Enhanced thermoelectric performance by Cu addition in p-type Bi-Te alloys

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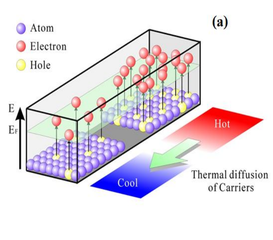
Introduction

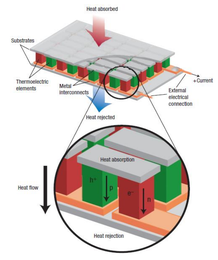
There are studies showing thermoelectric properties increase by cation addition on p-type Bi-Te alloy. Especially, $Bi_{0.5}Sb_{1.5}Te_3$ alloys are most widely used thermoelectric p-type materials for room-temperature applications. However, the analysis of Cu addition on p-type Bi-Te alloy($Bi_{0.5}Sb_{1.5}Te_3$) has not been verified yet. In this study, we investigated the influence of Cu addition in *p*-type $Cu_xBi_{0.5}Sb_{1.5}Te_3$ (x = 0, 0.0025, 0.005, 0.0075, 0.01) polycrystalline alloys on the electronic and thermal transport properties based on parabolic band modeling and Debye-Callaway model. It was found that the Cu addition increases the hole concentrations without modifying the band structure much and reduces the lattice and bipolar thermal conductivity quite effectively.

Experimental method

- We synthesized a series of Cu doped bismuth antimony telluride ($Cu_xBi_{0.5}Sb_{1.5}Te_3$, x = = 0, 0.0025, 0.005, 0.0075, 0.01) polycrystalline samples by solid-state reaction in a vacuum-sealed quartz tube with stoichiometric compositions.
- Stoichiometric amounts of Cu, Bi, Sb, Te shots (Copper : 99.99% Bismuth : 99.999%, Antimony: 99.999%, Tellurium : 99.999%,) were mixed and reacted in a vacuum-sealed quartz tube at 1050℃ for 18h.
- The polycrystalline samples were compacted using spark plasma sintering (SPS) at 400 ℃ for 5min under 60MPa.
- The S and σ were measured in the perpendicular direction to the SPS pressing direction using ZEM-3 from 300K to 520K.

Dimensionless figure of merit(zT) in Thermoelectrics



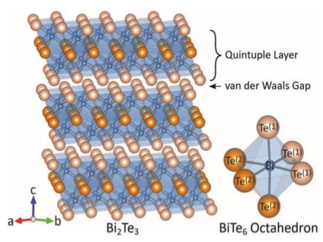


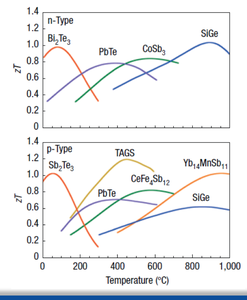
$$zT = \frac{\sigma S^2}{\kappa} \mathrm{T}$$

electrical conductivity σ [S/cm]
Seebeck coefficient, S [$\mu V/K$]
Thermal Conductivity [$W/m \cdot K$]
Absolute Temperature, T [K]

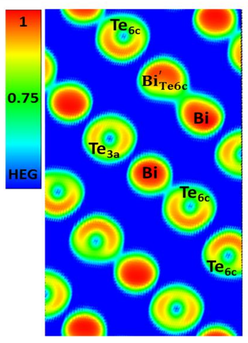
$P.F. = \sigma S^2$ *Power Factor*, $P.F.$ [mW/mK^2]

Seebeck coefficient is most important factor in thermoelectrics.





