calculated on 22 oxygen atoms, taking into account the valence states of Fe (based on structural data) and Mn (by structural and XANES data, see below) is: $(\text{Ce}_{1.72}\text{La}_{1.48}\text{Nd}_{0.17}\text{Pr}_{0.04}\text{Ca}_{0.57})_{3.98}\text{Mn}_{0.76}^{2+}\text{Fe}_{0.72}^{2+}\text{Mg}_{0.02}\text{Fe}_{0.48}^{3+}\text{Al}_{0.02}\text{Ti}_{2.935}\text{Nb}_{0.08}\text{Si}_{3.98}\text{O}_{22}$.

The simplified formula is $(\text{Ce}, \text{La}, \text{Ca})_4\text{Mn}(\text{Ti}, \text{Fe})_3(\text{Fe}, \text{Ti})(\text{Si}_2\text{O}_7)_2\text{O}_8$.

The idealised end-member formula, $\text{Ce}_3\text{CaMnFe}^{3+}\text{Ti}_3(\text{Si}_2\text{O}_7)_2\text{O}_8$, requires CaO 4.76, Ce₂O₃ 41.74, MnO 6.02, Fe₂O₃ 6.77, TiO₂ 20.33, SiO₂ 20.38, total 100.00 wt%.

Gladstone-Dale compatibility is $1 - (K_p/K_c) = 0.043$ (good) with D_{calc} ; 0.032 (excellent) with D_{meas} .

Table 1. Analytical data for christofschäferite-(Ce)

Constituent	wt%	Range	Probe Standard
CaO	2.61	2.24–2.98	Wollastonite
La ₂ O ₃	19.60	19.20–19.83	LaPO ₄
Ce ₂ O ₃	22.95	22.84–23.06	CePO ₄
Pr ₂ O ₃	0.56	0.43–0.68	PrPO ₄
Nd ₂ O ₃	2.28	2.01–2.50	NdPO ₄
MgO	0.08	0–0.20	Diopside
MnO*	4.39	4.27–4.51	MnTiO ₃
FeO**	4.18	6.74–7.26***	Fe ₂ O ₃
Fe ₂ O ₃ **	3.11		
Al ₂ O ₃	0.08	0–0.19	Al ₂ O ₃
TiO ₂	19.02	18.64–19.39	MnTiO ₃
Nb ₂ O ₅	0.96	0.83–1.11	Nb
SiO ₂	19.38	19.16–19.52	SiO ₂
Total	99.20		

*All Mn is bivalent within the error of the XANES method.
Total iron content (corresponding to 6.98 wt. % FeO) was apportioned between FeO and Fe₂O₃ in the proportions Fe²⁺:Fe³⁺ = 3:2, taking into account structural data (cation-ligand distances and bond valence calculations for cationic sites; see Authors' remarks). *For total iron considered as FeO. Analyst Alla A. Virus.

XANES data. The valency of Mn

Fine structure of the X-ray absorption spectrum near edge structure (XANES) is very sensitive to the electronic state of an absorbing atom, as well as to its local environment. In particular, this method has been repeatedly applied to the determination of the Mn valence states in minerals and inorganic compounds. Details of the method are described by Manceau *et al.* (2012).

In order to determine the state of Mn in christofschäferite-(Ce), its spectrum was compared with X-ray spectra of standard samples. XANES Spectra were recorded at the X-ray beamline of the Synchrotron Radiation Laboratory for Environmental Studies (SUL-X) of the synchrotron radiation source ANKA (Karlsruhe Institute of Technology, KIT). The storage ring operated at electron energy of 2.5 GeV. The radiation source of the SUL-X beamline is a 27 pole Wiggler. An Si(111) crystal pair was used in the double crystal monochromator with fixed beam height.

The following reference substances were used:

- for Mn(II) – MnSiO₃, MnCO₃, MnSO₄ • nH₂O and MnO;
- for Mn(III) – Mn₂O₃, MnPO₄ and henritermierite (Ca₃Mn_{1.9}Al_{0.1}(SiO₄)₂(OH)₄);
- for Mn(IV) – MnO₂;
- for Mn(VII) – K₂MnO₄.

