Electronic Supplementary Information (ESI)

Enhancement of Thermoelectric Properties of $CuFeS_2$ Through Formation of Spinel-type Microprecipitates

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Table S1. Lattice parameters of $Cu_{1-x}Cr_xFeS_2$ ($0 \le x \le 0.1$) described in the space group $I\bar{4}2d$.

Sample	***a*/Å**	***c*/Å**
$CuFeS_2$	5.2902(4)	10.4254(6)
$Cu_{0.98}Cr_{0.02}FeS_2$	5.2911(1)	10.4310(5)
$Cu_{0.96}Cr_{0.04}FeS_2$	5.2896(5)	10.4254(8)
$Cu_{0.94}Cr_{0.06}FeS_2$	5.2888(7)	10.4219(3)
$Cu_{0.92}Cr_{0.08}FeS_2$	5.2896(3)	10.4261(2)
$Cu_{0.9}Cr_{0.1}FeS_2$	5.2908(4)	10.4286(3)

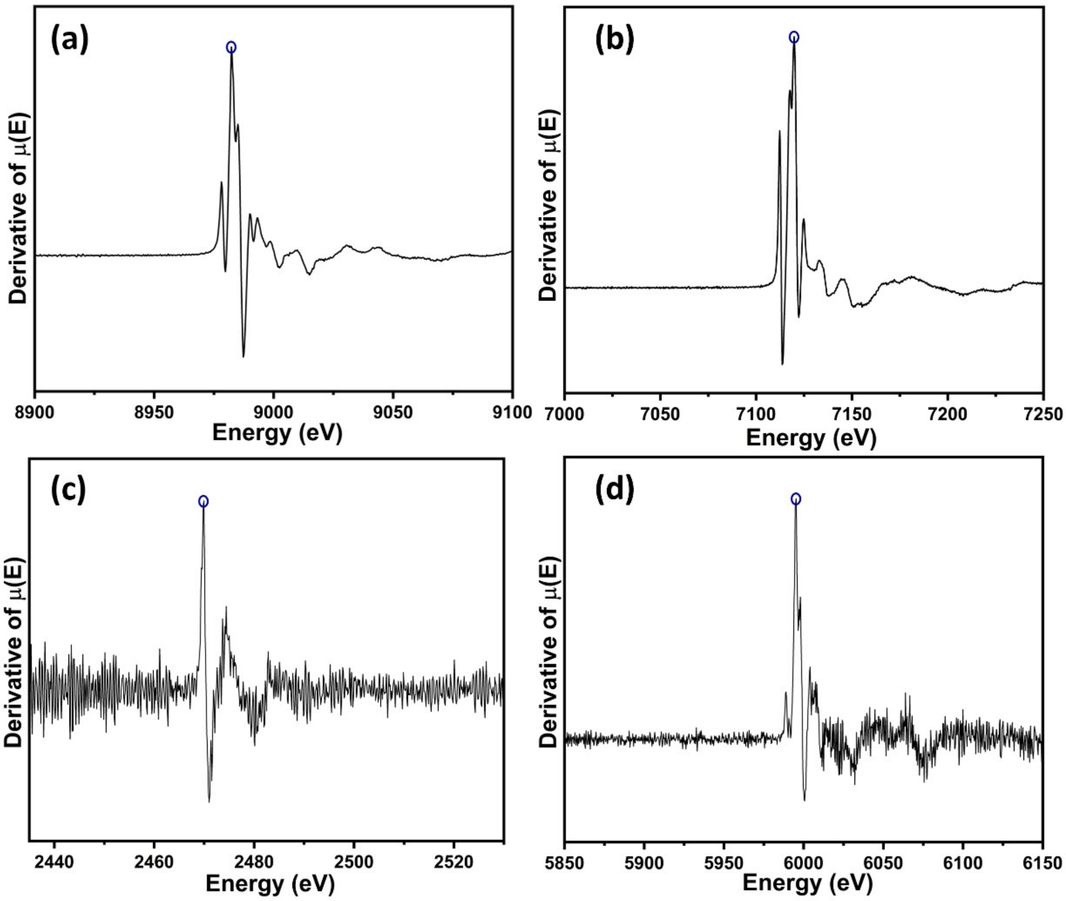

Figure S1. The first derivative of the absorption (μ(E)) of the (a) copper (b) iron (c) chromium and (d) sulfur spectra for $Cu_{0.92}Cr_{0.08}FeS_2$. The K-edge absorption energies were extracted from the maxima as shown by blue circles.

