

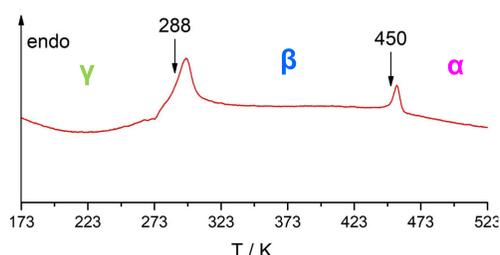


Abstract

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. 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 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.

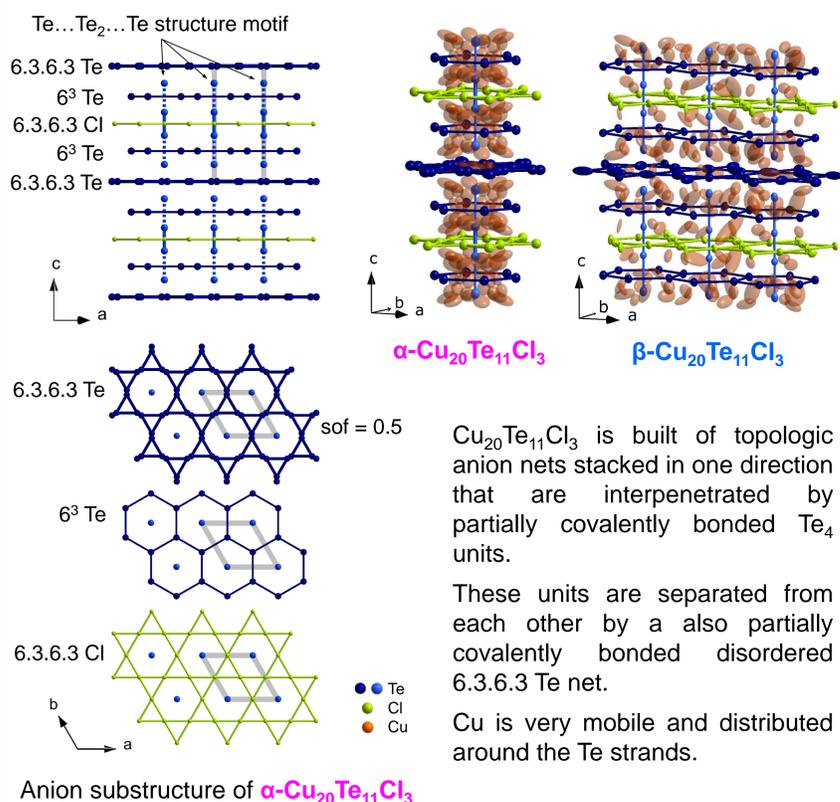
Polymorphism

Two endothermic signals in DCS can be assigned the γ - β - and β - α -phase transition



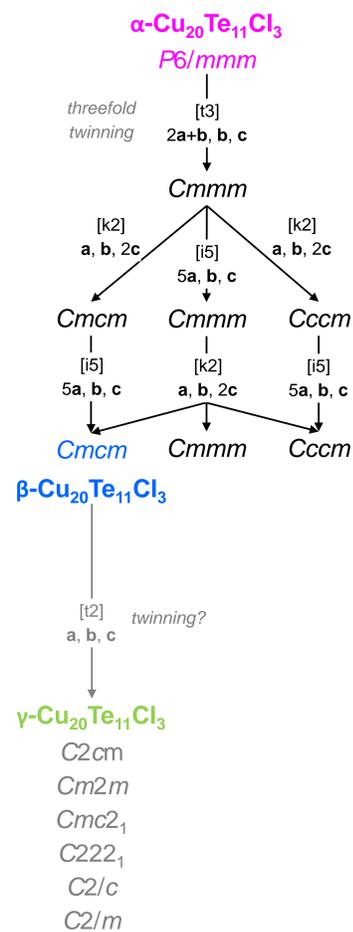
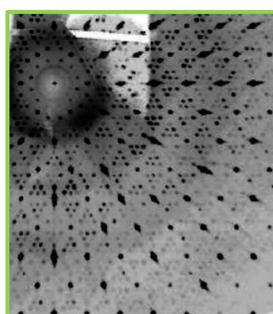
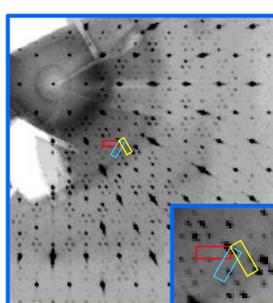
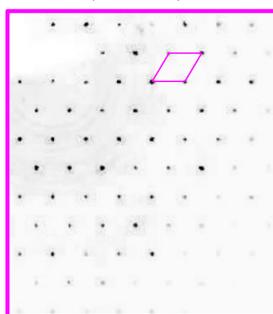
T / K

Crystal structure



Temperature-dependent single crystal XRD

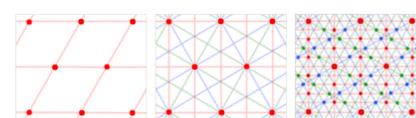
(h k l=0-4)



The diffraction image of $\beta\text{-Cu}_{20}\text{Te}_{11}\text{Cl}_3$ shows complex superstructure reflections.

The pattern can be derived by a 3-fold twinned C-centred orthorhombic unit cell.

Space group was determined by establishing a Bärnighausen tree featuring all possible symmetry reductions leading from $P6/mmm$ to the proposed unit cell. Possible resulting space groups are $Cmcm$, $Cmmm$ and $Cccm$. Best refinement results were achieved with $Cmcm$.



