Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Thermal stability of *p*-type Ag-doped Mg_3Sb_2 thermoelectric materials investigated by powder X-ray Diffraction

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Table S1. Rietveld refinement details of in-house *in situ* PXRD data for the as-pressed pellet 1 in two cycles of heating and cooling.

T(K)_heating		303-1	398-1	498-1	598-1	698-1
$t_{exp.}$(min)		52	52	52	52	52
No. of points		6573	6573	6573	6573	6573
No. of reflections (Mg_3Sb_2)		69	69	69	69	66
No. of parameters		26	29	32	29	32
R_f (Mg_3Sb_2) (%)		6.06	6.41	6.46	8.04	8.46
R_{Bragg} (Mg_3Sb_2) (%)		9.95	10.2	10.3	12.6	15.6
R_p (%)		19.8	20.1	19.4	19.9	21.2
R_{wp} (%)		24.5	25.2	23.6	23.3	24.0
χ^2		47.2	25.2	19.9	19.9	20.3
Wt.% Mg_3Sb_2		99.42(0.83)	99.26(0.87)	98.60(0.76)	97.87(0.76)	97.17(0.78)
Wt.% Sb		0.58(0.09)	0.74(0.09)	1.40(0.07)	2.13(0.07)	2.83(0.07)
Mg_3Sb_2	*a*=*b* (Å)	4.56882(16)	4.57552(17)	4.57790(13)	4.58171(11)	4.58596(10)
	c (Å)	7.23568(29)	7.24843(30)	7.25668(23)	7.26656(20)	7.27658(17)
	Volume (Å^3)	130.803(8)	131.418(9)	131.705(7)	132.103(6)	132.531(5)

T(K)_cooling	598-2	498-2	398-2	343-2
$t_{exp.}$(min)	52	52	52	52
No. of points	6573	6573	6573	6573
No. of reflections (Mg_3Sb_2)	66	65	65	65
No. of parameters	30	29	37	29
R_f (Mg_3Sb_2) (%)	8.19	8.52	8.46	8.77
R_{Bragg} (Mg_3Sb_2) (%)	13.6	13.8	12.9	14.2
R_p (%)	21.3	20.9	19.9	20.8

R_{wp} (%)		24.4	24.3	23.7	24.5
χ^2		22.0	23.2	24.1	26.1
Wt.% Mg_3Sb_2		96.46(0.78)	96.45(0.77)	95.43(0.76)	96.39(0.78)
Wt.% Sb		3.54(0.08)	3.55(0.08)	4.57(0.10)	3.61(0.09)
Mg_3Sb_2	a=b (Å)	4.57982 (9)	4.57373(9)	4.56788(9)	4.56435(9)
	c (Å)	7.26490(17)	7.25301(17)	7.24161(17)	7.23494(16)
	Volume (Å^3)	131.964(5)	131.398(5)	130.857(5)	130.534(5)

T(K)_heating		398-3	498-3	598-3	698-3
$t_{exp.}$(min)		52	52	52	52
No. of points		6573	6573	6573	6573
No. of reflections (Mg_3Sb_2)		65	66	65	66
No. of parameters		39	30	33	31
R_f (Mg_3Sb_2) (%)		8.20	8.51	7.94	8.60
R_{Bragg} (Mg_3Sb_2) (%)		12.9	14.2	13.4	14.3
R_p (%)		19.8	21.4	21.2	21.1
R_{wp} (%)		23.5	24.8	24.3	23.9
χ^2		24.1	24.3	22.5	21.0
Wt.% Mg_3Sb_2		95.44(0.75)	96.40(0.79)	96.54(0.78)	96.73(0.77)
Wt.% Sb		4.56(0.10)	3.60(0.09)	3.46(0.08)	3.27(0.08)
Mg_3Sb_2	a=b (Å)	4.56781(9)	4.57394(9)	4.58002(9)	4.58569(9)
	c (Å)	7.24151(16)	7.25347(17)	7.26492(16)	7.27624(16)
	Volume (Å^3)	130.851(5)	131.419(5)	131.976(5)	132.510(5)