Table S2. The energy positions of Cu, Fe, S and Cr K-edge absorption edges in $Cu_{1-x}Cr_xFeS_2$ ($0 \leq x \leq 0.1$).

Sample (nominal composition)	Cu K edge (eV)	Fe K edge (eV)	S K edge (eV)	Cr K edge (eV)
$CuFeS_2$	8982.3	7120.1	2469.8	-
$Cu_{0.98}Cr_{0.02}FeS_2$	8982.3	7119.8	2469.8	5995.3
$Cu_{0.96}Cr_{0.04}FeS_2$	8982.3	7120.1	2469.8	5995.1
$Cu_{0.94}Cr_{0.06}FeS_2$	8982.3	7119.8	2469.8	5995.3
$Cu_{0.92}Cr_{0.08}FeS_2$	8982.3	7119.8	2469.9	5995.3
$Cu_{0.9}Cr_{0.1}FeS_2$	8982.3	7120.1	2469.7	5995.1

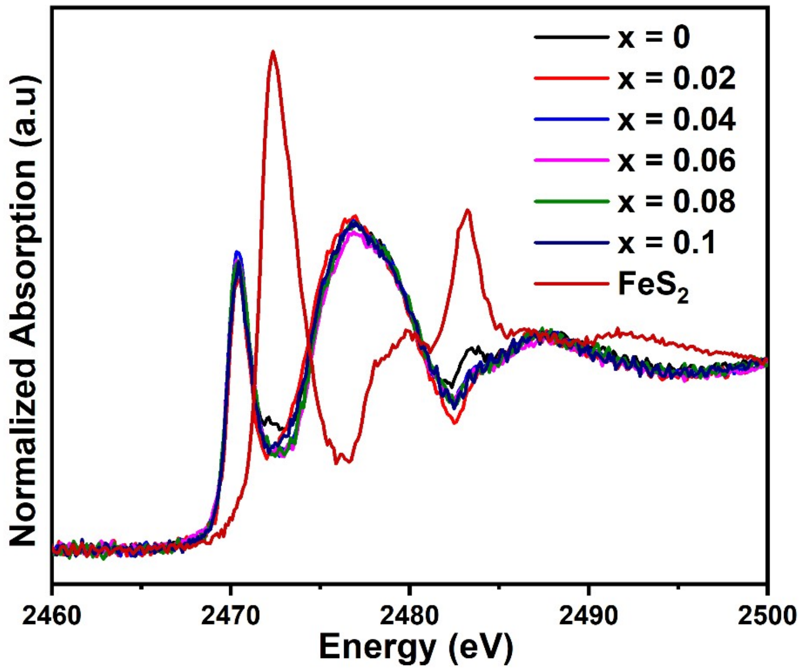

Figure S2. Sulfur absorption spectra for $Cu_{1-x}Cr_xFeS_2$ ($0 \leq x \leq 0.1$) and FeS_2.

