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New insights into the crystal chemistry of zemannite: Trigonal rather than hexagonal symmetry due to ordering within the host-guest structure

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Abstract

The microporous crystal structure of zemannite, $Mg(H_2O)_6[Zn^{2+}Fe^{3+}(TeO_3)_3]_2 \cdot nH_2O$, $n \le 3$, was re-investigated based on single-crystal X-ray diffraction data measured at 298 ± 0.5 K, 200 ± 1 K and 100 ± 3 K. So far, zemannite was described in space group $P6_3$ exhibiting a pronounced *pseudosymmetry* ($P6_3/m$). All refinements confirm the $[Zn^{2+}Fe^{3+}(TeO_3)_3]^{1-}$ framework topology with the extra-framework constituents (Mg atoms and H₂O molecules) being located within the channels along [001]. Measurements on a sample from the type locality revealed the unexpected occurrence of 00l reflections with l=2n+1, which clearly violate the 6_3 screw-axis symmetry. The minor but significant intensities of the low-order 00l reflections are assigned to the small differences in the scattering power between the Fe and Zn atoms; thus, the Zn and Fe cations are partly ordered between crystallographically distinct sites within the framework. In addition, the low symmetry allows a full order of the extra-framework atoms for the first time. A series of comparative refinement models were performed in the space groups $P6_3/m$, $P6_3$, $P\overline{6}$, and P3. A fully ordered arrangement of the extra-framework guest atoms confirms the earlier postulated theoretical structure model with a hexahydrated Mg^{2+} ion besides additional interstitial H_2O molecules. The final refinements in space group P3 yield $R1 \le 0.025$ for the entire data sets measured at the distinct temperatures ($2\theta_{max} = 101.4^\circ$, MoK α radiation). The polarity of the arrangement in the channels is restricted to individual domains of equal twin fractions related by a mirror plane parallel to (0001).

Keywords Zemannite · Single-crystal X-ray diffraction · Space-group symmetry P3 · Cation ordering · Extra-framework constituents

Introduction

The crystal structure of the mineral zemannite, Mg(H₂O)₆ $[Zn^{2+}Fe^{3+}(TeO_3)_3]_2 \cdot nH_2O$ ($n \le 3$, Z = 1), is the archetype of a family of microporous compounds. Their structural similarities are based on a porous honeycomb-shaped framework structure that is based on $X^{4+}O_3$ building units of tetravalent lone-pair cations ($X = Te^{4+}$, Se⁴⁺). It shows hexagonal symmetry in idealized basic metrics following an apparent $P6_3/m$ symmetry, with $P6_3$ suggested last as the most likely symmetry. The topologically zeolite-like structure exhibits a negatively charged framework with the one-dimensional open pores along the [001] axis accommodating a variable

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Herta S. Effenberger herta.silvia.effenberger@univie.ac.at number of extra-framework cations and H_2O molecules (cf. Eder et al. 2023a for an overview of various representatives).

Zemannite is named in honour of Josef Zemann (1923-2022) as a tribute to his early and extensive work on tellurite minerals (Mandarino and Williams 1961; Mandarino et al. 1969). As a pioneer he established the essential features of the stereochemistry of Te⁴⁺ ions in oxidotellurate(IV) compounds (Zemann 1968, 1971, 1974). Zemannite represents the archetype structure and first representative of this structure type, with molecular H₂O and hydrated guest cations inside the host framework. The type locality of this mineral, the Bambolla mine in Moctezuma (Sonora, Mexico), is a famous Au-Te deposit, from where up to now more than a dozen new minerals containing Te⁴⁺ or Te⁶⁺ atoms have been described (cf. Table S1 of the supplementary material; Braith et al. 2001; Jacobson et al. 2018). Matzat (1967) solved the crystal structure of this rare mineral species, proposed a structure model of the framework topology in the space-group symmetry $P6_3/m$, but assigned Na⁺ ions as the charge-compensating extra-framework constituents. The apparent Na content was derived from a semi-quantitative electron

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probe micro-analysis (EPMA), which in turn led to the establishment of $\{(Zn,Fe)_2[TeO_3]_3\}Na_xH_{2-x}, yH_2O$ as the first formula (Mandarino and Williams 1961; Mandarino et al. 1969).

An analogue chemical formula was postulated for the isostructural mineral kinichilite, originally described as the Mn^{2+} analogue of zemannite (Hori et al. 1981). The crystal structures and the chemical composition of both these minerals were re-investigated by Miletich (1989, 1993, 1995a). As a result, a revision of both the formulas was required. The electron-density maps determined from X-ray diffraction investigations clearly demonstrated the presence of centrally located $[Mg(H_2O)_6]^{2+}$ complexes besides H₂O molecules within the 1D micropores of the host framework. Host and guest units are solely bound by hydrogen bonds. The revised formula for zemannite was reported as $Mg_{0.5}[Zn^{2+}Fe^{3+}(TeO_3)_3] \cdot 4.5H_2O$ (Z=2), kinichilite is the isostructural Zn-free Mn²⁺Fe³⁺ analogue. A similar stoichiometry was later confirmed for the so far youngest accepted natural representatives of the zemannite group: keystoneite, $Mg(H_2O)_6[Ni^{2+}Fe^{3+}(TeO_3)_3]_2 \cdot 2H_2O$ (Missen et al. 2021) and ilirneyite, Mg(H₂O)₆[Zn²⁺Mn³⁺(TeO₃)₃]₂·3H₂O (Pekov et al. 2018). Most recently the new mineral wortupaite has been approved (IMA2022-107) and described as being crystallographically related to the zemannite structure family (Missen et al. 2023).

All up to now published crystallographic investigations mentioned too short distances for the extra-framework positions requiring partial occupations going along with an at least local violation of the parental $P6_3/m$ symmetry. Also, the cation distribution of the M1 and M2 positions within the octahedral framework remained uncertain. Miletich (1995a) suggested for the extra-framework constituents [i.e., $Mg^{2+}(H_2O)_6$ octahedra and molecular H_2O] a plausible ordering scheme, which was compatible with the periodicity along the *c*-axis direction. The scheme avoided any too short distances, but required the violation of the parental $P6_3/m$ symmetry. Any ordering scheme within the channels suggested the breaking of the local symmetry (i.e., the loss of centrosymmetry and of the mirror plane). However, the X-ray intensities did not give any evidence of a specific subgroup symmetry. Most recent re-investigations on zemannite (Cametti et al. 2017; Missen et al. 2019b) suggest the acentric space group $P6_3$ as the most appropriate symmetry, which was supported by ab initio simulations (Cametti et al. 2017). In addition, Missen et al. (2021) propose the same acentric $P6_3$ symmetry for the crystal structure of keystoneite, but the distribution of extra-framework atoms still requires partial site occupations ($\leq 50\%$) within the channels.

The high degree of flexibility with regard to the arrangement of atoms inside the channels was already suspected with the very first zemannite-like synthetic compounds (Wildner 1991; 1993; Miletich 1995b). Meanwhile it was manifested in innumerable further analogue phases (cf. the summary in Table S2, for the most recently described compounds see Eder et al. 2023a). The analogue phase representatives show a remarkable diversity in terms: (i) number and type of cations within the channel (e.g., Na⁺, K⁺, Mg²⁺, Sr²⁺, Ba²⁺), (*ii*) number of H₂O molecules within the channel, and (iii) occupation of the octahedrally coordinated sites in the framework by a variety of divalent and trivalent cations including both mono- and multi-cationic framework arrangements. This concerns also the distribution of cations in the channel (along the channel axis or even displaced, bonding to the channel-wall atoms), besides the pure hydrogen bonding of fully hydrated ion complexes. Even examples with neutral charged frameworks without any incorporated channel species have been described (Wontcheu and Schleid 2003; Kong et al. 2010). At best, these variations are also associated with deviations in the bulk but also local symmetries, which include both centrosymmetric (e.g., P6₃/m, Wildner 1993; Miletch 1995b) and acentric examples (e.g., P63, Johnston and Harrison 2011; Missen et al. 2019b; or $P2_1$, Eder et al. 2023b) besides superstructures of the zemannite aristotype (e.g., Johnston and Harrison 2011; Eder et al. 2023a, b) and even one-dimensionally modulated variations (Eder et al. 2023a).

