Electronic Supplementary Information

Thermoelectric properties of Ag-doped CuS nanocomposites synthesized by a facile polyol method

Tarachand[a], S. Hussain[b], N. P. Lalla[a], Y.-K. Kuo[c], A. Lakhani[a], V. G. Sathe[a], U. Deshpande[a] and G. S. Okram[a]

[a]UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore-452001, India
[b]UGC-DAE Consortium for Scientific Research, Kalpakkam Node, Kokilamedu-603104, India [c]Department of Physics, National Dong Hwa University, Hualien 97401, Taiwan.

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X-ray Diffraction (XRD) Lab source XRD measurements were performed for all samples in powder form using Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (0.154 nm) in the angle range of 20-80° in θ - 2θ geometry (Figure S1); X-rays were detected using a fast counting detector based on silicon strip technology (Bruker LynxEye detector). Synchrotron radiation XRD data with λ = 0.876 Å (E = 15.77 keV) was collected at BL-18B (Indian beamline), Photon Factory, Tsukuba, Japan, with a beam current of 401 mA in the angle range of 5° - 21.5° for angular step of 0.005° with a point detector (Cyberstar) on powdered samples.
Average crystallite size of $Cu_{1-x}Ag_xS$; x = 0, 0.1, 0.2, 0.5, 0.75 and 1 samples are calculated from Scherrer's formula: $L = \frac{K\lambda}{\beta \cos \theta}$
where K, λ, β and θ are shape factor (~0.9), X-ray wavelength, full width half maxima of diffraction peaks and Bragg's angle respectively.

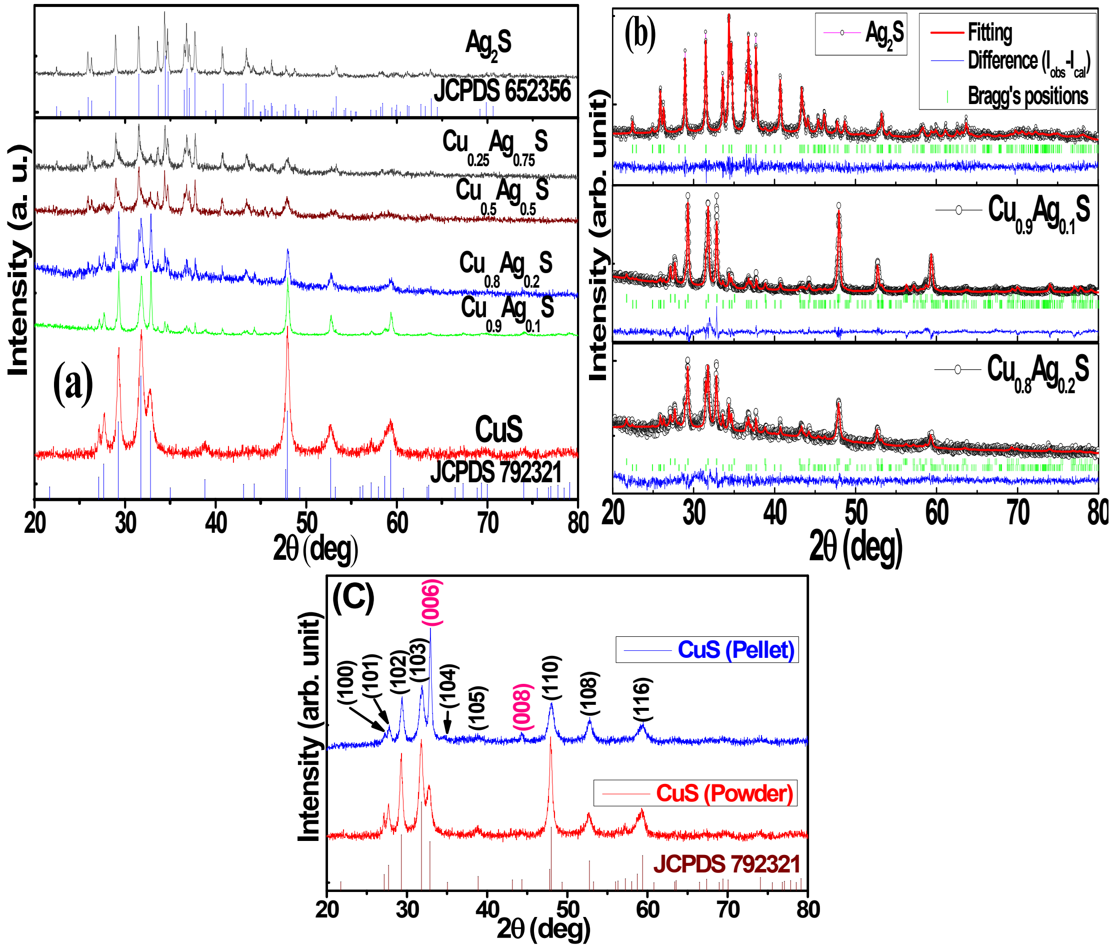

Figure S1. (a) XRD data of $Cu_{1-x}Ag_xS$, where x = 0 – 1 collected from lab source XRD with λ = 1.54 Å, (b) Rietveld refinement of powder XRD of x = 0.1, 0.2 and 1, and (c) XRD patterns of pure CuS in both powder and pellet forms as indicated.