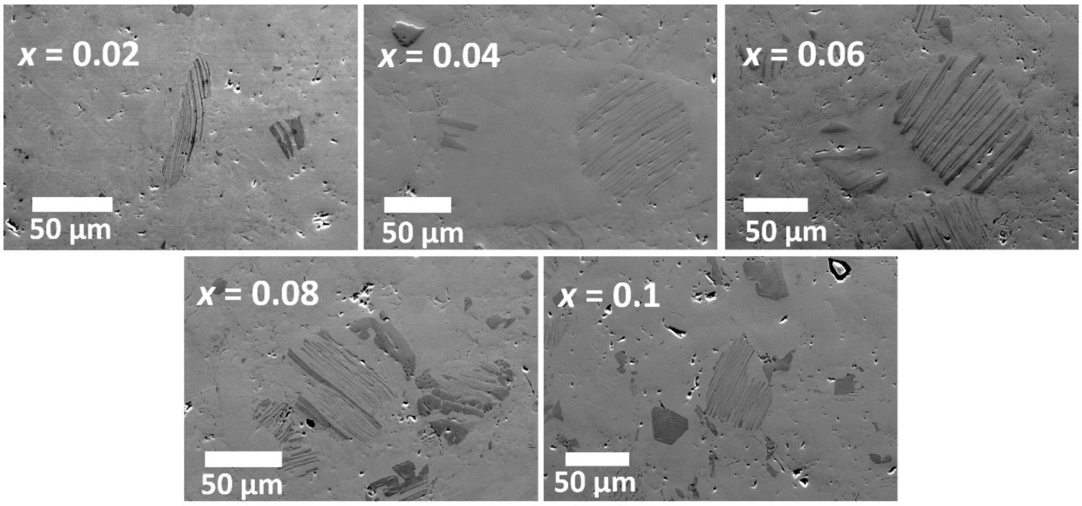

Figure S3. SEM images of $Cu_{1-x}Cr_xFeS_2$ ($0.02 \leq x \leq 0.1$) samples showing the spinel-type secondary phase.

Calculation of the compositions of chalcopyrite phase:

$$Cu_{0.98}Cr_{0.02}FeS_2 = bCu_xFe_yS_2 + cCu_uFe_vCr_wS_4 \quad (1)$$

with

$$0.98 = xb + uc \quad \text{for Cu} \quad (2)$$

$$0.02 = wc \quad \text{for Cr} \quad (3)$$

$$1 = yb + vc \quad \text{for Fe} \quad (4)$$

$$2 = 2b + 4c \quad \text{for S} \quad (5)$$

Taking the values of u, v and w from EDS, b, c, x and y were evaluated for all the samples and the final balanced equations are shown below:

- ***x* = 0.02**;
  $Cu_{0.98}Cr_{0.02}FeS_2 = 0.9755[Cu_{0.9977}Fe_{1.0116}S_2] + 0.0122[Cu_{0.5438}Fe_{1.0761}Cr_{1.6353}S_4]$
- ***x* = 0.04**;
  $Cu_{0.96}Cr_{0.04}FeS_2 = 0.9476[Cu_{0.9887}Fe_{1.0279}S_2] + 0.0261[Cu_{0.8878}Fe_{0.9870}Cr_{1.529}S_4]$
- ***x* = 0.06**;
  $Cu_{0.94}Cr_{0.06}FeS_2 = 0.9091[Cu_{0.9549}Fe_{1.0499}S_2] + 0.0454[Cu_{1.5822}Fe_{0.9998}Cr_{1.3206}S_4]$
- ***x* = 0.08**;
  $Cu_{0.92}Cr_{0.08}FeS_2 = 0.9011[Cu_{0.9884}Fe_{1.0511}S_2] + 0.0494[Cu_{0.5918}Fe_{1.0678}Cr_{1.6189}S_4]$
- ***x* = 0.1**;
  $Cu_{0.9}Cr_{0.1}FeS_2 = 0.8796[Cu_{0.9758}Fe_{1.0662}S_2] + 0.0602[Cu_{0.691}Fe_{1.0306}Cr_{1.6611}S_4]$

Table S3. EDS composition of the main and secondary spinel phases in all the samples; and the calculated composition of the main phase and Cu:Fe ratio.

Nominal composition	EDS composition of main phase*	EDS composition of spinel secondary phase[#]	Main phase composition (calculated)	Cu/Fe ratio in main phase (calculated)
$Cu_{0.98}Cr_{0.02}FeS_2$	$Cu_{1.21}Fe_{1.02}S_2$	$Cu_{0.54}Fe_{1.08}Cr_{1.64}S_4$	$Cu_{0.998}Fe_{1.012}S_2$	0.986
$Cu_{0.96}Cr_{0.04}FeS_2$	$Cu_{1.21}Fe_{1.03}S_2$	$Cu_{0.89}Fe_{0.99}Cr_{1.523}S_4$	$Cu_{0.989}Fe_{1.028}S_2$	0.962
$Cu_{0.94}Cr_{0.06}FeS_2$	$Cu_{1.19}Fe_{1.05}S_2$	$Cu_{1.582}Fe_{1.00}Cr_{1.32}S_4$	$Cu_{0.955}Fe_{1.050}S_2$	0.910
$Cu_{0.92}Cr_{0.08}FeS_2$	$Cu_{1.20}Fe_{1.04}S_2$	$Cu_{0.59}Fe_{1.07}Cr_{1.62}S_4$	$Cu_{0.988}Fe_{1.051}S_2$	0.940
$Cu_{0.9}Cr_{0.1}FeS_2$	$Cu_{1.19}Fe_{1.04}S_2$	$Cu_{0.69}Fe_{1.03}Cr_{1.66}S_4$	$Cu_{0.976}Fe_{1.066}S_2$	0.915

