Supplementary information for

Indium thiospinel $In_{1-x}\square_x In_2S_4$ – structural characterization and thermoelectric properties

Paweł Wyżga[a,b], Igor Veremchuk[b], Cameliu Himcinschi[c], Ulrich Burkhardt[b], Wilder Carrillo-Cabrera[b], Matej Bobnar[b], Christoph Hennig[d,e], Andreas Leithe-Jasper[b], Jens Kortus[c], Roman Gumeniuk*[a]

[a] Institut für Experimentelle Physik, TU Bergakademie Freiberg, Leipziger Str. 23, 09599 Freiberg, Germany

[b] Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Straße 40, 01187 Dresden, Germany

[c] Institut für Theoretische Physik, TU Bergakademie Freiberg, Leipziger Str. 23, 09599 Freiberg, Germany

[d] Institute of Resource Ecology, HZDR, 01314 Dresden, Germany

[e] Rossendorf Beamline BM20, ESRF, 38043 Grenoble, France

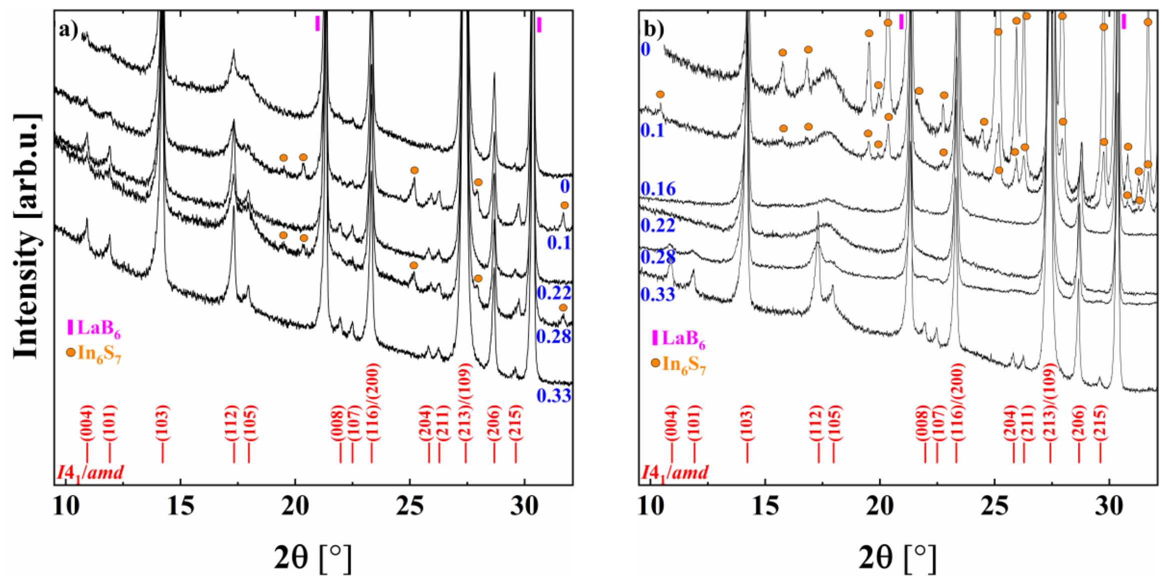

Figure S1. PXRD of x = 0 - 0.33 samples after: a) pre-synthesis (batch B1); b) annealing (batch B3). LaB_6 as internal standard.

Table S1. Selected crystallographic data for $In_{1-x}\square_xIn_2S_4$ samples (B3) at 293 K obtained from Rietveld refinement.