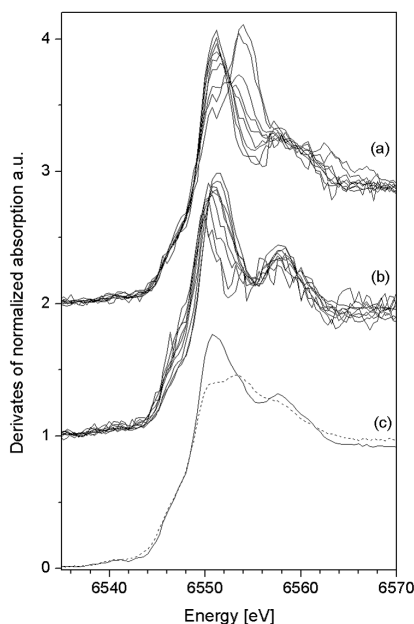


Fig. 4. Mn K-edge XANES spectra of grain 1 (a) and grain 2 (b) of christofschäferite-(Ce) with different orientations of the grains to the incoming beam (10 – 80° in 10° steps, and 45°); (c) shows the average spectrum for the 18 scans over the two grains in different orientations (solid line) and the Mn K-edge XANES spectrum of a powdered part of grain 2 which represent random orientation. The deviation between the averaged spectrum and the spectrum of randomly orientated crystallites might be due to the limited number of orientations in the 18 scans. The noise in the spectra of (a) and (b) is due to the short scanning time that was chosen.

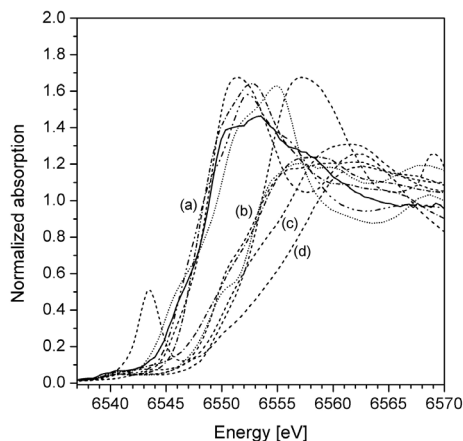


Fig. 5. Mn K-edge XANES spectra of christofschäferite-(Ce) (powdered; solid line) compared to spectra of (a) di-, (b) tri-, (c) tetra- and (d) heptavalent Mn compounds. With increasing Mn valency the flanks of the absorption edges shift to higher energy. The flanks of the sample spectra are within the range of the flanks for the divalent reference compounds. Spectra of reference compounds are (a) MnCO_3 (dashed), $\text{MnSO}_4 \cdot n\text{H}_2\text{O}$ (dash-dotted), MnSiO_3 (dash-double-dotted), MnO (dotted); (b) MnPO_4 (dashed), Mn_2O_3 (dash-dotted), $\text{Ca}_3\text{Mn}_2^{3+}\text{Al}_{0.1}(\text{SiO}_4)_2(\text{OH})_4$ (henritermierite) (dotted); (c) MnO_2 (dashed); (d) K_2MnO_4 (dashed).

All reference substances were prepared as pellets intermixed with cellulose for measurements in transmission mode using ionization chambers as detectors. XANES spectra were recorded in energy steps of 5 eV from -150 to -50 eV and of 2 eV from -50 to -20 eV prior to the edge, steps of 0.3 eV from -20 to +20 eV across the edge, and with a k step of 0.05 from k 2.29 to at least k 12 (+20 to about +550 eV) above the edge. At each spot, up to three scans were performed to improve measurement statistics.

Two grains of christofschäferite-(Ce) were mounted on Kapton tape. A series of measurements with different angles of the sample to the incoming beam were performed for both grains and a strong angular dependence of the XANES spectra was detected (Fig. 4). To obtain a spectrum that represents random orientation, a grain of christofschäferite-(Ce) was crushed and measured. Its spectrum is compared to the average spectrum of the 18 scans at different orientations in Figure 5c. The energy position of the flanks of the absorption edge in the spectra of the two sample grains matches best with the flanks of the divalent Mn-reference compounds (Fig. 5). The absorption edges of higher valency Mn-compounds are shifted to higher energies. In addition, the position of the first strong peaks in the derivatives matches best with those of the divalent reference compounds (Fig. 6).

To conclude, the most part of Mn in christofschäferite-(Ce) is bivalent. Because there is variability of edge position within a certain valence for different compounds, one cannot unequivocally say for an unknown sample whether a small shift is due to the variability for divalent compounds or admixture of Mn species of other valencies. Hence, small contributions of other valencies are possible, but at maximum would be in the range of about 10 to 15%.

