



Article

Kozłowskiite, ideally $\text{Ca}_4\text{Fe}^{2+}\text{Sn}_3(\text{Si}_2\text{O}_7)_2(\text{Si}_2\text{O}_6\text{OH})_2$, a new kristiansenite-type mineral from Szklarska Poręba, Lower Silesia, Poland

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Abstract

Kozłowskiite, ideally $\text{Ca}_4(\text{Fe}^{2+}\text{Sn}_3)(\text{Si}_2\text{O}_7)_2(\text{Si}_2\text{O}_6\text{OH})_2$, is a new mineral isostructural with kristiansenite and silesiaite, found as a band in the core of a zoned silesiaite–kristiansenite crystal from the granitic pegmatite at Szklarska Poręba, Lower Silesia, Poland. In tiny pieces kozłowskiite is pale brownish, with a calculated density of $3.775 \text{ g}\cdot\text{cm}^{-3}$ and a mean refractive index ~ 1.727 . The triclinic crystal structure was determined with space-group symmetry $C1$: $a = 10.0183(2)$, $b = 8.3861(1)$, $c = 13.3395(2) \text{ Å}$, $\alpha = 89.956(1)$, $\beta = 109.039(2)$, $\gamma = 89.979(1)^\circ$ and $V = 1059.40(3) \text{ Å}^3$, although, similarly to kristiansenite, it is metrically monoclinic (Laue group $2/m$) with α and γ angles equal to 90° and $a = 10.0170(3)$, $b = 8.3860(2)$, $c = 13.3421(4) \text{ Å}$, $\beta = 109.050(3)^\circ$ and $V = 1059.40(5) \text{ Å}^3$. The seven strongest reflections in the calculated powder X-ray diffraction pattern are [d in Å (I) hkl]: 5.190 (73.2) 111 , $1\bar{1}1$; 4.569 (30.0) $\bar{2}02$; 3.153 (64.7) 004 ; 3.094 (28.1) $\bar{3}11$, $\bar{3}\bar{1}1$; 3.089 (100) $\bar{2}22$, $\bar{2}22$; 2.595 (27.2) $\bar{2}22$, 222 ; and 2.141 (30.6) $\bar{3}31$, $\bar{3}31$. Electron microprobe analysis gave (in wt.%) SiO_2 39.46, ZrO_2 0.35, SnO_2 31.13, Al_2O_3 0.35, Sc_2O_3 2.65, total Fe as Fe_2O_3 5.06 (= $\text{Fe}_2\text{O}_{3\text{calc}}$, 2.26; FeO_{calc} , 2.52), MnO 0.71, CaO 18.42 and $\text{H}_2\text{O}_{\text{calc}}$ 1.48, sum 99.33. The empirical formula on the basis of $26\text{O} + 2(\text{OH})$ and 16 cations ($Z = 2$) is $\text{Ca}_{4.00}(\text{Sn}_{2.52}\text{Sc}_{0.47}\text{Fe}_{0.43}^{2+}\text{Fe}_{0.34}^{3+}\text{Mn}_{0.12}^{2+}\text{Al}_{0.08}\text{Zr}_{0.03})_{\Sigma 4.00}(\text{Si}_{2.00}\text{O}_7)_2(\text{Si}_{2.00}\text{O}_6\text{OH})_2$. The crystal structure of kozłowskiite was refined to an $R_1 = 2.12\%$ for 4887 reflections with $I > 2\sigma I$. The Ca and Si sites are occupied solely by Ca and Si, respectively, and three of four M sites: $M2$, $M3$ and $M4$, are dominated by Sn. Four hydrogen atoms present in the kozłowskiite unit cell are shared among the O17–O27 and O47–O37 oxygen atoms where O17 and O47 are OH groups forming relatively strong hydrogen bonds.

Keywords: kozłowskiite, crystal chemistry, crystal structure, Raman spectrum

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Introduction

Kozłowskiite, ideally $\text{Ca}_4(\text{Fe}^{2+}\text{Sn}_3)(\text{Si}_2\text{O}_7)_2(\text{Si}_2\text{O}_6\text{OH})_2$ ($Z = 2$), is a new mineral isostructural with kristiansenite, $\text{Ca}_5\text{ScSn}(\text{Si}_2\text{O}_7)(\text{Si}_2\text{O}_6\text{OH})$ and silesiaite, $\text{Ca}_2\text{Fe}^{3+}\text{Sn}(\text{Si}_2\text{O}_7)(\text{Si}_2\text{O}_6\text{OH})$ ($Z = 4$), found in pegmatites at Szklarska Poręba, Lower Silesia, Poland (IMA2021-081; Pieczka *et al.*, 2022). The mineral is named after Andrzej Kozłowski, an Emeritus Professor at the Faculty of Geology, Department of Geochemistry, Mineralogy and Petrology, University of Warsaw, Poland, born in 1946. He is an eminent Polish geologist specialising in geochemistry, mineralogy, petrology and mineral deposits, and one of the first Polish geologists to study pegmatites of the Karkonosze granite massif, including those exposed in the Szklarska Poręba Huta quarry, i.e. the type locality for silesiaite and kozłowskiite. Professor A. Kozłowski is also the main promoter of the Inter-Institute Analytical Complex for Minerals and Synthetic Substances of the University of Warsaw (2000), which made electron-probe

microanalysis possible for many Polish researchers and yielded international scientific collaboration.

In the classification of Strunz and Nickel (2001), kozłowskiite classifies along with kristiansenite and silesiaite in class 09.BC: Sorosilicates with Si_2O_7 groups, without non-tetrahedral anions, cations in octahedral [6] and higher coordination. In the classification of Dana (Gaines *et al.*, 1997), it belongs to the class 56.02: Sorosilicate Si_2O_7 groups and O, OH, F and H_2O with cations in [4] and/or $>[4]$ coordination, group 04: Cuspidine–Wohlerite. The silesiaite + kozłowskiite holotype (specimen SP5) is deposited in the collection of the Mineralogical Museum of University of Wrocław, catalogue number MMUWr IV7929. The postal address of the museum is as follows: University of Wrocław, Faculty of Earth Science and Environmental Management, Institute of Geological Sciences, Mineralogical Museum, 50-205 Wrocław, Cybulskiego, Poland.

Occurrence

Kozłowskiite was collected around 2002 in a pegmatite of the Karkonosze granite in the Szklarska Poręba Huta quarry (50.82778°N , 15.48944°E) in Lower Silesia, SW Poland. The Karkonosze granite is the largest Variscan pluton in the Western Sudetes at the north-eastern margin of the Bohemian Massif.

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The pluton is considered as a syn-collisional to magmatic arc intrusion on the margin of a continental platform neighbouring oceanic crust, formed by relatively reduced, K-rich, calc-alkaline, highly evolved, mostly peraluminous I- to transitional I-S-type magmas (Mazur *et al.*, 2007; Mikulski, 2007; Slaby and Martin, 2008) of ~320–315 Ma (Machowiak and Armstrong, 2007; Kryza *et al.*, 2014; Kusiak *et al.*, 2014). The main rocks of the massif are biotite-bearing, porphyritic to equigranular granite associated with a small volume of two-mica granite, subordinate granophyre granite, and numerous lamprophyre and aplite dykes (Berg, 1923; Borkowska, 1966). Pegmatites occur within various granite facies, although they are particularly abundant in the porphyritic type and also penetrate the metamorphic cover.

The Szklarska Poręba Huta quarry, located within the town Szklarska Poręba, is currently the only place in the Polish part of the massif where granite is exploited, mainly as dimension stone. Small bodies of granitic NYF-type pegmatite in the form of lenses and nests up to several tens of centimetres across are relatively frequent within the coarsely-crystalline porphyritic to equigranular granite; smaller nests and mineralised quartz veinlets are frequent in finely crystalline aplogranite (Pieczka *et al.*, 2015). Here, the pegmatitic assemblage is commonly overprinted by W–Sn–Mo–Bi hydrothermal mineralisation (Karwowski *et al.*, 1973; Kozłowski *et al.*, 1975; Olszyński *et al.*, 1976; Pieczka and Gołębiewska, 2012). Kozłowskiite was found in an ore-mineralised pegmatite specimen related to aplogranite, in which kristiansenite and silesiaite had been recognised previously (Pieczka *et al.*, 2017; Evans *et al.*, 2018). The mineral is accompanied by quartz, albite, andradite, allanite-(Ce), zircon, Sn-bearing titanite, malayaite, fergusonite-(Y), Sc-bearing columbite, clinocllore, bismuthinite, chalcopyrite and pyrite.

Kozłowskiite is a hydrothermal mineral that preceded the crystallisation of the silesiaite–kristiansenite assemblage.

