Thermoelectric Properties of Gd and Se Double Substituted Tetrahedrite

Umasankar Rout, and Ramesh Chandra Mallik[*]

Thermoelectric Materials and Devices Laboratory, Department of Physics, Indian Institute of Science, Bangalore, 560012, India

1. X-ray diffraction

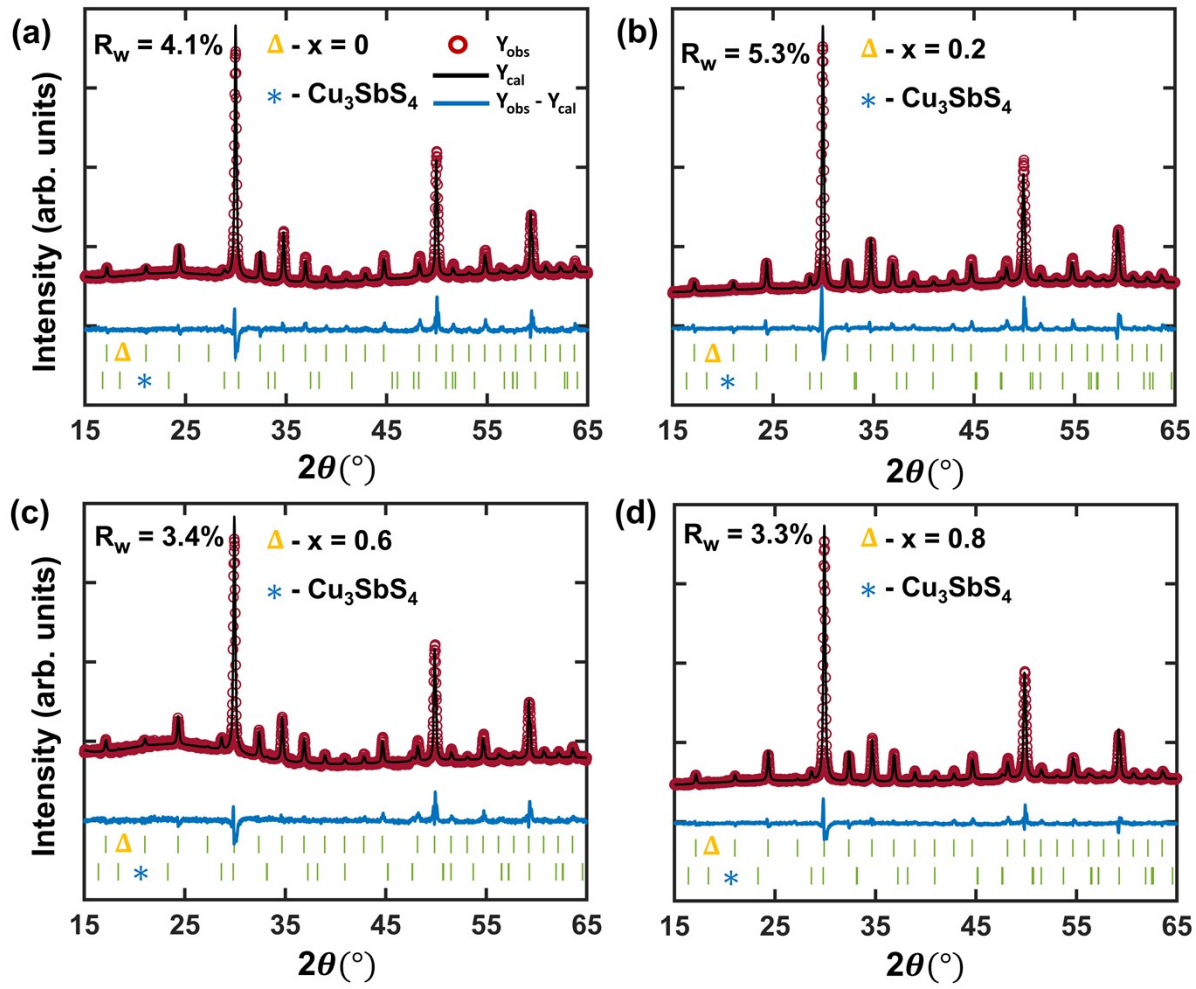

Fig. S1 Rietveld refined patterns of the samples (a) x = 0, (b) x = 0.2, (c) x = 0.6, and (d) x = 0.8.