X-ray diffraction data and crystal structure

Powder X-ray diffraction data for christofschäferite-(Ce) (Table 2) were collected using a Stoe IPDS II single-crystal diffractometer equipped with an image plate detector using the Gandolfi method, at the following conditions: $\text{MoK}\alpha$ -radiation, voltage of 45 kV, current of 30 mA, exposure time of 60 minutes; the distance between sample and detector was 200 mm. The standard software Stoe X-Area 1.42; Stoe WinXPOW 2.08 was used for the data processing.

The crystal structure of christofschäferite-(Ce) (Figs. 7–8, Tables 3–6) is similar to that of other chevkinite-group minerals. Sheets of small and distorted Ti-centred octahedra (with

Христофшеферит-(Ce), $(\text{Ce,La,Ca})_4\text{Mn}^{2+}(\text{Ti,Fe}^{3+})_3(\text{Fe}^{3+},\text{Fe}^{2+},\text{Ti})(\text{Si}_2\text{O}_7)_2\text{O}_8$ –
 новый минерал группы чевкинита из вулканической области Айфель (Германия)

Table 2. X-ray powder diffraction data for christofschäferite-(Ce)

I_{rel}	d_{obs}	d_{calc} *	hkl
24	10.96	10.90	001
4	9.31	9.27	-101
7	6.55	6.57	200
21	5.47	5.45	002
39	4.90	4.88	-111
65	4.64	4.63	-202
5	3.90	3.93, 3.86, 3.86	-112, 211, 202
8	3.772	3.769	-302
19	3.633	3.633	003
78	3.480	3.484	310
81	3.169	3.186, 3.151	311, -312
43	3.095	3.098	-113
15	2.999	2.998	401
37	2.883	2.892, 2.874	113, -411
100	2.730	2.724	004
27	2.609	2.610	402
34	2.530	2.535, 2.531	-122, -304
5	2.356	2.350	114
10	2.322	2.317	-404
19	2.247	2.253, 2.241	023, 403
46	2.169	2.172, 2.170	-421, -513
10	2.102	2.103, 2.099	-323, -422
20	2.072	2.074, 2.068	421, -115
21	1.973	1.976, 1.967, 1.966, 1.965	024, -514, -224, -423
8	1.863	1.866, 1.859, 1.858, 1.858	521, 513, 215, 131
13	1.828	1.830, 1.828, 1.827, 1.823	414, -231, 224, 305
21	1.789	1.791, 1.791, 1.785	-721, -614, 710
46	1.737	1.740, 1.739, 1.737, 1.736, 1.734	603, 504, 315, 025, -622
35	1.711	1.715, 1.714, 1.712, 1.710, 1.707	232, 711, 331, -605, -332
28	1.672	1.675, 1.674, 1.671, 1.668	-233, 206, -801, -623
28	1.631	1.635, 1.629, 1.627	332, -714, -333
6	1.553	1.556, 1.556, 1.553, 1.552	-531, 703, -126, -813
14	1.523	1.526, 1.525, 1.524, 1.524, 1.523, 1.522	811, -217, -326, -117, 721, 316

*Calculated from single-crystal data.

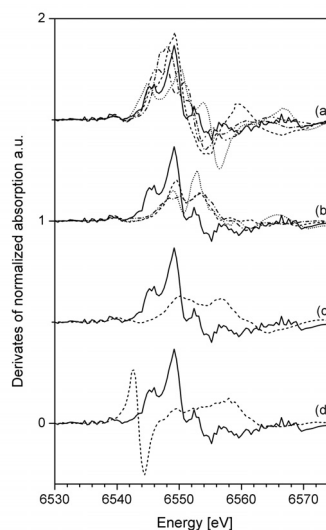


Fig. 6. Derivatives of Mn K-edge XANES spectra of christofschäferite-(Ce) (powdered; solid line) compared to spectra of (a) di-, (b) tri-, (c) tetra- and (d) heptavalent Mn compounds. With increasing Mn valency the flanks of the absorption edges shift to higher energy. The first strong peaks of the derivatives matches best with the peaks for the divalent reference compounds (a). The derivatives of the higher valent Mn compounds are shifted to higher energies. Spectra of reference compounds are (a) MnCO_3 (dashed), $\text{MnSO}_4 \cdot n\text{H}_2\text{O}$ (dash-dotted), MnSiO_3 (dash-double-dotted), MnO (dotted); (b) MnPO_4 (dashed), Mn_2O_3 (dash-dotted), henritermierite, $\text{Ca}_3\text{Mn}_{1.9}\text{Al}_{0.1}(\text{SiO}_4)_2(\text{OH})_4$ (dotted); (c) MnO_2 (dashed); (d) K_2MnO_4 (dashed).

