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High thermoelectric performance of $(AgCrSe_2)_{0.5}(CuCrSe_2)_{0.5}$ nano-composites having all-scale natural hierarchical architectures

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Supplementary information

S1 : Analysis of powder X-ray difffraction (XRD) data- Calculated Bragg peak positions for pure $AgCrSe_2$ and $CuCrSe_2$

Calculated Peak Positions for $AgCrSe_2$

h	k	l	2Θ (in degree)	d (Å)	Intensity
0	0	6	25.399	3.504	11.78
1	0	1	28.225	3.15918	337.79
0	1	2	29.186	3.05733	605.45
1	0	4	32.773	2.73044	579.96
0	1	5	35.248	2.54416	288.67
0	0	9	38.507	2.336	82.07
1	0	7	41.217	2.18849	902.71
0	1	8	44.606	2.02974	390.62
1	1	0	49.357	1.8449	723.24
1	1	3	51.158	1.78411	70.34
1	0	10	52.027	1.75635	54.23
0	0	12	52.165	1.752	66.92
0	1	11	56.019	1.64026	158.82

1	1	6	56.311	1.63245	7.37
0	2	1	57.83	1.59314	42.81
2	0	2	58.373	1.57959	92.66
0	2	4	60.517	1.52866	92.28
2	0	5	62.096	1.49354	50.56
1	1	9	64.287	1.44782	101.57
1	0	13	64.53	1.44296	4.57
0	2	7	66.199	1.41056	179.64
0	0	15	66.677	1.4016	45.36
2	0	8	68.698	1.36522	83.52
0	1	14	69.05	1.35911	52.46
0	2	10	74.536	1.27208	15.15
1	1	12	74.65	1.27042	100.36
2	0	11	77.863	1.22583	43.5
1	0	16	78.67	1.21526	2.84
2	1	1	79.41	1.20578	22.77
1	2	2	79.879	1.19988	56.76

Calculated Peak Positions for $CuCrSe_2$

h	k	l	2Θ (in degree)	d (Å)	Intensity
0	0	6	27.565	3.23333	58.71
1	0	1	28.441	3.13567	350.28
0	1	2	29.559	3.01957	267.74
1	0	4	33.694	2.65785	352.88
0	1	5	36.522	2.45831	86.92
0	0	9	41.876	2.15556	11.02
1	0	7	43.285	2.08859	353.71
0	1	8	47.105	1.92773	514.06
1	1	0	49.656	1.8345	500.28
1	1	3	51.757	1.76486	60.9
1	0	10	55.449	1.65578	42.47
0	0	12	56.911	1.61667	16.34
1	1	6	57.733	1.59557	44.95
0	2	1	58.219	1.58342	50.97
2	0	2	58.854	1.56783	35.25
0	1	11	59.939	1.54203	34.55
0	2	4	61.355	1.50978	52.85
2	0	5	63.192	1.47025	14.37
1	1	9	66.923	1.39705	16.45

0	2	7	67.955	1.37832	74.25
1	0	13	69.539	1.35075	15.77
2	0	8	70.851	1.32892	114.59
0	0	15	73.11	1.29333	30.99
0	1	14	74.666	1.27018	4.66
0	2	10	77.613	1.22915	10.7
1	1	12	78.853	1.2129	25.22
2	1	1	79.976	1.19867	30.44