[*] Author to whom correspondence to be addressed: rcmallik@iisc.ac.in

Table S1 Rietveld refinement results for Gd and Se double substituted samples.

Sample	Lattice parameters, a=b=c (in Å)	$Cu_{12}Sb_4S_{13}$(in wt %)	Cu_3SbS_4(in wt %)	Theoretical Density (in g cm^{-3})	Measured Density (g cm^{-3})	Rw
x = 0	10.324(6)	97.56(3)	2.4(3)	4.93(2)	4.86 (98.5%)	4.1%
x = 0.2	10.331(7)	96.84(8)	3.1(5)	4.92(7)	4.86 (98.7%)	5.3%
x = 0.4	10.336(1)	97.91(2)	2.0(8)	4.96(4)	4.88 (98.3%)	4.1%
x = 0.6	10.339(4)	96.30(7)	3.6(9)	5.10(2)	4.91 (96.2%)	3.4%
x = 0.8	10.345(4)	97.04(8)	2.9(5)	5.12(5)	4.93 (96.2%)	3.3%

The Uiso values were fixed in the Rietveld refinement, the Uiso for the host and substituent were kept the same (The Uiso values were referred from ICSD #14619), and the site occupancies (SOFs) were first calculated from the observed EPMA value and further refined. While refining the SOF, we allowed only those refined values that were physically meaningful. The refined occupancies and positions are provided with observed standard deviations.

Table S2 The Wyckoff sites and atomic coordinates (x, y, z) for the $Cu_{11.95}Gd_{0.05}Sb_4S_{13}$ sample.

Atoms	**Site**	**x**	**y**	**z**	**SOF**	**Uiso**
Gd	12d	0.5	0.25	0	0.0017	0.0213
Cu(1)	12d	0.5	0.25	0	0.9665(±3×10^{-4})	0.0213
Cu(2)	12e	0	0	0.2198(±2×10^{-4})	1	0.0630
Sb	8c	0.2685(±4×10^{-4})	0.2685(±4×10^{-4})	0.2685(±4×10^{-4})	0.9576(±2×10^{-4})	0.0213
S(1)	24g	0.8832(±2×10^{-4})	0.8830(±2×10^{-4})	0.3674(±3×10^{-4})	1	0.0205
S(2)	2a	0	0	0	1	0.0201

Table S3 The Wyckoff sites and atomic coordinates (x, y, z) for the $Cu_{11.95}Gd_{0.05}Sb_4S_{12.8}Se_{0.2}$ sample.

Atoms	Site	x	y	z	SOF	Uiso
Gd	12d	0.5	0.25	0	0.0017	0.0213
Cu(1)	12d	0.5	0.25	0	0.9653(±2×10^{-4})	0.0213
Cu(2)	12e	0	0	0.2169(±3×10^{-4})	1	0.0630
Sb	8c	0.2687(±6×10^{-4})	0.2687(±6×10^{-4})	0.2687(±6×10^{-4})	0.9448(±8×10^{-4})	0.0213
Se	24g	0.8722(±5×10^{-4})	0.8722(±5×10^{-4})	0.3856(±5×10^{-4})	0.0158	0.0205
S(1)	24g	0.8852(±7×10^{-4})	0.8852(±7×10^{-4})	0.3653(±4×10^{-4})	0.9833	0.0205
S(2)	2a	0	0	0	1	0.0201

Table S4 The Wyckoff sites and atomic coordinates (x, y, z) for the $Cu_{11.95}Gd_{0.05}Sb_4S_{12.6}Se_{0.4}$ sample.

