

MS17-2-3 Cross-shaped diffuse scattering in $K_2Cu_3Te_4O_{12}$ and $Na_2Cu_3Te_4O_{12}$
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Abstract

$K_2Cu_3Te_4O_{12}$ and $Na_2Cu_3Te_4O_{12}$ were obtained in solid state reactions with water as a mineralizer. Both crystal structures

can be derived from a tetragonal family structure ($P4/ncc$; $a_0 = 8.426(9) \text{ \AA}$, $c_0 = 6.403(6) \text{ \AA}$ ($K_2Cu_3Te_4O_{12}$) and $a_0 = 8.298(2) \text{ \AA}$, $c_0 = 6.1633(12) \text{ \AA}$ ($Na_2Cu_3Te_4O_{12}$)) with positional disorder of Te and K/Na around the same crystallographic site, and of the O atoms. In the diffraction patterns of $K_2/Na_2Cu_3Te_4O_{12}$, diffuse streaks in two perpendicular directions resulting in cross-like shapes on the $l = n + \frac{1}{3}$ and $l = n + \frac{2}{3}$ ($n \in \mathbb{Z}$) planes are observed (Figure 1). Even though the family structures of $K_2Cu_3Te_4O_{12}$ and $Na_2Cu_3Te_4O_{12}$ are isotypic, the orientation of the streaks is different: In $K_2Cu_3Te_4O_{12}$ they are parallel to $[100]$, in $Na_2Cu_3Te_4O_{12}$ parallel to $[110]$ with respect to the family structure. The crystal structure of $K_2Cu_3Te_4O_{12}$ is built from ordered ${}^1_{\infty}[K_2Te_4O_{12}]$ -rods with the sequence [...K-Te-Te-K-Te-Te...] oriented along $[001]$, which are connected by the Cu atoms. These rods have a translational period c_{rod} of $3c_0$ and the rod group $P2/c11$. The ${}^1_{\infty}[K_2Te_4O_{12}]$ -rods have two possible orientations, which differ by a rotation of 90° around $[001]$ (Figure 2; K/Te at different z values are drawn lighter/darker).

The cross-shaped diffuse scattering can be explained by dividing the structure into two substructures, each consisting of all rods with the same orientation, which are disordered independently from each other. For each substructure, the

disorder can be modelled by a variable stacking of layers oriented in (100) or (010) . The rods of an adjacent layer are translated by $\pm \frac{1}{6} c_{rod}$ or $+\frac{1}{2} c_{rod}$, though the $+\frac{1}{2}$ contact is not realized since it would lead to a K...K distance of only $3.301(9) \text{ \AA}$. The $\pm \frac{1}{6}$ layer pairs are symmetrically equivalent and therefore the stacking can be described by order-disorder (OD) theory [1]. One of the two maximum degree of order (MDO) polytypes [2] (consisting of only either $+\frac{1}{6}$

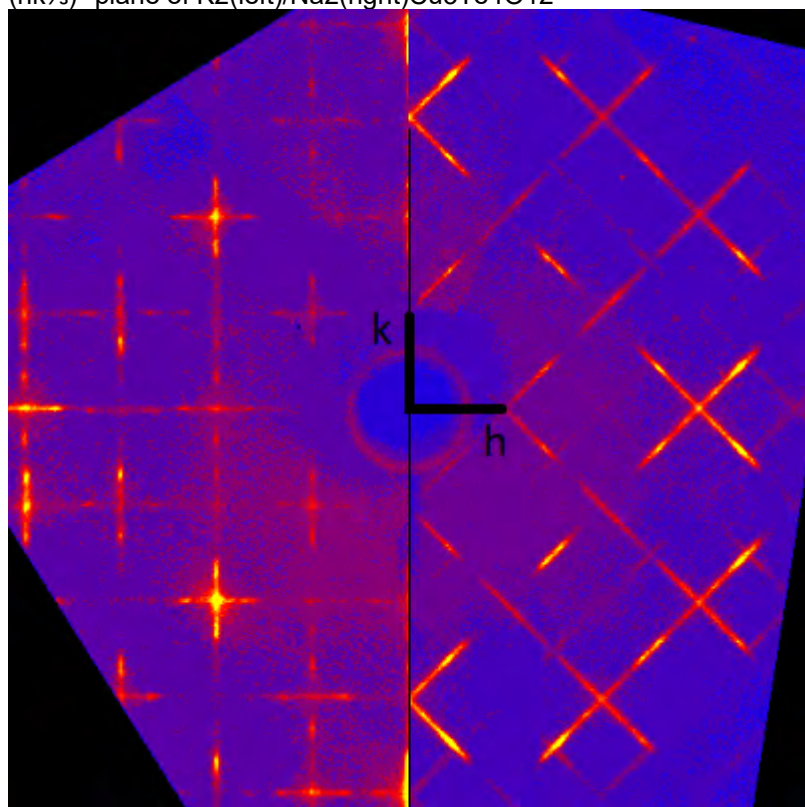
or $-\frac{1}{6}$ contacts; space group $P1$, $a = a_0$, $b = 3b_0$, $c = 3c_0$) is in accordance with the characteristic reflections, making it the preferred stacking.

For $Na_2Cu_3Te_4O_{12}$, the situation is more complicated. The smaller size of the Na atoms allows $+\frac{1}{2} c_{rod}$ contacts as well. It is not possible to use OD-theory for modelling because not all pairs of layers are equivalent. For both structures the disordered stacking of layers is modelled using DIFFAX [3] and is compared with precession images of the single crystal diffraction studies.

References

- [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.* **A38**, 491–498 (1982).
- [3] Treacy, M. M. J., Newsam, J. M., Deem, M. W. A General Recursion Method for Calculating Diffracted Intensities From Crystals Containing Planar Faults. *Proc. Roy. Soc. Lond.* **A433**, 499–520 (1991).

$(hk\frac{1}{3})^*$ plane of K2(left)/Na2(right)Cu3Te4O12



Simplified family structure of K2Cu3Te4O12

