# Se/S anion engineering of $Cu_{6.4}Te_{2.2}Se_{1.8-x}S_x$ as a low-tellurium thermoelectric material for cooling applications


**Adrianna Lis[1], Oleksandr Cherniushok[1], Mykola Maksymuk[1], G. Jeffrey Snyder[2], Krzysztof T. Wojciechowski[1], Taras Parashchuk[1]**

*[1]Thermoelectric Research Laboratory, Department of Inorganic Chemistry, Faculty of Materials Science and Ceramics, AGH University of Krakow, Mickiewicza Ave. 30, 30-059 Krakow, Poland*

*[2]Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA*


## Introduction

Thermoelectric materials for near-room-temperature cooling are predominantly based on $Bi_2Te_3$ compounds. However, their high tellurium content raises concerns related to cost, limited elemental availability, and environmental impact, which may restrict their large-scale application. Cu-based chalcogenides have emerged as promising low-tellurium alternatives due to their intrinsically low thermal conductivity and favorable electronic transport properties. Nevertheless, their highest thermoelectric performance is typically achieved well above room temperature, limiting their application in solid-state cooling. In this work, Se/S anion engineering is applied to the $Cu_{6.4}Te_{2.2}Se_{1.8-x}S_x$ system to shift its optimal thermoelectric performance toward lower temperatures and enable its potential use in near-room-temperature cooling.

## Structural analysis

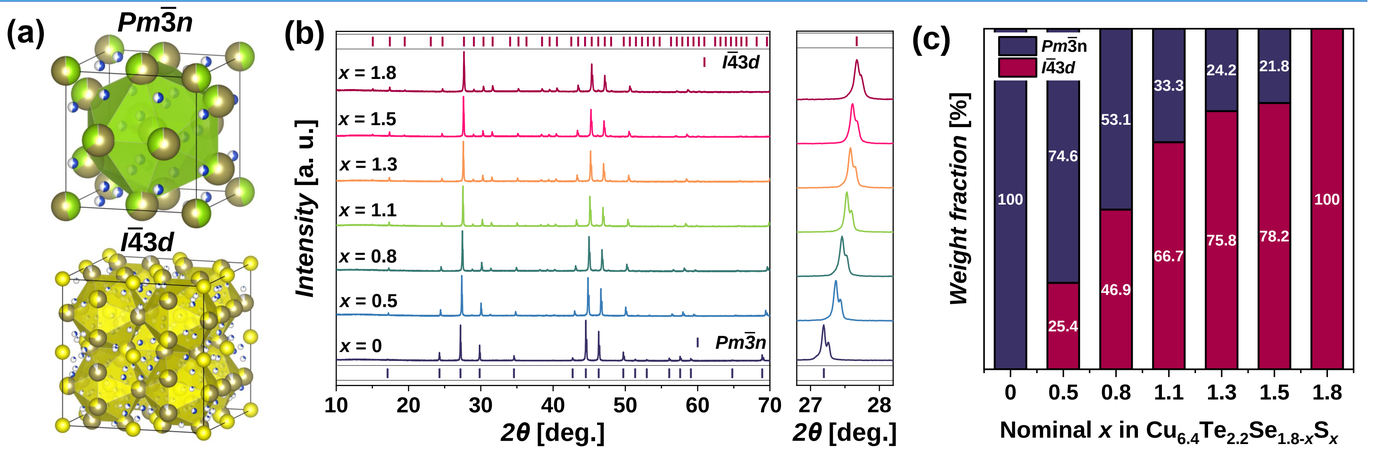



**Fig. 1** (a) Crystal structures of the $Pm\bar{3}n$ and $I\bar{4}3d$ phases. (b) Powder X-ray diffraction patterns of the $Cu_{6.4}Te_{2.2}Se_{1.8-x}S_x$ materials. (c) Refined weight fractions of the two phases for all samples.