T(K)_cooling		598-4	498-4	398-4	303-4
$t_{exp.}$(min)		52	52	52	52
No. of points		6573	6573	6573	6573
No. of reflections (Mg_3Sb_2)		65	65	65	65
No. of parameters		29	32	38	38
R_f (Mg_3Sb_2) (%)		8.21	8.43	8.51	8.65
R_{Bragg} (Mg_3Sb_2) (%)		13.6	14.8	13.2	14.1
R_p (%)		21.5	21.6	20.4	21.9
R_{wp} (%)		24.7	24.9	24.1	25.6
χ^2		23.1	24.6	25.5	29.0
Wt.% Mg_3Sb_2		96.28(0.78)	96.26(0.80)	95.18(0.77)	95.91(0.82)
Wt.% Sb		3.72(0.08)	3.74(0.09)	4.82(0.11)	4.09(0.10)
Mg_3Sb_2	a=b (Å)	4.57970(9)	4.57362(9)	4.56768(9)	4.56080(9)
	c (Å)	7.26473(17)	7.25281(17)	7.24141(17)	7.22834(17)
	Volume (Å^3)	131.954(5)	131.388(5)	130.841(5)	130.212(5)

Table S2. Rietveld refinement details of in-house *in situ* PXRD data for the powdered sample (from pellet 2) in two cycles of heating and cooling.

T(K)_heating		303-1	398-1	498-1	598-1	698-1	723-1
$t_{exp.}$(min)		52	52	52	52	52	52
No. of points		6573	6573	6573	6573	6573	6573
No. of reflections (Mg_3Sb_2)		69	71	69	69	69	69
No. of parameters		27	23	27	27	30	27
R_f (Mg_3Sb_2) (%)		5.79	6.83	5.76	6.58	6.84	6.94
R_{Bragg} (Mg_3Sb_2) (%)		11.1	16.9	10.9	11.8	11.9	12.2
R_p (%)		17.3	17.3	17.5	18.5	19.1	19.0
R_{wp} (%)		20.5	20.6	21.0	21.9	22.4	22.3
χ^2		14.6	14.8	15.0	14.7	15.6	15.3
Wt.% Mg_3Sb_2		99.35(0.46)	99.38(0.46)	99.13(0.46)	97.67(0.69)	97.16(0.72)	97.01(0.71)
Wt.% Sb		0.65(0.04)	0.62(0.04)	0.87(0.05)	2.33(0.07)	2.84(0.07)	2.99(0.07)
Mg_3Sb_2	*a*=*b* (Å)	4.55838 (11)	4.56308 (11)	4.56719 (11)	4.57193 (10)	4.57669 (9)	4.57782 (9)
	c (Å)	7.22769 (22)	7.23736 (22)	7.24531 (21)	7.25388 (18)	7.26312 (17)	7.26539 (17)
	Volume (Å^3)	130.062(6)	130.505(6)	130.884(6)	131.310(5)	131.752(5)	131.858(5)

T(K)_cooling		698-2	598-2	498-2	343-2
$t_{exp.}$(min)		52	52	52	52
No. of points		6573	6573	6573	6573
No. of reflections (Mg_3Sb_2)		69	69	67	67
No. of parameters		31	29	31	30
R_f (Mg_3Sb_2) (%)		7.05	6.82	6.80	7.09
R_{Bragg} (Mg_3Sb_2) (%)		12.1	12.2	11.6	12.4
R_p (%)		18.7	18.7	18.1	18.0
R_{wp} (%)		22.1	21.7	21.5	21.2
χ^2		15.0	15.4	15.5	16.2
Wt.% Mg_3Sb_2		97.00(0.71)	96.83(0.69)	96.85(0.69)	96.37(0.45)
Wt.% Sb		3.00(0.07)	3.17(0.07)	3.15(0.07)	3.63(0.08)
Mg_3Sb_2	*a*=*b* (Å)	4.57702(9)	4.57235(8)	4.56765(8)	4.56051(8)
	c (Å)	7.26368(16)	7.25387(15)	7.24477(15)	7.23027(15)
	Volume (Å^3)	131.781(5)	131.335(4)	130.900(4)	130.230(4)