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Table S1 Refined Wyckoff positions and occupations of Cu and S atoms at different Wyckoff sites in unit cell of CuS.

Atoms	Wyckoff sites	Wyckoff positions (x,y,z)	Occupation
Cu1	2d	2/3, 1/3, 0.25	0.49715
Cu2	4f	1/3, 2/3, 0.10806	0.98827
S1	2c	1/3, 2/3, 0.25	0.50380
S2	4e	0, 0, 0.06193	1.01183

Table S2 Calculated lattice parameters for $Cu_{1-x}Ag_xS$, where x = 0 – 0.75 using crystallographic relations for hexagonal system such as

$$d_{hkl} = \frac{1}{\left(\frac{4(h^2+hk+k^2)}{3a^2} + \frac{l^2}{c^2}\right)^{\frac{1}{2}}}$$

and $2d\sin\theta = n\lambda$ for most prominent peaks centered at 29.3° (hkl=102), 31.9° (103) and 32.7° (006).

Sample name	a (Å)	c (Å)
CuS pure	3.791	16.393
$Cu_{0.9}Ag_{0.1}S$	3.796	16.359
$Cu_{0.8}Ag_{0.2}S$	3.796	16.340
$Cu_{0.5}Ag_{0.5}S$	3.795	16.364
$Cu_{0.25}Ag_{0.75}S$	--	16.336

Table S3 Obtained parameters from Rietveld refinement of $Cu_{1-x}Ag_xS$; x=0, 0.1, 0.2 and 1. Errors are written in parentheses.

Parameters	CuS (**H**exagonal)	$Cu_{0.9}Ag_{0.1}S$ (Mix Phase)	$Cu_{0.8}Ag_{0.2}S$ (Mix Phase)	Ag_2S (**M**onoclinic)
a (Å), **H**;	3.791(1)	3.795(1)	3.796(1)	--
M	--	4.228(3)	4.232(2)	4.230(1)
b (Å), **H**;	3.791(1)	3.795(1)	3.796(1)	--
M	--	6.936(4)	6.933(3)	6.932(2)
c (Å) **H**;	16.390(3)	16.365(3)	16.372(4)	--
M	--	7.874(5)	7.872(3)	7.875(2)
V (Å^3) **H**;	204.313	204.118	204.280	--
M	--	227.704	227.728	227.691
ρ (g.cm^{-3}) **H**;	3.114	3.174	3.109	--
M	--	7.225	7.228	7.229
Phase-fraction; **H**;	100%	90.98%	80.45%	--
M	--	09.02%	19.55%	100%

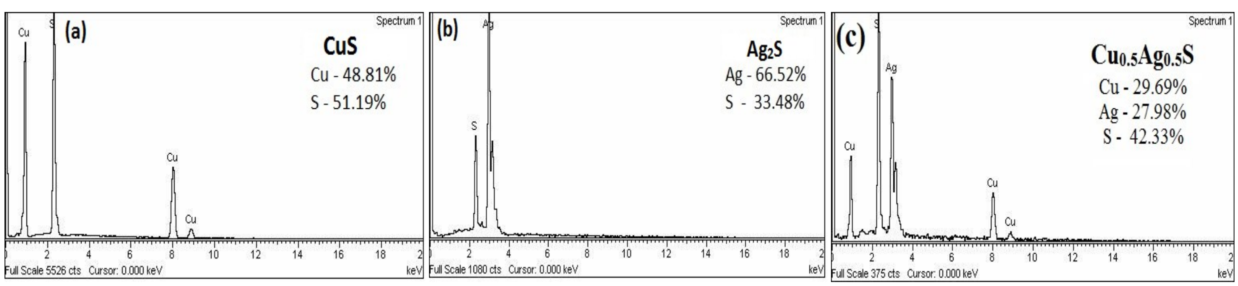

Figure S2. EDAX of cold pressed pellets of (a) CuS, (b) Ag_2S and (c) $Cu_{0.5}Ag_{0.5}S$.