## Microstructural analysis

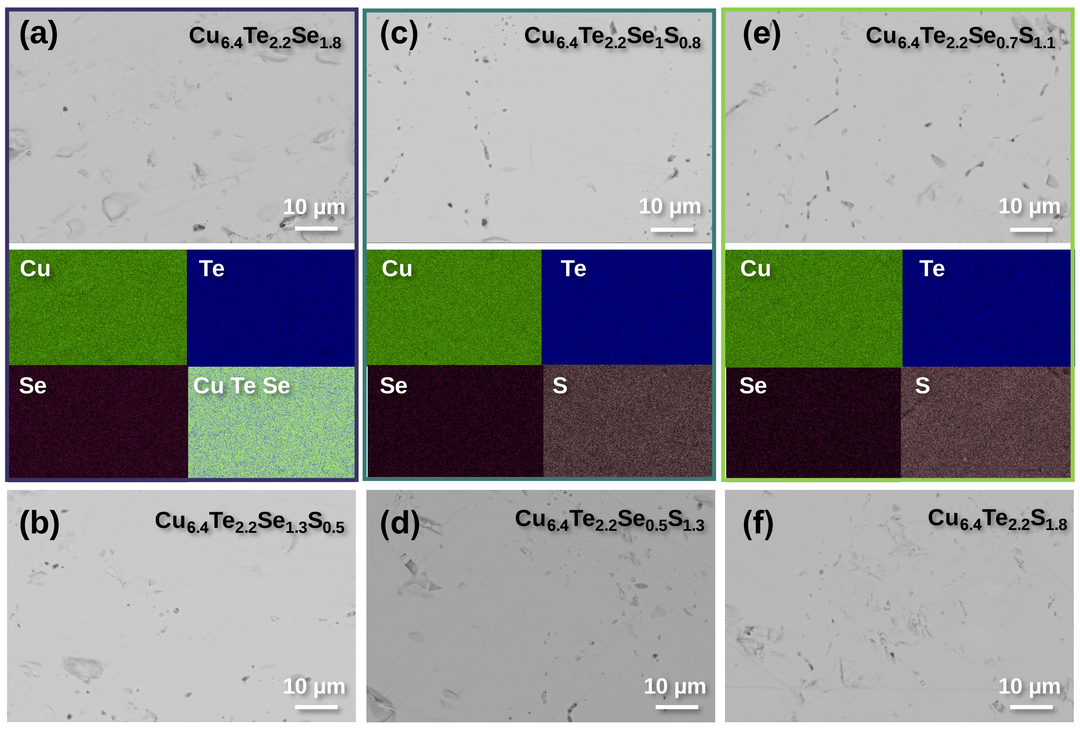



**Fig. 2** SEM micrographs and corresponding EDS elemental distribution maps of selected $Cu_{6.4}Te_{2.2}Se_{1.8-x}S_x$ samples: (a) x = 0, (b) *x* = 0.5, (c) *x* = 0.8, (d) *x* = 1.3, (e) *x* = 1.1, and (f) *x* = 1.8.