T(K)_heating	398-3	498-3	598-3	698-3	723-3

$t_{exp.}$(min)		52	52	52	52	52
No. of points		6573	6573	6573	6573	6573
No. of reflections (Mg_3Sb_2)		67	67	69	69	69
No. of parameters		34	27	32	32	32
R_f (Mg_3Sb_2) (%)		6.87	7.08	6.50	6.82	7.38
R_{Bragg} (Mg_3Sb_2) (%)		12.4	12.5	11.3	11.6	12.8
R_p (%)		18.1	18.7	18.2	18.6	19.0
R_{wp} (%)		21.3	22.1	21.5	21.9	22.2
χ^2		15.7	16.1	14.6	14.5	14.8
Wt.% Mg_3Sb_2		96.18(0.44)	96.82(0.70)	96.92(0.68)	96.97(0.70)	96.93(0.71)
Wt.% Sb		3.82(0.08)	3.18(0.07)	3.08(0.07)	3.03(0.07)	3.07(0.07)
Mg_3Sb_2	*a*=*b* (Å)	4.56329(8)	4.56756(8)	4.57224(8)	4.57705(9)	4.57814(8)
	c (Å)	7.23555(15)	7.24504(16)	7.25397(15)	7.26375(16)	7.26556(16)
	Volume (Å^3)	130.484(4)	130.900(4)	131.330(4)	131.784(5)	131.880(4)

T(K)_cooling		698-4	598-4	498-4	398-4	308-4
$t_{exp.}$(min)		52	52	52	52	52
No. of points		6573	6573	6573	6573	6573
No. of reflections (Mg_3Sb_2)		69	69	67	66	66
No. of parameters		30	30	29	29	29
R_f (Mg_3Sb_2) (%)		6.87	7.27	7.03	7.15	7.47
R_{Bragg} (Mg_3Sb_2) (%)		11.7	12.6	12.6	12.6	13.2
R_p (%)		18.6	19.1	18.7	18.5	18.7
R_{wp} (%)		21.8	22.2	21.8	21.4	22.2
χ^2		14.3	15.3	15.4	15.5	16.2
Wt.% Mg_3Sb_2		96.70(0.70)	96.66(0.71)	96.50(0.69)	95.88(0.45)	96.62(0.46)
Wt.% Sb		3.30(0.07)	3.34(0.07)	3.50(0.08)	4.12(0.09)	3.38(0.07)
Mg_3Sb_2	*a*=*b* (Å)	4.57725(8)	4.57250(8)	4.56795(8)	4.56337(8)	4.55886(8)
	c (Å)	7.26369(15)	7.25430(15)	7.24469(15)	7.23568(14)	7.22714(15)
	Volume (Å^3)	131.794(4)	131.351(4)	130.916(4)	130.491(4)	130.080(4)

Table S3. Rietveld refinement details of PXRD data at room temperature for pellet 1.

T(K)_@RT	before *in situ*	after *in situ*	after Hall	after Seebeck
$t_{exp.}$(min)	52	52	52	52
No. of points	6573	6573	6573	6573
No. of reflections (Mg_3Sb_2)	69	65	86	86
No. of parameters	26	38	44	41
R_f (Mg_3Sb_2) (%)	6.06	8.65	10.1	9.22

R_{Bragg} (Mg_3Sb_2) (%)		9.95	14.1	16.8	16.5
R_p (%)		19.8	21.9	24.2	23.2
R_{wp} (%)		24.5	25.6	29.1	29.1
χ^2		47.2	29.0	57.8	52.8
Wt.% Mg_3Sb_2		99.42(0.83)	95.91(0.82)	97.05(0.84)	96.69(0.83)
Wt.% Sb		0.58(0.09)	4.09(0.10)	2.95(0.10)	3.31(0.10)
Mg_3Sb_2	*a*=*b* (Å)	4.56882(16)	4.56080(9)	4.56640(4)	4.56610(5)
	c (Å)	7.23568(29)	7.22834(17)	7.23878(8)	7.23773(9)
	Volume (Å^3)	130.803(8)	130.212(5)	130.720(2)	130.684(2)

Table S4. Rietveld refinement details of multi-temperature synchrotron PXRD data for the powdered sample (from pellet 2) before in-house powder *in situ* PXRD measurements.