Appearance and physical properties

Kozłowskiite was recognised in a zoned silesiaite–kristiansenite crystal in a band at the core with sizes of $40\ \mu\text{m} \times 10\ \mu\text{m}$ and atypical enrichment in Sn above 2.5 atoms per formula unit (apfu), calculated in relation to $Z=2$ (Fig. 1). Kristiansenite crystals from Szklarska Poręba are usually highly inhomogeneous, composed of numerous thin alternating Sc-dominant (dark grey in back-scattered electron images, BSE) and Fe-dominant (light grey) bands. The observed oscillatory zoning seems to be a characteristic feature of kristiansenite-type minerals. It is also marked in the holotype kristiansenite from an amazonite pegmatite at Heftetjern, Tørdal, Telemark, Norway (Raade *et al.*, 2002). However, zoning in the kristiansenite holotype is restricted to only the bands with more Sc- or those that are Fe^{3+} -bearing, compositionally corresponding always to kristiansenite. In tiny pieces kozłowskiite is pale brownish; by analogy to kristiansenite it is likely to have a white streak and a Mohs hardness ≈ 6 . No cleavage, parting, tenacity, or fracture was observed. Density and optical properties could not be measured due to the extremely small amount of the mineral. Density calculated on the basis of empirical formula and refined unit-cell volume is $3.775\ \text{g}\cdot\text{cm}^{-3}$. Kozłowskiite is biaxial, with a mean refractive index close to a value of 1.727 calculated from the Gladstone-Dale relation (Mandarino, 1979, 1981) using the empirical formula and calculated density. The value is comparable with the type kristiansenite mean refractive index of 1.74 (Raade *et al.*, 2002).

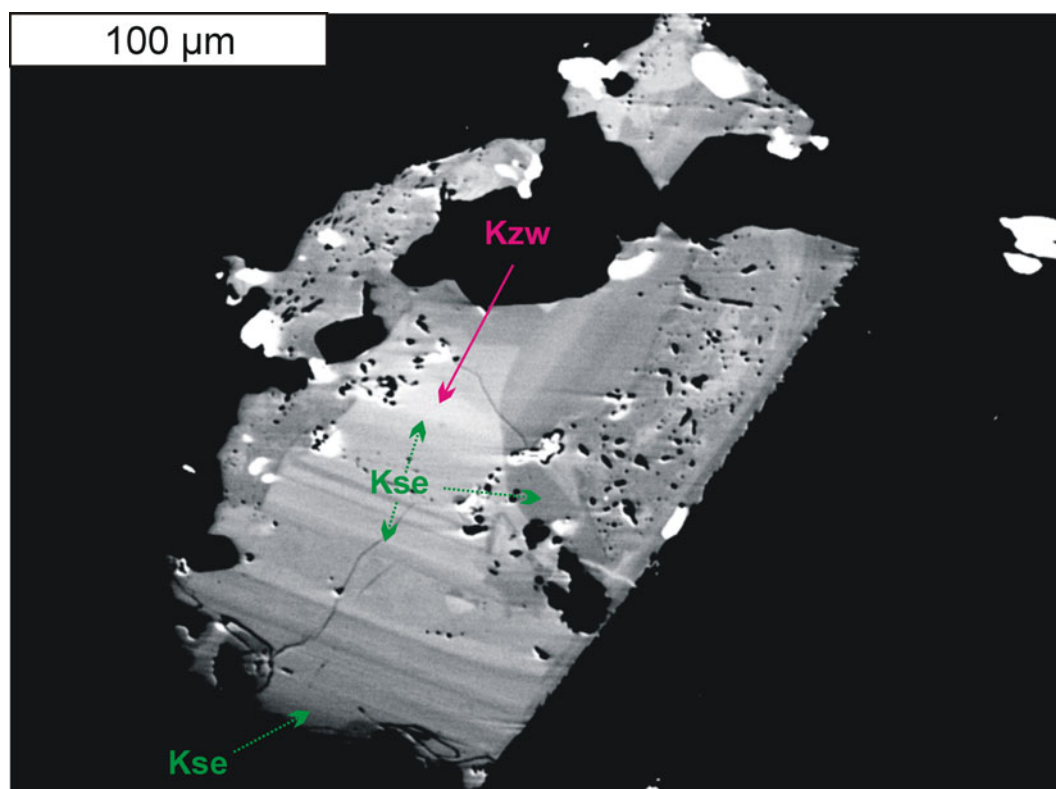


Fig. 1. Back-scattered electron image of type kozłowskiite (Kzw) (specimen number MMUWr IV7929). The Kzw band is overgrown by kristiansenite (Kse) and silesiaite (all other zones that are not labelled). White patches are inclusions of cassiterite and fersmite. Abbreviations of mineral names according to Warr (2021).

Table 1. Chemical data for kozłowskiite (in wt.%).

Constituent	Mean	Range	S.D.	Reference material
SiO ₂	39.46	39.15–39.72	0.21	diopside
ZrO ₂	0.35	0.21–0.48	0.10	zircon
SnO ₂	31.13	30.48–31.38	0.37	cassiterite
Al ₂ O ₃	0.35	0.28–0.41	0.05	orthoclase
Sc ₂ O ₃	2.65	2.33–3.08	0.29	Sc
Fe ₂ O ₃ *	2.26	1.61–3.43	0.70	hematite
FeO *	2.52	2.25–2.61	0.15	
MnO	0.71	0.65–0.76	0.04	rhodonite
CaO	18.42	18.36–18.49	0.05	diopside
H ₂ O _(calc.)	1.48	1.47–1.49		
Total	99.33			

S.D. – standard deviation; * total Fe measured as Fe₂O₃ was equal to 5.06 wt.% (range: 4.51–5.93 wt.%; S.D.: 0.53 wt.%).

Composition of kozłowskiite

Quantitative chemical analyses of kozłowskiite were performed at the Inter-Institute Analytical Complex for Minerals and Synthetic Substances at the University of Warsaw, Poland, using a Cameca SX 100 electron microprobe (EMPA) operating in wavelength-

dispersive X-ray spectrometry mode (WDS) with an accelerating voltage of 15 kV, a beam current of 20 nA, peak count-time of 20 s, background time of 10 s and a beam diameter of 2 µm (number of analyses $N = 5$). Reference materials, analytical lines, diffracting crystals and mean detection limits (element wt.%) were as follows: albite – Na (TAP, $K\alpha$, 0.02); diopside – Mg (TAP, $K\alpha$, 0.02), Si (TAP, $K\alpha$, 0.03) and Ca (PET, $K\alpha$, 0.04); orthoclase – Al (TAP, $K\alpha$, 0.03); rutile – Ti (PET, $K\alpha$, 0.09); rhodonite – Mn (LIF, $K\alpha$, 0.12); hematite – Fe (LIF, $K\alpha$, 0.12); LiNbO₃ – Nb (PET, $L\alpha$, 0.10); LiTaO₃ – Ta (TAP, $M\alpha$, 0.10); cassiterite – Sn (LPET, $L\alpha$, 0.07); zircon – Zr (LPET, $L\alpha$, 0.07); and pure Sc – Sc (LPET, $K\alpha$, 0.02). The contents of Na, Mg, Ti, Nb and Ta were below the detection limits. The raw data were reduced with the PAP routine of Pouchou and Pichoir (1991). The presence of H₂O was not analysed for due to the scarcity of the type material. The hydrogen atom positions were found from the Fourier-difference map during the X-ray structure analysis, and their parameters were refined using the riding model (Sheldrick, 2015b). The hydrogen atoms participate in the formation of hydrogen bonds, indicating the presence of 2 hydroxyls in the formula. Atomic contents in the empirical formula of kozłowskiite were normalised in relation to 26O + 2(OH) with a $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$