XRD pattern for the hot pressed $(AgCrSe_2)_{0.5}(CuCrSe_2)_{0.5}$ pellets

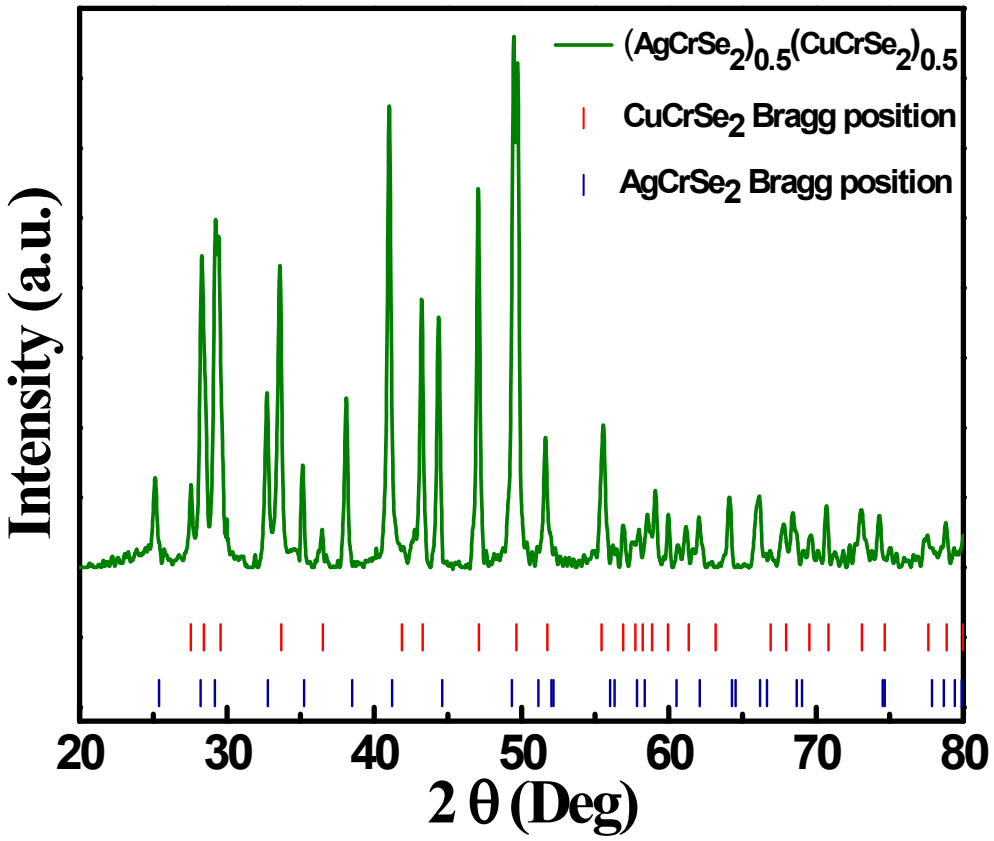

Figure S1: XRD pattern for the hot pressed $(AgCrSe_2)_{0.5}(CuCrSe_2)_{0.5}$ pellets

From Figure S1, it can be seen that there are multiple oriented peaks in the XRD spectra of hot pressed $(AgCrSe_2)_{0.5}(CuCrSe_2)_{0.5}$ pellets, which suggest the absence of any kind of texturing in the hot pressed pellets.

S2: Thermal diffusivity (D) and specific heat (C_p) data used for the estimation of thermal conductivity (k)

The temperature dependence of thermal diffusivity (D) and specific heat (Cp) data for all samples is shown in Fig. S2, for pure samples the presence of transitions can be clearly seen at 365 K (for $CuCrSe_2$) and 450 K (for $AgCrSe_2$). In the composite sample data, transition features for both $CuCrSe_2$ and $AgCrSe_2$ components can be clearly seen. It may be noted that the experimentally obtained high temperature Cp values were found to be 0.4 J/gm K, 0.3 J/gm K and 0.33 for $CuCrSe_2$, $AgCrSe_2$ and composite samples compares very well with theoretically estimated Dulong-Petit value. The Dulong-Petit Cp values were respectively found to be 0.37 J/gm K, 0.31 J/gm K and 0.32 for $CuCrSe_2$, $AgCrSe_2$ and composite samples.