*Normalized to 2 Sulphur atoms per formula unit in $CuFeS_2$. The overlap of the K_α and L_α characteristic lines of Cu and Fe, may result in uncertainties in the quantitative at.% determined by EDS and exhibiting a slight Cu excess as reported previously.[1,2]

[#] Normalized to 4 Sulphur atoms per formula unit in $[Cu, Fe, Cr]_3S_4$

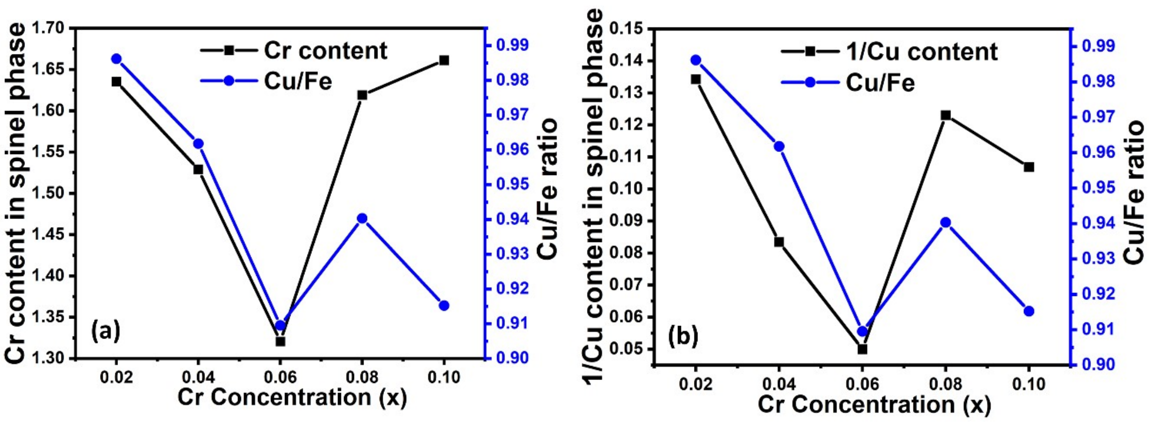

Figure S4. The dependence of (a) Cr content and (b) 1/Cu in the spinel secondary phase, on the Cu:Fe ratio in the main phase plotted as a function of nominal Cr concentration (*x*).

Table S4. Room temperature Hall measurement data of $Cu_{1-x}Cr_xFeS_2$ ($0 \leq x \leq 0.1$) samples.

Sample	Charge carrier concentration ($\times 10^{19}$ cm^{-3})	Charge carrier mobility (cm^2 V^{-1} s^{-1})
$CuFeS_2$	1.4(2)	16(2)
$Cu_{0.98}Cr_{0.02}FeS_2$	5.8(2)	15(1)
$Cu_{0.96}Cr_{0.04}FeS_2$	3.8(4)	11(1)
$Cu_{0.94}Cr_{0.06}FeS_2$	2.9(2)	12(1)
$Cu_{0.92}Cr_{0.08}FeS_2$	4.4(4)	18(2)
$Cu_{0.9}Cr_{0.1}FeS_2$	5.8(4)	15(1)

Calculation Details:

- **Lorenz number**:

The electronic part of the thermal conductivity (κ_e) was calculated from the Wiedemann-Franz relation:

$$\kappa_e = L\sigma T \tag{S1}$$

L is the temperature-dependent Lorenz number and T is the temperature. The temperature-dependent Lorenz number was evaluated from the following relation:

$$L = \left(\frac{k_B}{e}\right)^2 \left(\frac{\left(r + \frac{7}{2}\right) F_{r+5/2}(\eta)}{\left(r + \frac{3}{2}\right) F_{r+1/2}(\eta)} - \left[\frac{\left(r + \frac{5}{2}\right) F_{r+3/2}(\eta)}{\left(r + \frac{3}{2}\right) F_{r+1/2}(\eta)} \right]^2 \right) \tag{S2}$$

