The order-disorder (OD) structures of $Rb_2Zn(TeO_3)(CO_3)\cdot H_2O$ and $Na_2Zn_2Te_4O_{11}$

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The crystal chemistry of oxidotellurates(IV) is dominated by the stereochemically active $5s^2$ electron lone pair at the Te^{IV} atom. Its large space consumption often leads to the formation of modular structure units like clusters, chains, layers or channel structures.

Two newly discovered compounds, $Rb_2Zn(TeO_3)(CO_3)\cdot H_2O$ and $Na_2Zn_2Te_4O_{11}$, both were synthesized in a solid state reaction under the presence of water as a mineralizer. They both crystallize with order-disorder (OD) structures [1] comprising of layers and feature a high stacking fault probability. Both cases are unusual in that the OD character is due to different translation lattices of the adjacent layers.

$Rb_2Zn(TeO_3)(CO_3)\cdot H_2O$ is built of an alternation of two kinds of crystal-chemical layers A^1 and A^2 (both non-polar with respect to the stacking direction) extending parallel to (100). The A^1 layers (Te1, Rb1, Zn1) possess higher (pseudo-)symmetry ($A(1)2/m1$) than the A^2 layers (Rb2, CO_3, H_2O) ($P(1)2_1/c1$), which leads to an ambiguity in the arrangement of the layers, as the A-centering of the A^1 layers results in higher translational symmetry. Of the two possible MDO (maximum degree of order) polytypes [2], the preference for the MDO_2 (...$A^1A^{2+}A^1A^{2-}$... ; Fig. 1a) stacking can be identified in the diffraction pattern (Fig. 1b) as well as diffuse streaks due to stacking disorder.

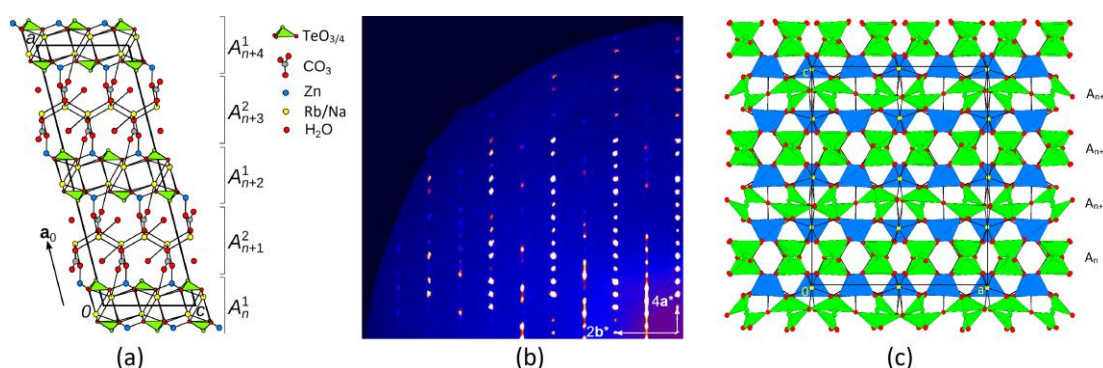Fig. 1: (a) The crystal structure of $Rb_2Zn(TeO_3)(CO_3)\cdot H_2O$ viewed down [010]. (b) $(h2l)^*$ plane of $Rb_2Zn(TeO_3)(CO_3)\cdot H_2O$. The reciprocal basis vectors are given with respect to the MDO_2 polytype. (c) The crystal structure of $Na_2Zn_2Te_4O_{11}$ viewed down [010].

$Na_2Zn_2Te_4O_{11}$ can be considered as a category I OD structure built of one kind of non-polar layers A_n. The layers are formed by $[Te_4O_{11}]$-groups, the Na and Zn atoms are located at the layer interfaces and assigned to both adjacent layers. The A_{2n} ($n \in \mathbb{Z}$) layers have the (idealized) $P2_12(2)$ symmetry with $a=2b$, the A_{2n+1} layers $P22_1(2)$ symmetry with $b=2a$ (the lattices are rotated by 90°). The different basis vectors of adjacent layers result in two equivalent ways of placing the A_{n+1} layer relative to the A_n layer. The diffraction pattern consists of sharp reflections of the family structure and diffuse characteristic reflections of the preferred MDO_2 polytype (Fig. 1c). Another feature of the diffraction pattern are non-space group extinctions which can be explained by the diffraction patterns of the two substructures each formed by the A_{2n} and A_{2n+1} ($n \in \mathbb{Z}$) layers, respectively.

[1] Dornberger-Schiff, K., Grell-Niemann, H. On the Theory of Order-Disorder (OD) Structures. *Acta Crystallogr.* **14**, 167–177 (1961).

[2] Dornberger-Schiff, K., Grell, H. Geometrical Properties of MDO Polytypes and Procedures for Their Derivation. II. OD Families Containing OD Layers of M > 1 Kinds and Their MDO Polytypes. *Acta Crystallogr*. A**38**, 491–498 (1982).