Effective mass and Seebeck coefficient correlation in DFT calculation



An electron localization function(ELF) map of Bi_2Te_3

$$DOS(E) = \frac{1}{2\pi^2}\left(\frac{2m_d^*}{\hbar^2}\right)^{3/2} E^{1/2} \longrightarrow m_d^* = (m_x m_y m_z)^{1/3} = (N_V)^{2/3} m_b^*$$

increse in DOS — *increse in* m_d^*

$$S = \frac{2k_B^2}{3e\hbar^2}\left(\frac{\pi}{3n}\right)^{2/3} m_d^* T$$

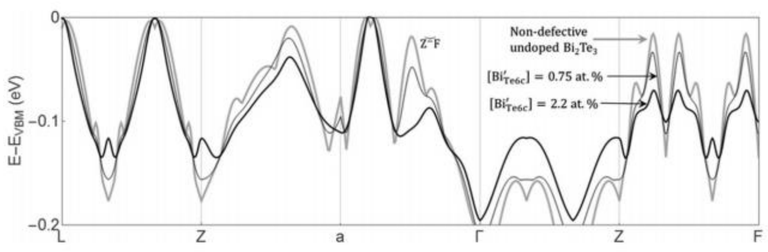
increse in Seebeck coefficient

$$\frac{1}{m_b^*} = \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k^2}$$

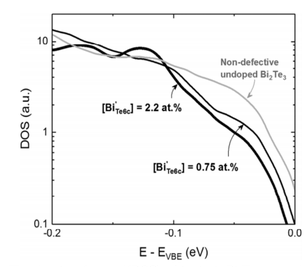
increse in m_b^*

$$\frac{1}{m_b^*} = \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k^2} \rightarrow \textbf{correlation between } m_b^* \textbf{ and band stucture}$$

m_b^* : *Band effective mass*
m_d^* : *Density of state effective mass*
N_V : *The number of equivalent degenerated valleys of the band structure.*



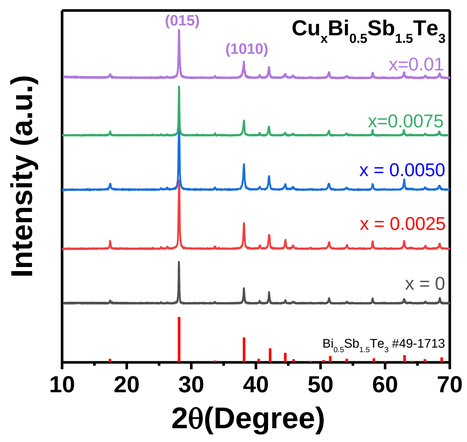
The valence band structure of Bi_2Te_3 with antisite defects.



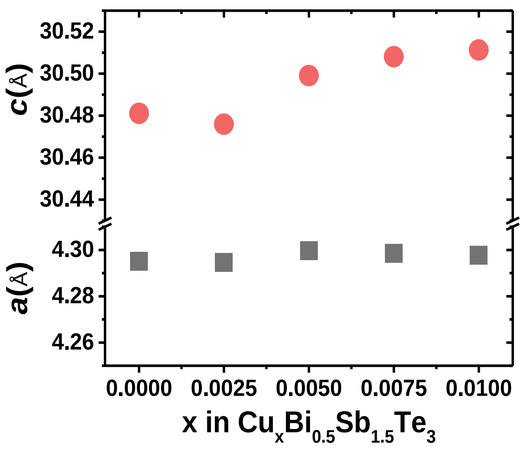
The density of stated(DOS) of intrinsic Bi_2Te_3 near the VBE

