Supplementary Information

Promoted crystallisation and cationic ordering in thermoelectric $Cu_{26}V_2Sn_6S_{32}$ colusite by eccentric vibratory ball milling

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Table S1. Rietveld analysis of sample milled for 1 hour + SPS

Colusite $Cu_{26}V_2Sn_6S_{32}$	Weight fraction in sample (%)	94(2)	Digenite $Cu_{2-x}S$	Weight fraction in sample (%)	5(1)
	Space group	$P\bar{4}3n$		Space group	$Fm\bar{3}m$
	a (nm)	1.0781(9)		a (nm)	0.5561(2)
	R-Bragg	5.51		R-Bragg	15.5
Covellite CuS	Weight fraction in sample (%)	1(1)			
	Space group	$P6_3/mmc$			
	a (nm)	0.3794(6)			
	c (nm)	1.6331(4)			
	R-Bragg	17.3			

Conventional Rietveld factors (as defined in FullProf software):

R_p	17.3
R_{wp}	18.2
R_{exp}	12.97
χ^2	1.97

Table S2. Rietveld analysis of sample milled for 3 hours + SPS

Colusite $Cu_{26}V_2Sn_6S_{32}$	Weight fraction in sample (%)	95(2)	Digenite $Cu_{2-x}S$	Weight fraction in sample (%)	3(1)
	Space group	$P\bar{4}3n$		Space group	$Fm\bar{3}m$
	a (nm)	1.0779(0)		a (nm)	0.5556(0)
	R-Bragg	6.57		R-Bragg	27.3
Covellite CuS	Weight fraction in sample (%)	2(1)			
	Space group	$P6_3/mmc$			
	a (nm)	0.3793(2)			
	c (nm)	1.6355(2)			
	R-Bragg	26.1			

Conventional Rietveld factors (as defined in FullProf software):

R_p	17.9
R_{wp}	20.7
R_{exp}	14.03
χ^2	2.18

Table S3. Rietveld analysis of sample milled for 6 hours + SPS

Colusite $Cu_{26}V_2Sn_6S_{32}$	Weight fraction in sample (%)	99(1)*
	Space group	$P\bar{4}3n$
	a (nm)	1.0763(9)
	R-Bragg	3.70

* contamination by SiO_2

Conventional Rietveld factors (as defined in FullProf software):

R_p	15.7
R_{wp}	16.0
R_{exp}	12.36
χ^2	1.67

Table S4. Rietveld analysis of sample milled for 12 hours + SPS

Colusite $Cu_{26}V_2Sn_6S_{32}$	Weight fraction in sample (%)	99(1)*
	Space group	$P\bar{4}3n$
	a (nm)	1.0761
	x_{Cu2}	0.2544(2)
	x, y, z_{Cu3}	0.2546(3)
	x, y, z_{S1}	0.1252(7)
	x_{S2}	0.3790(3)
	y_{S2}	0.3681(3)
	z_{S2}	0.1251(6)
	R-Bragg	2.59

* contamination by WC

Conventional Rietveld factors (as defined in FullProf software):

R_p	15.5
R_{wp}	15.1
R_{exp}	11.63
χ^2	1.68

Table S5. Cationic elemental analysis from EDS analysis on the colusite matrix normalised for 26 Cu

	Cu	V	Sn
1h + SPS	26	1.30	7.74
3h + SPS	26	1.549	7.15
6h + SPS	26	1.68	6.74
12h + SPS	26	2.06	6.23