Nominal *x*	**0.33**	**0.28**	**0.28**		**0.22**
Type of refinement	single-phase	single-phase	two-phase		single-phase
Composition,	$In_{2.67}S_4$,[a]	$In_{2.69(1)}S_4$,[a]	$In_{2.67}S_4$,[b]	$In_{2.72}S_4$,[b]	$In_{2.72(1)}S_4$,[a]
molar mass /g·mol^{-1}	434.5	437.8	434.5	440.6	440.6
Space group, no. of formula unit Z	$I4_1/amd$ (no. 141), 12			$Fd\bar{3}m$ (no. 227), 8	
a /Å	7.6194(1)	7.6160(1)	7.6192(1)	10.7685(1)	10.75811(5)
c /Å	32.327(1)	32.293(1)	32.329(1)	-	-
V /Å^3	1876.8 (1)	1873.1(1)	1876.8(1)	1248.73(3)	1245.11(1)
d /g·cm^{-3}	4.6129	4.6526	4.6129	4.6867	4.6991
λ /Å			0.4591		
$2\theta_{max}$ /°; sinθ/λ (max)			41, 0.763		
R_P, R_{wp} /%	2.67, 3.82	4.14, 6.11	4.15, 5.82		3.85, 5.46
Phase fraction /%	-	-	27.5(7)	72.5(7)	-

a – refined composition.
b – composition was fixed.

Table S2. Fractional positions, isotropic displacement parameters (U_{iso}) and site occupancy factors (SOF) of atoms for $In_{1-x}\square_x In_2S_4$ samples (B3) at 293 K obtained from Rietveld refinement.

Atoms	*x/a*	*y/b*	*z/c*	U_{iso} [pm^2]	SOF
		single-phase *x* = 0.33 (*I*4$_1$/*amd*)			
In1 (8*c*)	0	0	0	143(8)	1
In2 (8*e*)	0	1/4	0.20436(9)	91(4)	1
In3 (16*h*)	0	0.5192(2)	0.33272(9)	123(5)	1
S1 (16*h*)	0	0.506(2)	0.2509(5)	120(20)	1
S2 (16*h*)	0	0.007(1)	0.0788(5)	90(20)	1
S3 (16*h*)	0	0.022(1)	0.4126(5)	86(17)	1
		single-phase *x* = 0.28 (*I*4$_1$/*amd*)			
In1 (8*c*)	0	0	0	150(30)	1
In2 (8*e*)	0	1/4	0.2058(4)	102(14)	0.83(1)
In3 (16*h*)	0	-0.0098(9)	0.3328(4)	188(18)	1
In4 (4*a*)	0	1/4	7/8	250[a]	0.42(2)
S1 (16*h*)	0	-0.006(3)	0.2513(9)	110[a]	1
S2 (16*h*)	0	0.014(3)	0.080(1)	110[a]	1
S3 (16*h*)	0	0.019(3)	0.414(1)	110[a]	1
		two-phase *x* = 0.28 (*I*4$_1$/*amd*)			
In1 (8*c*)	0	0	0	140(20)[b]	1
In2 (8*e*)	0	1/4	0.2045	140(20)[b]	1
In3 (16*h*)	0	0.519	0.3325	140(20)[b]	1
S1 (16*h*)	0	0.5116	0.2491	110(60)[b]	1
S2 (16*h*)	0	0.0109	0.0805	110(60)[b]	1
S3 (16*h*)	0	0.026	0.414	110(60)[b]	1
		two-phase *x* = 0.28 (*Fd*$\bar{3}$*m*)			
In1 (8*b*)	3/8	3/8	3/8	161(11)	0.72
In2 (16*c*)	0	0	0	169(8)	1
S (32*e*)	0.2426(3)	0.2426(3)	0.2426(3)	98(15)	1
		single-phase *x* = 0.22 (*Fd*$\bar{3}$*m*)			
In1 (8*b*)	3/8	3/8	3/8	155(9)	0.72(1)
In2 (16*c*)	0	0	0	206(5)	1
S (32*e*)	0.2428(2)	0.2428(2)	0.2428(2)	114(9)	1

a - refinement yielded U_{iso} with unreliable error and thus the parameter was fixed.
b - U_{iso} were not stable and thus they were refined as: $U_{In1} = U_{In2} = U_{In3}$ and $U_{S1} = U_{S2} = U_{S3}$.