Atoms	Site	x	y	z	SOF	Uiso
Gd	12d	0.5	0.25	0	0.0017	0.0213
Cu(1)	12d	0.5	0.25	0	0.9983	0.0213
Cu(2)	12e	0	0	0.2187(±6×10^{-4})	0.9672(±6×10^{-4})	0.0630
Sb	8c	0.2694(±4×10^{-4})	0.2694(±4×10^{-4})	0.2694(±4×10^{-4})	0.9538(±5×10^{-4})	0.0213
Se	24g	0.8767(±2×10^{-4})	0.8767(±2×10^{-4})	0.3703(±3×10^{-4})	0.0325	0.0205
S(1)	24g	0.8844(±3×10^{-4})	0.8844(±3×10^{-4})	0.3635(±3×10^{-4})	0.9675	0.0205
S(2)	2a	0	0	0	1	0.0201

Table S5 The Wyckoff sites and atomic coordinates (x, y, z) for the $Cu_{11.95}Gd_{0.05}Sb_4S_{12.4}Se_{0.6}$ sample.

Atoms	Site	x	y	z	SOF	Uiso
Gd	12d	0.5	0.25	0	0.0015	0.0213
Cu(1)	12d	0.5	0.25	0	0.9985	0.0213
Cu(2)	12e	0	0	0.2171(±2×10^{-4})	1	0.0630
Sb	8c	0.2685(±3×10^{-4})	0.2685(±3×10^{-4})	0.2685(±3×10^{-4})	0.9754(±6×10^{-4})	0.0213
Se	24g	0.8788(±2×10^{-4})	0.8788(±2×10^{-4})	0.3689(±3×10^{-4})	0.0558	0.0205
S(1)	24g	0.8841(±5×10^{-4})	0.8841(±5×10^{-4})	0.3653(±4×10^{-4})	0.9442	0.0205
S(2)	2a	0	0	0	1	0.0201

Table S6 The Wyckoff sites and atomic coordinates (x, y, z) for the $Cu_{11.95}Gd_{0.05}Sb_4S_{12.2}Se_{0.8}$ sample.

Atoms	Site	x	y	z	SOF	Uiso
Gd	12d	0.5	0.25	0	0.0015	0.0213
Cu(1)	12d	0.5	0.25	0	0.9975	0.0213
Cu(2)	12e	0	0	0.2171(±5×10^{-4})	0.9952(±3×10^{-4})	0.0630
Sb	8c	0.2688(±3×10^{-4})	0.2688(±3×10^{-4})	0.2688(±3×10^{-4})	0.9738(±4×10^{-4})	0.0213
Se	24g	0.8848(±2×10^{-4})	0.8848(±2×10^{-4})	0.3689(±5×10^{-4})	0.0861	0.0205
S(1)	24g	0.8867(±2×10^{-4})	0.8867(±2×10^{-4})	0.3687(±4×10^{-4})	0.9362(±6×10^{-4})	0.0205
S(2)	2a	0	0	0	1	0.0201

Table S7 Lattice parameters a and b (in Å) of the Cu_3SbS_4 phase in the double substituted samples.

Samples	a=b (Å)	c (Å)
x = 0	5.389(4)	10.568(9)
x = 0.2	5.381(9)	10.814(5)
x = 0.4	5.386(5)	10.803(1)
x = 0.6	5.399(7)	10.794(5)
x = 0.8	5.393(4)	10.811(2)