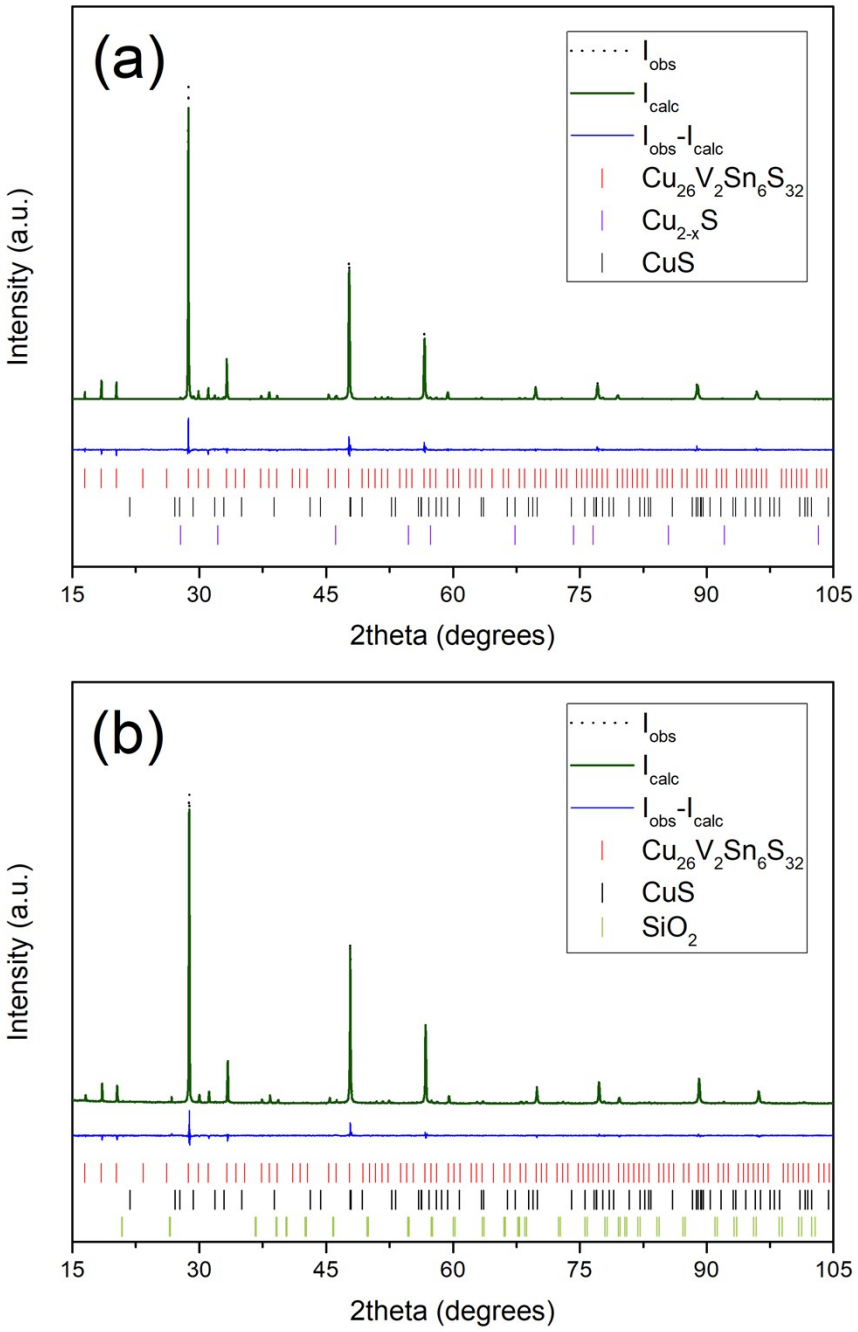

Figure S1. Rietveld refinements of the XRPD patterns of (a) 3h+SPS and (b) 6h+SPS samples.

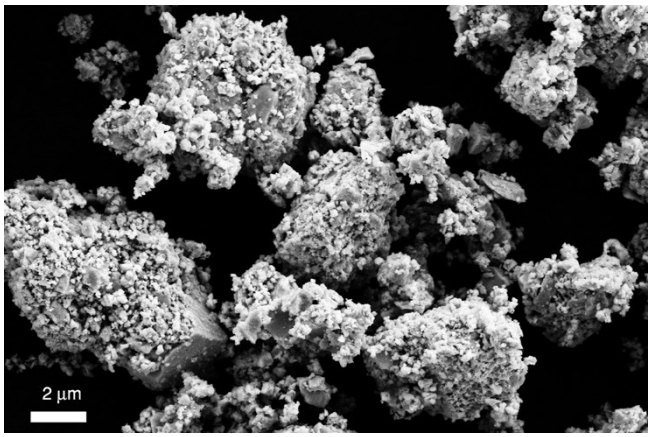

Figure S2. Typical micrography of as- milled powders (3h).

