

Zemannite, $\text{Mg}(\text{H}_2\text{O})_6[\text{Zn}^{2+}\text{Fe}^{3+}(\text{TeO}_3)_3]_2 \cdot n\text{H}_2\text{O}$, $n \leq 3$: Trigonal symmetry enables a fully ordered host-guest structure

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The microporous crystal structure of zemannite was originally described in space group $P6_3/m$ (Matzat 1967; Mandarino et al. 1967; Miletich 1995), later revised to $P6_3$ (Cametti et al. 2017; Missen et al. 2019). Most recently the diffraction pattern of a single-crystal sample was re-investigated using a high-sensitivity Dectris Pilatus pixel detector (Effenberger et al. 2023). Unexpectedly, several uneven low-order $00l$ reflections showed unequivocally verifiable weak intensities clearly violating the 6_3 screw-axis reflection conditions. These observations promoted detailed X-ray crystallographic investigation to be resumed.

The crystal-structure type of zemannite is characterised by a honey-comb like $[\text{Zn}^{2+}\text{Fe}^{3+}(\text{TeO}_3)_3]^{1-}$ framework building channels along $[001]$. It consists of $M_2\text{O}_9$ dimers formed by two face-sharing MO_6 octahedra, $M = (\text{Zn}^{2+}, \text{Fe}^{3+})$ with $\text{Zn}^{2+}:\text{Fe}^{3+} \sim 1:1$. These dimers are linked by $(\text{Te}^{4+}\text{O}_3)^{2-}$ figures and form the channel walls. The channels are filled by the extra-framework constituents, i.e. $0.5 [\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ cations per formula unit in addition to up to 1.5 interstitial H_2O molecules. So far, none of the space-group symmetries $P6_3/m$ or $P6_3$ was compatible with a fully ordered atomic arrangement. In space group $P6_3/m$ there is one $M = (\text{Zn}^{2+}\text{Fe}^{3+})$ position, thus an order of the M atoms is impossible. However, the ionic radii of the two M cations differ suggesting a tentative order and, furthermore, $\text{Fe}^{3+}_2\text{O}_9$ dimers besides $\text{Zn}^{2+}_2\text{O}_9$ dimers are not likely. Ordering of the extra-framework atoms is impossible within the given symmetry constraints for both space groups mentioned above. In the acentric space group the M position splits into two sites, $M1$ and $M2$; an order between Zn^{2+} and Fe^{3+} might be possible but could not be proofed so far (Cametti et al. 2017).

For this work X-ray diffraction data were collected at 298 ± 0.5 K, 200 ± 1 K, and 100 ± 3 K ($2\theta_{\text{max}} = 101.4^\circ$, $\text{MoK}\alpha$ radiation). Careful inspections of the entire images did not show any evidence for satellite reflections in the surrounding of the Bragg-peak positions. Furthermore, there is no hint neither for diffuse scattering nor for the appearance of superstructure reflections. Thus, an incommensurately modulated atomic arrangement or disorder phenomena in neighbouring channels are not likely.

A series of comparative refinement models were performed in the space groups $P6_3/m$ and its subgroups $P6_3$, $P\bar{6}$, and $P3$. Order of the Fe and Zn atoms in the framework is possible in all subgroups of $P6_3/m$. Due to mirror planes parallel to (0001) , space group $P\bar{6}$ allows Fe_2O_9 or Zn_2O_9 dimers, which contradicts the results of *ab initio* calculations (Cametti et al. 2017). A fully ordered atomic arrangement of the one-dimensional extra-framework atoms is possible in $P3$ only (Fig. 1). Refinements confirm the earlier postulated theoretical structure model with $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ octahedra alternating with interstitial H_2O molecules along $[001]$ (Miletich, 1995). The interaction between these structural units as well as the bonding between the host and guest atoms is achieved solely by hydrogen bonds. The final refinements in space group $P3$ yield $R1 \sim 0.025$ for the entire data sets.

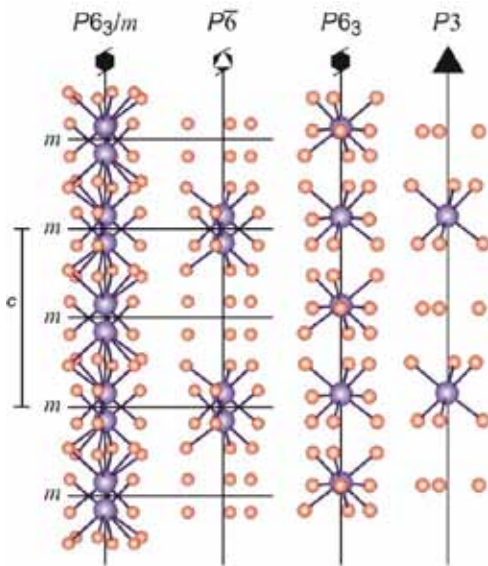


Figure 1. The extra-framework atoms and their distribution (full site multiplicity in the respective space group is shown). Mg and O atom position are shown as blue and red spheres, respectively. In $P3$ full order is achieved without the necessity of partial site occupations.

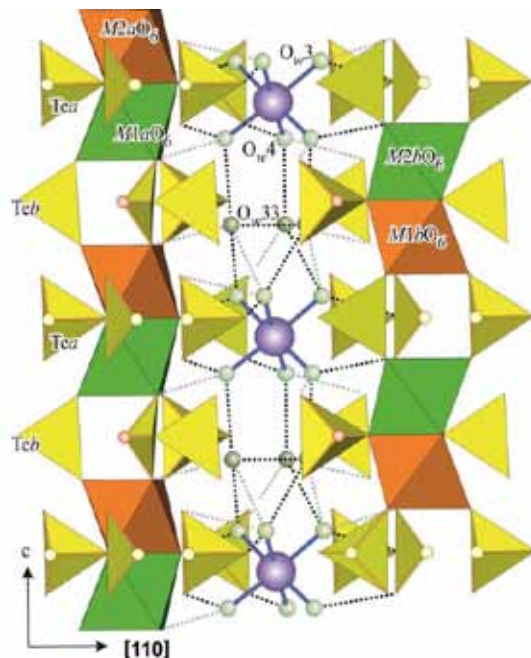


Figure 2. Detail of the atomic arrangement (space-group symmetry $P3$): the host structure consists of M_2O_9 dimers and TeO_3 groups. $M^{2+}O_6$ octahedra with $M = (Zn^{2+}, Fe^{3+})$ are shown in green and $M = (Fe^{3+}, Zn^{2+})$ in brown shades. – The channel is filled by $Mg^{[6]}$ atoms (blue) and H_2O molecules (O atoms in shades of green). Short and long O-H...O hydrogen bridges are indicated as dotted black and grey lines.

In accordance with the observed violation of the 6_3 screw axis, it is evident from crystal-structure refinements and crystal chemical considerations, that the atomic arrangement of zemannite is best described in space group $P3$. Zn^{2+} and Fe^{3+} ions are not fully ordered in the individual MO_6 octahedra but show a predominant occupation that explains the violation of the 6_3 screw axis. It is to be mentioned that neighbouring M_2O_9 dimers are differently orientated with Zn^{2+} respectively Fe^{3+} centred octahedra pointing upwards and downwards, respectively (Fig. 2). In contrast, symmetry $P6_3$ cause a parallel orientation of all dimers.

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