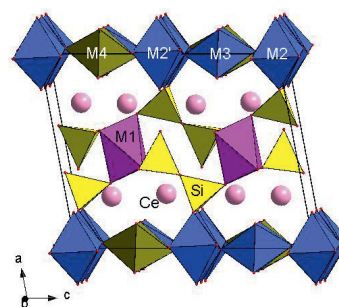


Fig. 7. Polyhedral representation of the crystal structure of christofschäferite-(Ce).

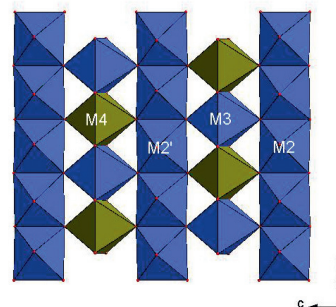


Fig. 8. The octahedral layer in the structure of christofschäferite-(Ce).

Table 3. Fractional site coordinates, equivalent displacement factors (U_{eq}) and site multiplicities (W) in the crystal structure of christofschäferite-(Ce)

Site	x/a	y/b	z/c	U_{eq} (Å ²)	W
A1	0.39299(2)	-0.25	0.26638(2)	0.00593(5)	2e
A2	0.81886(2)	-0.25	0.73890(2)	0.00448(4)	2e
A3	0.10733(3)	-0.25	0.73407(3)	0.0193(1)	2e
A4	0.68134(4)	-0.25	0.26116(3)	0.0364(2)	2e
M1	0.24991(5)	-0.25	0.49998(4)	0.0075(1)	2e
M2	0	0	0	0.0072(1)	2a
M2'	0.5	0	0	0.0102(2)	2c
M3	0.24994(5)	-0.25	0.00033(5)	0.0094(2)	2e
M4	0.74998(5)	-0.25	0.00015(5)	0.0102(2)	2e
Si1	0.0504(1)	-0.25	0.2672(1)	0.0046(2)	2e
Si2	0.4494(1)	-0.25	0.7326(1)	0.0058(2)	2e
Si3	0.8949(1)	-0.25	0.4537(1)	0.0055(2)	2e
Si4	0.6050(1)	-0.25	0.5465(1)	0.0059(2)	2e
O1	0.8968(2)	-0.25	0.9770(3)	0.0073(6)	2e
O2	0.7725(2)	-0.0035(6)	0.1255(2)	0.0133(6)	4f
O3	0.5129(5)	-0.25	0.6231(5)	0.0262(4)	2e
O4	0.9368(2)	-0.25	0.5974(2)	0.0062(5)	2e
O5	0.6052(3)	-0.25	0.0233(3)	0.016(1)	2e
O6	0.6757(3)	-0.0250(5)	0.5952(2)	0.0136(5)	4f
O7	0.9848(3)	-0.25	0.3749(4)	0.0137(4)	2e
O8	0.5211(3)	0.0126(6)	0.1852(2)	0.0189(7)	4f
O9	0.4023(2)	-0.25	1.0100(3)	0.0066(5)	2e
O10	0.0200(2)	-0.0152(5)	0.1850(2)	0.0119(5)	4f
O11	0.7273(2)	-0.0047(5)	0.8741(2)	0.0104(5)	4f
O12	0.5632(3)	-0.25	0.4023(3)	0.0152(9)	2e
O13	0.3327(2)	-0.25	0.6778(2)	0.0046(6)	2e
O14	0.0989(3)	-0.25	-0.0099(3)	0.0093(6)	2e
O15	0.1689(3)	-0.25	0.3205(3)	0.0096(7)	2e
O16	0.1739(3)	0.0261(9)	0.5960(3)	0.0284(6)	4f

Table 4. Anisotropic displacement parameters (Å²) for christofschäferite-(Ce)