The question of the true symmetry of zemannite arises from the ordering of the channel atoms. The hexagonal $P6_3/m$ and $P6_3$ symmetries reflect the overall symmetry of the host framework, which is not consistent with the actual arrangement of the guest molecules in the channels, neither in zemannite itself nor in any of the isostructural minerals. Corresponding structural refinements always result in partially occupied sites for both, the position of the Mg atoms and of the H₂O molecules. Cametti et al. (2017) investigated the behaviour of the crystal structure with increasing temperature. At 125 °C the H₂O molecules not bounded to the Mg atoms are released. Their careful study of the dehydration behaviour sheds light on the differences of the H₂O content, which had been reported in different studies for various zemannite samples.

In this study a re-investigation of the crystal structure of zemannite was carried out at room and low-temperature conditions (down to 100 K) using a microfocus X-ray tube besides a sensitive hybrid pixel detector. The present investigations aimed recording tentative superstructure phenomena, potential appearance of lattice modulations or diffuse scattering, or any deviation from the Laue symmetry 6/m. The overarching aim was to unravel the symmetry relationship between the host framework and the extra-framework guest constituents in this microporous guest–host structure.

Experimental

Single-crystal X-ray diffraction data were collected from an euhedrally shaped crystal, which is $30 \times 40 \times 60 \ \mu\text{m}^3$ in size and bright orange in colour. It is a co-type sample of zemannite from the type locality, the Bambolla mine (Moctezuma, Sonora, Mexico), deposited in the Zemann collection hosted at the Institut für Mineralogie und Kristallographie der Universität Wien (specimen no. RVG/#38). Morphologically, it shows a hexagonal prism and a hexagonal dipyramid. The orientation of the morphology with respect to the atomic arrangement was verified by single-crystal X-ray diffraction. The occurring faces follow two trigonal prisms and four trigonal pyramids: {1010}, {0110}, {1012}, {0112}, {1012}, and {0112}, according to trigonal symmetry. The atomic ratio Fe:Mn:Zn = 1.06:0.08:0.86 within the investigated specimen was found from EPMA, as earlier reported in detail by Miletich (1995b). For X-ray data collection the crystal was mounted on a MiTeGen kapton loop. Diffraction images were recorded on a Stoe StadiVari-diffractometer system using MoKα radiation: 100 W air-cooled Incoatec IuS microfocus source, operated at 50 kV and 1 mA, beam diameter ~ 110 µm FWHM (full with at half maximum), and a Dectris Pilatus 300 K pixel detector with a 450 µm silicon layer, set to a detector-tocrystal distance of 60 mm. In addition to room temperature (RT, 298.0 \pm 0.5 K), in-situ low-temperature measurements at 200 ± 1 K and 100 ± 3 K were performed using an Oxford CryoSystems nitrogen-gas Cryostream cooler. With the implemented resistive heating, a stable temperature of the N2 flow was achieved on the sample; encapsulation in a dry air stream prevents from persistent icing problems. For better comparability all data sets were recorded with almost equivalent datacollection parameters (i.e., 0.5° ω -rotation per frame, 45 to 50 s exposure time per frame, full coverage of the reciprocal space at $3^{\circ} < 2\theta < 101.36^{\circ}$). Data processing including indexing, integration, corrections for Lorenz-polarization effects, and crystal absorption (multi-scan method), was performed using the X-AREA software (Stoe & Cie 2002). Details of data collection, data reduction, and results of the final structure refinements are given in Table 1.

Structure refinements were performed with the programme suites JANA (Petříček et al. 2014) and SHELXL-97 (Sheldrick 1997, 2008). Various attempts were based on: (i) distinct space-group symmetries $P6_3/m$ (176), $P6_3$ (173), P6 (174), and P3 (143); (ii) variations of the scattering functions (neutral and charged atoms); (iii) distinct occupations of the M positions by Fe and/or Zn atoms; (iv) various constraints of positional parameters, displacement parameters, and site-occupation factors of the framework and/or extraframework sites. Furthermore, variations of the data sets truncated in the order of diffraction (high- and low-order with varying 2θ limits) were chosen, in order to account for the influence of the ratio core to bounding electrons. The atomic coordinates of the framework atoms published by Cametti et al. (2017) served as the starting set of structure refinement. For the refinements in $P6_3$ and P3 the origin of the unit cell was shifted by the vector [0, 0, 0.1] relative to the z/c coordinates of Cametti et al. (2017), in order to avoid the influence of the symmetry of the trigonometric functions for the calculation of structure factors at special z values (i.e., along the polar c-axis). The atom labelling follows Cametti et al. (2017), who indicate mirrored sites derived from symmetry reduction $P6_3/m$ to $P6_3$ by double

Table 1 Instrumental parameters for the single-crystal Xray data collection of zemannite, $Mg(H_2O)_6[Zn^{2+}Fe^{3+}(TeO_3)_3]_2 nH_2O$, $n \le 3$, data reduction, and final structure refinements in space group P3

Temperature	RT	200 K	100 K
a [Å]	9.4125(12)	9.4002(12)	9.3911(12)
<i>c</i> [Å]	7.6525(9)	7.6455(9)	7.6341(9)
V [ų] / Z	587.1 / 1	585.1 / 1	583.1 / 1
$\rho_{\text{calc}} [\text{g cm}^{-3}] / \mu(\text{Mo}K\alpha) [\text{mm}^{-1}]$	4.19 / 10.7	4.21 / 10.7	4.22 / 10.7
No. scans / images / $2\theta_{max}$ (MoK α radiation) [°]	79 / 6560 / 101.4	58 / 5480 / 101.4	59 / 5515 / 101.4
Rotation angle ω per image [°] / exposure time per frame [s]	0.5 / 45	0.5 / 50	0.5 / 50
Measured reflections	77444	66101	65735
Unique reflections (<i>n</i>) / reflections with $F_o > 4\sigma(F_o)$	8404 / 7674	8291 / 7795	8266 / 7831
$R_{int} = \sum F_o^2 - F_o^2(\text{mean}) / \sum F_o^2$	0.0338	0.0297	0.0324
Extinction parameter k: $F_c^* = F_c \cdot k [1+0.001 \cdot F_c^2 \lambda^3 / \sin(2\vartheta)]^{-1/4}$	0.0013(2)	0.00160(16)	0.00123(16)
$R1 = \sum (F_o - F_c) / \sum F_o (\text{unique/observed})$	0.025 / 0.021	0.019 / 0.021	0.020/0.018
$wR2 = \left[\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w F_o^4 \right]^{1/2}$	0.056	0.046	0.045
GooF = { $\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)$ } ^{0.5}	1.05	1.04	1.08
Number of variable parameters (<i>p</i>) / max Δ/σ	88 / < 0.001	94 / < 0.001	99 / < 0.001
Final difference Fourier map [eÅ-3]	-1.59 to +1.96	-1.64 to +1.73	-1.55 to +1.64
Twin ratio	0.537(2): 0.463	0.5352(18): 0.4648	0.5380(17): 0.4020
Weight parameter a / b	0.0268 / 0.86	0.0183 / 1.18	0.0167 / 1.25

 $w = 1/\{\sigma^2(F_o^2) + [a \times P]^2 + b \times P\}; P = ([\max(0, F_o^2)] + 2 \times F_c^2/3)$

digits (e.g., atoms O_w3 and O_w33). Following the further symmetry reduction from $P6_3$ to P3, independent sites are labelled "a" and "b". Positions and site-occupations for all extra-framework sites were found individually from difference Fourier summations for each space-group symmetry $P6_3/m$, $P6_3$, $P\overline{6}$, and P3. Twinning was considered for all acentric space groups, following a

$$\left(\begin{array}{rrr}1 & 0 \ 0 \\ 0 & 1 \ 0 \\ 0 & 0 \ \overline{1}\end{array}\right)$$

twin law as set for a twin plane parallel to (00.1), thus corresponding to the former mirror plane in $P6_3/m$. Refining a twin fraction according to merohedral twinning reduced in all cases the *R* values significantly and allowed a smoothing of the final difference Fourier summations.