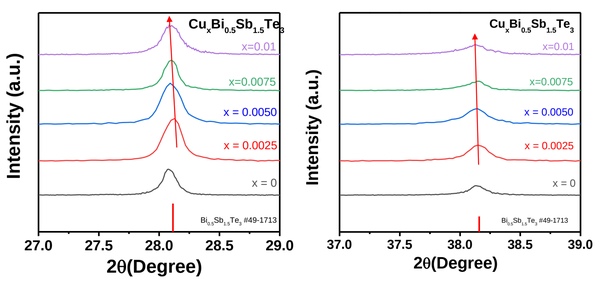
Structural Analysis

XRD patterns



Lattice parameters

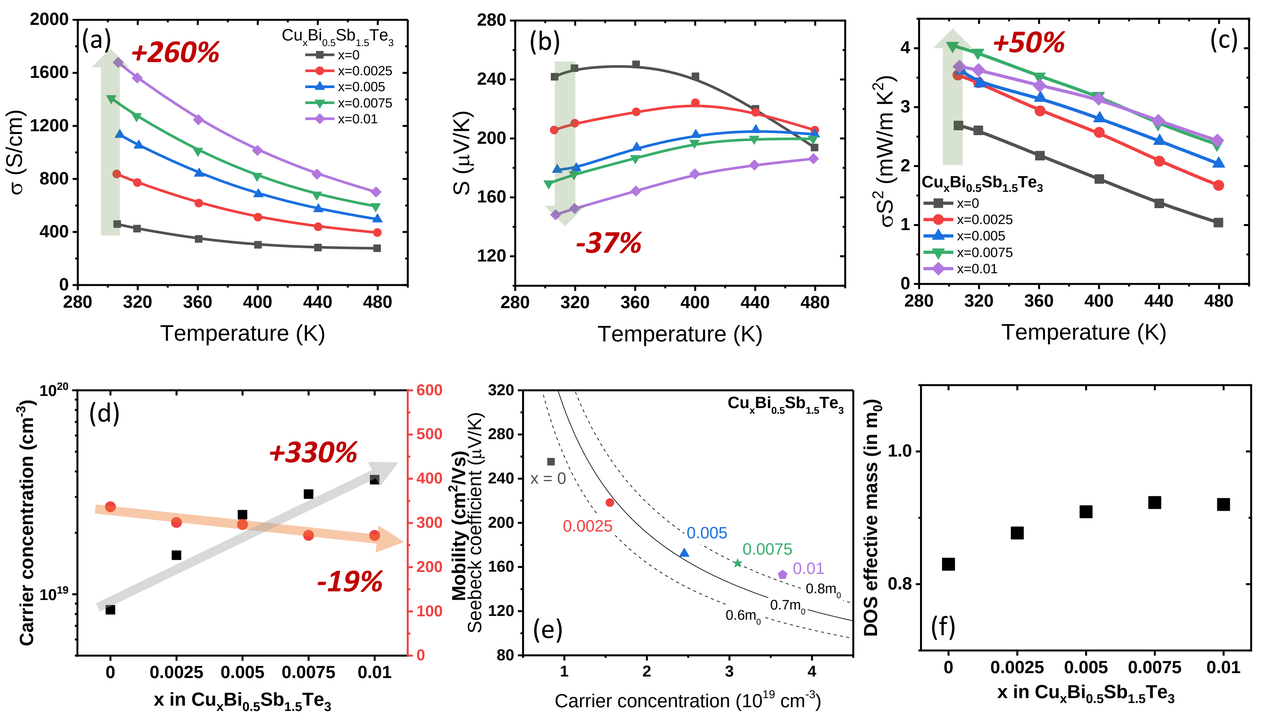




x in $Cu_xBi_{0.5}Sb_{1.5}Te_3$	a (Å)	c (Å)
0	4.2951	30.4811
0.0025	4.2946	30.4759
0.005	4.2996	30.4991
0.0075	4.2986	30.5081
0.01	4.2977	30.5113