Site	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
A1	0.0075(1)	0.0031(1)	0.0072(1)	0	0.0013(1)	0
A2	0.0046(1)	0.0039(1)	0.0051(1)	0	0.0012(1)	0
A3	0.0096(1)	0.0404(3)	0.0079(1)	0	0.0014(1)	0
A4	0.0042(2)	0.1008(7)	0.0045(1)	0	0.0014(1)	0
M1	0.0090(2)	0.0081(3)	0.0048(1)	0	0.0002(2)	0
M2	0.0058(2)	0.0124(3)	0.0032(1)	-0.0066(2)	0.0002(2)	0.0005(2)
M2'	0.0068(3)	0.0198(4)	0.0037(1)	-0.0095(2)	0.0005(2)	-0.0009(2)
M3	0.0077(2)	0.0115(3)	0.0082(2)	0	0.0001(2)	0
M4	0.0086(3)	0.0160(4)	0.0062(2)	0	0.0020(2)	0
Si1	0.0033(4)	0.0062(4)	0.0038(3)	0	-0.0001(2)	0
Si2	0.0052(4)	0.0077(5)	0.0042(3)	0	-0.0002(3)	0
Si3	0.0066(4)	0.0070(4)	0.0031(3)	0	0.0013(3)	0
Si4	0.0072(4)	0.0070(5)	0.0033(3)	0	0.0006(3)	0
O1	0.006(1)	0.009(1)	0.008(1)	0	0.004(1)	0
O2	0.008(1)	0.024(1)	0.009(1)	0.001(1)	0.001(1)	-0.004(1)
O3	0.031(1)	0.034(1)	0.020(1)	0	0.022(7)	0
O4	0.006(1)	0.008(1)	0.003(1)	0	-0.001(2)	0
O5	0.005(1)	0.034(2)	0.009(1)	0	0.002(1)	0
O6	0.025(1)	0.008(1)	0.007(1)	0.008(1)	0.001(1)	-0.002(1)
O7	0.017(1)	0.013(1)	0.016(1)	0	0.015(1)	0
O8	0.021(1)	0.030(2)	0.005(1)	-0.022(1)	0.001(1)	-0.001(1)
O9	0.004(1)	0.003(1)	0.012(1)	0	-0.001(1)	0
O10	0.017(1)	0.013(1)	0.005(1)	-0.011(1)	0.002(1)	0.001(1)
O11	0.007(1)	0.017(1)	0.007(1)	0.004(1)	0.001(1)	0.002(1)
O12	0.013(1)	0.025(2)	0.007(1)	0	0.001(1)	0
O13	0.003(1)	0.003(1)	0.007(1)	0	-0.003(1)	0
O14	0.007(1)	0.007(1)	0.014(1)	0	0.002(1)	0
O15	0.012(1)	0.009(1)	0.006(1)	0	-0.003(1)	0
O16	0.029(1)	0.045(1)	0.010(1)	0.028(1)	-0.001(1)	0.003(1)

Христофшеферит-(Ce), $(\text{Ce}, \text{La}, \text{Ca})_4\text{Mn}^{2+}(\text{Ti}, \text{Fe}^{3+})_3(\text{Fe}^{3+}, \text{Fe}^{2+}, \text{Ti})(\text{Si}_2\text{O}_7)_2\text{O}_8$ –
 новый минерал группы чевкинита из вулканической области Айфель (Германия)

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Table 5. Bond lengths (Å) in coordination polyhedra of christofschäferite-(Ce)

