$Cu_3Se_yTe_{2-y}$: A new representative of transition metal chalcogenides

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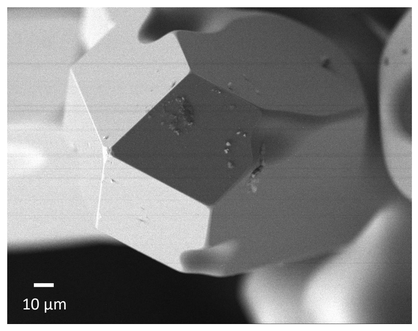
Motivation

The field of thermoelectric materials has experienced great research interest over the last decades due to their ability of creating an electric field when a heat gradient is applied. Therefore, they open up promising applications in the conversion of waste heat to increase efficiencies in all energy related processes. Except for the well known Bi_2Te_3 ,which shows high thermoelectric performance especially in temperature ranges near room temperature, various other materials have been studied.[1] The classes of coinage metal chalcogenides and chalcogenide halides revealed various suitable candidates because of their high ionic conductivity, low band gaps as well as low thermal conductivity.[2,3] The new solid solution $Cu_3Se_yTe_{2-y}$ with y = 0.4 – 1.4 crystalizes in a cubic space group where the copper atoms are distorted tetrahedrally coordinated by the chalcogenide atoms. The cell volume as a function of selenium content shows good agreement with Vegard's law and the material is thermally stable up to 673 K. Due to its narrow band gap on the order of a few millivolts combined with a relatively low thermal conductivity it shows reasonable thermoelectric performance in the range close to room temperature.

Synthesis

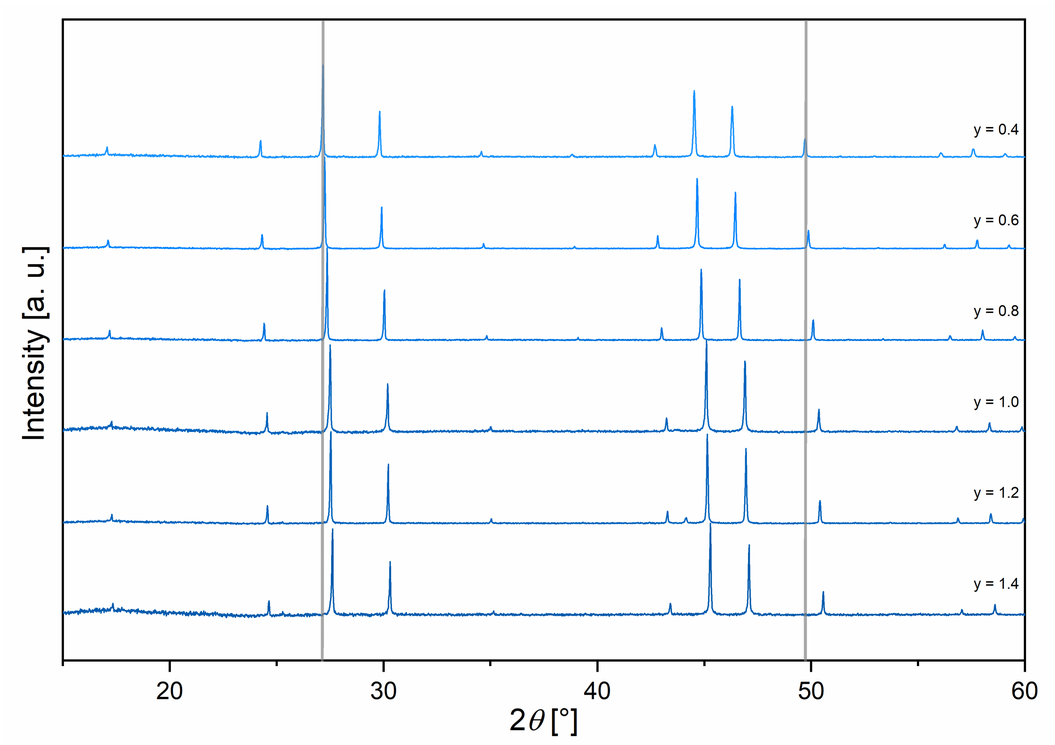
single- and polycrystalline samples are grown at 723 K in a copper chloride supported solid state reaction under inert conditions