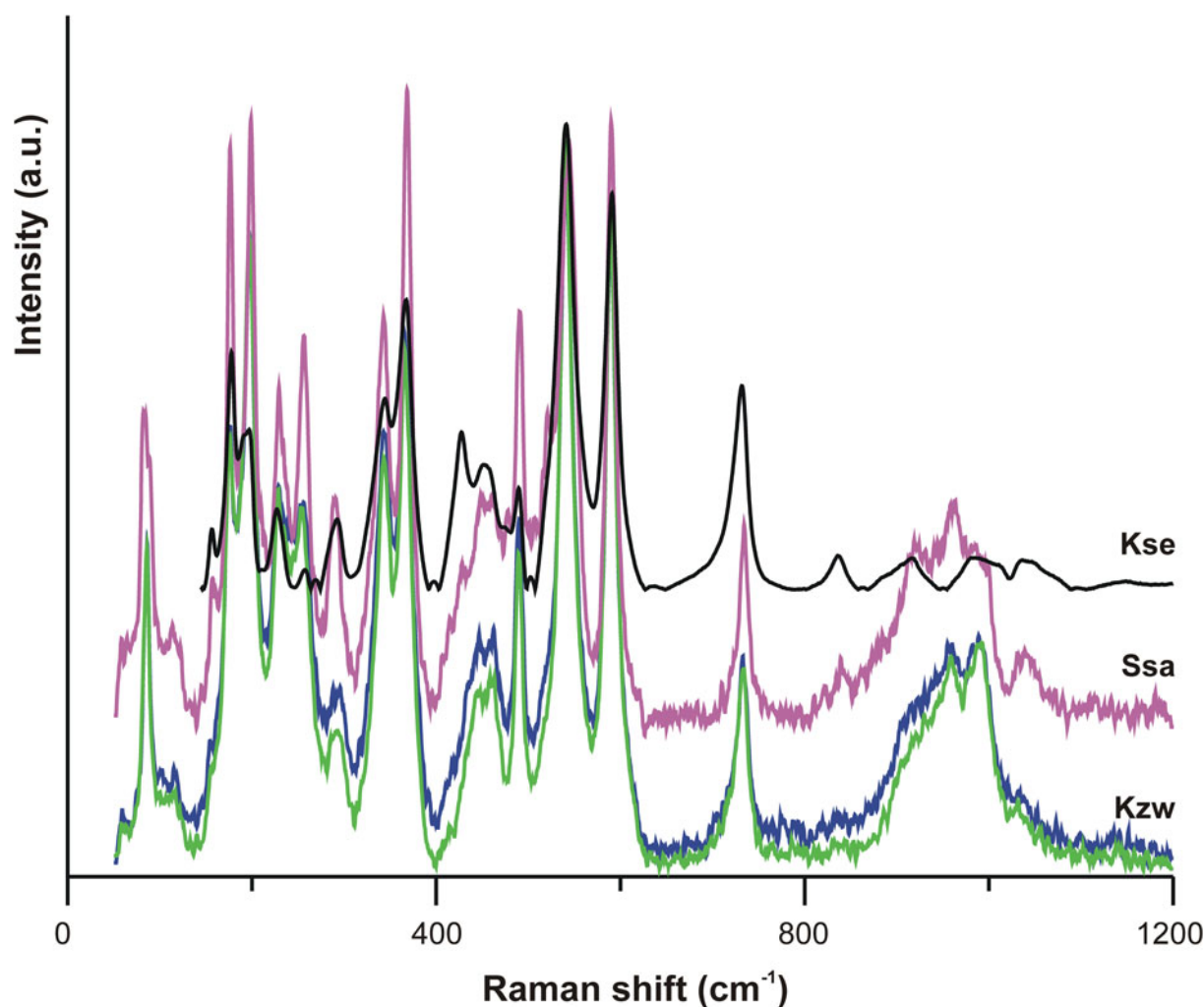


Fig. 2. Raman spectra of kozłowskiite (Kzw; green and blue) compared to the spectrum of silesiaite (Ssa, magenta) and kristiansenite (Kse; black; RRUFF database R090022, <https://ruff.info/>). Kozłowskiite and silesiaite originate from the Szklarska Poręba Huta quarry, kristiansenite from the Heftetjern pegmatite, Tørdal, Telemark, Norway.

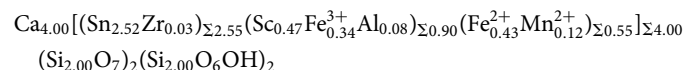
Table 2. Data and experimental details for the selected crystal.

Crystal data	
Ideal formula	$\text{Ca}_4(\text{Fe}_{1.60}\text{Sn}_{2.40})(\text{Si}_2\text{O}_7)_2(\text{Si}_2\text{O}_6\text{OH})_2$
Refined formula	$\text{Ca}_4(\text{Fe}_{1.68}\text{Sn}_{2.32})(\text{Si}_2\text{O}_7)_2(\text{Si}_2\text{O}_6\text{OH})_2$
Crystal dimensions (mm)	$0.036 \times 0.021 \times 0.003$
Crystal system, space group	Triclinic (pseudomonoclinic), C1
Temperature (K)	293.29(10)
a , b , c (Å)	10.0183(2), 8.3861(1), 13.3395(2)
α , β , γ (°)	89.956(1), 109.039(2), 89.979(1)
V (Å ³)	1059.40(3)
Z	2
Calculated density (g cm ⁻³)	3.775
μ (mm ⁻¹)	5.397
Data collection	
Crystal description	Plate, pale brownish
Instrument	XtalLAB Synergy-S (Rigaku Oxford Diffraction) four circle diffractometer with a mirror monochromator
Radiation type, wavelength (Å)	MoK α , 0.71073
Number of frames	2818 frames in 22 runs
θ range (°)	3.244 to 29.999
Absorption correction	Multi-scan (ABSPACK; Oxford Diffraction, 2006) <i>CrysAlisPro</i> 1.171.40.67a (Rigaku Oxford Diffraction, 2019). Empirical absorption correction using spherical harmonics. Frame scaling
$T_{\min}$, $T_{\max}$	0.90175, 1.00000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15772, 5705, 4887
R_{int}	0.0274
Data completeness (%)	98.5
Indices range of h , k , l	$-14 \leq h \leq 14$, $-11 \leq k \leq 11$, $-18 \leq l \leq 18$
Refinement	
Refinement method	Full-matrix least-squares on F^2
Number of reflections, parameters, restraints	5705, 276, 5
R_1 [$I > 2\sigma(I)$], $R_1(\text{all})$	0.0212, 0.0274
wR_2 [$I > 2\sigma(I)$], $wR_2(\text{all})$	0.0359, 0.0369
GoF	0.935
No. of refined parameters	276
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e ⁻ Å ⁻³)	0.479, -0.482

$R_{\text{int}} = \sum |F_o^2 - F_o^2(\text{mean})| / \sum |F_o^2|$; $\text{GoF} = S = \{ \sum [w(F_o^2 - F_c^2)^2] / (n - p + r) \}^{1/2}$; $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$, where a is 0.0015, b is 0.0000 and P is $[2F_c^2 + F_o^2] / 3$

ratio leading to 16 cations pfu. Compositional data on holotype material are given in Table 1.

The empirical formula of kozłowskiite presented in the form of valence groups of octahedral cations is



The formula clearly indicates that a surplus of tetravalent octahedral cations above 2 apfu, which is typical for the kristiansenite structure, is connected with an equal amount of divalent cations, suggesting the substitution $2\text{M}^{3+} = \text{M}^{2+} + \text{M}^{4+}$ in accord with the valency-imposed double site-occupancy (Hatert and Burke, 2008). The simplified formula of kozłowskiite is $\text{Ca}_4[(\text{Sc}, \text{Fe}^{3+})_{2-2x}\text{Fe}_x^{2+}\text{Sn}_{2+x}]_{\Sigma 4}(\text{Si}_2\text{O}_7)_2(\text{Si}_2\text{O}_6\text{OH})_2$; $x > 0.5$, and the ideal formula is $\text{Ca}_4(\text{Fe}^{2+}\text{Sn}_3)(\text{Si}_2\text{O}_7)_2(\text{Si}_2\text{O}_6\text{OH})_2$, which requires (in wt.%) CaO 17.99, FeO 5.76, SnO₂ 36.26, SiO₂ 38.55 and H₂O 1.44, Total 100.

Raman spectroscopy

Raman spectra of kozłowskiite were collected in back-scattered geometry with a Horiba Labram HR spectrometer integrated with an Olympus BX 41 confocal microscope. The system was calibrated using the Rayleigh line. The spectra were recorded in the range of 50–4000 cm⁻¹ using the 532 nm line of a solid-state Nd-YAG laser (10 mW), and 1800 grating on a randomly orientated section of the type crystal mounted in epoxy resin that was

used previously for microprobe analysis and later partly extracted for X-ray diffraction structural studies. Prior to the Raman measurements, the carbon coating of the disc was removed. The Raman measurements were carried out by an accumulation of two scans, each with an acquisition time of 600 s at the microscope magnification $\times 100$; the minimum lateral and depth resolution ≈ 1 μm , and an estimated analytical spot size of ~ 5 μm .

The spectrum of kozłowskiite (Fig. 2) is close to those of kristiansenite and silesiaite, which confirms that the three species (kristiansenite, silesiaite and kozłowskiite) share a common structure. No indication of OH groups was observed in the spectrum, which is similar to silesiaite and kristiansenite. The bands at Raman shifts of 1036, 989, 961 and 935 (broader) cm⁻¹ correspond to asymmetric Si–O stretch, 838 and 733 (medium) cm⁻¹ to symmetric Si–O stretch, 590 (strong), 542 (strong), 515, 491 (strong), 467 (broader), 445, 426, 367 (strong) and 344 (strong) to ν_4 Si–O modes, and 291, 257 (medium), 242, 228 (medium), 215, 198 (strong), 177 (strong), 160, 117, 94 and 86 (medium) cm⁻¹ to Si–O bending modes.

Powder X-ray diffraction data

Powder X-ray diffraction data could not be collected due to the scarcity of material. Therefore, they were only calculated from the refined single-crystal structure using the program *Diamond* Version 3.2k (Putz and Brandenburg, 2014). The seven strongest reflections are [d in Å (I) hkl]: 5.190 (73.2) 111, $\bar{1}\bar{1}1$; 4.569 (30.0) $\bar{2}02$; 3.153 (64.7) 004; 3.094 (28.1) $\bar{3}11$, $\bar{3}\bar{1}1$; 3.089 (100)

Table 3. Atomic coordinates, occupancy, equivalent and anisotropic displacement parameters ($\text{\AA}^2$) for non-hydrogen atoms for kozłowskiite.

