

Polymorphism in $\text{Cu}_{20}\text{Te}_{11}\text{Cl}_3$

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Coinage metal polychalcogenide halides are an intriguing class of materials, and many representatives are solid ion conductors and thermoelectric materials. The compounds show high ion mobility, polymorphism, and various attractive interactions in the cation and anion substructures. $\text{Cu}_{20}\text{Te}_{11}\text{Cl}_3$ is trimorphic, with order-disorder phase transitions occurring at 288 and 450 K. As shown in Figure 1, the α - β -phase transition occurs via symmetry reduction from the hexagonal to the orthorhombic crystal system that is attended by twinning and additional quintuplication of the **a**- and duplication of the **c**-axis. [1]

$\text{Cu}_{20}\text{Te}_{11}\text{Cl}_3$ is identified as a solid Cu-ion conductor that features dynamic disorder in the cation and statistical disorder in the anion substructure. The compound structurally fits well into the class of

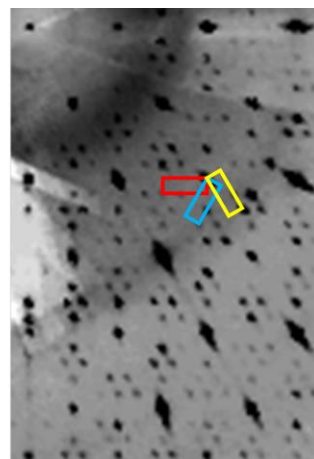
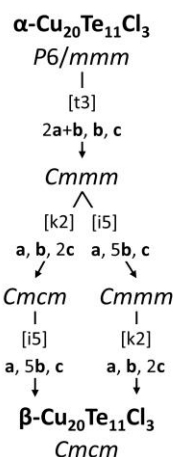


Figure 1. Projection of five planes (hk0-4) of the single crystal XRD pattern data of $\beta\text{-Cu}_{20}\text{Te}_{11}\text{Cl}_3$ and Bärnighausen tree for the symmetry reduction from α - to $\beta\text{-Cu}_{20}\text{Te}_{11}\text{Cl}_3$.

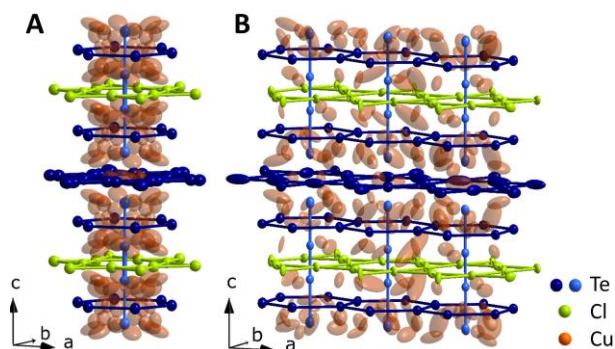


Figure 2. Structure features of α - and $\beta\text{-Cu}_{20}\text{Te}_{11}\text{Cl}_3$.

coinage metal polychalcogenide halides because it is built of topologic anion nets stacked in one direction that are interpenetrated by partially covalently bonded chalcogene strands just like the other representatives $\text{Cu}_{9.1}\text{Te}_4\text{Cl}_3$ and $\text{Ag}_{10}\text{Te}_4\text{Br}_3$. [2, 3] A new structure feature also containing covalently bonded chalcogen is the disordered 6.3.6.3 Te net. This net can be described by a disordered arrangement of $[\text{Te}_2]^{2-}$ dumbbells. Structure features of α - to $\beta\text{-Cu}_{20}\text{Te}_{11}\text{Cl}_3$ are shown in Figure 2.

- [1] Vogel A, Nilges T. Ion Dynamics and Polymorphism in $\text{Cu}_{20}\text{Te}_{11}\text{Cl}_3$. *Inorg. Chem.* 60(20), 15233–15241 (2021).
- [2] Vogel A, Miller T, Hoch C, Jakob M, Oeckler O, Nilges T. $\text{Cu}_{9.1}\text{Te}_4\text{Cl}_3$: A Thermoelectric Compound with Low Thermal and High Electrical Conductivity. *Inorg. Chem.* 58(9), 6222–6230 (2019).
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A.V. acknowledges support by DFG under Germany's Excellence Strategy (EXC 2089/1-390776260). We thank Dr. Jens Meyer and Tom Faske of STOE & Cie GmbH, Darmstadt, Germany, for the conduction of high-temperature single-crystal measurements on one of their newly developed measuring systems.