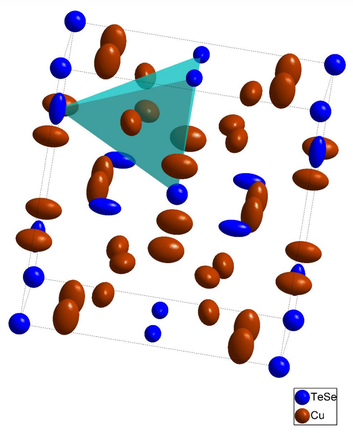
SEM/EDX/XPS

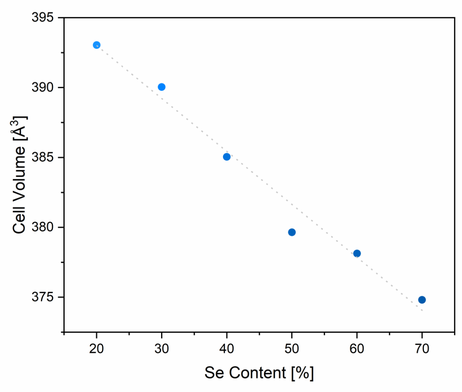


- tendency in **Se:Te ratio was proven** by EDX
- less then 1 at% Cl is detected in the crystals by EDX
- higher amounts of chlorine detected on surface by XPS
  ➡ surface defects may stabilize the crystals

Crystallographic Characterization

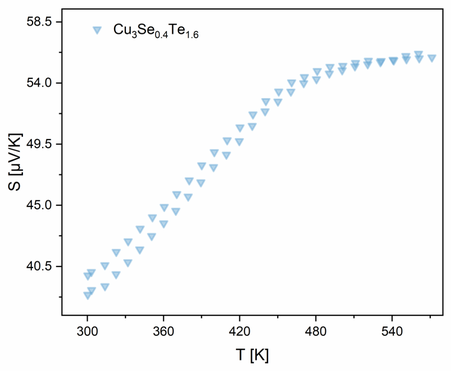


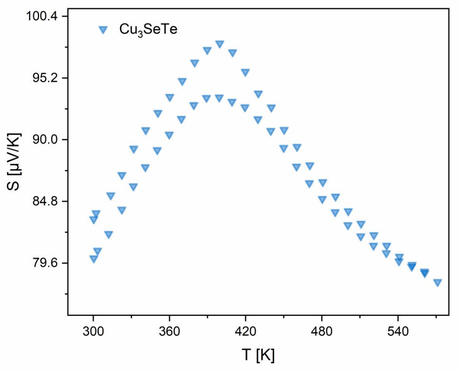


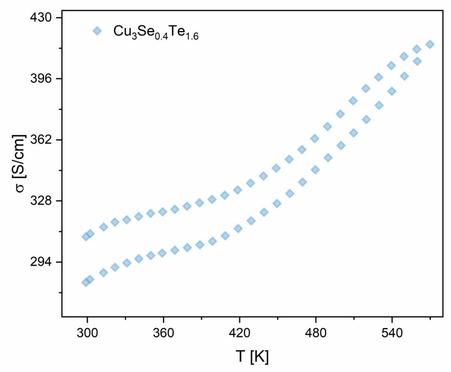


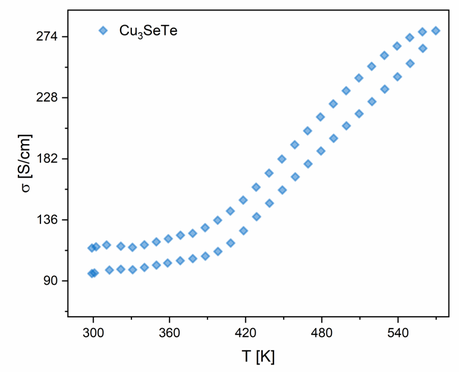
- $Cu_3Se_yTe_{2-y}$ crystalizes in cubic space group $\boldsymbol{Pm\bar{3}n}$ **(No. 223),** copper distorted tetrahedraly coordinated
- solid solution behaves in agreement to Vegard's law for 20% - 70% selenium content
- lattice parameters ranging from **a = 7.2100(4) Å** for y = 1.4 to **a = 7.3250(6) Å** for y = 0.4