Site	Atom	Occupancy	x/a	y/b	z/c	$U_{\text{iso}}^*/U_{\text{eq}}$	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ca1	Ca	1	0.3994(3)	0.1471(3)	0.8821(2)	0.01573(16)	0.0102(3)	0.0084(2)	0.0245(4)	0.0000(2)	0.0000(3)	-0.00015(19)
Ca2	Ca	1	0.5998(3)	0.1457(3)	0.6179(2)	0.01653(17)	0.0091(3)	0.0084(2)	0.0270(4)	0.0000(2)	-0.0011(3)	0.00023(19)
Ca3	Ca	1	0.6011(3)	0.8492(3)	0.1148(2)	0.01573(16)	0.0102(3)	0.0084(2)	0.0245(4)	0.0000(2)	0.0000(3)	-0.00015(19)
Ca4	Ca	1	0.4002(3)	0.8479(3)	0.3911(2)	0.01653(17)	0.0091(3)	0.0084(2)	0.0270(4)	0.0000(2)	-0.0011(3)	0.00023(19)
M1	Sn,Fe	Sn _{0.276(4)} Fe _{0.724(4)}	0.14509(13)	0.23375(14)	0.64134(10)	0.00596(9)	0.00652(14)	0.00662(13)	0.00429(14)	-0.00056(8)	0.00115(10)	0.00193(8)
M2	Sn,Fe	Sn _{0.619(4)} Fe _{0.381(4)}	0.85793(8)	0.23301(8)	0.86119(6)	0.00539(7)	0.00565(12)	0.00593(10)	0.00435(12)	0.00063(7)	0.00128(8)	-0.00119(7)
M3	Sn,Fe	Sn _{0.672(5)} Fe _{0.328(5)}	0.85806(9)	0.76154(10)	0.36185(7)	0.00596(9)	0.00652(14)	0.00662(13)	0.00429(14)	-0.00056(8)	0.00115(10)	0.00193(8)
M4	Sn,Fe	Sn _{0.755(4)} Fe _{0.245(4)}	0.14297(7)	0.76342(7)	0.14072(6)	0.00539(7)	0.00565(12)	0.00593(10)	0.00435(12)	0.00063(7)	0.00128(8)	-0.00119(7)
Si11	Si	1	0.1671(3)	0.4201(3)	0.8684(2)	0.00606(15)	0.0053(4)	0.0060(3)	0.0071(4)	-0.0005(2)	0.0024(3)	-0.0005(2)
Si12	Si	1	0.3740(3)	0.5300(4)	1.0719(2)	0.00673(15)	0.0061(4)	0.0075(3)	0.0066(4)	0.0002(3)	0.0022(3)	-0.0005(2)
O11	O	1	0.1886(10)	0.2755(10)	0.7968(8)	0.0090(4)	0.0098(10)	0.0089(8)	0.0090(10)	-0.0008(7)	0.0038(8)	0.0003(6)
O12	O	1	0.1743(9)	0.5945(9)	0.8182(6)	0.0100(4)	0.0110(10)	0.0082(8)	0.0102(10)	0.0013(7)	0.0025(8)	-0.0014(7)
O13	O	1	0.0237(9)	0.4024(10)	0.9011(7)	0.0091(4)	0.0061(10)	0.0092(8)	0.0129(10)	-0.0011(7)	0.0043(8)	-0.0008(6)
O14	O	1	0.3028(8)	0.4004(9)	0.9789(6)	0.0099(4)	0.0092(10)	0.0084(8)	0.0101(10)	0.0000(7)	0.0002(8)	-0.0010(6)
O15	O	1	0.2556(10)	0.5679(9)	1.1282(7)	0.0101(4)	0.0098(10)	0.0089(8)	0.0141(10)	0.0020(7)	0.0071(8)	0.0017(7)
O16	O	1	0.4130(8)	0.6903(8)	1.0198(6)	0.0090(4)	0.0094(10)	0.0091(8)	0.0087(10)	0.0000(7)	0.0033(8)	-0.0020(7)
O17	O	1	0.5178(9)	0.4510(9)	1.1538(6)	0.0113(4)	0.0105(11)	0.0140(9)	0.0085(10)	0.0004(7)	0.0017(8)	0.0023(7)
H17	H	1	0.499(6)	0.426(6)	1.211(3)	0.014*						
Si21	Si	1	0.8346(3)	0.4224(3)	0.6345(2)	0.00594(15)	0.0053(4)	0.0061(3)	0.0067(4)	0.0005(2)	0.0024(3)	0.0003(2)
Si22	Si	1	0.6280(3)	0.5301(4)	0.4314(2)	0.00762(15)	0.0070(4)	0.0084(3)	0.0074(4)	0.0001(3)	0.0025(3)	0.0014(2)
O21	O	1	0.8282(9)	0.5944(9)	0.6858(6)	0.0110(4)	0.0124(10)	0.0091(8)	0.0106(10)	-0.0006(7)	0.0025(8)	0.0003(7)
O22	O	1	0.8145(10)	0.2758(9)	0.7069(7)	0.0091(4)	0.0101(10)	0.0100(8)	0.0065(9)	0.0013(7)	0.0019(8)	-0.0010(7)
O23	O	1	0.9755(9)	0.4014(10)	0.6005(7)	0.0105(4)	0.0089(10)	0.0109(8)	0.0124(10)	0.0014(7)	0.0045(8)	0.0011(7)
O24	O	1	0.6984(8)	0.3981(9)	0.5267(6)	0.0099(4)	0.0089(10)	0.0088(8)	0.0088(8)	0.0003(7)	0.0003(8)	0.0011(6)
O25	O	1	0.7432(10)	0.5632(10)	0.3744(8)	0.0111(4)	0.0112(11)	0.0105(8)	0.0132(10)	-0.0004(7)	0.0062(9)	0.0005(7)
O26	O	1	0.5874(9)	0.6868(9)	0.4838(6)	0.0102(4)	0.0108(10)	0.0098(8)	0.0100(10)	-0.0007(7)	0.0035(8)	0.0015(7)
O27	O	1	0.4857(9)	0.4541(9)	0.3474(7)	0.0125(4)	0.0114(11)	0.0165(9)	0.0076(10)	0.0004(8)	0.0003(9)	-0.0021(7)
Si31	Si	1	0.8343(3)	0.5748(3)	0.1340(2)	0.00606(15)	0.0053(4)	0.0060(3)	0.0071(4)	-0.0005(2)	0.0024(3)	-0.0005(2)
Si32	Si	1	0.6283(3)	0.4659(4)	-0.0701(2)	0.00673(15)	0.0061(4)	0.0075(3)	0.0066(4)	0.0002(3)	0.0022(3)	-0.0005(2)
O31	O	1	0.8127(10)	0.7196(9)	0.2056(8)	0.0090(4)	0.0098(10)	0.0089(8)	0.0090(10)	-0.0008(7)	0.0038(8)	0.0003(6)
O32	O	1	0.8260(9)	0.3982(9)	0.1842(6)	0.0100(4)	0.0110(10)	0.0082(8)	0.0102(10)	0.0013(7)	0.0025(8)	-0.0014(7)
O33	O	1	0.9766(9)	0.5932(10)	0.1027(7)	0.0091(4)	0.0061(10)	0.0092(8)	0.0129(10)	-0.0011(7)	0.0043(8)	-0.0008(6)
O34	O	1	0.6990(8)	0.5970(8)	0.0252(6)	0.0099(4)	0.0092(10)	0.0084(8)	0.0101(10)	0.0000(7)	0.0002(8)	-0.0010(6)
O35	O	1	0.7449(10)	0.4325(9)	-0.1250(7)	0.0101(4)	0.0098(10)	0.0089(8)	0.0141(10)	0.0020(7)	0.0071(8)	0.0017(7)
O36	O	1	0.5882(8)	0.3070(8)	-0.0164(6)	0.0090(4)	0.0094(10)	0.0091(8)	0.0087(10)	0.0000(7)	0.0033(8)	-0.0020(7)
O37	O	1	0.4870(9)	0.5419(9)	-0.1521(6)	0.0113(4)	0.0105(11)	0.0140(9)	0.0085(10)	0.0004(7)	0.0017(8)	0.0023(7)
Si41	Si	1	0.1662(3)	0.5747(3)	0.3674(2)	0.00594(15)	0.0053(4)	0.0061(3)	0.0067(4)	0.0005(2)	0.0024(3)	0.0003(2)
Si42	Si	1	0.3720(3)	0.4648(4)	0.5715(2)	0.00762(15)	0.0070(4)	0.0084(3)	0.0074(4)	0.0001(3)	0.0025(3)	0.0014(2)
O41	O	1	0.1734(9)	0.3986(9)	0.3164(6)	0.0110(4)	0.0124(10)	0.0091(8)	0.0106(10)	-0.0006(7)	0.0025(8)	0.0003(7)
O42	O	1	0.1902(9)	0.7200(9)	0.2965(7)	0.0091(4)	0.0101(10)	0.0100(8)	0.0065(9)	0.0013(7)	0.0019(8)	-0.0010(7)
O43	O	1	0.0241(9)	0.5911(10)	0.3995(7)	0.0105(4)	0.0089(10)	0.0109(8)	0.0124(10)	0.0014(7)	0.0045(8)	0.0011(7)
O44	O	1	0.3026(8)	0.5944(9)	0.4775(6)	0.0099(4)	0.0089(10)	0.0088(8)	0.0088(8)	0.0003(7)	0.0003(8)	0.0011(6)
O45	O	1	0.2539(10)	0.4314(10)	0.6269(8)	0.0111(4)	0.0112(11)	0.0105(8)	0.0132(10)	-0.0004(7)	0.0062(9)	0.0005(7)
O46	O	1	0.4119(9)	0.3048(9)	0.5195(7)	0.0102(4)	0.0108(10)	0.0098(8)	0.0100(10)	-0.0007(7)	0.0035(8)	0.0015(7)
O47	O	1	0.5147(9)	0.5441(9)	0.6542(7)	0.0125(4)	0.0114(11)	0.0165(9)	0.0076(10)	0.0004(8)	0.0003(9)	-0.0021(7)
H47	H	1	0.501(7)	0.544(6)	0.715(3)	0.015*						

$\bar{2}22$, $\bar{2}22$; 2.595 (27.2) $\bar{2}22$, $\bar{2}22$; and 2.141 (30.6) $\bar{3}31$, $\bar{3}31$. Full calculated powder X-ray diffraction data has been deposited with the Principal Editors of *Mineralogical Magazine* and is available as Supplementary material (Table S1).