T(K)_heating			300	400	500	600	650	700	730
$t_{exp.}$(min)			5	5	5	5	5	5	5
No. of points			7728	7728	7727	7727	7726	7726	7726
No. of reflections (Mg_3Sb_2)			1024	1044	972	957	972	967	948
No. of parameters			58	50	44	55	52	56	59
R_f (Mg_3Sb_2) (%)			1.97	2.65	3.84	4.59	4.34	6.56	7.47
R_{Bragg} (Mg_3Sb_2) (%)			6.00	16.4	6.35	3.92	3.60	8.28	9.80
R_p (%)			8.12	8.71	9.93	11.3	11.7	11.6	10.6
R_{wp} (%)			11.0	11.4	12.4	13.5	13.5	13.0	11.9
χ^2			6.18	6.41	7.20	8.24	8.17	7.47	6.24
Wt.% Mg_3Sb_2			95.43 (1.20)	93.44 (1.21)	90.68 (1.20)	88.04 (1.26)	86.13 (1.23)	84.23 (1.17)	84.49 (1.08)
Wt.% Sb			1.27 (0.04)	1.72 (0.05)	4.11 (0.06)	5.79 (0.07)	7.01 (0.08)	8.18 (0.09)	9.06 (0.09)
Wt.% MgO			3.30 (0.13)	4.84 (0.15)	5.21 (0.16)	6.18 (0.19)	6.86 (0.20)	7.59 (0.20)	6.45 (0.17)
Mg_3Sb_2	*a*=*b* (Å)		4.56449 (9)	4.57289 (9)	4.58097 (8)	4.58903 (7)	4.59316 (5)	4.59687 (5)	4.59892 (4)
	c (Å)		7.23590 (16)	7.25312 (16)	7.26843 (13)	7.28431 (13)	7.29243 (10)	7.30006 (9)	7.30448 (7)
	Volume (Å^3)		130.559 (5)	131.352 (5)	132.095 (4)	132.850 (4)	133.238 (3)	133.592 (2)	133.792 (2)
	B_{iso}	Mg1	0.948 (152)	0.757 (153)	1.468 (156)	1.991 (174)	2.405 (187)	3.122 (199)	3.356 (187)
		Mg2	0.787 (73)	1.418 (83)	1.846 (85)	2.492 (99)	2.801 (104)	2.936 (104)	3.033 (95)
		Sb1	0.723 (16)	1.033 (19)	1.524 (19)	1.967 (23)	2.012 (24)	2.266 (23)	2.503 (22)

T(K)_cooling			700	600	500	400	300
$t_{exp.}$(min)			5	5	5	5	5
No. of points			7725	7725	7725	7724	7724
No. of reflections (Mg_3Sb_2)			957	933	931	9202	916
No. of parameters			50	48	49	44	49
R_f (Mg_3Sb_2) (%)			6.43	5.45	4.00	3.55	2.29
R_{Bragg} (Mg_3Sb_2) (%)			6.42	7.27	4.51	5.04	5.55
R_p (%)			11.0	10.6	10.7	10.3	8.93
R_{wp} (%)			12.6	12.2	12.3	12.2	11.2
χ^2			8.14	8.84	9.33	10.5	8.83
Wt.% Mg_3Sb_2			84.01(1.21)	83.62(1.18)	82.69(1.14)	82.98(1.14)	83.88(0.99)
Wt.% Sb			9.69(0.11)	9.67(0.10)	9.46(0.10)	9.56(0.10)	9.31(0.09)
Wt.% MgO			6.30(0.18)	6.70(0.19)	7.85(0.20)	7.46(0.20)	6.82(0.16)
Mg_3Sb_2	a=b (Å)		4.59658(4)	4.58861(4)	4.58056(4)	4.57224(4)	4.56360(3)
	c (Å)		7.29955(8)	7.28311(8)	7.26691(7)	7.25031(7)	7.23316(6)
	Volume (Å^3)		133.566(2)	132.803(2)	132.044(2)	131.264(2)	130.459(2)
	B_{iso}	Mg1	3.547(211)	2.980(192)	2.141(161)	1.763(152)	1.065(112)
		Mg2	2.437(100)	2.235(92)	1.817(84)	1.364(75)	0.968(57)
		Sb1	2.357(23)	1.994(21)	1.536(18)	1.131(16)	0.718(11)

Table S5. Rietveld refinement details of multi-temperature synchrotron PXRD data for the powdered sample (from pellet 2) after in-house powder *in situ* PXRD measurements.