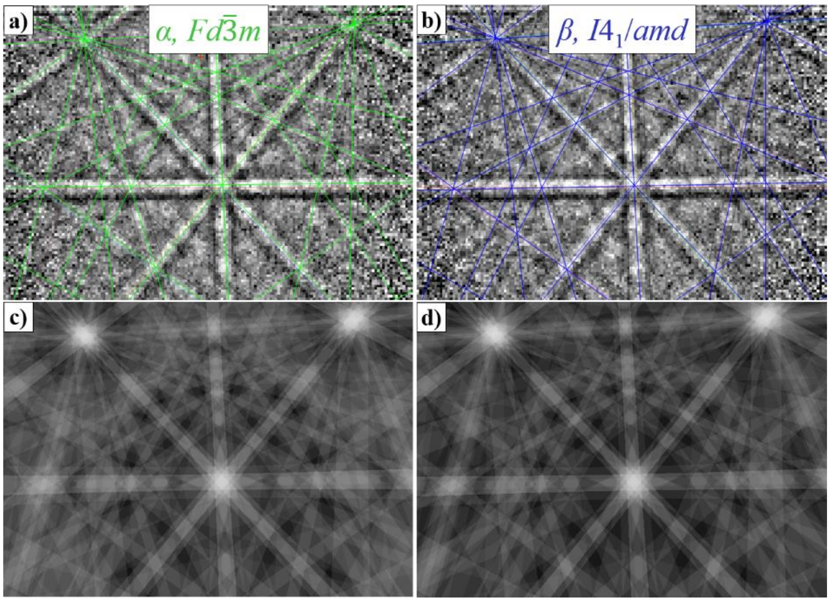

Figure S2. Experimental (a,b) and simulated (c,d) Kikuchi patterns for $In_{0.67}\square_{0.33}In_2S_4$ single crystal. Patterns a) and b) were assigned to $Fd\bar{3}m$ and $I4_1/amd$ space group, respectively. Color code as for Figure 6.

Table S3. List of all Raman modes [cm^{-1}] observed for $In_{1-x}\square_{x}In_2S_4$ (x = 0.16, 0.22, 0.28, 0.33) samples (batch B3 + single crystal). Values in parenthesis indicate modes observed only for some grains. Modes in green are visible only for the β polymorph.

This work					Literature – measured values		
x = 0.33 (single crystal)	x = 0.33	x = 0.28	x = 0.22	x = 0.16	β-In_2S_3 [1]	$FeIn_2S_4$ (cubic)[2]	$MnIn_2S_4$ (cubic)[2]
64	64		67	67	61		
73	72	71			70		
85	84			79		82	87
91	90	(89)					
102	100	(100)	100	100	102	96	102
116	115	(113)	(112)		113		
122	121						
137	135	(134)			137		
171	~171		170			167	166
181	177	174		~178	180	182	180
198	193	189	~206	~211	196		
219	~219				217	231	221
246	244	244	243	~252	244	253	245
267	265	261	260	~268	266	271	261
309	307	306	304	~295	306	313	303
327	324	320	~333	~332	326	329	320
369	365	364	361	~360	367	370	353