A1-O12	2.488(4)	M2'-O9	1.958(2) x2
A1-O6	2.492(3) x2	M2'-O5	1.993(3) x2
A1-O11	2.497(2) x2	M2'-O8	2.022(2) x2
A1-O8	2.566(4) x2	M2'-O9	1.958(2) x2
A1-O9	2.868(3)	Mean	1.991
Mean	2.558		
		M3-O2	2.001(3) x2
A2-O4	2.420(3)	M3-O14	2.002(4)
A2-O11	2.531(3) x2	M3-O11	2.004(3) x2
A2-O6	2.599(3) x2	M3-O9	2.020(3)
A2-O10	2.647(3) x2	Mean	2.005
A2-O1	2.654(3)		
A2-O15	2.958(1) x2	M4-O2	1.968(3) x2
Mean	2.654	M4-O11	1.968(3) x2
		M4-O5	1.999(4)
A3-O16	2.480(4) x2	M4-O1	2.026(3)
A3-O2	2.491(3) x2	Mean	1.982
A3-O4	2.495(2)		
A3-O10	2.566(3) x2	Si1-O15	1.586(4)
A3-O14	2.861(3)	Si1-O7	1.606(5)
Mean	2.554	Si1-O10	1.637(3) x2
		Mean	1.617
A4-O12	2.419		
A4-O2	2.535(3) x2	Si2-O13	1.567(3)
A4-O16	2.604 (4) x2	Si2-O3	1.604(7)
A4-O8	2.629(4)	Si2-O8	1.647(3) x2
A4-O5	2.647(3) x2	Mean	1.633
A4-O13	2.964(1) x2		
Mean	2.655	Si3-O4	1.589(2)
		Si3-O7	1.611(5)
M1-O13	2.076(2)	Si3-O16	1.618(5) x2
M1-O15	2.084(3)	Mean	1.609
M1-O6	2.232(3) x2		
M1-O16	2.253(5) x2	Si4-O12	1.594(3)
Mean	2.188	Si4-O3	1.619(7)
		Si4-O6	1.633(3) x2
M2-O14	1.969(3) x2	Mean	1.620
M2-O1	1.975(2) x2		
M2-O10	2.021(2) x2		
Mean	1.988		

minor admixtures of Fe^{3+} , Al and Nb) lie parallel to the (100) plane. These sheets are interleaved with a layer consisting of Si_2O_7 groups and larger M1O_6 octahedra with a mean cation-anion distance of 2.188 Å. *REE* and subordinate Ca occupy the sites A1 – A4 with coordination numbers from 8 to 10. The rare earth ions fill the channels, which are formed through the linkage of heteropolyhedral and octahedral layers.

Based on the interatomic distances (Table 5) and bond valence calculations (Table 6), we consider the following occupancy of octahedral sites:

M1 – Mn^{2+} with subordinate Fe^{2+} ;

M2, M2' and M3 – Ti with subordinate Fe^{3+} , Fe^{2+} and minor Nb;

M4 – Fe^{3+} , Fe^{2+} and Ti with mean charge about +3.

The site M1 with the mean cation-anion distance of 2.188 Å and the mean charge close to 2 is the only site that can contain Mn^{2+} . The crystal-chemical formula of christofschäferite-(Ce), taking into account chemical data, is $^{\text{X}}(\text{Ce}, \text{REE}, \text{Ca})_2^{\text{VIII}}(\text{Ce}, \text{REE}, \text{Ca})_2^{\text{VI}}(\text{Mn}, \text{Fe}^{2+})^{\text{VI}}(\text{Ti}, \text{Fe}, \text{Al})_4(\text{Si}_2\text{O}_7)_2\text{O}_8$.

Discussion

The chevkinite group unites monoclinic oxosilicates with the general formula $A_2B_2M_5(\text{Si}_2\text{O}_7)_2\text{O}_8$ where A and B are large cations like REE^{3+} , Sr or Ca with coordination numbers from 8 to 10 and M are octahedral cations (Ti, Fe^{2+} , Fe^{3+} , Zr, Cr^{3+} , Mg, Nb, Mn^{2+} , Al). In the crystal structures of these minerals, alternating octahedral and heteropolyhedral layers are coplanar with the plane (001). The A and B cations are situated in channels between the layers.

All chevkinite-group minerals are monoclinic. Among them, representatives of two structural types are distinguished (Table 7) which are different in unit-cell parameters, number of M sites, mutual orientation of coordination polyhedra, cation ordering, as well as in X-ray powder-diffraction patterns.

Chevkinite enriched in Mn is known from a number of localities including Stokkøya, Norway (2.65 wt.% MnO; Segalstad, Larsen, 1978), the pit number 17, Ilmeny Mountains, South Urals (1.34 wt.% MnO; Makarochkin *et al.*, 1959) and exocontact zone of western part of Khibiny alkaline pluton (2.71 wt.% MnO; Shlyukova, Burova, 1959). However these values correspond to Mn contents less than 0.5 Mn atoms per formula unit.