Transmission electron microscopy (TEM) TEM images and selected area electron diffraction (SAED) of CuS nanodisks were recorded using transmission electron microscopy by drop-casting the well-sonicated solution of a few milligrams of nanoparticles dispersed in about 4 ml methanol on copper grid coated with an amorphous carbon film. TEM measurements were performed with a TECHNAI-20-G^2 operating at a 200 kV accelerating voltage**.**

Field emission scanning electron microscopy (FESEM) FESEM images of CuS NDs were collected using Carl Zeiss AURIGA FIBSEM in secondary emissions mode operated at 4.0 kV applied voltage. Sample was prepared by sprinkling of a small amount of the powder on a conducting tape. Then tap the holder to from the sides to remove the loose powders and followed by gold coating for a thickness of 1 nm by sputtering.

X-ray photoelectron spectroscopy (XPS) XPS measurements were performed on an X-ray photoelectron spectroscope (SPECS, Germany) using Al K_α radiation with an anode voltage of 13 kV and an emission current of

22.35 mA. Powder sample was consolidated into pellet by applying 500 MPa pressure. A full-scan survey spectrum was recorded with an energy of 40 eV and high-resolution spectra were recorded with energy of 30 eV.

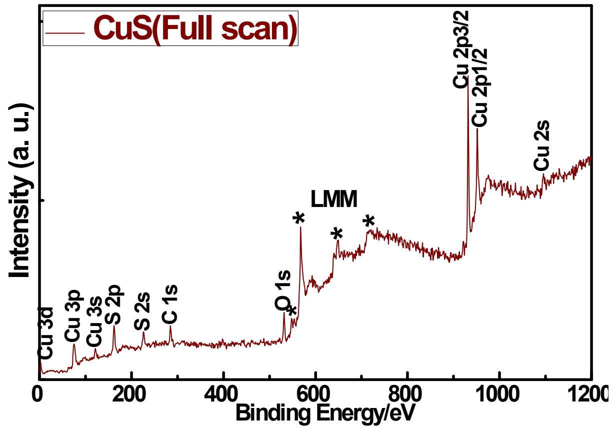

Figure S3. Full scan XPS survey of synthesized CuS nanoparticles.

Raman spectroscopy Room temperature Raman spectroscopic measurement was performed using Jobin Yvon Horibra LABRAM HR-800 Visible instrument equipped with an Ar ion laser of wavelength 473 nm and a CCD detector giving over all spectral resolution of ~1 cm^{-1}. Powder sample was consolidated into pellet by applying 500 MPa pressure and data was recorded for 120 second in air.

Table S4. Obtained density (mass/volume) for all consolidated pellets $Cu_{1-x}Ag_xS$; x = 0 - 1 nanocomposites. Estimated error in the calculation is ±0.05.

Sample name	CuS	x=0.05	x=0.1	x=0.2	x=0.5	x=0.75	x=1 (Ag_2S)
Density ($g.cm^{-3}$)	3.01	4.58	4.61	5.03	5.64	6.45	7.19

Table S5. Hall coefficient for pure CuS obtained from the slope of Hall resistivity (ρ_{xy}) versus applied magnetic field graph at fixed temperatures (10, 50, 100, 200 and 300 K) and calculated charge carrier density (n) and mobility (μ), using $\sigma = ne\mu$ and $R_H = 1/ne$ relation.

Temperature	CuS (pure)			$Cu_{0.9}Ag_{0.1}S$		
	R (cm^3C^{-1}) x 10^{-4}	n (cm^{-3}) x10^{21}	μ ($cm^2V^{-1}.Sec^{-1}$)	R (cm^3C^{-1}) x10^{-4}	n (cm^{-3}) x10^{21}	μ ($cm^2V^{-1}.Sec^{-1}$)
10 K	+ 8.0516	7.7518	1.4197	+9.7347	6.4116	2.4283
50 K	+ 7.9953	7.8065	1.3520	+8.9871	6.9450	2.0648
100 K	+ 7.0069	8.9076	1.1159	+8.8644	7.0411	1.8060
200 K	+6.8382	9.1275	0.9665	+6.9363	8.9989	1.1744
300 K	+ 13.3821	4.6641	1.7504	+6.4692	9.6481	0.9770

Table S6. Thermoelectric power factor, thermal conductivity and figure of merit for $Cu_{1-x}Ag_xS$; x = 0-0.75 nanocomposites at 300 K.