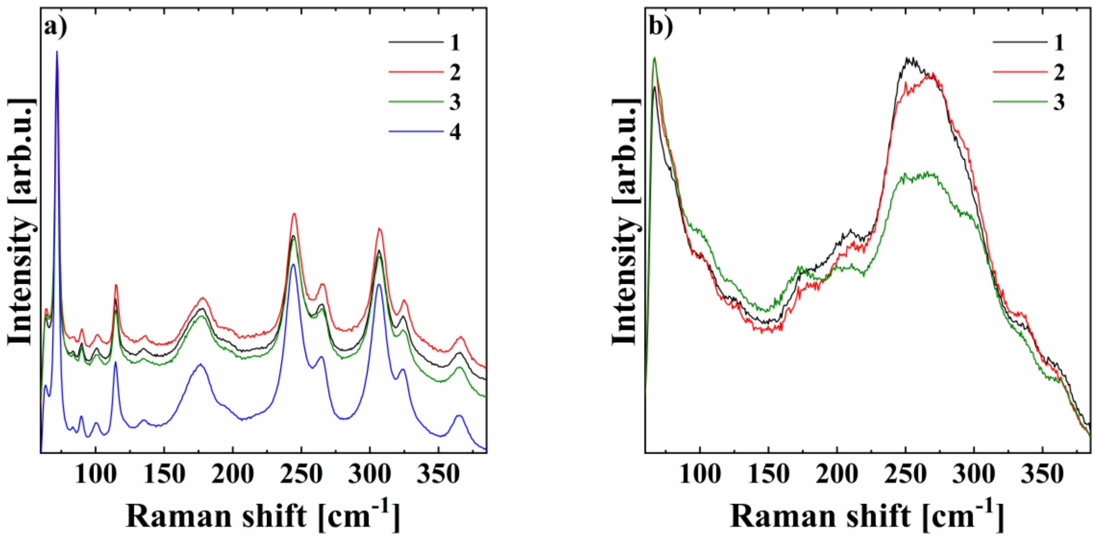

Figure S3. Raman spectra collected from different grains of $In_{1-x}\square_{x}In_2S_4$-samples (batch B3). a) x = 0.33, b) x = 0.16.