For the final refinements, ionic atomic scattering functions for Mg²⁺, Fe³⁺, Zn²⁺, and neutral ones for O and Te atoms were taken from Wilson (1992). Tables 1, 2, 3 and 4 provide the details of the final structure refinements in space group P3, fractional coordinates, and the results for the bonding geometries derived from them. Figure 1 provides a view of the crystal-structure topology with its crystallographic individual sites. The anisotropic displacement parameters (ADPs), the principle mean square atomic displacements, and also the results of refinements in the parental structure with space group $P6_3/m$ are summarized in Tables S3, S4, and S5 (cf. supplementary material). Figure S1 visualizes the thermal displacements as compared between 298 K, 200 K, and 100 K. Bond strengths were determined using the parameters for Te⁴⁺–O from Mills and Christy (2013), for all other bond types those from Brese and O'Keeffe (1991). Bond valences for mixed occupations were derived following the suggestions given by Bosi (2014). Further details of the crystal structure investigations may be obtained from the joint CCDC/FIZ Karlsruhe online deposition service: https://www. ccdc.cam.ac.uk/structures/? by quoting the deposition numbers CSD-2244025 (room temperature), and CSD-2244030 (200 K), and CSD-2244032 (100 K).

Results and discussion

Lattice features and X-ray crystallography

Apart from the tentative order of the Fe³⁺ and Zn²⁺ ions within the MO_6 octahedra and the order of the atoms in the channel relative to the host framework, the main features of the crystal structure of zemannite were known for more than five decades. However, the additional structural details are expected to cause a very limited contribution to the entire scattering power only. Therefore, great attention was paid for the re-investigation to both, the individual recorded diffraction patterns and the reciprocal space (reconstructed from the more than 5400 collected frames).

Superstructure reflections have been observed for individual synthetic zemannite analogue phases. Examples include a fourfold $2 \times 2 \times 1$ supercell in Ba M^{2+} (SeO₂)₃·3H₂O, M = Mg, Mn, Co, and in CsMn₂(TeO₃)₃·H₂O (Johnston and Harrison 2011; Eder et al. 2023a), a rhombohedral superstructure such as in Na₂Cu₂(TeO₃)₃·1.5H₂O (Eder et al. 2023a), or a monoclinic twofold supercell in K(Mn,Cu)(TeO₃)₃·2H₂O (Eder et al. 2023b). Even a first example of an incommensurately modulated structure belonging to the zemannite-group has been reported (i.e., K₂Co₂(TeO₃)₃·2.5H₂O) with a modulation along c^* -axis as due to the misfit of periodicities between the host and guest atoms (Eder et al. 2023a). Therefore, particular attention was paid to a tentative occurrence of any features in the reciprocal space beyond the Bragg reflections based on the average cell. A focus was set onto the hk0 and hk1 planes as indicative for comparable superstructures within the *ab* plane, and along the c^* direction, which would evidence for a periodicity change along the channel direction.

None of the three measurements at RT, 200 K, and 100 K gave any indication of the occurrence of a commensurate superstructure. In addition, no satellite reflections were observed around the known Bragg peak positions, which would have indicated an incommensurately modulated arrangement. The recorded X-ray diffraction images do not provide any evidence for a diffuse scattering, that might indicate a relative disorder of atoms in neighboring channels, such as recently exemplified by the channel fillings in pezzottaite (Ende et al. 2021).

Nevertheless, a careful examination of the diffraction patterns recorded with the employed sensitive hybrid detector system reveals unexpected intensities violating the reflection conditions for a 6₃-screw axis (i.e., reflections 001, 003, and 005). Figure 2 shows a section through the reconstructed reciprocal space, which reveals unequivocally slight but clearly observable intensities for these 00*l* reflections with l = 2n + 1. Most pronounced are those at low diffraction angles: Integrated intensities correspond to $I \approx 7 \sigma(I)$ and $\approx 22\sigma(I)$ for the 001 and 003 reflection. The intensities for these two reflections are maintained over the entire temperature range; only the intensity of the 005 reflection increased from the data set taken at RT to 200 K continuously by a factor of 2.5. The possibility of multiple diffraction according to the Renninger effect was ruled out, as the violations were observed independently from the investigated sample and the orientation of the crystal with respect to the incident X-ray beam.

Assuming the l=2n+1 extinction rule for 00*l* reflections to be correct, it suggests either the presence of a 6_3 axis, or a 2_1 axis in case of monoclinic or orthorhombic lattice symmetry. At most, a metrically non-hexagonal lattice with γ deviating from 120° would be a clear indication of

Table 2 Fractional atomic coordinates and equivalent isotropic displacement parameter (exp $[2\pi^2 \Sigma_{i=1}^3 \Sigma_{j=1}^3 U_{ij} a_i^* a_j^* h_i h_j]$) obtained from the final refinements in P3

Atom	Site occupation	Temperature	Multiplicity Wyckoff letter site symmetry		x	у	Ζ _ν	U _{equiv} /U _{iso}	Σs
Tea T	Te _{1.0}	RT	3d	1	0.49744(4)	0.04104(4)	0.6*	0.01122(5)	4.01
		200 K			0.49734(4)	0.04091(4)	0.6*	0.00846(4)	4.00
		100 K			0.49709(3)	0.04065(3)	0.6*	0.00597(4)	3.97
Teb Te _{1.0}	Te _{1.0}	RT	3 <i>d</i>	1	0.50214(4)	0.95924(4)	0.10160(6)	0.01057(4)	3.86
		200 K			0.50251(4)	0.95948(3)	0.10176(6)	0.00804(4)	3.79
		100 K			0.50246(3)	0.95949(3)	0.10201(5)	0.00581(4)	3.83
M1a	Fe ³⁺ _{1/3} Zn ²⁺ _{2/3}	RT	1b	3	1/3	2/3	0.4102(2)	0.0107(2)	2.12
		200 K			1/3	2/3	0.41009(19)	0.00757(17)	2.06
		100 K			1/3	2/3	0.41063(17)	0.00493(16)	2.04
M2a	Fe ³⁺ _{2/3} Zn ²⁺ _{1/3}	RT	1b	3	1/3	2/3	0.78912(19)	0.0089(2)	2.83
		200 K			1/3	2/3	0.78921(18)	0.00580(17)	2.94
		100 K			1/3	2/3	0.78880(18)	0.00436(17)	3.00
M1b	$Fe^{3+}_{2/2}Zn^{2+}_{1/2}$	RT	1 <i>c</i>	3	2/3	1/3	0.9110(2)	0.0108(2)	2.65
	215 115	200 K			2/3	1/3	0.9110(2)	0.0095(2)	2.61
		100 K			2/3	1/3	0.91095(21)	0.00687(19)	2.61
M2b	$Fe^{3+}_{1/2}Zn^{2+}_{2/2}$	RT	1c	3	2/3	1/3	0.29310(19)	0.0109(2)	2.30
	1/3 2/3	200 K			2/3	1/3	0.29259(19)	0.00836(19)	2.26
		100 K			2/3	1/3	0.29317(17)	0.00607(19)	2.27
O1a	0	RT	3 <i>d</i>	1	0.4933(5)	0.8382(5)	0.6060(7)	0.0110(5)	1.89
014	01.0	200 K	2.a		0.4933(4)	0.8379(4)	0.6072(6)	0.0085(4)	1.89
		100 K			0.4929(4)	0.8379(4)	0.6098(5)	0.0058(4)	1.88
O1h	0	PT	3.1	1	0.5026(5)	0.1613(5)	0.1023(8)	0.0132(5)	1.82
010	01.0	200 K	54	1	0.5020(5)	0.1617(4)	0.1023(0)	0.0101(5)	1.02
		200 K 100 K			0.5024(5)	0.1610(4)	0.1017(7) 0.1024(7)	0.0077(4)	1.00
$\Omega^2 a$	0	PT	3.1	1	0.5017(4)	0.1010(4)	0.1024(7) 0.4275(7)	0.0077(4)	1.00
020	01.0	200 K	54	1	0.6485(6)	0.1305(6)	0.4278(7)	0.0170(3)	2.00
		200 K 100 K			0.0483(0)	0.1395(0)	0.4278(7)	0.0130(4)	2.00
024	0		2.4	1	0.0492(3)	0.1383(0)	0.4238(0)	0.0097(4)	1.97
020	$O_{1.0}$	X1 200 K	54	1	0.3537(7)	0.8587(7)	0.9129(7)	0.0103(3)	1.00
		200 K			0.3320(0)	0.8543(0)	0.9140(7)	0.0113(4)	1.00
022	0	100 K	2.1		0.3316(3)	0.8342(6)	0.9155(7)	0.0096(4)	1.89
022a	$O_{1.0}$	R1 200 K	54	1	0.6534(8)	0.1432(8)	0.7852(7)	$= U_{equiv}(O2a)$	1.82
		200 K			0.6546(6)	0.1448(7)	0.7830(7)	$= U_{equiv}(02a)$	1.78
0221	0	100 K	2		0.6534(6)	0.1453(6)	0.7842(6)	$= U_{equiv}(O2a)$	1.82
0226	$O_{1.0}$	RI 200 K	3	1	0.3394(7)	0.8593(8)	0.2742(7)	$= U_{equiv}(O2b)$	1.//
		200 K			0.3404(7)	0.8621(7)	0.2765(7)	$= U_{equiv}(O2b)$	1.73
	2.5.21	100 K			0.3401(6)	0.8625(6)	0.2763(6)	$= U_{equiv}(O2b)$	1.74
Mg	$Mg^{2+}_{1.0}$	RT	1 <i>a</i> 3		0.0	0.0	0.5203(3)	0.0164(3)	2.01
		200 K			0.0	0.0	0.5219(3)	0.0115(2)	2.30
		100 K			0.0	0.0	0.5233(2)	0.0081(2)	2.16
Ow3	O _{1.0}	RT	3 <i>d</i>	1	0.0759(8)	-0.1221(8)	0.7059(9)	0.0449(6)	0.29
		200 K			0.0699(8)	0.1277(9)	0.6990(10)	0.0402(10)	0.32
		100 K			0.0684(8)	-0.1290(8)	0.6980(9)	0.0330(9)	0.33
Ow4	O _{1.0}	RT	3 <i>d</i>	1	0.1995(7)	0.0687(7)	0.3610(7)	$= U_{iso}(Ow3)$	0.38
		200 K			0.1995(3)	0.0670(4)	0.3660(5)	0.0260(5)	0.39
		100 K			0.1997(3)	0.0663(3)	0.3675(4)	0.0183(4)	0.39
Ow33	O _{0.785(11)}	RT	3 <i>d</i>	1	0.1852(11)	0.0457(10)	0.0152(11)	$= U_{iso}(Ow3)$	0.00
	O _{0.750(12)}	200 K			0.1849(15)	0.0508(15)	0.0086(15)	0.050^{*}	0.00
	O _{0.708(12)}	100 K			0.1802(12)	0.0537(14)	0.0076(14)	0.040^{*}	0.00