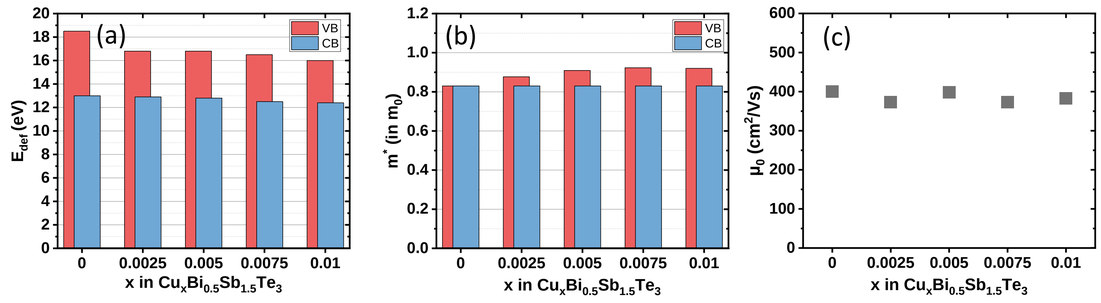
Cu addition in $Bi_{0.5}Sb_{1.5}Te_3$

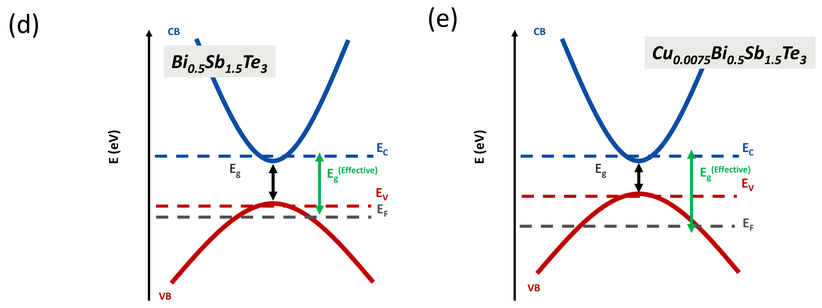
Electrical properties



(a) Electrical conductivity, (b) Seebeck coefficient, (c) power factor, (d) hall carrier concentration and mobility, (e) pisarenko plot, (f) density of state effective mass of $Cu_xBi_{0.5}Sb_{1.5}Te_3$.

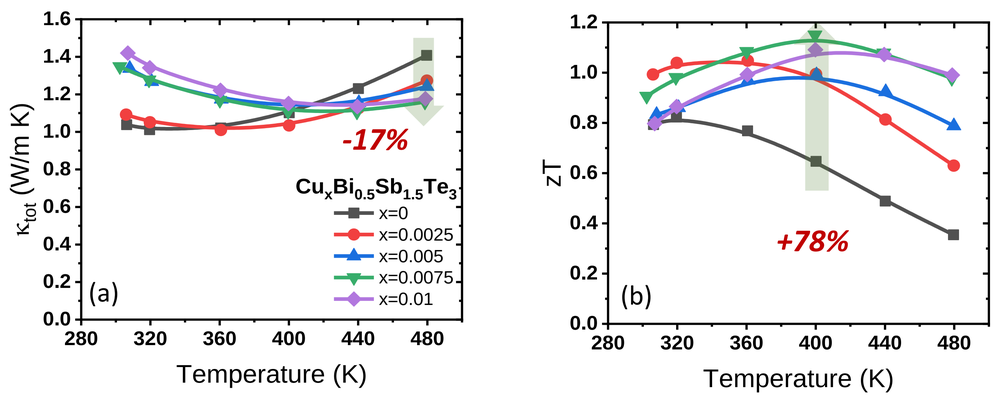
Parabolic band modeling





(a) Deformation potential, (b) density of state effective mass, (c) non-degenerate mobility of $Cu_xBi_{0.5}Sb_{1.5}Te_3$, schematic band diagram of (d) $Bi_{0.5}Sb_{1.5}Te_3$, and (e) $Cu_{0.0075}Bi_{0.5}Sb_{1.5}Te_3$

Thermal conductivity & *zT*



(a) Total thermal conductivity and (b) *zT* of $Cu_xBi_{0.5}Sb_{1.5}Te_3$.

Conclusion

- Through the correlation between density of effective mass and band structure, the change in band structure was observed and a schematic diagram was drawn.
- The Cu atoms are inserted between the layers of the Bi-Te material to make a larger difference in mass and lattice constant compared to other substitutional doping.
- As Cu addition increased, Carrier concentration increases and Mobility decreases.
- Through the addition of Cu, zT increased in the whole temperature range by high power factor value and thermal conductivity reduction effect at high temperature.
- $Cu_{0.0075}Bi_{0.5}Sb_{1.5}Te_3$ exhibited the highest zT value of 1.15 at 400 K.