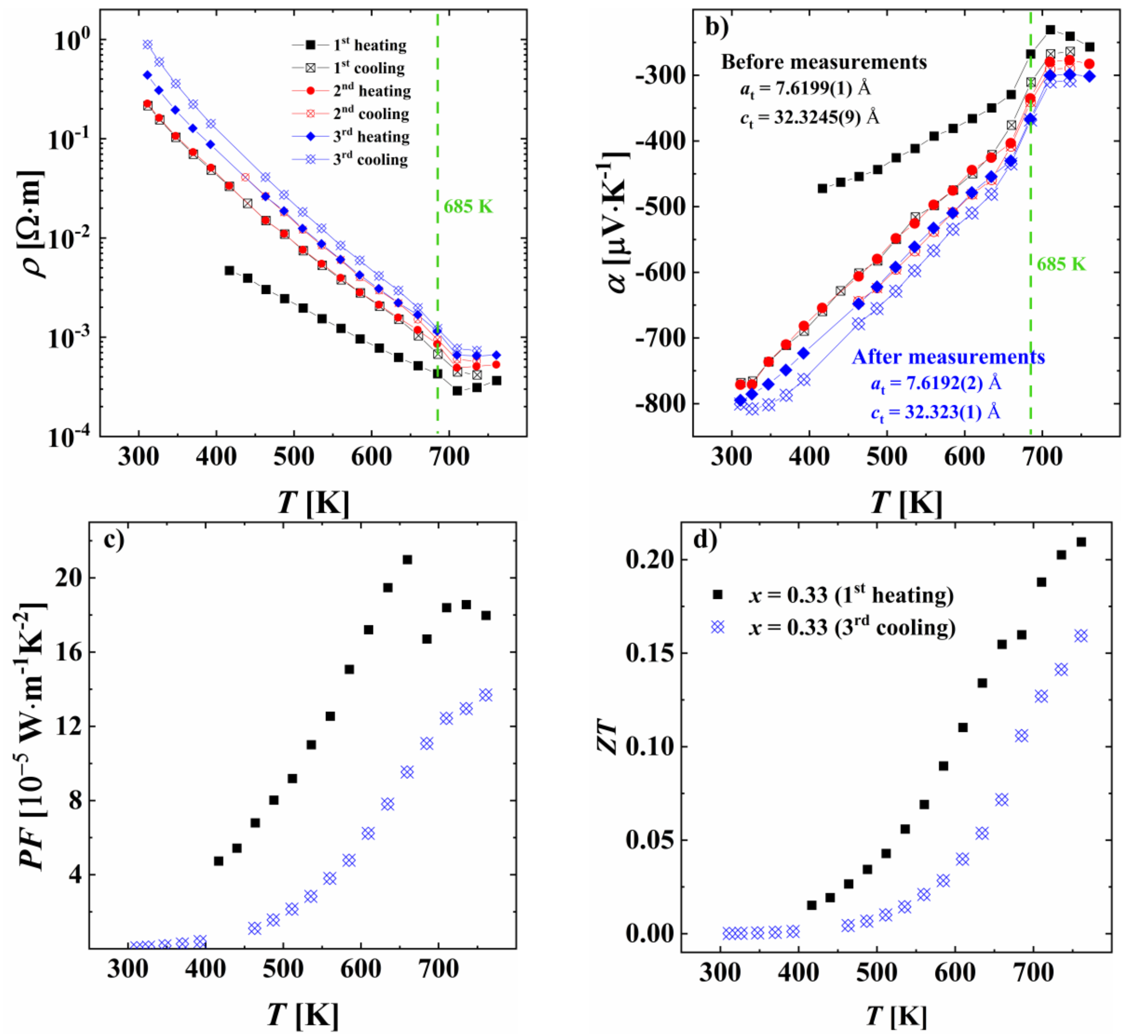

Figure S4. Cyclic TE measurement of $x = 0.33$ sample: a) electrical resistivity, b) Seebeck coefficient, c) power factor and d) *ZT* parameter. Lines are guide for the eye.

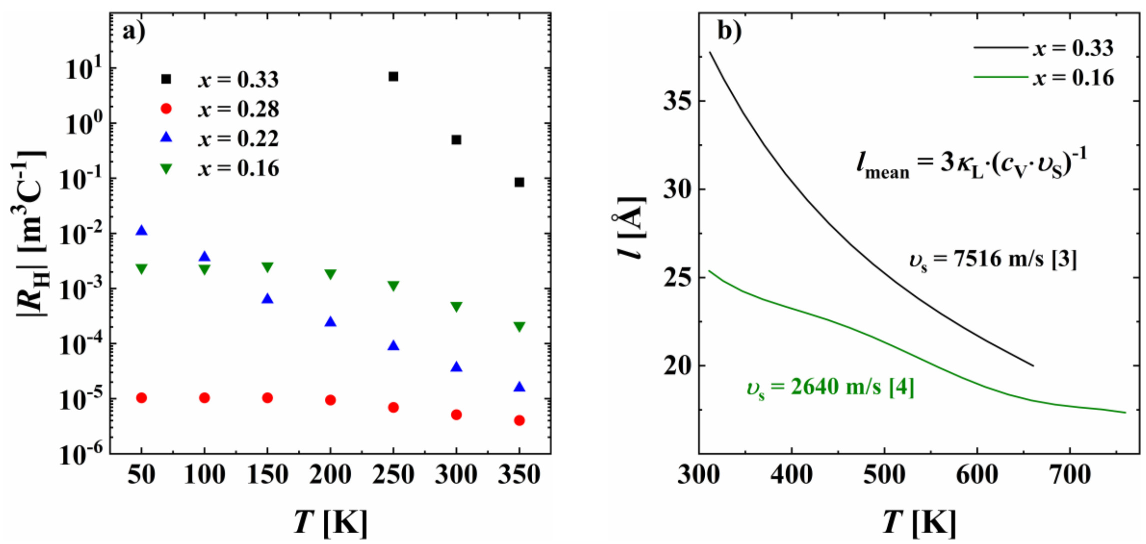

Figure S5. a) Temperature dependence of Hall coefficient R_H for $In_{1-x}\square_xIn_2S_4$ (x = 0.16, 0.22, 0.28, 0.33) samples. b) Estimation of phonon mean free path for $In_{0.67}\square_{0.33}In_2S_4$ and $In_{0.84}\square_{0.16}In_2S_4$.

References

1 K. Kambas, J. Spyridelis and M. Balkanski, *Phys. Status Solidi*, 1981, **105**, 291–296.

2 M. Guc, V. V. Ursaki, I. V. Bodnar, D. V. Lozhkin, E. Arushanov, V. Izquierdo-Roca and A. Pérez Rodríguez, *Mater. Chem. Phys.*, 2012, **136**, 883–888.

3 M. Amlouk, M. A. Ben Said, N. Kamoun, S. Belgacem, N. Brunet and D. Barjon, *Jpn. J. Appl. Phys.*, 1999, **38**, 26–30.

4 V. Krasnenko and M. G. Brik, *Mater. Res. Express*, 2014, **1**, 015905.