Data collected at RT (first row), 200 K (second row), and 100 K (third row). Sum of bond valences (*s*) were added (in v.u.), contributions of the H atoms were neglected, parameters for Te⁴⁺–O bonds from Mills and Christy (2013), for all other bond types from Brese and O'Keeffe (1991)

*Fixed parameter

Table 3 Interatomic bond distances (in \mathring{A}) and angles (in \degree) for the data collection at RT, 200 K, and 100 K

Temperature		RT	200 K	100 K
Tea–O2a		1.822(5)	1.815(4)	1.827(4)
Tea-O1a		1.886(4)	1.890(4)	1.895(3)
Tea-O22a		1.915(5)	1.922(5)	1.912(4)
< Tea-O>		1.874	1.876	1.878
O-Tea-O		93.9(2) to 98.6(3)	93.88(17) to 98.8(2)	94.05(16) to 98.79(17)
Tea…O2b		2.854(6)	2.887(5)	2.888(5)
Tea…O22b		2.961(6)	2.939(5)	2.935(5)
Tea…O2a		3.217(7)	3.230(6)	3.236(5)
Tea…O22a		3.223(7)	3.224(6)	3.221(5)
Teb-O22b		1.876(6)	1.884(5)	1.881(5)
Teb-O1b		1.895(4)	1.901(3)	1.896(3)
Teb-O2b		1.896(5)	1.905(5)	1.901(5)
< Te <i>b</i> -O>		1.889	1.897	1.892
O-Te-O		93.9(2) to 98.9(2)	93.7(2) to 99.7(2)	93.72(16) to 98.43(19)
Teb…O22a		2.902(7)	2.907(6)	2.910(5)
Teb…O2a		2.941(7)	2.939(6)	2.919(5)
Teb…O22b		3.177(6)	3.205(6)	3.201(5)
Teb…O22b		3.285(6)	3.258(5)	3.250(5)
M1a–O22b	3×	2.062(6)	2.074(5)	2.078(5)
M1a–O1a	3×	2.161(5)	2.169(4)	2.173(4)
< <i>M</i> 1 <i>a</i> -O>		2.112	2.122	2.126
O22 <i>b</i> – <i>M</i> 1 <i>a</i> –O22 <i>b</i>		96.9(2)	97.8(2)	97.75(18)
O1 <i>a–M</i> 1 <i>a–</i> O1 <i>a</i>		77.4(2)	777.04(17)	76.41(15)
O22 <i>b</i> – <i>M</i> 1 <i>a</i> –O1 <i>a</i>		89.4(2), 94.9(2)	88.94(19), 94.56(19)	89.39(17), 94.72(16)
M2a–O2b	3×	1.956(6)	1.937(5)	1.940(5)
<i>M</i> 2 <i>a</i> –O1 <i>a</i>	3×	2.095(5)	2.090(4)	2.067(4)
< M2aO>		2.026	2.014	2.004
O2 <i>b</i> – <i>M</i> 2 <i>a</i> –O2 <i>b</i>		98.7(2)	97.6(2)	97.3(2)
O1 <i>a –M2a–</i> O1 <i>a</i>		80.3(2)	80.51(18)	81.08(15)
O2 <i>b</i> – <i>M</i> 2 <i>a</i> –O1 <i>a</i>		84.9(2), 95.0(2)	85.72(19), 95.31(19)	85.78(17), 95.08(17)
M1b-O22a	3×	1.960(5)	1.970(5)	1.962(4)
<i>M</i> 1 <i>b</i> –O1 <i>b</i>	3×	2.151(5)	2.150(4)	2.166(4)
< <i>M</i> 1 <i>b</i> -O>		2.056	2.06	2.064
O22 <i>a</i> – <i>M</i> 1 <i>b</i> –O22 <i>a</i>		98.0(3)	98.1(2)	97.8(2)
O1b-M1b-O1b		79.0(2)	79.1(2)	79.08(18)
O22a-M1b-O1b		87.5(2), 94.4(2)	87.7(2), 93.77(19)	87.73(19), 94.12(18)
M2b-O2a	3×	2.018(5)	2.027(4)	2.025(4)
M2b-O1b	3×	2.149(5)	2.151(5)	2.152(4)
< M2h-O>		2.084	2.089	2.089
$\Omega^2 a - M^2 b - \Omega^2 a$		96.5(3)	96.3(2)	97,17(19)
O1b-M2b-O1b		79.1(2)	79.01(19)	79.23(17)
$\Omega^2 a - M^2 b - \Omega^1 b$		88.0(2) 95.5(2)	88 0(2) 95 75(17)	87 50(16) 95 02(16)
$[M_1 a M_2 a \Omega_0]$ dimer		0010(2), 2010(2)		0,100(10), 90102(10)
$M1a \cdots M2a$		2.8929(15)	2.8986(14)	2.8870(15)
O22 <i>b</i> …O22 <i>b</i>		3.085(13)	3.127(9)	3.131(8)
01 <i>a</i> …01 <i>a</i>		2.702(7)	2.702(6)	2.688(6)
O2 <i>b</i> …O2 <i>b</i>		2.973(11)	2.915(8)	2.913(8)
[M1bM2bO ₆] dimer			(-)	
M1bM2b		2.9168(17)	2.9173(17)	2.9179(17)

Table 5 (continued)						
Temperature		RT	200 K	100 K		
O22a…O22a		2.959(11)	2.976(9)	2.957(9)		
01 <i>b</i> …01 <i>b</i>		2.736(7)	2.737(6)	2.744(5)		
O2a…O2a		3.010(11)	3.019(8)	3.037(8)		
$Mg-O_w4$	3×	2.048(6)	2.038(3)	2.038(3)		
$Mg-O_w3$	3×	2.156(7)	2.120(7)	2.107(5)		
< Mg-O>		2.102	2.079	2.073		
O–Mg–O		82.5(3) to 96.3(2)	83.6(3) to 94.2(2)	84.2(3) to 93.7(2)		

Bold font is used to mark average values

deviations from the hexagonal metrics. The precise values of the metric parameters for unconstrained triclinic refinements clearly show that there is no significant deviation from hexagonality, as expressed by the values for γ being 119.982 $\pm 0.005^{\circ}$ (at RT), 119.986 $\pm 0.005^{\circ}$ (at 200 K) and 119.962 $\pm 0.006^{\circ}$ (100 K), respectively. Moreover, the independently fitted values for the a_1 and a_2 axis are equivalent within the 3σ criterion of significance, and thus confirm in addition the hexagonal metrics of the lattice observed here. As the FWHM does not positively correlate with the 2θ -angle, also pseudomerohedral twinning is ruled out.