2. Microstructural analysis

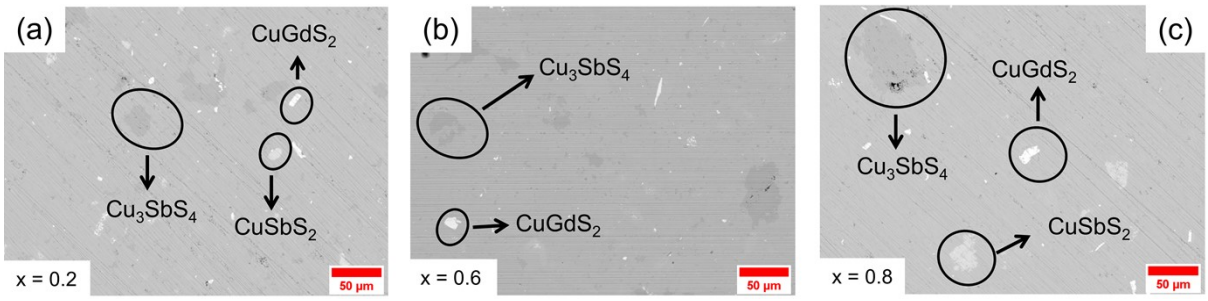

Fig. S2 Backscattered electron (BSE) image of the polished surface of the samples (a) x = 0.2, x = 0.6, and x = 0.8.

3. X-ray photoelectron spectroscopy

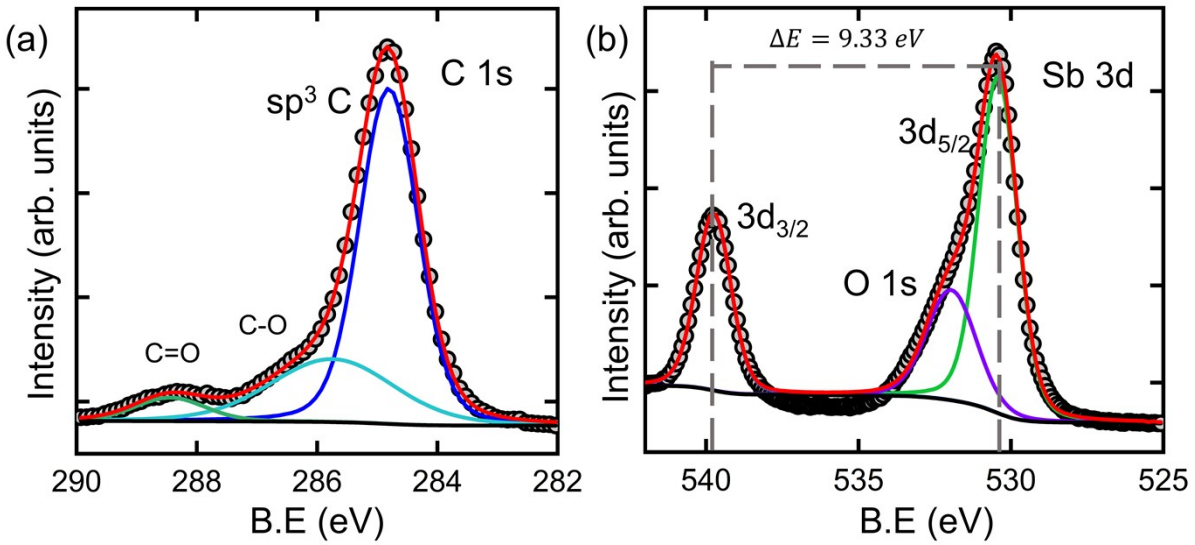

Fig. S3 X-ray photoelectron spectra corresponding to (a) C 1s and (b) Sb 3d lines in the sample x = 0.4 ($Cu_{11.95}Gd_{0.05}Sb_4S_{12.6}Se_4$).

Table S8 Binding energy and oxidation states for the XPS peaks for the elements Cu, Gd, Sb, S, and Se.