T(K)_heating	300	400	500	600	650	700	730
$t_{exp.}$(min)	5	5	5	5	5	5	5
No. of points	7727	7727	7727	7727	7727	7727	7726
No. of reflections (Mg_3Sb_2)	924	936	993	955	967	946	944
No. of parameters	56	54	51	44	51	52	50
R_f (Mg_3Sb_2) (%)	3.56	4.21	3.53	5.91	5.58	8.99	8.67
R_{Bragg} (Mg_3Sb_2) (%)	13.7	10.9	7.81	14.5	12.5	9.01	7.91
R_p (%)	9.60	10.0	12.2	10.9	11.4	11.2	11.2
R_{wp} (%)	12.1	12.3	14.6	12.7	13.1	12.8	12.5
χ^2	9.16	8.87	10.8	8.40	8.75	8.27	8.00
Wt.% Mg_3Sb_2	90.32 (1.26)	90.46 (1.30)	89.82 (1.50)	89.33 (1.32)	88.85 (1.35)	86.59 (1.31)	84.28 (1.25)
Wt.% Sb	5.53 (0.07)	5.69 (0.07)	6.04 (0.09)	5.89 (0.08)	6.60 (0.09)	7.93 (0.10)	9.58 (0.11)

Wt.% MgO			4.14 (0.16)	3.84 (0.16)	4.15 (0.19)	4.77 (0.18)	4.55 (0.20)	5.48 (0.21)	6.14 (0.21)
Mg_3Sb_2	*a*=*b* (Å)		4.56488 (4)	4.57320 (5)	4.58143 (6)	4.58914 (5)	4.59311 (5)	4.59671 (5)	4.59898 (4)
	c (Å)		7.23518 (8)	7.25180 (9)	7.26809 (11)	7.28388 10)	7.29200 (10)	7.29961 (9)	7.30437 (8)
	Volume (Å^3)		130.568 (2)	131.346 (2)	132.115 (3)	132.848 (3)	133.226 (3)	133.575 (3)	133.794 (2)
	B_{iso}	Mg1	1.070 (131)	1.370 (150)	1.620 (196)	2.893 (197)	2.649 (206)	3.235 (218)	3.537 (226)
		Mg2	0.876 (67)	1.331 (77)	1.288 (98)	2.103 (95)	2.254 (103)	2.563 (109)	2.790 (108)
		Sb1	0.712 (13)	1.117 (17)	1.292 (22)	1.900 (22)	2.068 (24)	2.379 (25)	2.506 (25)

T(K)_cooling			700	600	500	400	300
$t_{exp.}$(min)			5	5	5	5	5
No. of points			7726	7726	7726	7726	7726
No. of reflections (Mg_3Sb_2)			938	933	922	918	916
No. of parameters			49	50	48	41	54
R_f (Mg_3Sb_2) (%)			7.05	5.48	4.34	4.45	2.44
R_{Bragg} (Mg_3Sb_2) (%)			6.23	5.55	5.22	4.96	6.26
R_p (%)			11.2	11.0	10.6	10.4	9.57
R_{wp} (%)			12.6	12.8	12.4	12.2	11.7
χ^2			8.31	9.02	9.24	10.0	10.3
Wt.% Mg_3Sb_2			82.30(1.21)	82.87(1.22)	82.95(1.18)	83.08(1.17)	84.21(1.14)
Wt.% Sb			10.01(0.11)	9.90(0.11)	9.89(0.11)	9.95(0.11)	10.01(0.10)
Wt.% MgO			7.69(0.23)	7.23(0.21)	7.15(0.21)	6.98(0.20)	5.78(0.19)
Mg_3Sb_2	*a*=*b* (Å)		4.59654(4)	4.58875(4)	4.58068(4)	4.57246(4)	4.56401(3)
	c (Å)		7.29940(8)	7.28328(8)	7.26703(7)	7.25059(7)	7.23367(7)
	Volume (Å^3)		133.561(2)	132.814(2)	132.053(2)	131.282(2)	130.492(2)
	B_{iso}	Mg1	3.486(217)	3.200(200)	2.709(180)	1.771(151)	1.214(132)
		Mg2	2.703(107)	2.241(98)	1.729(86)	1.400(77)	0.930(66)
		Sb1	2.366(24)	1.955(22)	1.532(19)	1.111(16)	0.734(13)

Table S6. Rietveld refinement details of synchrotron PXRD data at 300 K for the powdered sample (from the as-synthesized pellet 5).