Table 4 Coordination of the O_w atoms and the relevant distances for hydrogen bonding for the data at RT, 200 K, and 100 K

Temperature	RT	200 K	100 K
O _w 3–Mg	2.156(7)	2.120(7)	2.107(5)
O _w 3–H…O1a	2.701(8)	2.677(8)	2.667(6)
O _w 3–H…O _w 33	2.738(8)	2.788(10)	2.799(11)
O _w 3…O _w 33'	2.970(9)	2.923(11)	2.879(11)
$O_w 3 \cdots O22a$	3.086(9)	3.041(9)	3.039(8)
Mg–O _w 3…O1a	122.2(3)	125.0(3)	126.0(3)
$Mg-O_w3\cdots O_w33$	112.9(4)	109.8(5)	108.1(4)
O _w 33…O _w 3…O1a	121.2(3)	120.3(4)	120.8(3)
O _w 4–Mg	2.048(6)	2.038(3)	2.038(3)
O _w 4–H…O _w 33	2.647(9)	2.736(12)	2.752(11)
O_w 4–H···O2 a	2.737(8)	2.750(5)	2.733(5)
$O_w 4 \cdots O22b$	2.936(8)	2.912(6)	2.900(5)
$Mg-O_w4\cdots O_w33$	124.4(3)	123.7(3)	122.6(2)
Mg– O_w 4····O2 <i>a</i>	120.6(3)	121.03(16)	121.17(14)
$O_w 33 \cdots O_w 4 \cdots O2a$	104.4(3)	102.9(3)	102.5(3)
O _w 33…H–O _w 4	2.647(10)	2.736(12)	2.752(11)
O _w 33–H…O1b	2.696(10)	2.719(13)	2.759(11)
O _w 33–H…O _w 33	2.718(16)	2.69(2)	2.607(17)
O _w 33…H–O _w 3	2.738(8)	2.788(10)	2.799(11)
O _w 33O _w 3'	2.970(9)	2.923(11)	2.879(11)
O _w 33…O2b	2.995(10)	3.049(3)	3.100(12)

Interatomic bond lengths are given in Å, bond angles in °

Comparative structure refinements

The crystal structure originally has been described in the parental space group $P6_3/m$, with the framework atoms located on four fully occupied positions: Te atoms on site 6h (point symmetry m.), M atoms on 4f (3..), O1 atoms on 6h(m.), and O2 atoms on the general site 12i (Matzat 1967; Miletich 1993, 1995b). For the framework an ordered arrangement is compatible with all structure refinements. The guest constituents are on partially occupied positions with site-occupation factors (s.o.f.s) significantly smaller than 1.0 (i.e., the Mg atoms are on 4e (3..) with a s.o.f. of ≈ 0.25 , the O_w3 and O_w4 atoms are on sites 12*i* with a s.o.f. of ≈ 0.33 ; Miletich 1995b). For an ordered atomic arrangement a violation of space-group symmetry $P6_3/m$ at least for the guest atoms is required (Miletich 1993, 1995b). Accordingly, unobtrusive anisotropies of the framework atoms but large ones for the guest atoms suggest at least minor deviations for the host framework. In contrast, for the positions of the guest atoms an extensive displacement is expected. It was considered that a tentative order between Zn and Fe atoms cause a violation of the mirror plane resulting in symmetry $P6_3$. Any ordering for the channel atoms Mg and O_w was considered theoretically being only possible in space group P3, but none of the ordering aspects could be verified experimentally at that time.

Cametti et al. (2017) succeeded in refining a softconstrained model in the acentric space group $P6_3$ and suggested the Te atoms on site 6c (1), M atoms on two independent sites 2b (3..), Mg atoms on site 2a with a s.o.f. about 0.5 - refined to 0.467(6), and all oxygen atoms located on the general site 6c. The positions of the O_w atoms belonging to the coordination sphere of the Mg²⁺ ion were labelled O_w3 and O_w4 , each of them occupied with s.o.f.s ≈ 0.5 , while the O_w33 atom of the interstitial free H₂O molecule shows a higher and flexible deficiency; the s.o.f. was refined to 0.31(3). Based on this $P6_3$ structure model, Missen et al. (2019b) re-refined the zemannite structure from synchrotron data, established a preferred ordering on the M sites ($M1 = Zn_{0.78}Fe_{0.22}$, $M2 = Zn_{0.18}Fe_{0.82}$) based on bond-valence calculations.

Fig. 1 The crystal structure of zemannite corresponding to the space-group symmetry P3 in a perspective view along the c-axis. The four different M sites correspond to the octahedra in green (M1a, M2b) and brown (M1b, M2a), thus representing the two different dimer types (a-type = $M1aM2aO_9$, b-type = $M1bM2bO_0$). The two individual TeO3 groups are displayed as the yellow (Tea) and brown (Teb) pyramidal units interlinking the dimers within the framework. The $Mg(H_2O)_6$ complexes inside the channels are depicted as turquoise octahedral groups. O_w33 atoms are visualized as red spheres. Programme ATOMS (Dowty 1997)



As a tribute of the observed violation of the reflection conditions corresponding to the 6_3 screw axis, a further symmetry reduction into the direct subgroup $P\overline{6}$ or via both space groups $P6_3$ and $P\overline{6}$ to P3 were considered. Space group $P\overline{6}$ allows Fe_2O_9 or Zn_2O_9 dimers only, which contradicts the ab initio calculations by Cametti et al. (2017). In addition, the $P\overline{6}$ symmetry is not compatible with an ordered arrangement of the channel atoms at all. The only symmetry, which is in accordance with all aspects mentioned above is P3, for which a model was established with the atoms M1a and M2a on 1b (3..), M1b and M2b on 1c (3..), Mg on 1a (3..), and the entire Te and O atoms on the general site 3d.

Many series of refinements were carried out with variations of (*i*) the space-group symmetries as mentioned above (including also *P*1), (*ii*) the occupations of the *M* sites with Fe and Zn atoms in variable proportions with fixed and variable s.o.f.s, (*iii*) variations of the scattering functions (for neutral and charged atoms), (*iv*) with or without constrained atomic coordinates and displacement parameters, and (*v*) variations in the 2θ range of Bragg reflections included

Fig. 2 Reciprocal lattice plane of the h0l layer reconstructed from the recorded frames of the data collection at 298 K. The plane direction represents equivalent orientations in the reciprocal space with c^* (vertical arrow) and a^* (horizontal arrow) originating from the origin O*. Yellow circles in (a) mark the violation of the forbidden reflections, which should exhibit zero intensities for the existence of a 6_3 screw axis along the hexagonal c axis. The image section shown in (b) shows the violation of the extinction up to the order l = 11, with the strongest intensity generally being found at low diffraction orders (e.g., 001, 003,005)





in the refinements. Refinements were carried out for data sets of 8266, 8291, and 8408 unique reflections collected at 100 K, 200 K, and 298 K. The ratio of unique reflections versus variable parameters amounts to 83, 88, and 95 in space group *P*3 for the refinements of the data sets measured at RT, 200 K, and 100 K. Merging of multiple measured and symmetry equivalent reflections result in internal R values correlating insignificantly with the considered Laue symmetry (e.g., R_{int} =0.037 for $P6_3/m$, 0.036 for $P6_3$, 0.034 for *P*3, but 0.024 for *P*1 for the RT refinement). The analogous trend was observed for the final *R*1 and *wR*2 values.

