

Structural diversity in new, synthetic zemannite-type phases

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The mineral zemannite (Matzat 1967; Fig. 1), named in honor of Prof. Josef Zemann (1923–2022), has a composition of $[\text{Zn}^{2+}\text{Fe}^{3+}(\text{TeO}_3)_3]_2[\text{Mg}(\text{H}_2\text{O})_6] \cdot n\text{H}_2\text{O}$ ($n \leq 3$), and is the mineral of the MinWien2023 conference. Synthetic zemannite-type phases can be obtained from hydrothermal reactions between transition metal oxides, tellurium dioxide and alkali metal carbonates. In comparison with the usual set-up for a hydrothermal experiment, the drastic reduction of the water content changes the role of water from a typical solvent to a mineralizer. Under these conditions, the formation of numerous new phases with zemannite-type structures was observed (Eder et al. 2023).

The crystal structures of the new zemannite-type phases were determined on basis of single-crystal X-ray diffraction. Like the mineral zemannite itself, the crystal structures of $\text{Fe}_2(\text{TeO}_3)_3$, $\text{Na}_2[\text{Ni}_2(\text{TeO}_3)_3](\text{H}_2\text{O})_{2.5}$, $\text{K}_2[\text{Ni}_2(\text{TeO}_3)_3](\text{H}_2\text{O})$, $\text{K}_2[\text{Zn}_2(\text{TeO}_3)_3](\text{H}_2\text{O})_2$, $\text{Rb}_{1.25}[\text{Co}_2(\text{TeO}_3)_3](\text{H}_2\text{O})_{1.5}$, $\text{Rb}_{1.24}[\text{Mn}_2(\text{TeO}_3)_3](\text{H}_2\text{O})_2$, and $\text{Na}_{1.79}\text{Mg}_{0.11}[\text{Mg}_2(\text{TeO}_3)_3](\text{H}_2\text{O})_{3.86}$ show hexagonal metrics, with $a \approx 9.3$ Å and $c \approx 7.7$ Å. Relative to this unit-cell, different kinds of superstructures are realized for $\text{Na}_2[\text{Cu}_2(\text{TeO}_3)_3](\text{H}_2\text{O})_{1.5}$ (threefold), $\text{K}_2[\text{Cu}_2(\text{TeO}_3)_3](\text{H}_2\text{O})_2$ (twofold), $\text{K}_2[\text{Co}_2(\text{TeO}_3)_3](\text{H}_2\text{O})_{2.5}$ (twofold and incommensurately modulated), $\text{Rb}_{1.5}[\text{Mn}_2(\text{TeO}_3)_3](\text{H}_2\text{O})_{1.25}$ (fourfold), and $\text{Cs}[\text{Mn}_2(\text{TeO}_3)_3](\text{H}_2\text{O})$ (fourfold).

The formation of these superstructures can be attributed to several influences. Variable water contents (compounds with zemannite-type structures are known for their zeolitic properties (Miletich 1995)), the space requirements of large alkali metal cations like Rb^+ or Cs^+ , and Jahn–Teller distortions of the coordination polyhedra of certain framework atoms like Cu^{II} or Mn^{III} play crucial roles in this respect.

Another aspect of zemannite-type crystal structures is the nature and distribution of the contents inside the large hexagonal channels perforating the framework. For most of the investigated phases, alkali metal cations and crystal water molecules are displaced up to 2 Å from the channel center and are disordered around the 6_3 axis (or other symmetry elements containing a threefold rotation axis). In the superstructures of $\text{Rb}_{1.5}[\text{Mn}_2(\text{TeO}_3)_3](\text{H}_2\text{O})_{1.25}$ and $\text{Cs}[\text{Mn}_2(\text{TeO}_3)_3](\text{H}_2\text{O})$, ordered channel-contents were observed. $\text{Fe}_2(\text{TeO}_3)_3$ has empty channels, which causes some Te^{IV} atoms of the framework to “tilt” towards the channel center. In $\text{Na}_{1.79}\text{Mg}_{0.11}[\text{Mg}_2(\text{TeO}_3)_3](\text{H}_2\text{O})_{3.86}$, both Na^+ and Mg^{2+} cations inhabit the channels together with H_2O molecules, and the superposition of their respective environments can be noticed in the crystal structure refinement.



Figure 1. Zemannite—the mineral of the meeting. Photo: S. Wolfsried

Eder F, Marsollier A, Weil M (2023): Structural studies on synthetic $A_{2-x}[\text{M}_2(\text{TeO}_3)_3] \cdot n\text{H}_2\text{O}$ phases ($A = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$; $M = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) with zemannite-type structures. - Mineral Petrol <https://doi.org/10.1007/s00710-023-00814-5>

Matzat E (1967): Die Kristallstruktur eines unbenannten zeolithartigen Tellurminerals, $\{(\text{Zn}, \text{Fe})_2[\text{TeO}_3)_3\} \text{Na}_x \text{H}_{2-x} \cdot y\text{H}_2\text{O}$. - Tschermaks Mineral Petrogr Mitt 12, 108–117

Miletich R (1995): The synthetic microporous tellurites $\text{Na}_2[\text{M}_2(\text{TeO}_3)_3] \cdot 3\text{H}_2\text{O}$ ($M = \text{Zn}, \text{Co}$): crystal structure, de- and rehydration, and ion exchange properties. - Monatsh Chem 126, 417–430