Sample name	$S^2\sigma$ ($\mu Wm^{-1}K^{-2}$)	κ ($Wm^{-1}K^{-1}$)	ZT
CuS pure	23.89	3.653	0.001962 (~0.002)
$Cu_{0.9}Ag_{0.1}S$	32.69	3.325	0.002945 (~0.003)

$Cu_{0.8}Ag_{0.2}S$	15.07	2.831	0.001597
$Cu_{0.5}Ag_{0.5}S$	3.8	2.345	0.000486
$Cu_{0.25}Ag_{0.75}S$	1.12	1.771	0.000190

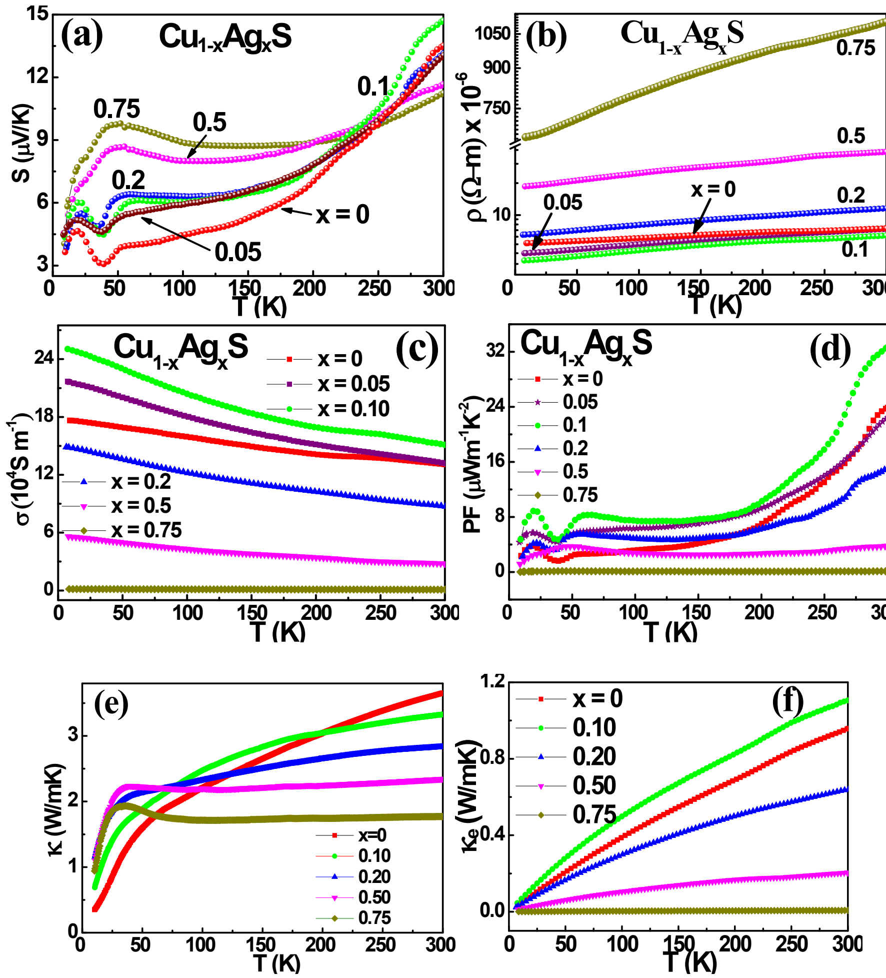

Figure S4. Temperature dependence of (a) Seebeck coefficient, (b) electrical resistivity, (c) electrical conductivity, (d) thermoelectric power factor, (e) total thermal conductivity and (f) electrical part of thermal conductivity of $Cu_{1-x}Ag_xS$: x = 0-0.75.

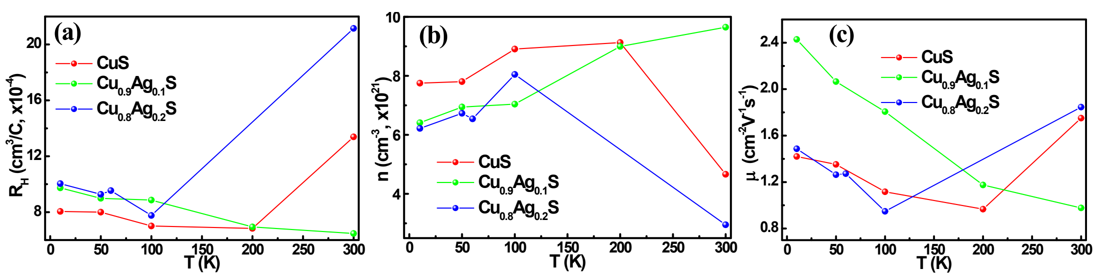

Figure S5 Temperature dependence of (a) Hall coefficient, (b) charge carrier concentration and (c) carrier mobility of $Cu_{1-x}Ag_xS$: x = 0, 0.1 and 0.2.