In most cases, titanium chevkinite-group minerals are metamict due to the presence of admixed thorium. In spite of this, representatives

Table 6. Bond valence calculations for christofschäferite-(Ce)

Site	A1	A2	A3	A4	M1	M2	M2'	M3	M4	Si1	Si2	Si3	Si4	V _i
O1		0.26 ^{↓→}				0.65 ^{(x2)↓→}			0.45 ^{↓→}					2.01
O2			0.40 ^{(x2)↓}	0.36 ^{(x2)↓}				0.60 ^{(x2)↓}	0.53 ^{(x2)↓}					1.89
			0.40 [→]	0.36 [→]				0.60 [→]	0.53 [→]					
O3											1.06 ^{↓→}		1.01 ^{↓→}	2.07
O4		0.49 ^{↓→}	0.40 ^{↓→}									1.10 ^{↓→}		1.99
O5				0.26 ^{(x2)↓}			0.62 ^{(x2)↓→}	0.49 ^{↓→}						1.99
				0.26 [→]										
O6	0.40 ^{(x2)↓}	0.30 ^{(x2)↓}			0.29 ^{(x2)↓}									0.98 ^{(x2)↓}
	0.40 [→]	0.30 [→]			0.29 [→]									0.98 [→]
O7										1.05 ^{↓→}		1.04 ^{↓→}		2.09
O8	0.33 ^{(x2)↓}			0.28 ^{↓→}			0.57 ^{(x2)↓}				0.94 ^{(x2)↓}			2.12
	0.33 [→]						0.57 [→]				0.94 [→]			
O9	0.15 ^{↓→}						0.68 ^{(x2)↓→}	0.57 ^{↓→}						2.08
O10		0.26 ^{(x2)↓}	0.33 ^{(x2)↓}				0.57 ^{(x2)↓}			0.97 ^{(x2)↓}				2.13
		0.26 [→]	0.33 [→]				0.57 [→]			0.97 [→]				
O11	0.40 ^{(x2)↓}	0.36 ^{(x2)↓}						0.60 ^{(x2)↓}	0.53 ^{(x2)↓}					1.89
	0.40 [→]	0.36 [→]						0.60 [→]	0.53 [→]					
O12	0.41 ^{↓→}			0.49 ^{↓→}									1.08 ^{↓→}	1.98
O13				0.11 ^{(x2)↓→}	0.46 ^{↓→}						1.17 ^{↓→}			1.85
O14			0.15 ^{↓→}			0.66 ^{(x2)↓→}		0.60 ^{↓→}						2.07
O15		0.11 ^{(x2)↓→}		0.45 ^{↓→}						1.11 ^{↓→}				1.78
O16			0.41 ^{(x2)↓}	0.30 ^{(x2)↓}	0.30 ^{(x2)↓}							1.02 ^{(x2)↓}		2.03
			0.41 [→]	0.30 [→]	0.30 [→]							1.02 [→]		
V _i	2.82	2.81	2.83	2.83	2.09	3.76	3.74	3.57	3.06	4.10	4.11	4.18	4.05	

Table 7. Predominant components in cationic sites of chevkinite-group minerals

Minerals with chevkinite-type unit cell (β = 100.3–100.7)									
	A1/A3	A2/A4	M1	M2/M2'	M3	M4	Space group	β, °	References
Christofschäferite-(Ce)	Ce/Ce	Ce/Ce	Mn	Ti/Ti	Ti	(Fe,Ti) ³⁺	P2 ₁ /a	100.58	This work
Chevkinite-Ce	Ce	Ce	Fe ²⁺	Ti	Ti	Ti	C2/m	100.54	Sokolova <i>et al.</i> , 2004
Maonipiungite-(Ce)	Ce	Ce	Fe ³⁺	Ti	Ti	Ti	C2/m	100.60	Yang <i>et al.</i> , 2002
Dingdaohengite-Ce	Ce	Ce	Ti	Ti	Ti	Fe ²⁺	P2 ₁ /a	100.64	Li <i>et al.</i> , 2005
Polyakovite-Ce	Ce	Ce	Mg	Ti	Cr	Cr	C2/m	100.54	Popov <i>et al.</i> , 2001
Strontiochevkinite	Sr	Sr	Fe ²⁺	Ti	Ti	Ti	P2 ₁ /a	100.32	Haggerty, Mariano, 1983
Minerals with perrierite-type unit cell (β = 113.5–114.2)									
	A1	A2	M1	M2	M3	Space group	β, °	References	
Perrierite-Ce	Ce	Ce	Fe ²⁺	Ti	Ti	C2/m	113.5	Gottardi, 1960	
Perrierite-La	La	La	Fe ²⁺	Ti	Ti	P2 ₁ /a	113.64	Chukanov <i>et al.</i> , 2011	
Matsubaraitite	Sr	Sr	Ti	Ti	Ti	C2/m	114.14	Miyajima <i>et al.</i> , 2002	
Hezuolinite	Sr	Sr	Zr	Ti	Ti	C2/m	114.10	Yang <i>et al.</i> , 2012	
Rengeite	Sr	Sr	Zr	Ti	Ti	P2 ₁ /a	114.22	Miyawaki <i>et al.</i> , 2002	