Single-crystal X-ray diffraction and structure determination

Sample preparation, data collection and refinement

The single crystal of kozłowskiite was cut using a Quanta 3D 200i (Thermo Fisher Scientific) scanning electron microscope equipped with a Ga⁺ ion gun, Pt precursor gas injection systems (GIS) and Omniprobe micromanipulator for *in situ* lift-out. An ion beam accelerating voltage of 30 kV and ion currents in the range of 60 nA to 1 nA were applied. The sample was then transferred via a micromanipulator to standard TEM copper half-ring grids. A FIB deposition process (from the Pt precursor) was used to attach the manipulator probe to the sample and the foil to the

grid, and then the crystal was transferred to a suitable microloop and placed on the goniometer base.

Single-crystal X-ray diffraction measurements were made at the Faculty of Chemistry, Jagiellonian University in Kraków on the kozłowskiite crystal of volume 0.036 mm × 0.021 mm × 0.003 mm. X-ray diffraction data for a single crystal were collected using XtalLAB Synergy-S (Rigaku Oxford Diffraction) four circle diffractometer with a mirror monochromator and a microfocus MoK α or CuK α radiation source. The data were collected at the controlled temperature of 293.3(1) K using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) to a maximum θ value of 33.515°. The obtained data sets were processed with *CrysAlisPro* 1.171.40.67a software (Rigaku Oxford Diffraction, 2019).

The phase problem was solved by direct methods with *SHELXT-2014/5* (Sheldrick, 2015a). Parameters of the obtained model were refined using *SHELXL-2018/3* (Sheldrick, 2015b). The figures presenting the kozłowskiite structure were prepared with *ORTEP-3* for Windows version 2020.1 software (Farrugia,

Table 4. Selected interatomic distances (Å) in kozłowskiite.

Ca1–O11	2.312(10)	Ca2–O46	2.330(8)	Si11–O11	1.601(9)	Si12–O16	1.619(8)
Ca1–O36	2.355(8)	Ca2–O45	2.346(9)	Si11–O12	1.620(8)	Si12–O15	1.629(9)
Ca1–O35	2.356(9)	Ca2–O22	2.358(10)	Si11–O13	1.639(9)	Si12–O14	1.629(8)
Ca1–O13	2.370(9)	Ca2–O23	2.370(9)	Si11–O14	1.655(8)	Si12–O17	1.637(9)
Ca1–O21	2.518(9)	Ca2–O12	2.565(9)	<Si11–O>	1.629	<Si12–O>	1.629
Ca1–O14	2.818(8)	Ca2–O24	2.778(7)				
Ca1–O33	2.824(10)	Ca2–O43	2.798(9)	Si21–O21	1.607(9)	Si22–O25	1.599(9)
< ^{VII} Ca1–O>	2.508	< ^{VII} Ca2–O>	2.506	Si21–O22	1.616(9)	Si22–O26	1.602(8)
Ca1–O12	3.167(9)	Ca2–O21	3.165(9)	Si21–O23	1.628(9)	Si22–O27	1.629(9)
Ca1–O34	3.219(8)	Ca2–O44	3.210(8)	Si21–O24	1.641(8)	Si22–O24	1.659(7)
Ca1–O37	3.494(9)	Ca2–O47	3.520(9)	<Si21–O>	1.623	<Si22–O>	1.622
< ^X Ca1–O>	2.743	< ^X Ca2–O>	2.744				
				Si31–O31	1.603(9)	Si32–O35	1.593(9)
Ca3–O16	2.319(8)	Ca4–O26	2.314(8)	Si31–O33	1.618(9)	Si32–O37	1.611(8)
Ca3–O31	2.338(10)	Ca4–O42	2.332(9)	Si31–O32	1.638(8)	Si32–O36	1.624(8)
Ca3–O15	2.369(9)	Ca4–O25	2.357(9)	Si31–O34	1.642(8)	Si32–O34	1.655(8)
Ca3–O33	2.374(9)	Ca4–O43	2.372(9)	<Si31–O>	1.625	<Si32–O>	1.621
Ca3–O41	2.581(9)	Ca4–O32	2.647(9)				
Ca3–O13	2.735(10)	Ca4–O23	2.683(9)	Si41–O42	1.607(8)	Si42–O45	1.611(9)
Ca3–O34	2.762(8)	Ca4–O44	2.745(7)	Si41–O43	1.621(9)	Si42–O46	1.619(8)
< ^{VII} Ca3–O>	2.497	< ^{VII} Ca4–O>	2.493	Si41–O41	1.637(9)	Si42–O44	1.632(7)
Ca3–O14	3.152(8)	Ca4–O24	3.150(8)	Si41–O44	1.657(8)	Si42–O47	1.635(9)
Ca3–O32	3.207(9)	Ca4–O41	3.231(9)	<Si41–O>	1.631	<Si42–O>	1.624
Ca3–O17	3.522(9)	Ca4–O27	3.508(9)				
< ^X Ca3–O>	2.736	< ^X Ca4–O>	2.734				
M1–O11	2.006(10)	M2–O22	1.992(9)	M3–O31	2.014(10)	M4–O42	2.009(9)
M1–O45	2.028(8)	M2–O16	2.036(8)	M3–O46	2.027(8)	M4–O36	2.019(8)
M1–O26	2.029(8)	M2–O35	2.061(8)	M3–O25	2.061(8)	M4–O15	2.028(8)
M1–O21	2.091(8)	M2–O12	2.092(8)	M3–O41	2.092(8)	M4–O17	2.054(8)
M1–O47	2.101(8)	M2–O37	2.103(8)	M3–O27	2.108(8)	M4–O32	2.070(8)
M1–O23	2.134(8)	M2–O13	2.118(8)	M3–O43	2.125(8)	M4–O33	2.127(8)
<M1–O>	2.065	<M2–O>	2.067	<M3–O>	2.071	<M4–O>	2.051

2012) and VESTA Version 3 Copyright 2006–2021 (Momma and Izumi, 2011). The programs were operated under the WinGX integrated system, version 2020.1 (Farrugia, 2012).

Kozłowskiite, $\text{Ca}_4\text{Fe}^{2+}\text{Sn}_3(\text{Si}_2\text{O}_7)_2(\text{Si}_2\text{O}_6\text{OH})_2$ ($Z = 2$), is isostructural with kristiansenite, $\text{Ca}_2\text{ScSn}(\text{Si}_2\text{O}_7)(\text{Si}_2\text{O}_6\text{OH})$ and silesiaite, $\text{Ca}_2\text{Fe}^{3+}\text{Sn}(\text{Si}_2\text{O}_7)(\text{Si}_2\text{O}_6\text{OH})$ ($Z = 4$). The space group symmetry was assigned as C1 [$a = 10.0183(2)$, $b = 8.3861(1)$, $c = 13.3395(2)$ Å, $\alpha = 89.956(1)^\circ$, $\beta = 109.039(2)^\circ$, $\gamma = 89.979(1)^\circ$ and $V = 1059.40(3)$ Å³ from 11,299 reflections measured in the θ range 3.216–33.797° at 293.3(1) K using MoK α radiation], however, similarly to kristiansenite (Ferraris *et al.*, 2001), the structure is metrically monoclinic (Laue group 2/m) with α and γ angles equal to 90° [$a = 10.0170(3)$, $b = 8.3860(2)$, $c = 13.3421(4)$ Å, $\beta = 109.050(3)^\circ$ and $V = 1059.40(5)$ Å³] from 11,137 reflections measured in the θ range 3.216–33.797°.

The preliminary crystal structure was solved in the monoclinic space group C2/c and then transformed to the unconventional space group C1 according to the structure of kristiansenite from Ferraris *et al.* (2001). The refinement of 276 structural parameters in C1 (positional and anisotropic displacement parameters for non-hydrogen atoms and positional parameters of hydrogen atoms) gave an R_1 index of 2.12% ($R_1[\text{all}] = 2.74\%$), $wR_2[\text{all}] = 3.69\%$, and

goodness of fit parameter $S = 0.935$. In general, the structure of kozłowskiite differs from kristiansenite (Ferraris *et al.*, 2001) by the choice of unit cell origin and the qualitative and quantitative chemical composition, however, it is difficult to compare their asymmetric units as in the paper by Ferraris *et al.* (2001) it has not been properly chosen (see Fig. S1 deposited with the Principal Editors of *Mineralogical Magazine* and available as Supplementary material).

Full details of the diffraction data measurement and structure solution are listed in Table 2. Refined atomic coordinates, equivalent and anisotropic displacement parameters, and occupancy for structural sites are given in Table 3, selected bond lengths are collected in Table 4 and assigned M -site populations are shown in Table 5. Bond valences calculated on the basis of the parameters given by Gagné and Hawthorne (2015) are shown in Table 6. Table 7 presents the geometrical parameters of hydrogen bonds and Table 8 the brief comparison of kozłowskiite with kristiansenite and silesiaite. The crystallographic information file has been deposited with the Principal Editor of *Mineralogical Magazine* and is available as Supplementary material (see below).

The kozłowskiite unit cell contains two formal units ($Z = 2$); each of them is composed of three types of cationic sites: 4 polyhedral Ca sites (Ca1 to Ca4), 4 octahedral M sites (M1 to M4), and 8 tetrahedral Si sites (Si11 to Si41 and Si12 to Si42) forming 4 disilicate groups (Si_2O_7) half of which is protonated ($\text{Si}_2\text{O}_6\text{OH}$). A projection of the kozłowskiite structure onto (010), with the disilicate groups and the other polyhedra of cations in different alternating (10 $\bar{1}$) planes is shown in Fig. 3. The M positions are occupied partially by Sn and Fe atoms; the M octahedra are isolated from each other and aligned in [101] rows. The hydrogen bonds (marked by dashed lines) connect [101] rows of disilicate groups. The asymmetric unit contents of kozłowskiite with the atom numbering scheme, and packing of the ions in the kozłowskiite structure viewed along [010] and [100] is presented in Fig. 4.