## Local thermoelectric homogeneity

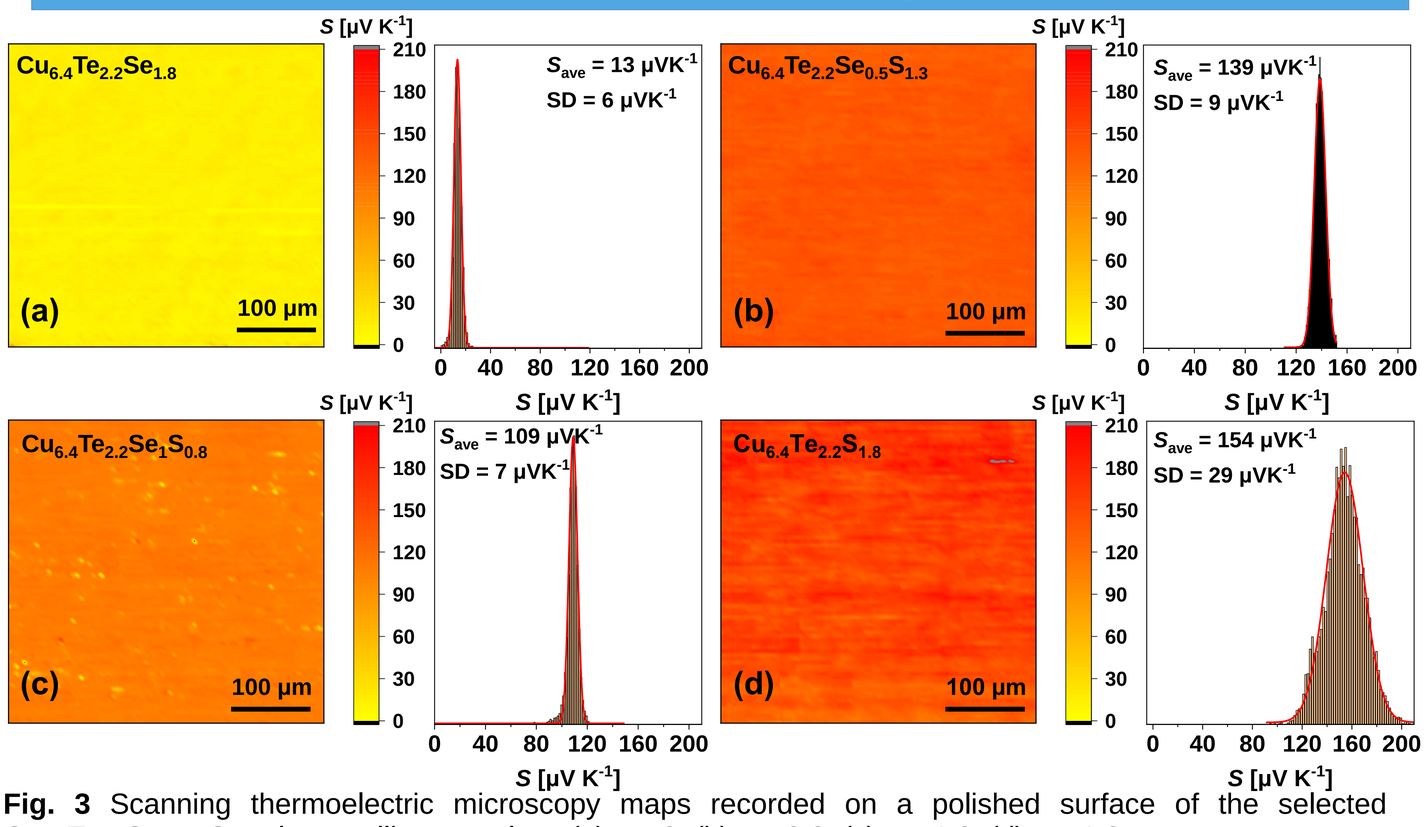