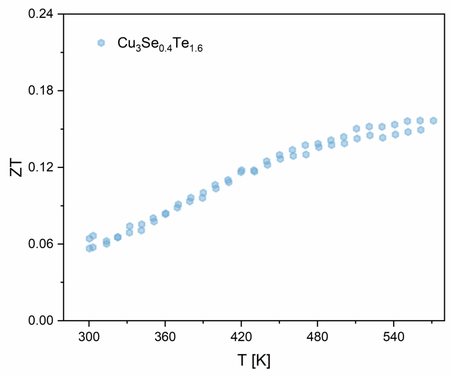
Thermoelectric Performance

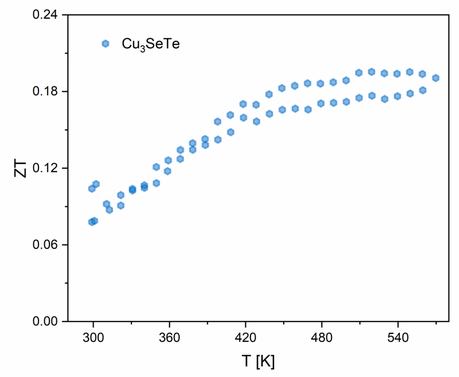






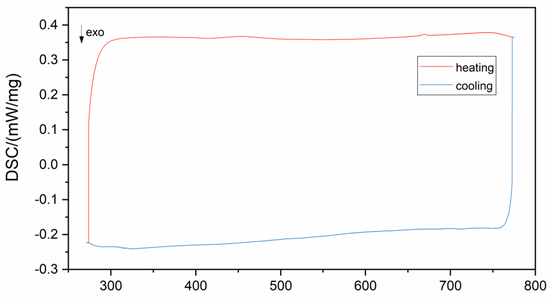


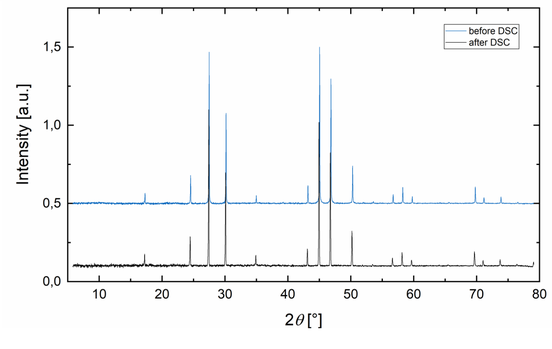




- maximum Seebeck coefficients of **98 µV/K** (y = 1) and **66 µV/K** (y = 0.4) were achieved
- band gaps are therefore estimated to **0.06 – 0.08 eV** by Goldshmid&Sharp's method
- electrical conductivities in a range between **~100 – 400 S/cm** combined with low thermal conductivities of **0.26 – 0.52 W/mK** enable thermoelectic figure of merit ZT of **0.2** already at 450 K

Thermal Analysis





- Cu_3SeTe shows no significant thermal effects between 273 K and 673 K
- after three consecutive DSC cycles up to 773 K, the formation of small amounts of Cu_2Se is observed
- this temperature stability would enable applications in a suited range near room temperature, e.g. for car exhausts

Conclusion

The system $Cu_3Se_yTe_{2-y}$ is synthesized and characterized in a range of y = 0.4-1.4. It crystalizes in the cubic space group $Pm\bar{3}n$, where the copper ions are distorted tetrahedrally coordinated by chalcogenide anions. The material is thermally stable up to 673 K. The reasonable electrical conductivity as well as the narrow band gap of ~0.06 – 0.08 eV identify the materials as suitable candidates for thermoelectric applications. In combination with the very low thermal conductivity of 0.26 –0.52 W/mK ZT values up to 0.19 could be reached already at 450 K. Nanostructuring and especially an improve in electrical conductivity by chemical doping would deliver promising approaches to further improve the materials thermoelectric performance at ambient temperatures.

References

[1] Mamur, H., et al. Renewable and Sustainable Energy Reviews. 824159-4169, **2018**.
[2] Nilges, T., et al. Nat Mater. 8(2)101-8, **2009.**
[3] Vogel, A., et al. Inorganic Chemistry. 58(9)6222-6230, **2019.**