Site assignment

The Ca1–Ca4 and Si11–Si24 sites are occupied solely by Ca and Si, respectively. The occupancy of Ca sites exclusively by Ca is corroborated by the refined <Ca–O> distances (Table 4) and calculated bond-valence sums (Table 6). The 7-fold-coordinated Ca polyhedra are highly distorted with Ca–O distances ranging from almost 2.312 Å up to 2.824 Å. The <^{VII}Ca1–O> to <^{VII}Ca4–O> averaged distances, 2.508, 2.506, 2.497 and 2.493 Å, are comparable with the appropriate distances in type kristiansenite (2.527, 2.513, 2.478 and 2.480 Å) (Ferraris *et al.*, 2001) and kristiansenite from Szklarska Poręba (2.498, 2.487, 2.504 and 2.501 Å) (Evans *et al.*, 2018). They are distinctly longer than the sum of Ca^{2+} and O^{2-} radii, 2.42–2.44 Å, evaluated using radii of seven-fold-coordinated Ca^{2+} and (3 or 4)-coordinated O^{2-} by Shannon (1976). The decreased values of BVS for ^{VII}Ca1–O to

Table 5. Refined M site-scattering values and assigned M -site populations for kozłowskiite.

Site	Refined site-scattering (epfu)	Refined <M–O> (Å)	Assigned site population (apfu)	Calculated site-scattering (epfu)	Calculated <M–O> (Å)
M1	32.6(1)	2.065	$\text{Sn}_{0.366}\text{Sc}_{0.247}\text{Fe}_{0.181}^{3+}\text{Fe}_{0.123}^{2+}\text{Al}_{0.044}\text{Mn}_{0.035}^{2+}\text{Zr}_{0.005}$	33.0	2.065
M2	40.9(1)	2.067	$\text{Sn}_{0.658}\text{Fe}_{0.136}^{2+}\text{Sc}_{0.087}\text{Fe}_{0.064}^{3+}\text{Mn}_{0.037}^{2+}\text{Al}_{0.015}\text{Zr}_{0.009}$	41.3	2.067
M3	42.1(1)	2.071	$\text{Sn}_{0.698}\text{Fe}_{0.159}^{2+}\text{Sc}_{0.046}\text{Mn}_{0.045}^{2+}\text{Fe}_{0.034}^{3+}\text{Zr}_{0.010}\text{Al}_{0.008}$	42.5	2.071
M4	44.1(1)	2.051	$\text{Sn}_{0.794}\text{Sc}_{0.090}\text{Fe}_{0.066}^{3+}\text{Fe}_{0.017}^{2+}\text{Al}_{0.016}\text{Zr}_{0.011}\text{Mn}_{0.005}$	44.5	2.051

Table 6. Bond-valence analysis for kozłowskiite (vu)*.

	Ca1	Ca2	Ca3	Ca4	M1	M2	M3	M4	Si11	Si12	Si21	Si22	Si31	Si32	Si41	Si42	Σ
O11	0.371				0.632				1.061								2.06
O12	0.046	0.200				0.531			1.010								1.79
O13	0.322		0.132			0.488			0.962								1.90
O14	0.108		0.048						0.923	0.987							2.07
O15			0.323					0.696		0.987							2.01
O16			0.365			0.639				1.013							2.02
O17			0.019					0.636		0.967							1.62
O21	0.224	0.046			0.491						1.045						1.81
O22		0.332				0.740					1.021						2.09
O23		0.322		0.150	0.433						0.990						1.90
O24		0.119		0.048							0.957	0.914					2.04
O25				0.333			0.593					1.066					1.99
O26				0.370	0.590							1.058					2.02
O27				0.020			0.507					0.987					1.51
O31			0.349				0.695						1.055				2.10
O32			0.042	0.164				0.602					0.965				1.77
O33	0.106		0.319					0.495					1.016				1.94
O34	0.040		0.124										0.955	0.923			2.04
O35	0.334					0.589								1.083			2.01
O36	0.334							0.718						1.000			2.05
O37	0.021					0.512								1.034			1.57
O41			0.192	0.039			0.536								0.967		1.74
O42				0.354				0.744							1.045		2.14
O43		0.113		0.321			0.479								1.008		1.92
O44		0.041		0.129											0.919	0.980	2.07
O45		0.342			0.592											1.034	1.97
O46		0.356					0.665									1.013	2.03
O47		0.019			0.477											0.972	1.57
Σ	1.91	1.89	1.91	1.93	3.22	3.50	3.48	3.89	3.96	3.95	4.01	4.03	3.99	4.04	3.94	4.00	

* Bond valence sums were calculated using the equation $S = \exp[(R_0 - R)/B]$, where R_0 and B are bond-valence parameters derived by Gagné and Hawthorne (2015), and R is the refined bond length.

Table 7. Geometrical parameters of hydrogen bonds in kozłowskiite (Å, °).

D–H...A (acceptor position)	D–H	H...A	D...A	∠DHA
O17–H17...O27 (x,y,z+1)	0.87(1)	1.88(3)	2.705(11)	158(5)
O47–H47...O37 (x,y,z+1)	0.877(1)	1.82(2)	2.687(11)	176(6)

^{VII}Ca4–O (1.79 to 1.82 valence units [vu], Table 6) suggest that several longer interactions should contribute to the bond-valence sums around the central Ca cations, according to the valence-sum rule. Ferraris *et al.* (2001) indicated (7+2)-coordination as more appropriate for all Ca sites in the kristiansenite structure. We checked more distant oxygen atoms around the Ca1 to Ca4 sites and found for each of them a possible coordination of 7 +

Table 8. Comparison of selected structural parameters in kristiansenite, silesiaite and kozłowskiite.

	Kristiansenite Ca ₂ Sc ₂ Sn ₂ (Si ₂ O ₇)(Si ₂ O ₆ OH)	Silesiaite Ca ₂ Fe ₂ ³⁺ Sn ₂ (Si ₂ O ₇)(Si ₂ O ₆ OH)	Kozłowskiite Ca ₄ Fe ²⁺ Sn ₃ (Si ₂ O ₇) ₂ (Si ₂ O ₆ OH) ₂
Idealised formula			
Z	4	4	2
Crystal system	triclinic	triclinic	triclinic
Space group	C1	C1	C1
a (Å)	10.028(1)	10.0080 (2)	10.0183(2)
b (Å)	8.408(1)	8.3622(1)	8.3861(1)
c (Å)	13.339(2)	13.2994(2)	13.3395(2)
α (°)	90.01(1)	89.987(1)	89.956(1)
β (°)	109.10(1)	109.095(2)	109.039(2)
γ (°)	90.00(1)	89.978(1)	89.979(1)
V (Å ³)	1062.7(3)	1051.77(3)	1059.40(3)
Idealised site-occupancies			
Ca1–Ca4	Ca	Ca	Ca
M1	Sc + Fe ³⁺	Fe ³⁺ + Sc	Fe ³⁺ + Sn + Fe ²⁺
M2	Sc + Sn	Fe ³⁺ + Sn	Sn + Fe ²⁺ + Fe ³⁺
M3	Sn + Sc	Sn + Fe ³⁺	Sn + Fe ²⁺
M4	Sn	Sn	Sn
Si11, Si12, Si21, Si22, Si31, Si32, Si41 & Si42	Si	Si	Si
Reference	Ferraris <i>et al.</i> (2001)	Pieczka <i>et al.</i> (2017)	This study
	Raade <i>et al.</i> (2002)	Pieczka <i>et al.</i> (in. prep.)	

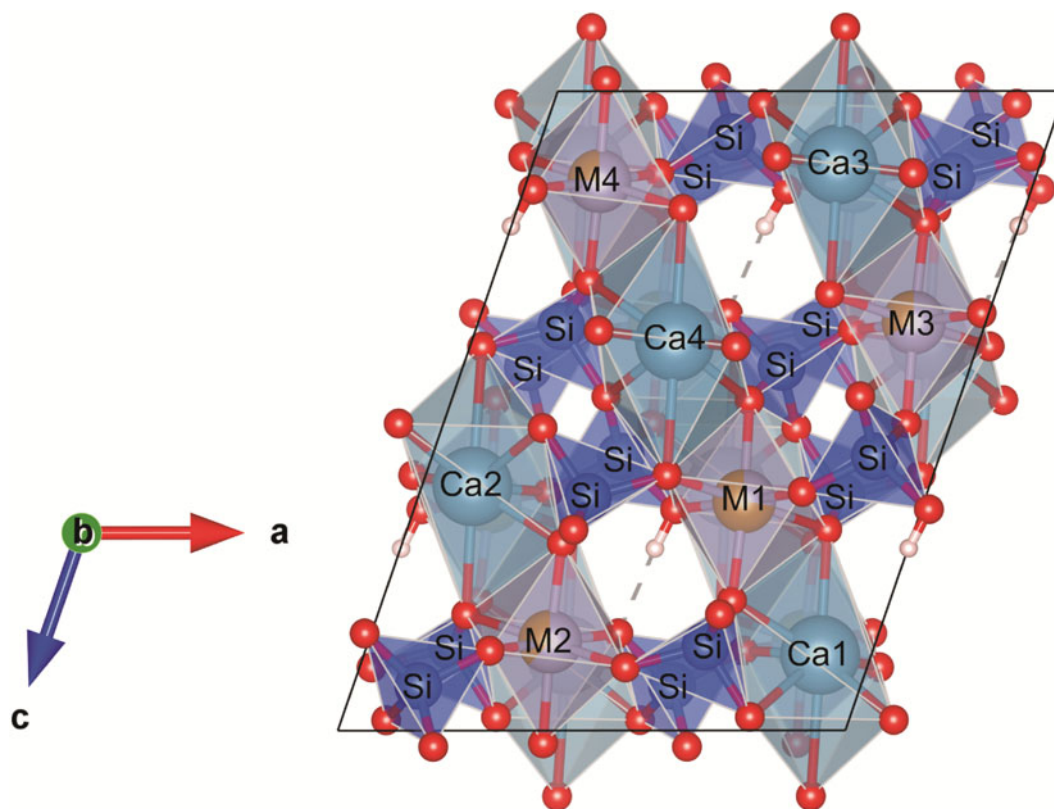


Fig. 3. Projection of the kozłowskiite structure onto (010) to be compared to figure 1 in Ferraris *et al.* (2001). The *M* positions are occupied partially by Sn (violet tint) and Fe (gold tint) atoms.