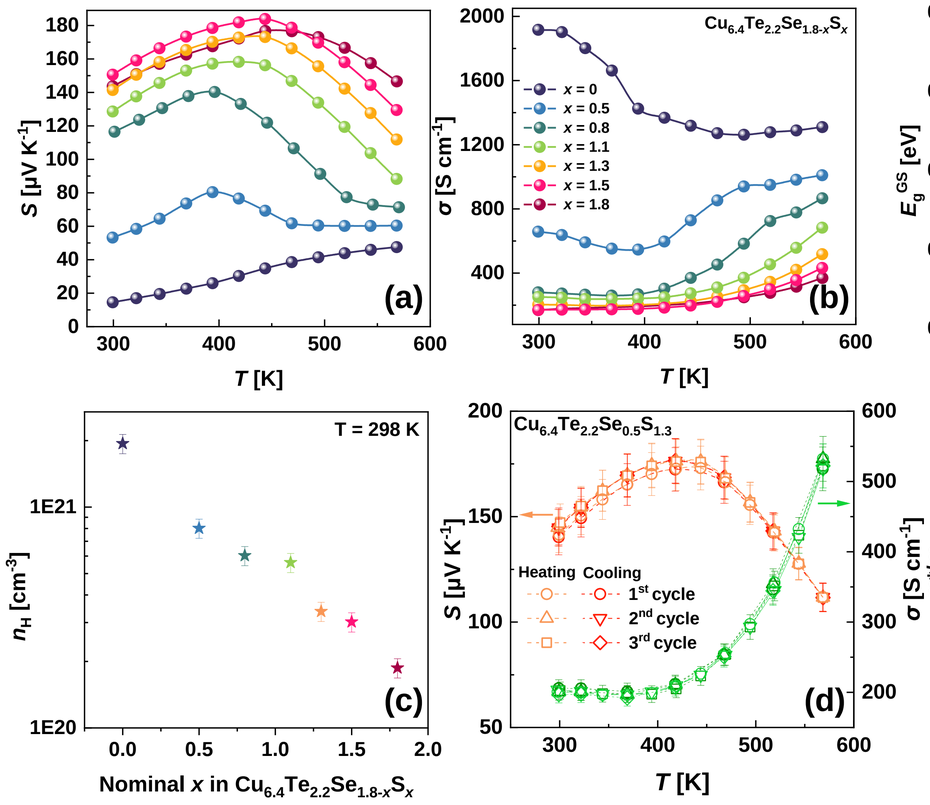
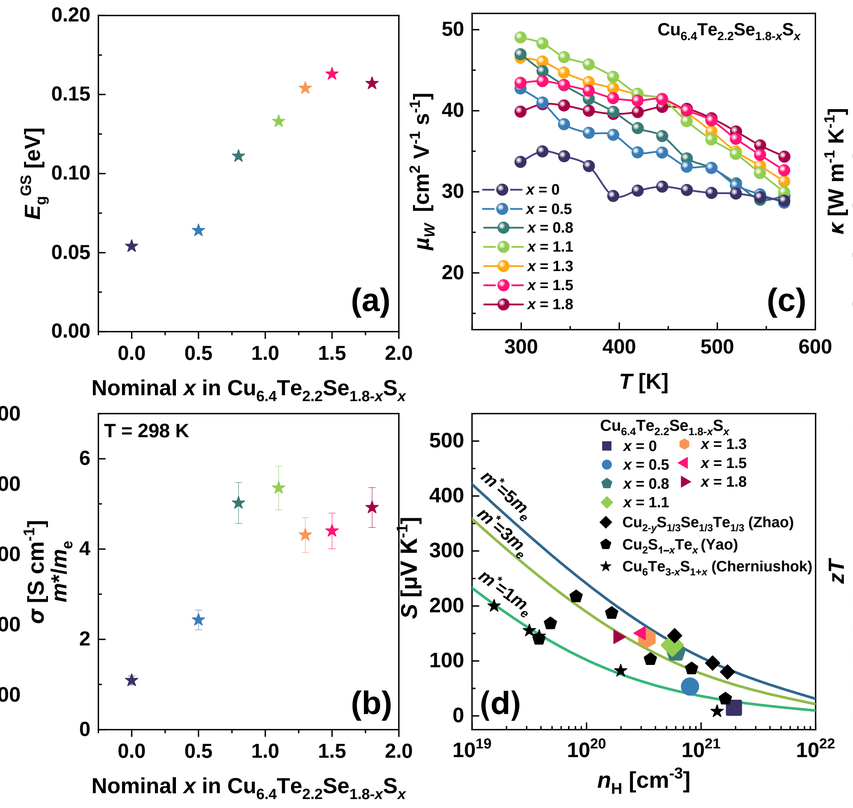