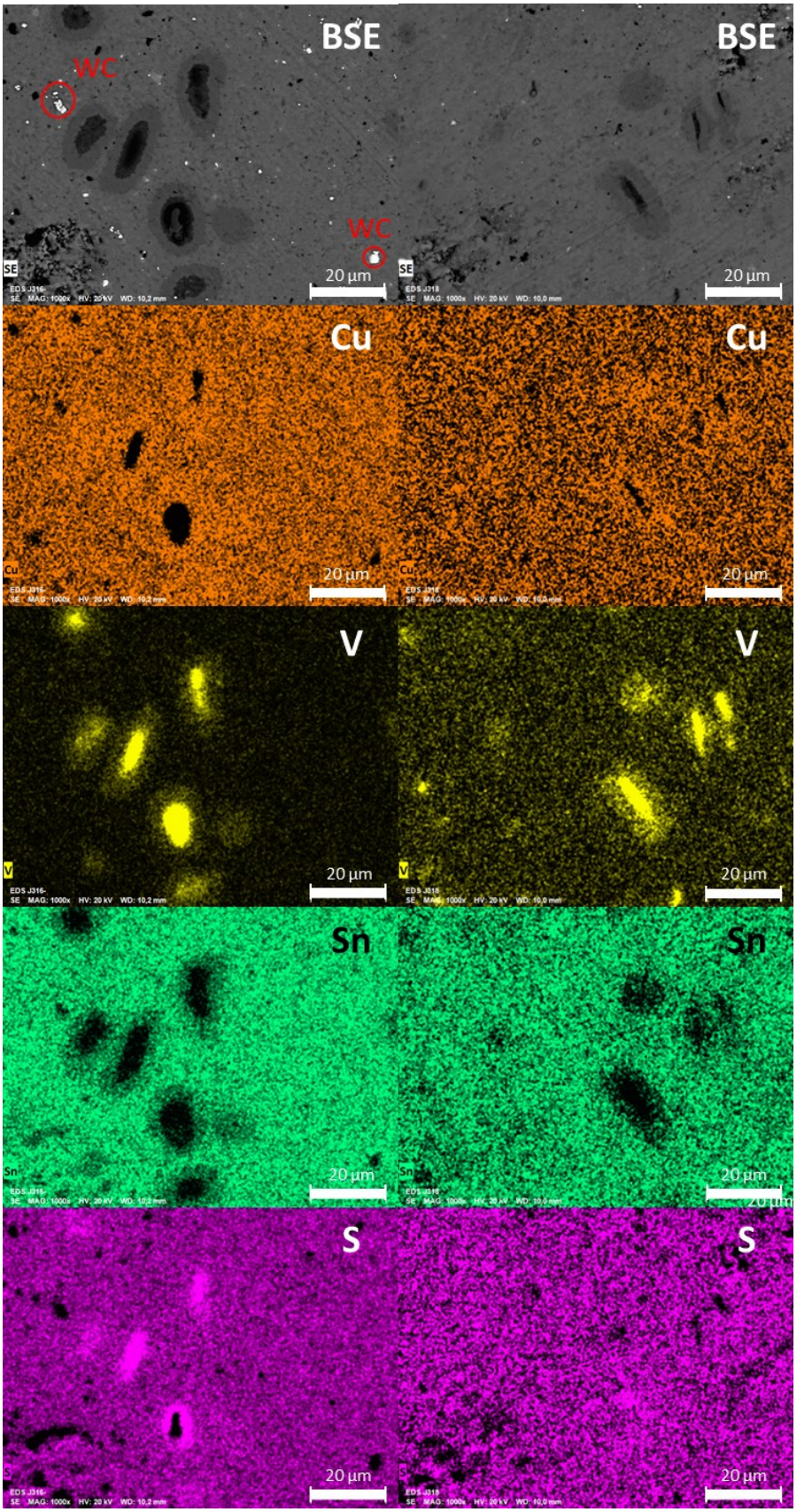

Figure S3. BSE micrographs and corresponding EDS elemental analysis maps for the samples 1h+SPS (left column) and 3h+SPS (right column)