2 + 1, i.e. with two additional oxygen atoms in the distance of ~ 3.2 Å and one in the distance of ~ 3.5 Å (Table 4). Although these additional Ca–O interactions could increase the BVS of Ca^{2+} up to 1.89–1.93 vu, they are still too small for a 2+ ion (Table 6). The $\langle^{\text{X}}\text{Ca1–O}\rangle$ to $\langle^{\text{X}}\text{Ca4–O}\rangle$ averaged distances of 2.734–2.744 Å are also much longer than ~ 2.59 Å, i.e. the length calculated for $^{\text{X}}\text{Ca–O}$. It seems that the main reason for the above incompatibility is the presence of significantly long Ca–O bonds to oxygen atoms interacting through hydrogen bonds (O17–H17...O27 and O47–H47...O37). In consequence, the contribution of these $^{\text{X}}\text{Ca–O}$ bonds in the BVS around Ca^{2+} cations is almost negligible (bond valences of only 0.019–0.021 vu, Table 6), and small deficiencies in the calculated BVS appear.

The eight Si sites (site symmetry 1, C_1) are occupied entirely by Si in distorted tetrahedra of oxygen atoms. The $\langle\text{Si–O}\rangle$ mean bond lengths vary in a narrow range of 1.621–1.631 Å (Table 4), and they are comparable with the kristiansenite (1.619–1.636 Å) described by Ferraris *et al.* (2001) and from Szklarska Poręba (1.615–1.643 Å; Evans *et al.*, 2018). Of course, the bonds formed by Si to bridging oxygen atoms O14, O24, O34 and O44 in Si_2O_7 and $\text{Si}_2\text{O}_6\text{OH}$ anions have the largest lengths reaching 1.629–1.659 Å.

The four *M* sites have diverse site occupants. Although in these positions, tetravalent Sn and Zr are dominating, the trivalent Fe, Sc and Al as well as divalent Mn and Fe are also frequent. The occupancies of the sites were refined in the system Sn vs. Fe. The refined total *M*-site scattering, 159.73 e^- , agrees well with 161.28 e^- calculated from the EMPA formula for $Z = 2$. The structure refinement separates the electrons among the *M1–M4* sites in the following way: 32.6(1); 40.9(1); 42.1(1); and 44.1(1) e^-

(Table 5), resulting from the refined Sn–Fe occupancies presented in Table 3. The real *M*-site fillings are more complex due to the diversified sets of cations at the *M* sites. To approximate these occupancies, we took into account the refined *M1* to *M4* site-scattering values and $\langle(\text{M1–M4})\text{–O}\rangle$ distances. Occupancies of the *M1* to *M4* sites were estimated in the system of complex $\text{Sn+Zr} - \text{Fe}^{3+} + \text{Sc+Al} - \text{Fe}^{2+} + \text{Mn}^{2+}$ cations. The tetravalent Sn+Zr complex cation features 49.863 electrons and calculated radius of 0.690 Å; the trivalent $\text{Fe}^{3+} + \text{Sc+Al}$ cation has 22.175 electrons and radius of 0.687 Å, and the divalent $\text{Fe}^{2+} + \text{Mn}^{2+}$ cation has 25.778 electrons and a radius of 0.791 Å [calculated radii of complex cations based on Shannon (1976) data]. The refined *M1–M4* site-scattering should satisfy the equations:

$$\begin{aligned} &^{M1-4}(\text{Sn} + \text{Zr}) \cdot 49.863 + ^{M1-4}(\text{Fe}^{3+} + \text{Sc} + \text{Al}) \cdot 22.175 \\ &+ ^{M1-4}(1 - \text{Sn} - \text{Zr} - \text{Fe}^{3+} - \text{Sc} - \text{Al}) \cdot 25.778 = ^{M1-4}\text{s.s.} \end{aligned}$$

where $^{M1-4}(\text{Sn} + \text{Zr})$, $^{M1-4}(\text{Fe}^{3+} + \text{Sc+Al})$ and $^{M1-4}(1 - \text{Sn} - \text{Zr} - \text{Fe}^{3+} - \text{Sc} - \text{Al})$ are contributions of tetravalent, trivalent and divalent cations at the *M1* to *M4* sites, and $^{M1-4}\text{s.s.}$ are the refined site-scattering at the sites. Because abundance, $^{M1-4}(\text{Fe}^{3+} + \text{Sc} + \text{Al})$, can be expressed as $^{M1-4}n \cdot 0.896$, where n is a contribution (0 to 1 or 0 to 100%) of the complex trivalent cation in the occupancy of the selected *M* site, and 0.896 is the total abundance of trivalent cations at the *M1–M4* sites, it is possible to match ^{M1}n , ^{M2}n , ^{M3}n and ^{M4}n to minimise differences between the refined and estimated $\langle\text{M1–O}\rangle$, $\langle\text{M2–O}\rangle$, $\langle\text{M3–O}\rangle$ and $\langle\text{M4–O}\rangle$ mean bond lengths. The results of such estimation presented in Table 5 indicate that at the average difference in the refined and

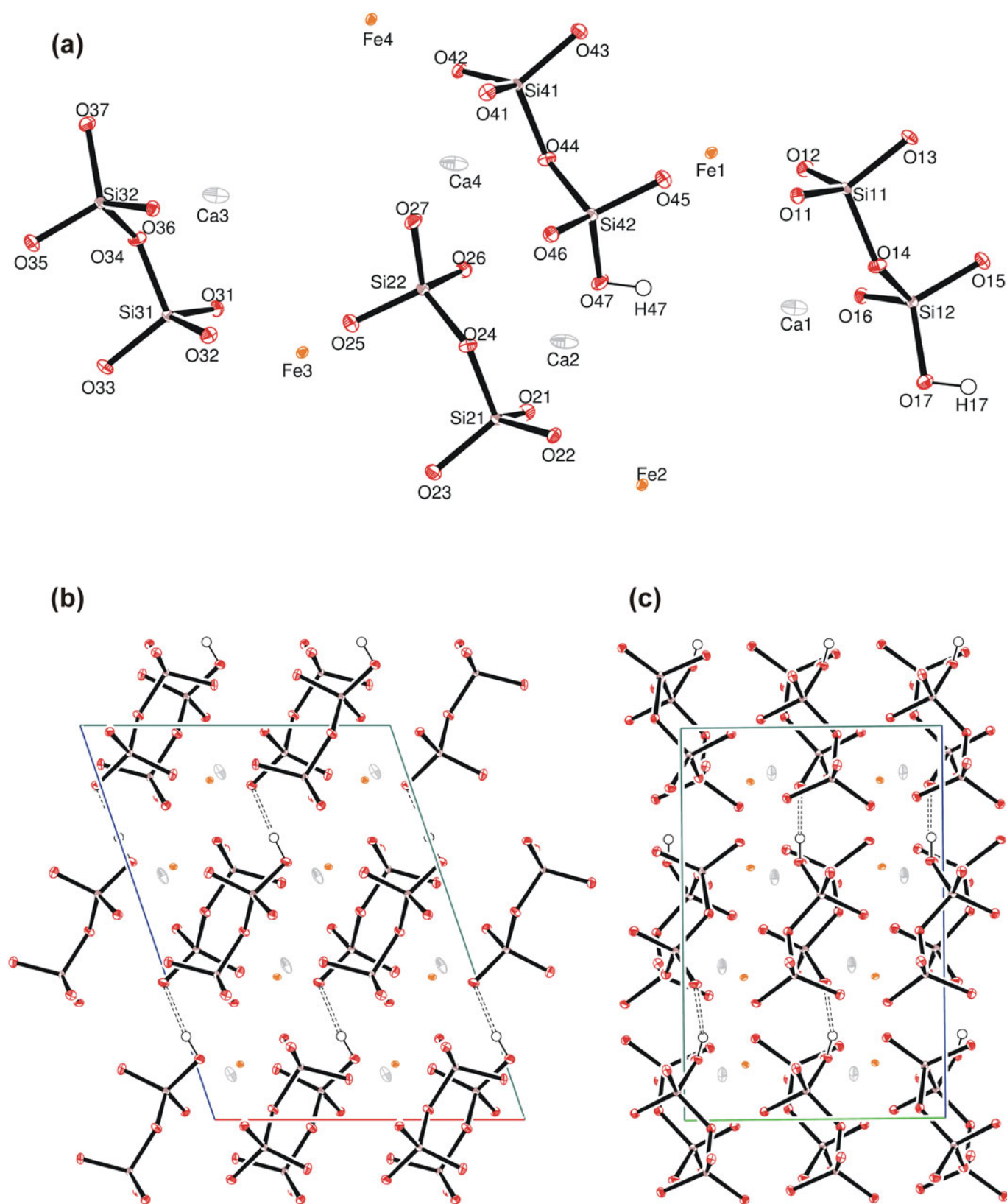


Fig. 4. (a) Asymmetric unit contents of kozłowskiite with the atom numbering scheme. Displacement ellipsoids are given at 50% probability level. (b) Packing of the ions in the structure of kozłowskiite viewed along [010] and (c) along [100]. Lattice directions **a**, **b**, and **c** are marked by red, green and blue lines, respectively.