Some displacement parameters of the oxygen atoms related by $P6_3/m$ symmetry were constrained for the final refinements in P3. The stronger mobility of the atoms at higher temperature required some constraints for the channel atoms for the data sets measured at RT and 200 K, respectively. The atomic coordinates of all atoms were allowed to vary individually by full-matrix least-squares refinements (see Tables 2 and S3). Moreover, attempts were considered to establish the hydrogen-bonding scheme within the channel, although the hydrogen-atom positions could not be assigned beyond doubt in the final difference Fourier summations. Large residual intensities in the final difference Fourier summations (between -1.5 and + 2.0 e⁻Å⁻³) are located in the close vicinity of the Te atoms and thus interpreted as an effect of truncation in the Fourier series.

The stereochemistry of the $[TeO_3]^{2-}$ group

One of the basic building blocks of the anionic framework is the $[Te^{4+}O_3]^{2-}$ unit (Fig. 1), which is present in the zemannite structure in the form of non-polymerized isolated groups, located on the former mirror plane in the archetype $P6_3/m$ framework. The degree of polymerisation plays a key role for the stereochemistry of tetravalent Te atoms in oxidotellurates(IV) with respect to a rather flexible coordination number for the polar arrangement of oxygen atoms (Zemann 1968, 1971, 1974; Christy and Mills 2013; Christy et al. 2016). As previously described for the zemannitestructure type, the geometry corresponds to a pyramidal $[TeO_3]^{2-}$ configuration with three short Te–O bonds (1.83) to 1.91 Å) that are clearly distinguishable from further Te-O contacts (> 2.89 Å), for both the Tea and Teb atoms in the P3 symmetry chosen here. Considering the further 2+2 weak Te–O contacts in accordance with Mills and Christy (2013) and Christy et al. (2016), the bond-valence sums of 3.97 v.u. (valence units; Tea) and 3.83 v.u. (Teb) are in almost perfect agreement with the theoretical value. As expected, the TeO₃ group is rather stiff and shows no significant geometrical variation across the entire temperature range down to 100 K.

In space group $P6_3/m$ the unique TeO₃ group shares corners with the unique MO_6 octahedra. The occupation of the *M* site by Fe³⁺ respectively Zn²⁺ atoms is expected to influence

the M-O bond lengths due to different atomic radii. Accordingly, the involved oxygen atoms O1 and O2 can be expected to show increased values for the relevant ADPs for the refinements in space group $P6_3/m$. Neither Miletich (1993, 1995b) nor Cametti et al. (2017) observed conspicuous magnitudes or anisotropies for the vibrational behaviour of the Te and *M* atoms in their refinements, while the $O2^{[1Te+1M]}$ atoms always exhibit a relatively large vibrational ellipsoid with a pronounced disc-shaped anisotropy; it is oriented with the shortest axis approximately perpendicular to the M...Te direction. To a lesser extent this behaviour can be observed for the O1^[1Te+2 M] atom, the displacement remains still large, but it is rather isotropic. Again, this vibrational behaviour is maintained for all of the independent atom sites at any of the measured temperatures notwithstanding the symmetry of the chosen structure model (cf. Fig. S1, Tables S3 to S5), which in turn provides strong evidence for originating from the substitution on the octahedrally coordinated M sites. Nevertheless, individual Te-O2 bonds reveal distinct differences (Table 3), which can be attributed to the various *M*-site occupation by divalent and trivalent cations and thus violating the former mirror-plane symmetry of the TeO₃ group.

The (Zn,Fe) ordering within the M_2O_9 dimers

The M_2O_9 dimers are formed by two face-sharing MO_6 octahedra. In natural samples they are occupied mainly by Zn²⁺ and Fe^{3+} ions (i.e., by two different kinds of atoms in the *di*and trivalent state respectively). Miletich (1993, 1995b) found minor substitutions by Mn²⁺ atoms, in addition confirming the absence of Fe²⁺ atoms by Mössbauer spectroscopy. However, many synthetic representatives crystallizing in the zemannite-type structure are known with the entire octahedrally coordinated sites occupied by the same kind of M^{2+} cations; thus the symmetry $\overline{6}$.. of the M_2O_0 dimer is maintained (e.g., Wildner 1993; Miletich 1995a; Eder et al. 2023a). The mutual occupation by M^{2+} and M^{3+} cations was suspected early on, corresponds to Pauling's demand for a minimized electrostatic repulsion in such a dimer. It results in the violation of the mirror plane and consequently the presence of a polar axis. As the effective ionic radii of ${}^{[6]}$ Fe³⁺ (0.645 Å) and ${}^{[6]}$ Zn²⁺ (0.74 Å) (Binder 1999) are not too diverse, cation ordering corresponding to a $[Fe^{3+}Zn^{2+}O_q]^{13-}$ dimer unit has been suggested. Cametti et al. (2017) performed ab inito calculations for distinct models of the Fe³⁺–Zn²⁺ distribution within these dimers, and confirmed the $[Fe^{3+}Zn^{2+}O_9]$ distribution in a $P6_3$ arrangement as the energetically most favourable. However, the coexistence of $[Fe^{3+}_{2}O_{9}]$ and $[Zn^{2+}_{2}O_{9}]$ dimers arranged in single columns along the *c*-axis direction was found to be energetically favourable, too.

Mutual refinements of U_{equiv} , s.o.f., and the scattering function was applied for an experimental verification of a tentative (partial) ordering of the M atoms. The space-group symmetry P3 splits the M site into four unique positions. However, none of the refinements was conclusive. The U_{equiv} values did not give a clear indication. The results of refinements with permuted combinations of the scattering functions for the sites M1a, M2a, M1b, and M2b being occupied exclusively by Fe or Zn atoms are not convincing at all. All attempts refining even for only one of the M sites the Fe:Zn ratio (considering ionic or neutral scattering curves) resulted in unstable refinements. Summarizing, all attempts finally suggested, that none of the *M* sites is exclusively occupied by only one type of atoms and that all four of them exhibit at least a partial substitution according to (Fe^{3+},Zn^{2+}) . In combination with crystal chemical considerations preferred occupations corresponding to $M1aM2aO_9 = (Fe_{1/3}Zn_{2/3})(Fe_{2/3}Zn_{1/3})O_9$ within the "a-type dimer" and $M1bM2bO_9 = (Fe_{2/3}Zn_{1/3})(Fe_{1/3}Zn_{2/3})$ within the "b-type dimer" is likely (see below). Moreover, their displacement parameters are rather similar showing them, as a general trend, being disc-shaped with the largest elongation in (0001). It is not surprising that they correlate positively with the applied temperature during data collection (Fig. 3, Tables S3 and S4). The smallest values were observed for the atom M2a, the largest ones for the atoms M1b and M2b.

An analysis of the average < M-O > bond distances show that < M2a-O > and < M1b-O > are slightly shorter than < M1a-O > and < M2b-O > . Considering the larger bond lengths indicating a preferred occupation by Zn²⁺ atoms, whereas the smaller ones a preferred occupation by Fe³⁺ atoms, for the sites M2a and M1b an excess of Fe³⁺ atoms whereas for the sites *M*1*a* and *M*2*b* an excess of Zn²⁺ atoms is expected. This suggests an inversion of the a- and b-type dimers: Fedominated site pointing towards the direction [001] and the Zn-dominated site towards [001] within the a-type dimer while the directions are inverted within the b-type dimer (Fig. 3). The bond-valence calculations in general support these findings. None of the *M* sites seem to be exclusively occupied by one type of atom, as the bond valence sum for the Zn²⁺ atoms is always larger than ideal 2.00 v.u. (2.08 to 2.49 v.u.), and that one for the Fe³⁺ atoms is smaller than 3.00 v.u. (ranging between 2.40 and 2.89 v.u.). Based on the considerations reported by Bosi (2014), the degree of Fe³⁺ substitution (=Zn_{1-x}Fe_x) can be derived as $x \approx 26$ at% for *M*1*a*, ~ 84 at% for *M*2*a*, ~ 53 at% for *M*1*b*, and ~12 at% for *M*2*b*.