T(K)	300-start	300-cooling1	300-cooling2
$t_{exp.}$(min)	5	5	5
No. of points	7740	7732	7729

No. of reflections (Mg_3Sb_2)			957	904	904
No. of parameters			46	53	51
R_f (Mg_3Sb_2) (%)			2.13	1.91	1.99
R_{Bragg} (Mg_3Sb_2) (%)			11.1	5.28	4.86
R_p (%)			8.20	9.61	9.61
R_{wp} (%)			10.8	12.0	12.0
χ^2			6.86	9.69	10.6
Wt.% Mg_3Sb_2			96.53(1.23)	90.60(1.19)	90.29(1.21)
Wt.% Sb			0.39(0.04)	5.85(0.07)	6.14(0.07)
Wt.% MgO			3.08(0.14)	3.55(0.15)	3.57(0.15)
Mg_3Sb_2	a=b (Å)		4.56310(10)	4.56469(7)	4.56471(6)
	c (Å)		7.23403(18)	7.23663(12)	7.23679(11)
	Volume (Å^3)		130.446(5)	130.584(3)	130.588(3)
	B_{iso}	Mg1	0.607(148)	1.103(127)	1.045(129)
		Mg2	0.676(71)	0.982(64)	0.950(65)
		Sb1	0.624(16)	0.753(13)	0.728(13)

Table S7. Rietveld refinement details of in-house *in situ* PXRD data after cooling down to RT for the powdered samples (from pellets 5 and 6).

Sample		Powdered sample (from pellet 5)	Powdered sample (from pellet 6)
T(K)		308	308
$t_{exp.}$(min)		30	30
No. of points		8995	8995
No. of reflections (Mg_3Sb_2)		56	58
No. of parameters		8	8
R_f (Mg_3Sb_2) (%)		9.21	13.2
R_{Bragg} (Mg_3Sb_2) (%)		9.79	14.1
R_p (%)		25.1	29.4
R_{wp} (%)		32.3	44.2
χ^2		17.9	35.7
Wt.% Mg_3Sb_2		97.46(0.85)	98.89(1.17)
Wt.% Sb		2.54(0.08)	1.11(0.09)
Mg_3Sb_2	a=b (Å)	4.55827(10)	4.55876(13)
	c (Å)	7.22620(20)	7.22614(28)
	Volume (Å^3)	130.029(6)	130.056(7)

Table S8. The nominal and actual compositions measured by SEM-EDS for the pellets 2 and 4. As the Ag doping content is close to the detection limit of SEM-EDS, only the actual compositions of Mg and Sb can be used for discussion. For major components (Mg and Sb), the combined errors

of SEM-EDS also limit the precision of the analysis results to ± 2 %. As can be seen in this table, there are no significant differences in the compositions of Mg and Sb among the EDS measurements, suggesting that the sample compositions are not changed after heat treatment.

Compositions (at.%)			Pellet 2 (as-synthesized)	Pellet 2 (after Hall measurements)	Pellet 2 (after Hall measurements & surface polished)	Pellet 4 (as-synthesized)		Pellet 4 (after heat treatment)	
						Top	Bottom	Top	Bottom
Nominal ($Mg_{2.985}Ag_{0.015}Sb_2$)		Mg	59.7						
		Sb	40						
		Ag	0.3						
Actual	Region 1	Mg	52.49	53.54	51.04	54.05	54.16	54.30	55.08
		Sb	47.00	45.66	48.46	45.41	45.25	44.94	44.33
		Ag	0.51	0.80	0.50	0.55	0.59	0.76	0.59
	Region 2	Mg	52.41	53.79	51.34	51.99	53.25	53.78	54.42
		Sb	47.12	45.36	48.00	47.25	46.29	45.64	44.84
		Ag	0.47	0.85	0.65	0.75	0.46	0.58	0.74
	Region 3	Mg	52.15	54.51	51.41	52.31	53.38	54.51	55.20
		Sb	47.28	44.75	48.09	47.16	46.03	44.84	44.21
		Ag	0.57	0.74	0.50	0.53	0.59	0.65	0.59
	Region 4	Mg	52.75	53.18	51.97	52.30	52.89	54.18	55.11
		Sb	46.80	45.81	47.56	47.30	46.60	45.19	44.29
		Ag	0.45	1.01	0.47	0.40	0.51	0.63	0.60
	Region 5	Mg	52.13	53.47	51.06	52.58	52.80	54.11	55.52
		Sb	47.48	45.67	48.29	46.96	46.63	45.29	43.90
		Ag	0.39	0.87	0.66	0.46	0.57	0.60	0.58
	Average	**Mg**	**52.39**	**53.70**	**51.36**	**52.65**	**53.30**	**54.18**	**55.07**
		Sb	**47.14**	**45.45**	**48.08**	**46.82**	**46.16**	**45.18**	**44.31**
		Ag	**0.48**	**0.85**	**0.56**	**0.54**	**0.54**	**0.64**	**0.62**

Table S9. The nominal and actual compositions measured by SEM-EDS for pellet 5 after in-house *in situ* PXRD measurements.