**Fig. 3** Scanning thermoelectric microscopy maps recorded on a polished surface of the selected $Cu_{6.4}Te_{2.2}Se_{1.8-x}S_x$ polycrystalline samples: (a) *x* = 0, (b) *x* = 0.8, (c) *x* = 1.3, (d) *x* = 1.8.

## Electronic transport




## Electronic transport mechanism




## Thermal transport & TE performance

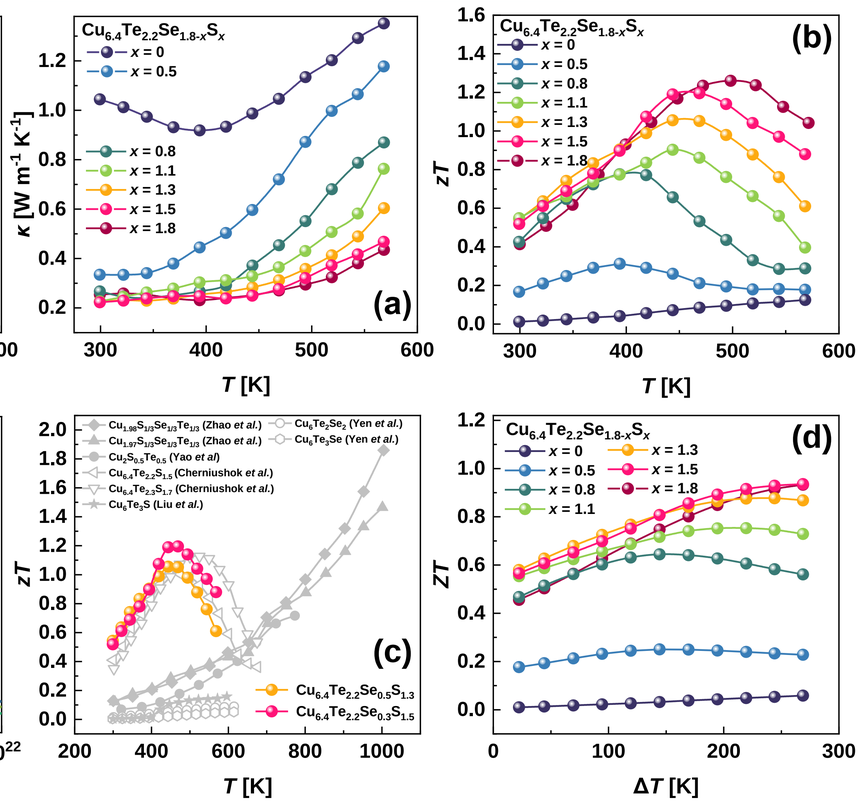



**Fig. 4** Temperature dependence of (a) Seebeck coefficient and (b) electrical conductivity. (c) Carrier concentration at 298 K as a function of S content. (d) Thermal cycling stability of $Cu_{6.4}Te_{2.2}Se_{0.5}S_{1.3}$.

**Fig. 5** Composition dependence of (a) $E_g^{GS}$ and (b) $m^*$. (c) Temperature-dependent weighted mobility. (d) Pisarenko plot with Kane-model calculations at 298 K.

**Fig. 6** Temperature dependence of (a) thermal conductivity and (b) *zT*. (c) Comparison of *zT* with other Cu-based chalcogenides. (d) Device *ZT* as a function of Δ*T*.

## Cooling performance

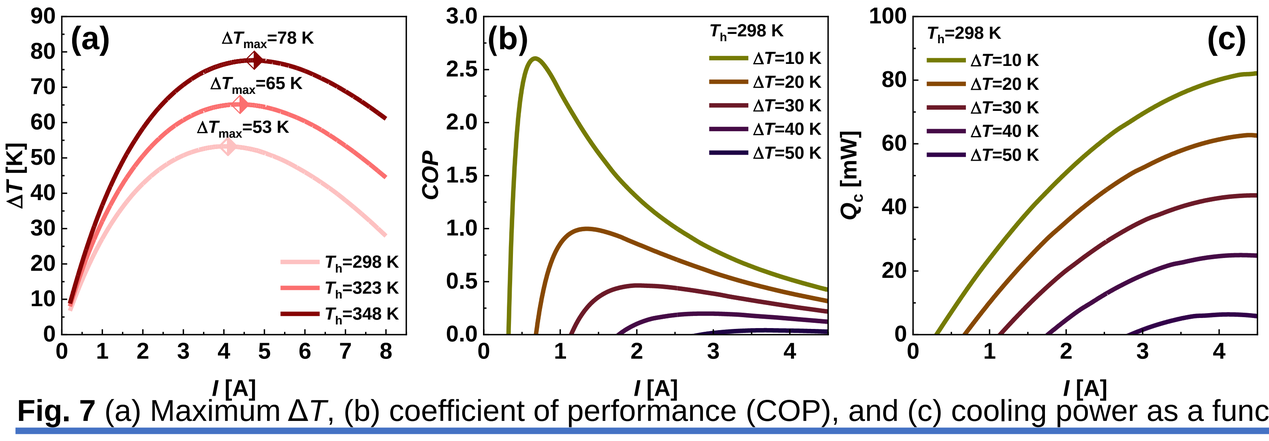



**Fig. 7** (a) Maximum Δ*T*, (b) coefficient of performance (COP), and (c) cooling power as a function of applied current for the $Cu_{6.4}Te_{2.2}Se_{0.5}S_{1.3}$ sample.

## Summary

- Se/S anion engineering effectively shifts the thermoelectric performance of $Cu_{6.4}Te_{2.2}Se_{1.8-x}S_x$ toward lower temperatures, through simultaneous modification of the electronic and thermal transport.
- The optimized $Cu_{6.4}Te_{2.2}Se_{0.5}S_{1.3}$ composition reaches $zT \approx 0.55$ near room temperature and a maximum $zT \approx 1.1$ at 450-500 K, while maintaining high weighted mobility.
- Device simulations predict $\Delta T_{max}$ = 53 K at $T_h$ = 298 K (up to 78 K at 348 K) and $COP_{max} \approx 2.6$ at ΔT = 10 K, demonstrating the potential of mixed-anion Cu-based chalcogenides for near-room-temperature solid-state cooling.


*The research was funded by the Foundation for Polish Science (FNP) under the First-Team programme, project no. FENG.02.02-IP.05-0012/25.*