This again supports the inverted ordering of the Fe³⁺ and Zn²⁺ ions within the dimers, with an "antiparallel" alignment of a- respectively b-type dimers in neighbouring columns (Fig. 3b). This model indeed violates the 6₃ arrangement suggested by the former authors (Cametti et al. 2017; Missen et al. 2019b) (Fig. 3a). Missen et al. (2019b) investigated the crystal chemistry of two zemannite samples based on synchrotron data and suggest from their refinements in space group $P6_3 M1 = Zn_{0.78}Fe_{0.22}$ and $M2 = Zn_{0.18}Fe_{0.82}$, respectively $M1 = Zn_{0.75}Fe_{0.25}$ and $M2 = Zn_{0.34}Fe_{0.66}$. It is a clear tendency of ordering between the two sites M1 and M2, but all dimers are arranged in a "parallel" fashion. However, the refinements are not entirely stringent, have issues, including certain uncertainties. They leave certain

Fig. 3 Detail of the framework structure in a view along [110] with the symbolized M_2O_9 dimers and the TeO₃ groups. The preferred distribution of M^{2+} (green) and M^{3+} (brown) is differentiated by colour. The image sections (a) and (b) show the differences for cation ordering required by a 6_3 screw axis (a) in contrast to the inverted order in half of the dimers, which in turn is compatible with a simple three-fold symmetry (b). Horizontal lines mark the levels of z/c = 0.25 and 0.75 with respect to the original setting in $P6_3/m$. Programme ATOMS (Dowty 1997)



uncertainties (e.g., by rather restricted resolution, $\sin\theta/\lambda \le 0.831 \text{ Å}^{-1}$), more or less inverted s.o.f.s on refining the occupancies corresponding to a Fe_{0.67}Zn_{0.33} distribution, questionable s.o.f.s for some of the extra-framework atoms, while the atom $O_w 33$ was not considered during the refinement, and the determination of hydrogen position although residual electron densities range between -1.8 and 2.8 e⁻/Å³ resulted in impossible hydrogen bonds. Moreover, the lack of restrictions to the atomic parameters of the framework atoms means that high correlations can be expected, which were not considered in their scope to affect the refinements of the s.o.f.s and ADPs.

The extra-framework $[Mg(H_2O)_6] \cdot nH_2O$ arrangement

The breakthrough in the knowledge of the occupation of the channels originated from the work of Miletich (1995b), who recognized hexahydrated Mg^{2+} cations for the compensation of the framework charges. The proposed scheme of the arrangement of H₂O molecules in the fully hydrated state of zemannite and the theoretical hydrogen bonding were confirmed by the later authors. Cametti et al. (2017) and Missen et al. (2019b) suggested as due to their refinements in $P6_3$ the interstitial H₂O molecules, which are not part of the coordination shell around the Mg²⁺ ions, to be located on the crystallographically independent site O_w33. Moreover, Cametti et al. (2017) and Missen et al. (2017) and Missen et al. (2019b) recognized

the variable H_2O content depending on humidity and temperature, which was attributed to the (partial) loss of this "free" interstitial H_2O molecule.

The structural refinements in space group P3 performed in this study enabled the proof of a fully ordering of the channel atoms Mg, O_w3 , O_w4 , and O_w33 for the first time. In contrast, all other symmetries $(P6_3/m, P6_3, P\overline{6})$ require (partial) occupation of the extra-framework atom positions; a possible order schema was discussed theoretically only (Fig. 4). The arrangement of the $[Mg(H_2O)_6]^{2+}$ complex and the interstitial H₂O molecules clearly violates any of the higher symmetries as breaking either the mirror-plane symmetry or the 6_3 screw axis. Following the results of the refinements in space group P3, the site-occupation factors and displacement parameters show again, as expected, a high correlation. Assuming a full occupation of the Mg site, U_{equiv} is $\leq 0.02 \text{ Å}^2$ as typical for Mg²⁺ ions in octahedral [6] coordination. A stoichiometric Mg content requires a full occupation of the O_w3 and O_w4 sites to form the $[Mg(H_2O)_6]^{2+}$ complexes. The electron density at the $O_w 33$ site is somewhat lower resulting in s.o.f.s of 0.71 to 0.79. It corresponds to a proven H₂O deficiency with n = 2.13 - 2.37 interstitial H₂O molecules p.f.u. (per formula unit) in contrast to ideal 3 H₂O p.f.u. in the fully hydrated state.

The arrangements of the O_w atoms found in the actual refinements correspond to the earlier reports. The ligands of the Mg²⁺ ions (atoms O_w 3 and O_w 4) are located on the

Fig. 4 Comparison of the arrangements of extra-framework atoms and the atomic distribution according to the full multiplicity of the individual sites in the space groups $P6_3/m$, $P\overline{6}$, $P6_3$, and P3. In $P6_3/m$, $P6_3$, and $P\overline{6}$ the Mg position (blue spheres) have s.o.f.s of 0.25 and 0.5, respectively. Only in P3 full order is achieved without assuming partial site occupations. Programme ATOMS (Dowty 1997)



central triad of the channel. The Mg-Ow distances correspond with those expected for $[Mg(H_2O)_6]^{2+1}$ complexes, and show a minor variation with temperature (cf. Table 3). The shortest O_w3…O and O_w4…O distances considered as hydrogen bonds involve O_w33, O1a, and O2a atoms as acceptors for hydrogen bonds. Their lengths do not correlate systematically with the variation of temperature. Decreasing temperature cause a decreasing hydrogen-bond lengths $O_w 3 \cdots O1a$, slightly increasing ones O_w3...O_w33 and O_w4...O_w33 but a variable one for $O_w 4 \cdots O2a$ (cf. Table 4). The $O1a \cdots O_w 3 \cdots O_w 33$ angle is somewhat larger than that of $O2a \cdots O_{w} 4 \cdots O_{w} 33$, but both agree with the expectations for a H₂O molecule. Further oxygen atoms were only identified at distances beyond 2.84 Å and thus are not considered for a significant participation in the hydrogen-bonding system but influence the deviations from linearity of the O-H···O bond only.

The interstitial free H₂O molecules H₂O_w33 are purely hydrogen bonded, and therefore it is the most flexible constituent within the channel. Each three O_w33 atoms per unit cell are arranged as a planar triangle between two $[Mg(H_2O)_6]^{2+}$ complexes; thus each O_w33 atom is simultaneously donor and acceptor of a O_w33...O_w33 hydrogen bond (Fig. 5). The O_w33...O_w33 distances shows the largest changes with temperature, it significantly shortens from 2.72 Å at RT to 2.61 Å at 100 K. As it was impossible to determine the H atom positions, it can only be speculated what kind of geometry exist for the O_w33 -H··· $O_w33 \leftrightarrow O_w33$ ···H- O_w33 hydrogen bridge, but a strong kinking of the H bonds with the H atoms being displaced off the channel axis appears very likely. At low temperature also a hydrogen bond forming a double minimum potential cannot be excluded. The O_w33 ··O1*b* distance exhibits a significant increase towards lower T. Thus this hydrogen-bond seems to be controlled by the weak acceptor role of the O1*b* atom. Any actual discussion of the hydrogen bonding is again speculative in the absence of knowledge of the hydrogen atom positions.

Both the s.o.f.s and displacement parameters indicate the high dynamic character of the H_2O_w33 molecule, which is responsible for changes in the hydration state at variable humidity or temperatures even below 100 °C (Cametti et al. 2017). Accordingly, the largest structural changes induced by temperature concerns the O_w atoms associated to extra-framework H_2O molecules. They are displaced between RT and 200 K by 0.042 to 0.100 Å, between RT and 100 K by 0.058 to 0.158 Å. The position of the Mg atom in the channel is much less affected (by 0.017 and 0.027 Å for the equivalent T ranges).