Compositions (at.%)			Top side of $Mg_{3.5}Sb_2$ pellet
Nominal ($Mg_{3.5}Sb_2$)		Mg	63.64
		Sb	36.36
Actual	Region 1	Mg	55.19
		Sb	44.81
	Region 2	Mg	56.58
		Sb	43.42
	Region 3	Mg	56.04
		Sb	43.96
	Region 4	Mg	56.24
		Sb	43.76
	Region 5	Mg	56.73
		Sb	43.27
	Region 6	Mg	56.48
		Sb	43.52
	Average	**Mg**	**56.21**
		Sb	**43.79**

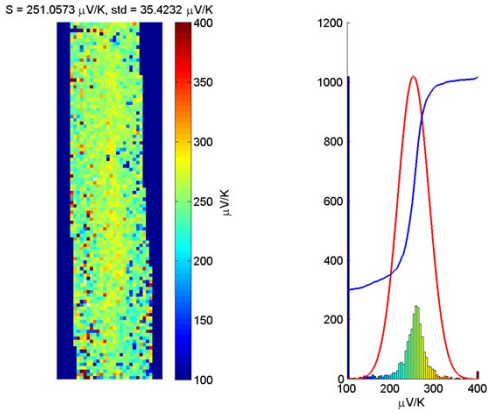

Fig. S1. Seebeck coefficient map and histogram from a PSM scan over the cross section of the as-synthesized pellet 2.

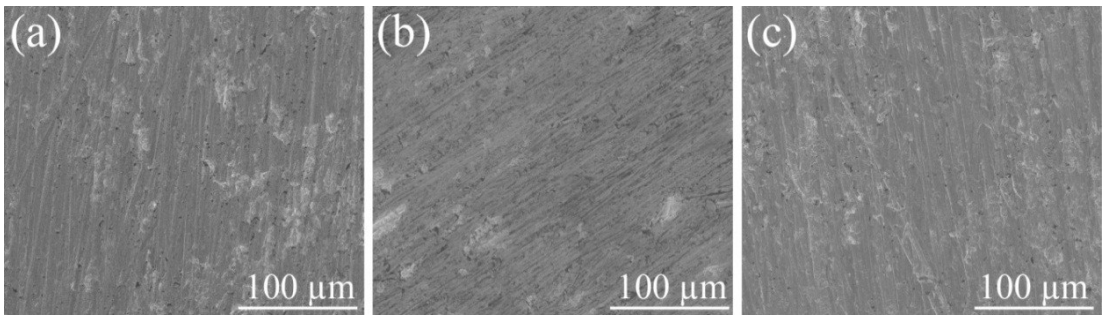

Fig. S2. SEM images of the surface (pellet 2): (a) without heat history, (b) after Hall measurements (the surface was not polished) and (c) after Hall measurements (the surface was polished).

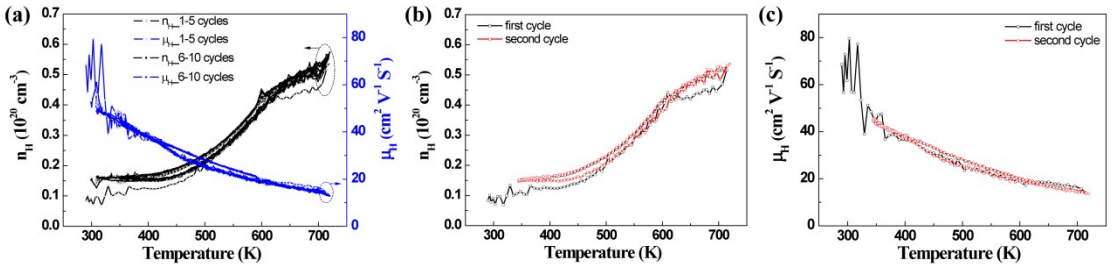

Fig. S3. (a) Temperature dependent Hall carrier concentration and Hall mobility for the total 10 cycles. (b) and (c) show the temperature dependence of Hall carrier concentration and Hall mobility in the first two cycles, respectively.