$a = 7.3 \text{ \AA}$
 $c = 14.8 \text{ \AA}$

$a = 7.3 \text{ \AA}$
 $b = 12.6 \text{ \AA}$
 $c = 14.8 \text{ \AA}$

$a = 36.4 \text{ \AA}$
 $b = 12.6 \text{ \AA}$
 $c = 29.6 \text{ \AA}$

$\gamma\text{-Cu}_{20}\text{Te}_{11}\text{Cl}_3$ has similar unit cell dimensions. The phase transition might occur via a *translationengleiche* symmetry reduction to the orthorhombic or monoclinic crystal system that is probably attended by additional twinning.

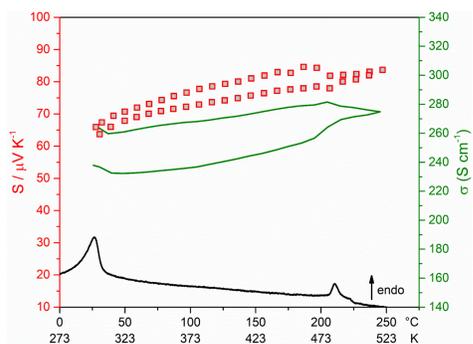
Structure refinement is still under investigation.

	$\alpha\text{-Cu}_{20}\text{Te}_{11}\text{Cl}_3$	$\beta\text{-Cu}_{20}\text{Te}_{11}\text{Cl}_3$
R1 / wR2 [$I > 3\sigma(I)$]	0.0387 / 0.0723	0.0353 / 0.0544
R1 / wR2 (all data)	0.0569 / 0.0794	0.0931 / 0.0874

Thermoelectric properties

$\text{Cu}_{20}\text{Te}_{11}\text{Cl}_3$ is thermoelectric compound.

With estimated thermal conductivity between 0.3 and 0.6 $\text{W m}^{-1} \text{K}^{-1}$ (typical for the substance class) we predict a maximum ZT value between 0.15 and 0.3 at 500 K.

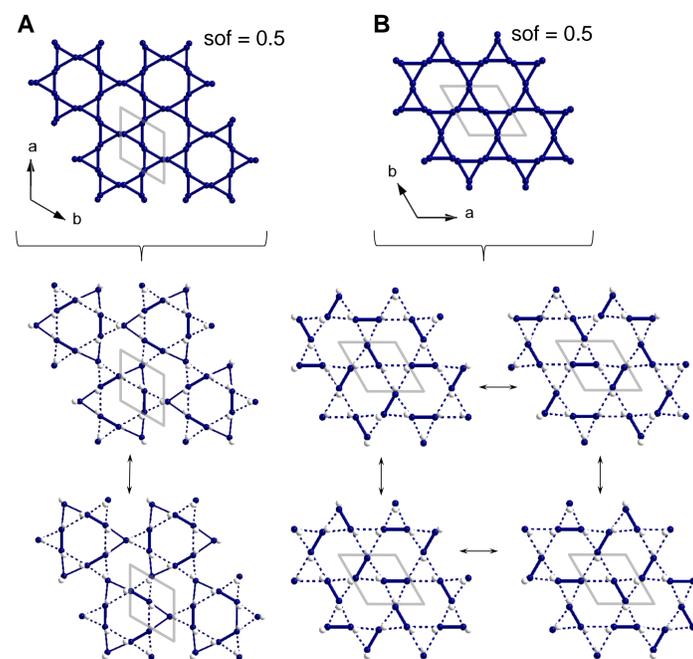


Disorder of the 6.3.6.3 Te net

The nature of the disordered net can be described by two different sets of resonance structures: $[\text{Te}_2]^{2-}$ dumbbells with additional coordinating Te^{2-} ions (A) or dumbbells only (B).

The total charge of the anion substructure differs between $[\text{Te}_{11}\text{Cl}_3]^{21-}$ (A) and $[\text{Te}_{11}\text{Cl}_3]^{20-}$ (B). We strongly favor model B because of the higher agreement with the measured and refined Cu content.

The picture shows $\alpha\text{-Cu}_{20}\text{Te}_{11}\text{Cl}_3$, but the net is not ordered in $\beta\text{-Cu}_{20}\text{Te}_{11}\text{Cl}_3$ and there is no hint towards ordering in $\gamma\text{-Cu}_{20}\text{Te}_{11}\text{Cl}_3$, so we assume static disorder here.



Conclusion

$\text{Cu}_{20}\text{Te}_{11}\text{Cl}_3$ shows an intriguing structure chemistry and is characterized by two order-disorder phase transitions. It is built of topologic anion nets stacked in one direction that are interpenetrated by partially covalently bonded chalcogene strands. A structure feature also containing covalently bonded chalcogen is the disordered 6.3.6.3 Te net. This net can be described by two models: a disordered arrangement of $[\text{Te}_2]^{2-}$ dumbbells or two statistically distributed distorted 6.3.6.3 Te nets in an opposite orientation. Ordering of that disordered 6.3.6.3 Te net might be achieved by modification of the cell parameters by the implementation of higher or lower homologues into the crystal structure.

References

- [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).
- [3] Lange S, Bawohl M, Wilmer D, Meyer H-W, Wiemhöfer H-D, Nilges T. Polymorphism, Structural Frustration, and Electrical Properties of the Mixed Conductor $\text{Ag}_{10}\text{Te}_4\text{Br}_3$. *Chem. Mater.* 19(6), 1401–1410 (2007).