Fig. 5 The hydrogen bonding scheme derived for the *P3* symmetry. The Mg atom is depicted in blue, the oxygen atoms of the H₂O molecules are given in shades of green. Strong hydrogen bonds (<2.8 Å) are shown as dotted lines in black, weak ones (>2.9 Å) as dotted lines in grey. Accep-

tor oxygen atoms belong to the octahedral framework units, which are preferentially occupied by either M^{2+} (green) or M^{3+} (brown). Programme ATOMS (Dowty 1997)

Bond valence considerations for the host-guest interaction

The framework-oxygen atoms deserve special attention with regard to the interaction of the guest molecules in the channels with the $[Zn^{2+}Fe^{3+}(TeO_3)_3]^-$ host framework. A general difference is that the atoms O1*a* and O1*b* are pyramidally [3] coordinated by framework cations (atoms Te, M^{2+} , and M^{3+}), while the atoms O2*a*, O2*b*, O22*a*, and O22*b* are angled [2] coordinated by only two framework cations (Te and M^{2+} or M^{3+}). The total bond strengths of the framework-oxygen atoms, excluding the bond contributions from the hydrogen bonds, range between 1.77 and 1.99 v.u.), clearly showing a bond-valence undersaturation, and thus give evidence of being acceptors for hydrogen bridges.

O…O distances < 2.8 Å are assumed as hydrogen bonds but some electrostatic interactions with the more distant O atoms (above 2.9 Å) has been considered. Acceptor atoms are (i) framework-oxygen atoms and (ii) channel-oxygen atoms. Considering O···O distances < 2.8 Å results in a nearly planar [3] coordination for the O_w3 atom (angular sum~356°) and a slightly pyramidal [3] coordination for the $O_w 4$ atom (angular sum ~ 349°). $O_w 33 \cdots O_w 3 \cdots O1a$ is somewhat large for a H₂O molecule (122°) but it fits the expectations for O_w33····O_w4····O2a (104°). A deflection by rather distant O atoms is common in stereochemical approaches. The situation is not that clear for the $O_{w}33$ atom. The $O_w 33 \cdots O_w 33$ distance is short and it is extremely short at low temperatures; this distance indicate doubtless a hydrogen bond. The second O-H bond might switch between O1b, O_w3 , or O2b. Thus each framework-oxygen atom is considered being involved in the hydrogen-bonding network but their role is definitely distinct (Fig. 5). It is remarkable that only half of the framework-oxygen atoms (O1a, O1b, and O2a) act as predominant acceptor atoms.

As discussed above, the <M1a-O> and <M2b-O> bond lengths are slightly longer than <M2a-O> and <M1b-O>. Thus the former are assumed being predominantly $Zn^{2+}O_6$ octahedra whereas the latter $Fe^{3+}O_6$ octahedra. At the same time the respective framework-oxygen atom is acceptor of an extremely weak hydrogen bond $(O_w33\cdots O22a=3.09 \text{ Å}, O_w33\cdots O2b=3.00 \text{ Å})$. It is not surprising, that these hydrogen bridges point to the interstitial O_w33 atom, which is the most flexible in terms of being more dynamic than the atoms O_w3 and O_w4 . Therefore, the atom O_w33 is involved in the early-stage dehydration process.

Considering the various degree of bond-valence undersaturation of the framework oxygen atoms, it is not surprising that the highest degree of undersaturation (for the atoms O1*a*, O1*b*, O2*b*, and O22*b*) refers to those hydrogen bridges from the O_w3 and O_w4 atoms, and thus represent the direct link to the $[Mg(OH_2)_6]^{2+}$ complexes. The differences in unsaturation of bond valences are comparatively small here in the archetype structure of zemannite. In many synthetic analogue phases, the bonding of the channel cations often takes place directly to the oxygen atoms on the channel wall (cf. examples given by Eder et al. 2023a). Accordingly, in many cases significantly higher differences are compensated by the direct bonding to the cations to the framework as compared to the relative weak hydrogen bonds from extra-framework H₂O molecules in the channels. In all of these cases, the cations in the channel are always localized at a position that no longer corresponds to the central symmetry axis of the channel.

Conclusions

Zemannite and representatives of this mineral group were studied by Cametti et al. (2017), Pekov et al. (2018), Missen et al. (2019b), and Missen et al. (2021) most recently, with remaining open questions concerning the order within the channels and the true distribution of cations on the octahedral framework sites. The observation of the violation of the so far undisputedly accepted 6_3 screw axis in this study was a definitely new aspect. Missen et al. (2019b) stated "the systemic absences to be most consistent" for their synchrotron data, which was at least a hidden hint for a possibly existing mismatch. The series of comparative structure refinements opens up the avenue for a new route along the $P6_3/m - P6_3 - P3$.

As previously reported, the performed approaches to determine the distribution of cations on the M sites was challenging and yielded partially contradicting results. In full agreement with Cametti et al. (2017), no reliable Fe^{3+} :Zn²⁺ distribution could be determined for the four crystallographic different M sites in space group P3 due to the high correlations of the variable parameters. The most reliable assignment is based on the individual bond lengths arguments, from which the estimated Fe:Zn distribution has been derived, thus amounting for the four M sites to vary between 0.12 and 0.84. In a good approximation a fully occupied Mg site within the channel is expected which requires a stoichiometric ratio $Fe^{3+}:Zn^{2+} = 1:1$ as reported earlier (Miletich 1995b; Cametti et al. 2017; Missen et al. 2019b). The final refinements were therefore approximated to $Fe_{1/3}Zn_{2/3}$ for the sites M1a and M2b, but to Fe_{2/3}Zn_{1/3} for the sites M1b and M2a. However, this distribution can be considered as the strongest argument explaining the violation of 6_3 symmetry. Differentiating between the a-type $[M1aM2aO_9]$ dimer and the b-type $[M1bM2bO_9]$ dimer, the distribution of the atoms Fe and Zn follows an inverted sequence comparing the two octahedral dimers, and thus breaks the 6_3 symmetry. It is obvious that the greatest scattering contrast can only be seen at the lowest diffraction angles and therefore the forbidden reflections exhibit the strongest intensities at the lowest orders of diffraction (i.e., l = 1, 3, 5 for 00l).

The arrangement of the extra-framework constituents follows the model originally proposed by Miletich (1995b) and later confirmed both by Cametti et al. (2017) and Missen et al. (2019b). It was not possible to locate the positions of the hydrogen atoms with respect to the residual electron densities due to high correlations. The arrangement of hexahydrated $[Mg(H_2O)_6]^{2+}$ complexes in addition to up to three interstitial "free" H₂O molecules per unit cell, clearly supports the revised symmetry of the host framework and is compatible with the violation of the mirror-plane symmetry (cf. Eder et al. 2023a). The confirmed atomic distribution follows a polar triad, and is thus clearly responsible for the overall symmetry in the space group P3. As a consequence, all positions of the extra-framework constituents (atoms Mg, O_w 3, and O_w 4) are located on fully occupied sites. The atom position O_w33 exhibit some vacancies, the s.o.f. scatters around 0.75 p.f.u.). It was found to be sensitive to variations on temperature and humidity (Cametti et al. 2017). Twinning follows the pseudo-mirror plane of the framework. It leads to the corresponding antiparallel orientation of the polar arrangement inside the channels in the opposite direction in the respective twin domain. The polarity of the arrangement in the channels is therefore restricted to individual crystal domains, which are related by twinning following the mirror plane parallel to (0001) with almost equal twin fractions.

The periodicity of the atoms inside the channels is fully compatible with the periodicity of the framework along the *c*-axis direction. Thus it matches the absence of any modulation and the lack of a superstructure. Moreover, as the arrangement of the extra-framework atoms follows the local three-fold symmetry, there is no need to consider superordinate periodicities. Accordingly, even superstructures within the *ab* plane directions, such as exemplified by Eder et al. (2023b), are absent. In addition, diffuse scattering is absent. Stereochemical interactions of bonding between the channel constituents and the anionic framework is evident. Since the orientation of the hydrogen bonds from the channel correlates with the bond strengths of the framework oxygen atoms, the arrangement in adjacent channels is therefore clearly influenced by the cation distribution within the framework. The arrangements in adjacent channels are obviously controlled in a cooperative manner that excludes any kind of disorder between adjacent channels in zemannite.

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