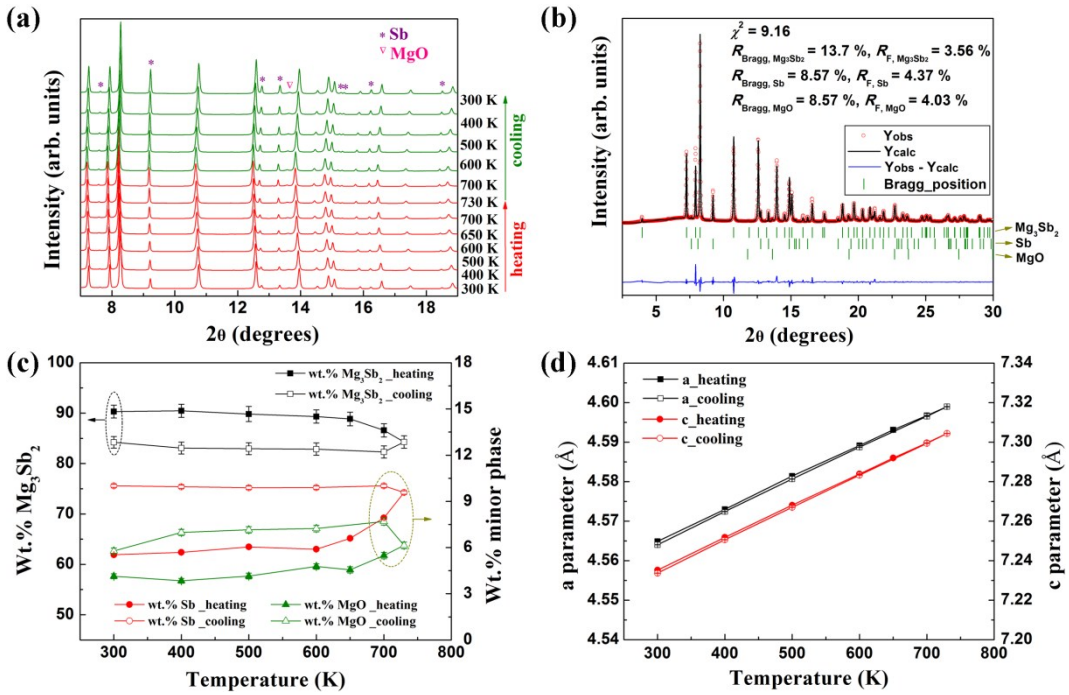

Fig. S4. (a) Multi-temperature synchrotron PXRD patterns, (b) the calculated and observed diffraction patterns at 300 K, (c) weight fractions of the Mg_3Sb_2, Sb and MgO phases, and (d) unit cell parameters of the Mg_3Sb_2 phase for the powdered sample (from pellet 2) after in-house powder *in situ* PXRD measurements. In (c) and (d), the error bars are smaller than the symbols.

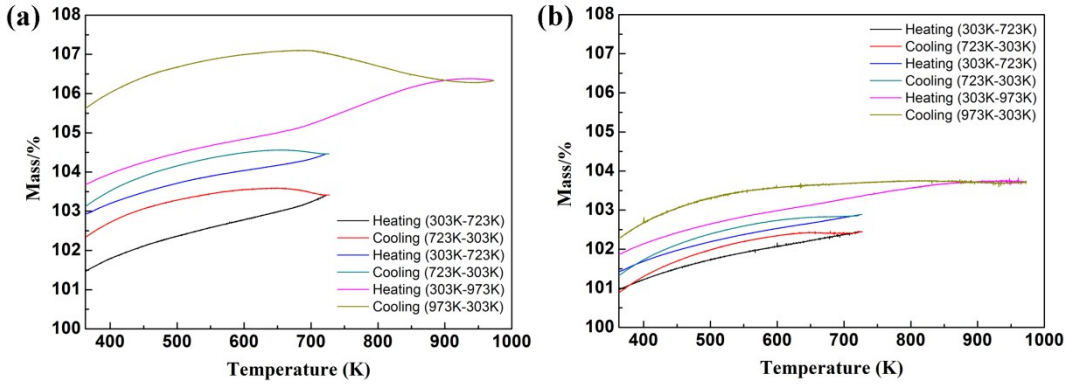

Fig. S5. TG data for the powdered samples (a) from pellet 2 before heat treatment and (b) from pellet 3 after all the HT thermoelectric properties measurements.