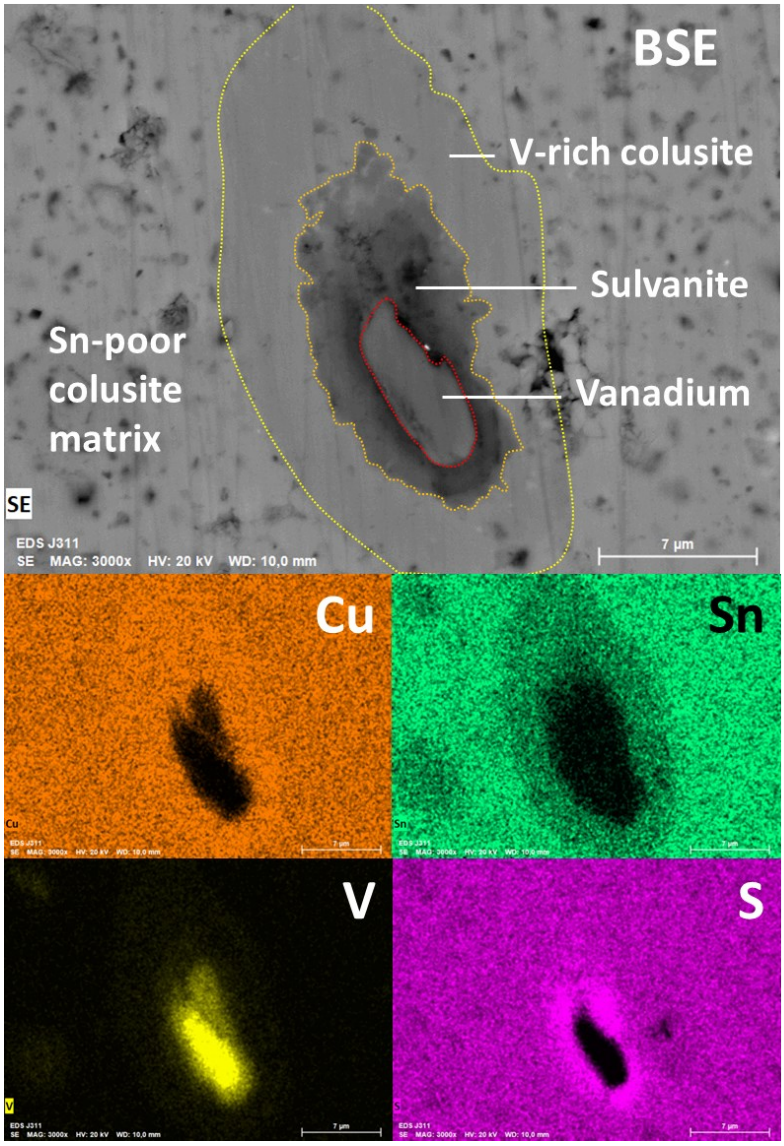

Figure S4. Backscattered SEM image of polished surface showing V-rich core-shell structures in 6h+SPS sample

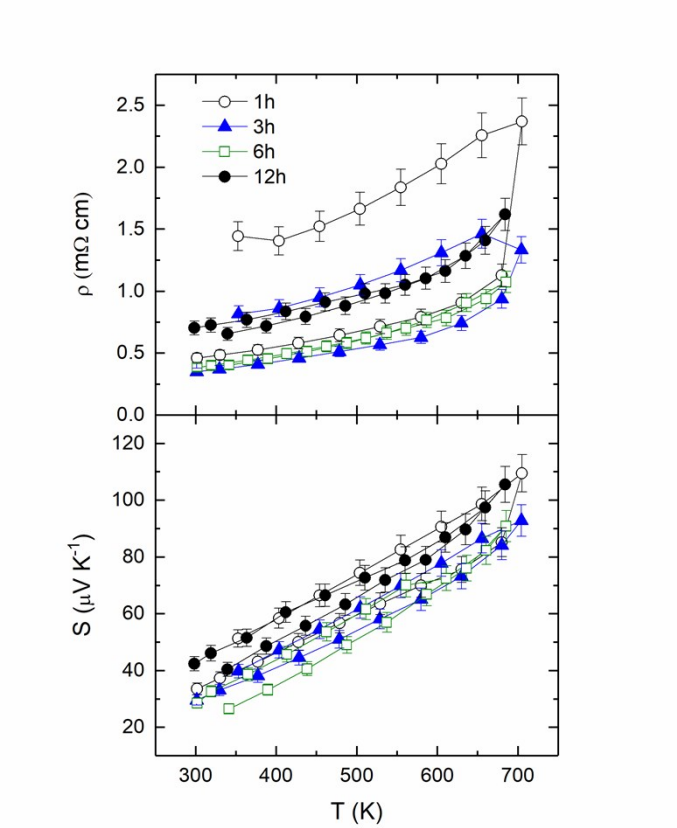

Figure S5. Heating and cooling measurements of the electrical resistivity and Seebeck coefficient with different ball-milling times