Elements	Peak	Binding Energy (in eV)	Oxidation State[#]
Cu	$2p_{1/2}$	952.42	+1
Cu	$2p_{3/2}$	932.59	+1
Gd	3d	1187.80	+3
Sb	$3d_{3/2}$	539.70	+3
Sb	$3d_{5/2}$	530.37	+3
S	$2p_{1/2}$	162.88	-2

S	$2p_{3/2}$	161.71	-2
Se	$3d_{3/2}$	55.74	-2
Se	$3d_{5/2}$	54.22	-2

4. Rama spectroscopy

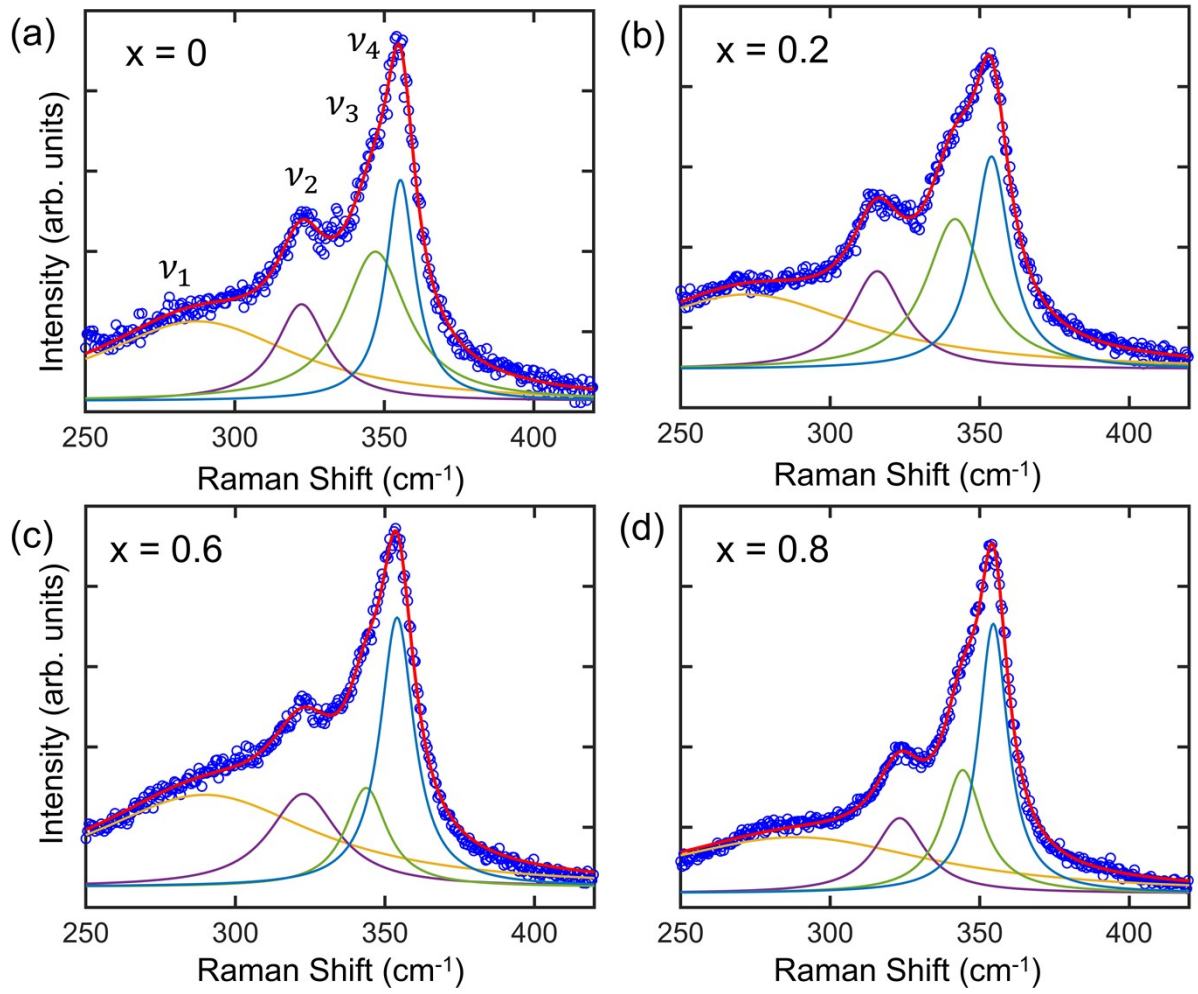

Fig. S4 Fitted Raman spectra for the samples (a) x = 0, (b) x = 0.2, (c) x = 0.6, and (d) x = 0.8 with four characteristic modes (ν_1 - ν_4) marked.