Христофшэферит-(Ce), (Ce,La,Ca)₄Mn²⁺(Ti,Fe³⁺)₃(Fe³⁺,Fe²⁺,Ti)(Si₂O₇)₂O₈ –
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Table 8. Comparative data for christofschäferite-(Ce) and related minerals with the chevkinite-type unit cell

Mineral	Christof-schäferite-(Ce)	Chevkinite-(Ce)	Dingdaohengite-(Ce)	Maonipiungite-(Ce)
Simplified formula	(Ce,La,Ca) ₄ Mn(Ti,Fe) ₃ (Fe,Ti)(Si ₂ O ₇) ₂ O ₈	(Ce,La,Ca) ₄ Fe ²⁺ ₂ (Ti,Fe ³⁺) ₃ (Si ₂ O ₇) ₂ O ₈	(Ce,La,Ca) ₄ Fe ²⁺ (Ti,Fe ³⁺) ₄ (Si ₂ O ₇) ₂ O ₈	(Ce,La,Ca) ₄ (Fe ³⁺ ,Ti,Fe ²⁺ ,□)(Ti,Fe ³⁺ ,Fe ²⁺ ,Nb)(Si ₂ O ₇) ₂ O ₈
Space group	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> 2 ₁ / <i>a</i> (pseudo <i>C</i> 2/ <i>m</i>)	<i>C</i> 2/ <i>m</i>
<i>a</i> , Å	13.3722	13.37 – 13.44	13.4656	13.456
<i>b</i> , Å	5.7434	5.66 – 5.74	5.7356	5.728
<i>c</i> , Å	11.0862	11.04 – 11.28	11.0977	11.083
β, °	100.580	100.20 – 100.61	100.636	100.60
Z	2	2	2	2
Strong lines of the X-ray powder-diffraction pattern:				
<i>d</i> , Å (<i>I</i> , %)	4.90 (39) 4.64 (65) 3.480 (78) 3.169 (81) 3.095 (43) 2.730 (100) 2.169 (46) 1.737 (46)	4.58 (40) 3.46 (40) 3.17 (100) 3.14 (100) 2.71 (100) 2.16 (50) 1.961 (50)	3.198 (68) 3.162 (46) 2.870 (52) 2.752 (100) 2.726 (98) 2.546 (54)	4.89 (35) 3.49 (80) 3.004 (40) 2.874 (40) 2.760 (40) 2.722 (100)
Optical data:				
α	1.945	1.90 – 2.01	1.978	1.937
β	2.015	1.92 – 2.02	No data	No data
γ	2.050	1.925 – 2.05	2.01	1.97
Optical sign, 2V, °	-70	-70 – -80	No data	(-); no data on 2V
Density, g cm ⁻³	4.8(1) (meas) 4.853 (calc)	4.53 – 4.67 (meas) 4.99 (calc)	4.83 (meas) 4.88 (calc)	4.88 (calc)
References	This work	Izett, Wilcox (1968); Segalstad, Larsen (1978); Feklichev (1989); Macdonald, Belkin (2002); Yang <i>et al.</i> (2002); Sokolova <i>et al.</i> (2004); Yang <i>et al.</i> (2007).	Li <i>et al.</i> (2005); Jinsha <i>et al.</i> (2008)	Yang <i>et al.</i> (2002); Shen <i>et al.</i> (2005)

of this group originating from young rocks of the Eifel volcanic area and depleted in Th have perfect crystal structures (see Chukanov *et al.*, 2011).

Comparative data for christofschäferite-(Ce) and some related minerals are given in Table 8.

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