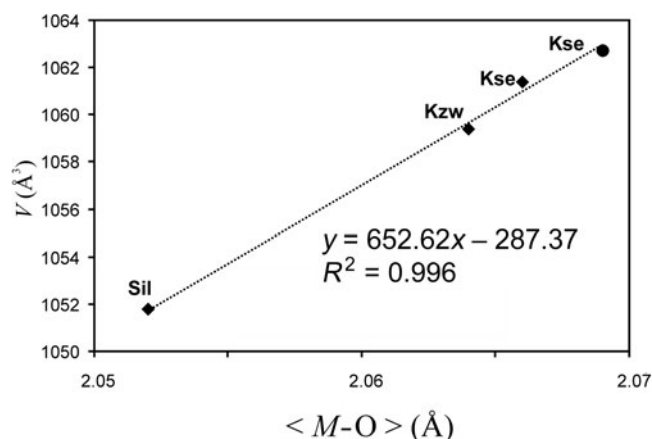


Fig. 5. Relationship between the refined unit-cell volume and averaged $\langle M-O \rangle$ distance in kristiansenite-group minerals. Symbols: full circle – kristiansenite from the Heftetjern pegmatite (Ferraris *et al.*, 2001); diamonds – kristiansenite, kozłowskiite and silesiaite from Szklarska Poręba (Evans *et al.*, 2018; this study). Abbreviations of the mineral names according to Warr, 2021).

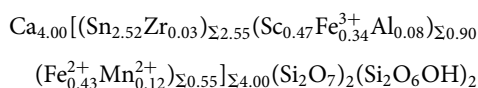
EMPA-estimated values of M^{1-4} s.s. at the level of $-0.4 e^-$ per site, the differences between the refined and estimated $\langle (M1-M4)-O \rangle$ distances are in the range of $\pm 0.001 \text{ \AA}$. The populations also indicate that three of four M sites: $M2$, $M3$ and $M4$, are formally dominated by tetravalent $\text{Sn}+\text{Zr}$ (mainly Sn), and the relative content of M^{4+} cations which may be related to the substitution $M^{4+} + M^{2+} \rightarrow 2 M^{3+}$ increases from 0.03 at the $M4$ site through 0.29 and 0.25 at $M3$ and $M2$ sites, respectively, up to 0.43 at the $M1$ site. The calculated values of BVS for $M1$, $M2$, $M3$ and $M4$ cations (3.22, 3.50, 3.48 and 3.89 vu; Table 6) are close to averaged valences of complex M cations at the sites (3.21, 3.50, 3.50 and 3.78) and corroborate the estimated populations.

The kozłowskiite unit cell ($Z=2$), similarly to kristiansenite and silesiaite, contains two hydrogen atoms shared among the O17–O27 and O47–O37 oxygen atoms. The geometric parameters of the hydrogen bonds are presented in Table 7.

Chemical formula

Difference-Fourier maps showed that H atoms are ordered at two sites (H17 and H47) and bonded to O17 and O47 oxygen atoms, respectively, therefore it can be expected that the maximum content of OH groups in minerals of the kristiansenite-type structure is 2 pfu for $Z=2$. Each of the OH groups is bonded to the Si12 and Si42 atoms and by hydrogen bond acceptors O27 and O37 to the Si22 and Si32 atoms, respectively, forming two protonated disilicate anions $(\text{Si}_2\text{O}_6\text{OH})^{5-}$.

The kozłowskiite empirical formula calculated in relation to $26\text{O} + 2(\text{OH})$ and 16 cations pfu, i.e. the same normalisation base as is suggested by the ideal compositions of kristiansenite and silesiaite, is:



In the formula, iron occurs in mixed-valence states indicating an oxidation ratio $\text{Fe}^{3+}/\text{Fe}_{\text{total}} = 0.45$. However, because direct determinations of FeO and Fe_2O_3 (e.g. using Mössbauer spectroscopy) as well as H_2O were not possible due to the scarcity of the

mineral, and the relationship among the constituents Fe^{2+} – Fe^{3+} and OH – O depends on the coupled substitution $\text{Fe}^{2+} + \text{OH}^- = \text{Fe}^{3+} + \text{O}^{2-}$, the question arises of whether a better solution with another $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$ ratio exists, which could lead to another ideal formula of the species. To investigate this possibility, we checked the effects of (1) oxidation of M^{2+} and (2) reduction of M^{3+} cations involved in the substitution.

Case (1) would be connected with partial deprotonation of OH groups participating in the hydrogen bonds due to the replacement of $M^{1,M4}\text{Fe}^{3+} + \text{O}_{17,\text{O}47} \rightarrow M^{1,M4}\text{Fe}^{2+} + \text{O}_{17,\text{O}47}\text{OH}$. As explained by Ferraris *et al.* (2001), the deprotonation of those OH groups would lead to two short distances between the donor (D) and acceptor (A) oxygens, e.g. in kozłowskiite, the O47(D)–O37(A) and the O17(D)–O27(A) distances are only 2.687 Å and 2.707 Å. Moreover, the formula of the oxidised mineral must take into account the distribution of M -type cations among the $M1$ – $M4$ sites (Table 5): $\text{Ca}_{4.00}[(\text{Sn}_{2.52}\text{Zr}_{0.03})_{\Sigma 2.55}(\text{Sc}_{0.47}\text{Fe}_{0.53}^{3+}\text{Al}_{0.08})_{\Sigma 1.09}(\text{Fe}_{0.24}^{2+}\text{Mn}_{0.12}^{2+})_{\Sigma 0.36}]_{\Sigma 4.00}(\text{Si}_2\text{O}_7)_{2.19}(\text{Si}_2\text{O}_6\text{OH})_{1.81}$, which would lead to the unbalanced idealised formula $\text{Ca}_4(\text{Sn}_3\text{Fe}^{3+})(\text{Si}_2\text{O}_7)_2(\text{Si}_2\text{O}_6\text{OH})_2$. These limitations definitely eliminate the possibility of the evolution of kozłowskiite towards solely Fe^{3+} -bearing species with a lowered OH content below 2 apfu. In contrast, each substitution related to at least partial reduction of M^{3+} -type cations would lead to an increase of OH content above the maximum amount of 2 OH groups pfu determined from difference-Fourier maps in structural studies.

A comparison of some structural and compositional parameters of kristiansenite (Ferraris *et al.*, 2001; Raade *et al.*, 2002), kozłowskiite (this study), and silesiaite (preliminary data are not yet published) presented in Table 8 provides additional arguments for the significant presence of M^{2+} -type cations (mainly Fe^{2+}) in kozłowskiite. Among the parameters the unit-cell volume draws special attention because at the same occupancy of the Ca and Si sites in the three minerals it can be expected that the difference in the volume is a result of varying M -site populations. In the minerals, the sites are populated by cations with radii ranging from 0.535 Å (Al^{3+}) up to 0.83 Å (Mn^{2+}), with Sc^{3+} (0.745 Å), Sn^{4+} (0.69 Å), Fe^{3+} (0.645 Å) and Fe^{2+} (0.78 Å) as the main occupants (ionic radii according to Shannon, 1976). The plot of the refined unit-cell volume versus averaged mean distance $\langle (M1-M4)-O \rangle$ (Fig. 5) for the kristiansenite from the Heftetjern pegmatite, Tørdal, Norway (Ferraris *et al.*, 2001), and kristiansenite, kozłowskiite and silesiaite from the Szklarska Poręba Huta pegmatite, Poland (Evans *et al.*, 2018; this study), i.e. for the four crystals representing the kristiansenite group of minerals, features a good linear relationship ascribed by the equation: $V = 652.6 \langle (M1-M4)-O \rangle - 287.4$ with $r^2 = 0.996$. This indicates that unit-cell volume increases proportionally to an averaged $\langle (M1-M4)-O \rangle$ distance, with the highest value for the Heftetjern kristiansenite showing $\langle (M1-M4)-O \rangle = 2.069 \text{ \AA}$. For the Szklarska Poręba Huta Fe^{3+} -enriched kristiansenite (2.066 Å), kozłowskiite (2.064 Å) and finally silesiaite (2.052 Å) the volume is slightly lower. The kozłowskiite $\langle (M1-M4)-O \rangle$ distance is comparable with the analogous distances in kristiansenite species (with M sites populated mainly by Sn and the relatively large Sc^{3+} cation) which confirms that the M sites in kozłowskiite must be populated, besides Sn, by a large octahedral cation. It can be only Fe^{2+} .

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