Where k_B is the Boltzmann's constant, η is the reduced Fermi energy that is obtained from Seebeck coefficient values via the relation:

$$S = \pm \frac{k_B}{e}\left(\frac{\left(r+\frac{5}{2}\right)F_{r+3/2}(\eta)}{(r+\frac{3}{2})F_{r+1/2}(\eta)} - \eta\right) \tag{S3}$$

Here, $F(\eta)$ is the reduced Fermi integral given by:

$$F_n(\eta) = \int_0^{\infty} \frac{x^n}{1+\ e^{x-\eta}}\,dx \tag{S4}$$

And $\eta = E_F/k_BT$ where E_F denotes the Fermi level. Assuming that the main scattering mechanism is acoustic phonon scattering, the value of r is taken as -1/2. The Lorenz number at each temperature value is therefore obtained by substituting η and r in equation (S2).

- **Mean sound velocity (v_m):**

$$v_m = \left[\frac{1}{3}\left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right)\right]^{-\frac{1}{3}}$$

and **average sound velocity (v_{avg}):**

$$v_{avg} = (2v_t + v_l)/3$$

where, v_l and v_t are the longitudinal and transverse velocities, respectively.

- **Shear modulus (G):**

$$G = dv_t^2$$

Where d and v_t are the density and transverse velocities respectively.

- **Young's modulus (E):**

$$E = \frac{dv_t^2\,(3v_l^2 - 4v_t^2)}{(v_l^2 - v_t^2)}$$

- **Debye temperature (θ_D):**

$$\theta_D = \frac{h}{k_B}\left(\frac{3N}{4\pi V}\right)^{1/3} v_m$$

where h is the Plank's constant, k_B is the Boltzmann's constant, N is the number of atoms in the unit cell, V is the volume of the unit cell and v_m is the mean sound velocity.

Table S5. Temperature dependent Lorenz number of $CuFeS_2$.

Temperature (K)	**Lorenz number (x 10^{-8} V^2 K^{-2})**
323	1.524
373	1.526
423	1.527
473	1.527
523	1.528
573	1.531
623	1.538
673	1.563

Table S6. Temperature dependent Lorenz number of $Cu_{0.98}Cr_{0.02}FeS_2$.

Temperature (K)	**Lorenz number (x 10^{-8} V^2 K^{-2})**
323	1.616
373	1.611
423	1.609
473	1.608
523	1.604

573	1.606
623	1.607
673	1.611

Table S7. Temperature dependent Lorenz number of $Cu_{0.96}Cr_{0.04}FeS_2$.

Temperature (K)	**Lorenz number (x 10^{-8} V^2 K^{-2})**
323	1.549
373	1.547
423	1.545
473	1.543
523	1.539
573	1.535
623	1.540
673	1.553

Table S8. Temperature dependent Lorenz number of $Cu_{0.94}Cr_{0.06}FeS_2$.

Temperature (K)	**Lorenz number (x 10^{-8} V^2 K^{-2})**
323	1.539
373	1.538
423	1.536
473	1.535
523	1.533

573	1.533
623	1.536
673	1.542

Table S9. Temperature dependent Lorenz number of $Cu_{0.92}Cr_{0.08}FeS_2$.

Temperature (K)	Lorenz number (x 10^{-8} V^2 K^{-2})
323	1.620
373	1.610
423	1.601
473	1.595
523	1.591
573	1.588
623	1.583
673	1.584

Table S10. Temperature dependent Lorenz number of $Cu_{0.9}Cr_{0.1}FeS_2$.

Temperature (K)	Lorenz number (x 10^{-8} V^2 K^{-2})
323	1.641
373	1.630
423	1.626
473	1.623
523	1.623
573	1.625

623	1.629
673	1.6385

References:

1 S. Tippireddy, F. Azough, F. T. Tompkins, A. Bhui, R. Freer, R. Grau-Crespo, K. Biswas, P. Vaqueiro and A. V. Powell, *Chem Mater*, 2022, **34**, 5860–5873.

2 S. Tippireddy, F. Azough, Vikram, A. Bhui, P. Chater, D. Kepaptsoglou, Q. Ramasse, R. Freer, R. Grau-Crespo, K. Biswas, P. Vaqueiro and A. V. Powell, *J Mater Chem A*, 2022, **10**, 23874–23885.