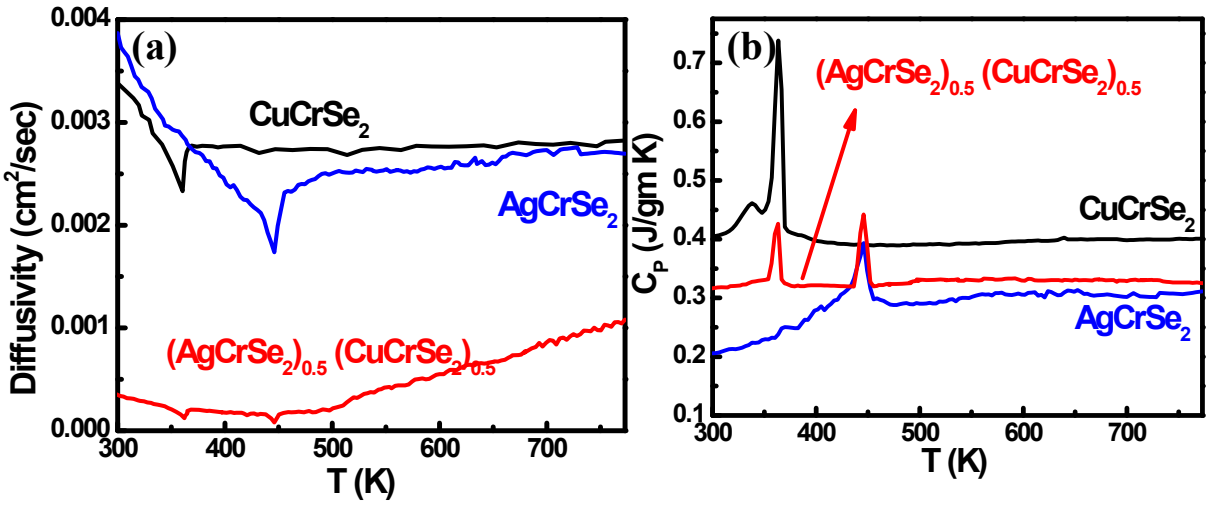

Figure S2: (a) Thermal diffusivity (D) and (b) specific heat (Cp) results for $AgCrSe_2$, $CuCrSe_2$ and $(AgCrSe_2)_{0.5}(CuCrSe_2)_{0.5}$ samples.

Thermal conductivity (k) can be calculated from the C_p and thermal diffusivity (D), using the following relation $k = C_p \times D \times d$, Where, Cp is the specific heat and D is the thermal

diffusivity and d is the density of the sample. In the calculation of thermal conductivity the mass density (estimated using Archimedes method) used for pure $CuCrSe_2$, $AgCrSe_2$ and composite samples were respectively 6.31, 6.69 and 6.49 gm/cc.

S3: Estimation of the band gap

Room temperature optical diffused reflectance measurements were performed on hot pressed samples to estimate the optical energy gap of the materials. The spectra were taken in the mid IR range (400- 7000 cm^{-1}) using a FTIR spectrometer (Bruker 80 V). The reflectance versus wave number data were used to estimate the band gap by converting reflectance to the absorption data according to Kubelka-Munk equations $\alpha/S = (1-R)^2/(2R)$, where R is the reflectance, α and S are the absorption and scattering coefficient respectively.

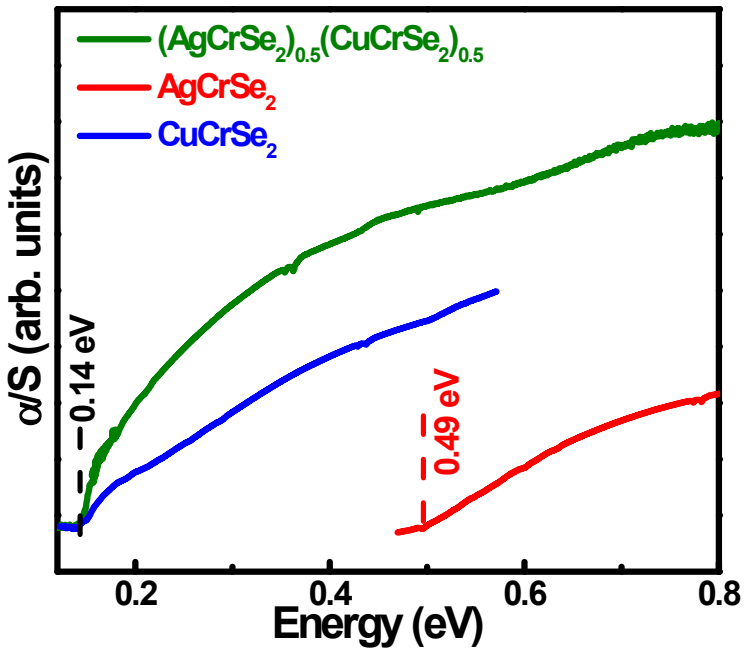

Figure S3: Electronic absorption spectra for the samples

The plots of α/S versus energy for pure $AgCrSe_2$, $CuCrSe_2$ and $(AgCrSe_2)_{0.5}(CuCrSe_2)_{0.5}$ composite samples are shown in Figure S3. From Fig. S3 it can be seen that for pure $AgCrSe_2$ and $CuCrSe_2$ the band gap values are 0.49 eV and 0.14 eV respectively, which are very close to the reported values.[1,2] For $(AgCrSe_2)_{0.5}(CuCrSe_2)_{0.5}$ sample both band gap corresponding to pure $AgCrSe_2$ and $CuCrSe_2$ are clearly seen in the data.