5. Thermoelectric properties

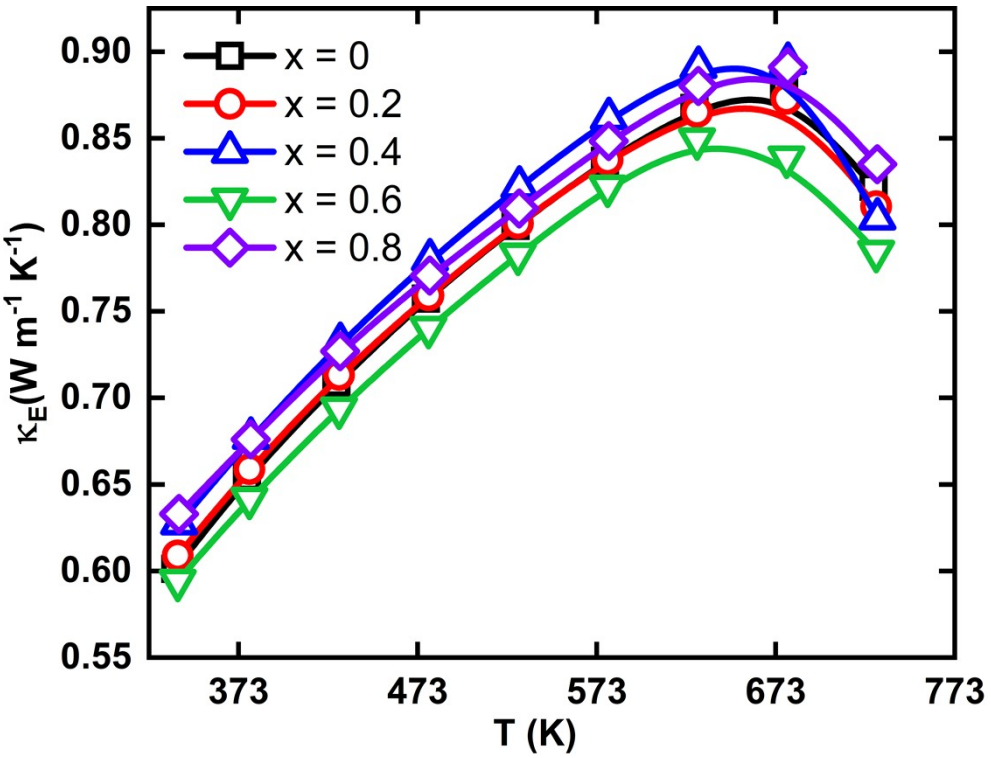

Fig. S5 Temperature dependence of electronic part of thermal conductivity (κ_E) of the samples $Cu_{11.95}Gd_{0.05}Sb_4S_{13-x}Se_x$ (x = 0, 0.2, 0.4, 0.6 and 0.8).

Table S9. Values of prefactors of the Callaway model

Sample	A (s^3)	B (s K^{-1})	L (m)
x = 0	2.11×10^{-40}	5.65×10^{-18}	6×10^{-6}
x = 0.2	3.51×10^{-40}	2.13×10^{-18}	6×10^{-6}
x = 0.4	2.83×10^{-40}	5.95×10^{-18}	6×10^{-6}
x = 0.6	2.29×10^{-40}	4.47×10^{-18}	6×10^{-6}
x = 0.8	2.23×10^{-40}	4.70×10^{-18}	6×10^{-6}