S4: Details of stability test of $(AgCrSe_2)_{0.5}(CuCrSe_2)_{0.5}$ samples at high current density

Figure S4: (a) Photo graph of the test chamber (b) Inside view of the test chamber and details of electrical connections to the sample. (c) Sample photograph before stability test (d) Sample photograph after stability test.

The details of the stability test of $(AgCrSe_2)_{0.5}(CuCrSe_2)_{0.5}$ are shown in Fig. S4. In order to perform the stability measurement of $(AgCrSe2)_{0.5}(CuCrSe2)_{0.5}$ samples, we have measured the resistivity of these samples at 773 K by applying a constant high current density (~ 50 A/cm^2) in a specially home-made test set up (Shown in Fig. S4(a)) and electrical contacts were taken by four fingers of silver (pressure contact) shown in Fig. S4(b). Before starting the four probe resistivity measurement, the chamber was first evacuated to 2×10^{-2} mbar pressure and then purged with argon gas to atmospheric pressure. At room temperature, unidirectional current of 2 Amp (current density ~ 50 A/cm^2) was applied on the sample and voltage was measured. Subsequently the sample temperature was raised to 773 K (heating rate ~ 13 K/min) and after achieving a stabilized temperature of 773K, the resistivity measurement was measured as a function of time. The constant current was applied using Keithley 2400 source meter and voltage was measured using Keithley 2182A nano-voltmeter. The data was collected (using Labview software) for 12 hrs at an interval of 20 seconds. The recorded data shown in Fig. 9 (b) suggest that sample is stable at high current density ~ 50 A/cm^2. It is important to note that during resistivity measurement current was kept continuously ON for more than 12 hours.

S5: Transmission electron microscope image of $(AgCrSe_2)_{0.5}(CuCrSe_2)_{0.5}$ samples after performing 12 hrs annealing at 773K

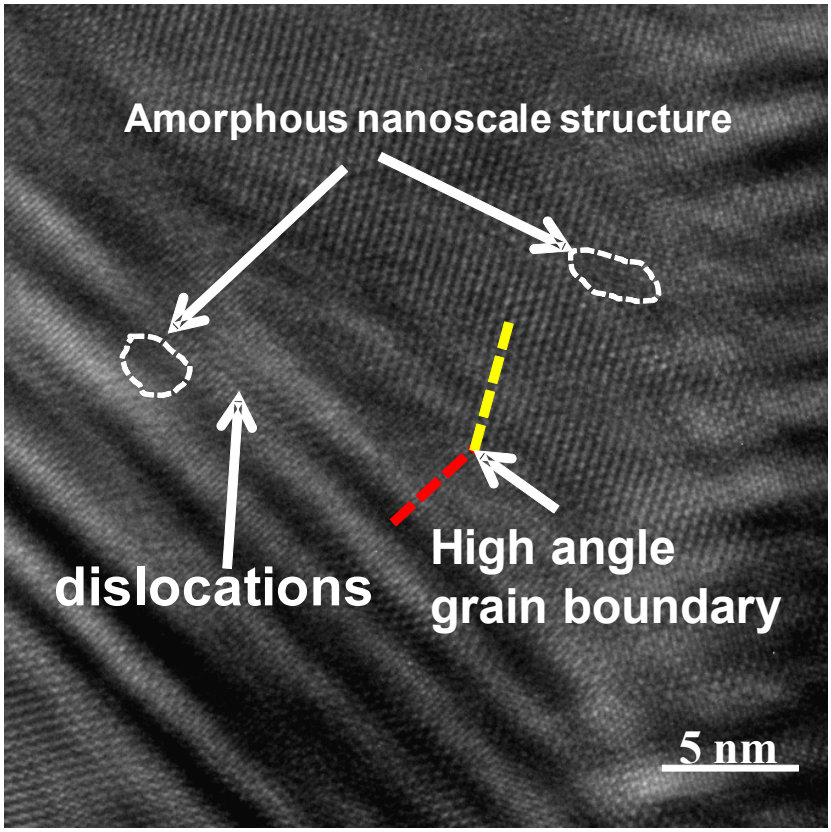

Figure S5. Transmission electron microscope (TEM) image of $(AgCrSe_2)_{0.5}(CuCrSe_2)_{0.5}$ samples after 12 hrs of annealing at 773 K.. In the image, region inside white dotted lines shows the presence of nanoscale features with amorphous structure.