Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information

Structural evolution, optical gap and thermoelectric properties of $CH_3NH_3SnBr_3$ hybrid perovskite, prepared by mechanochemistry.

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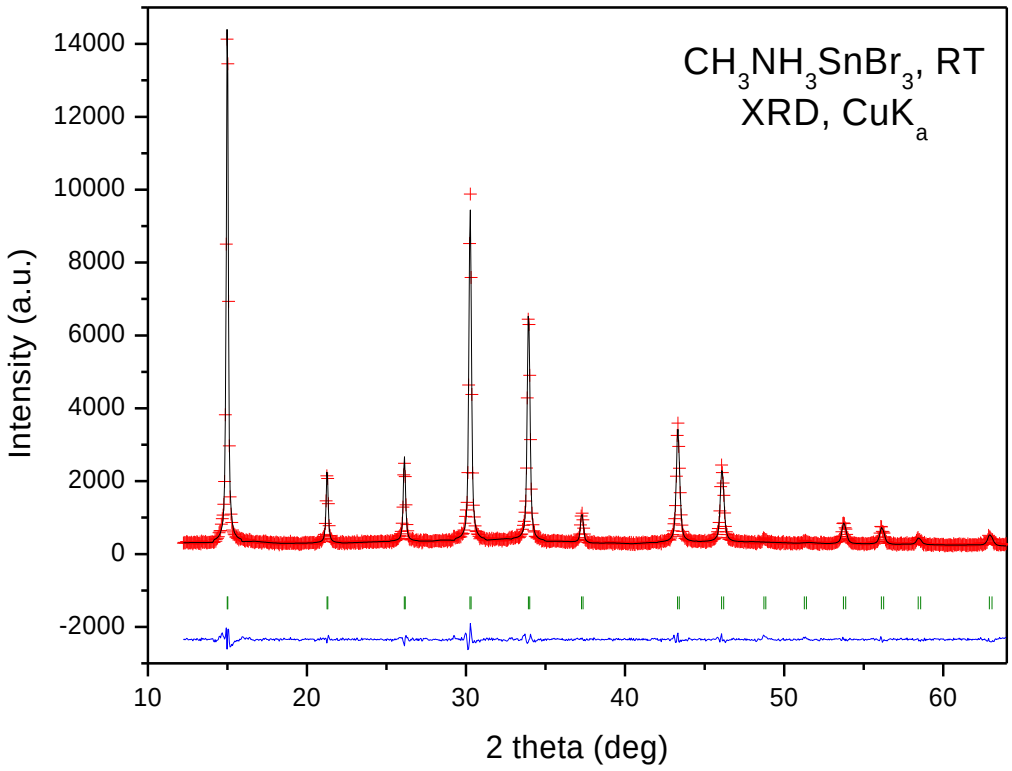
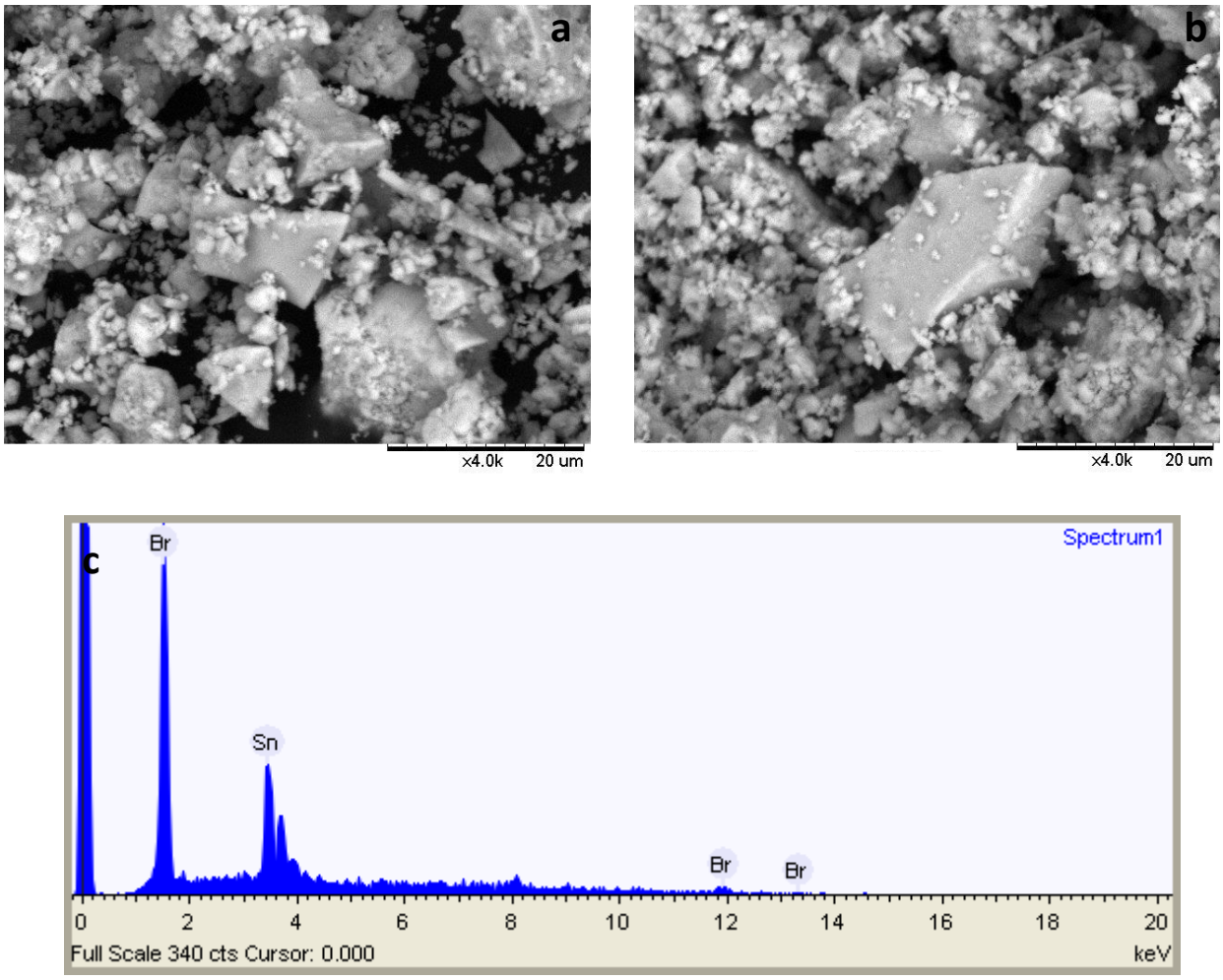


Figure S1: Le Bail fit of laboratory X-ray diffraction pattern of $MASnBr_3$ prepared by mechano-chemical synthesis.



Element	Weight %	Calc.
Bromine	61.6	66.88
Tin	38.4	33.12

Figure S2: a) and b) Two selected SEM images of the as-prepared sample, and c) EDX spectrum with the determined weight (%) of Sn and Br.

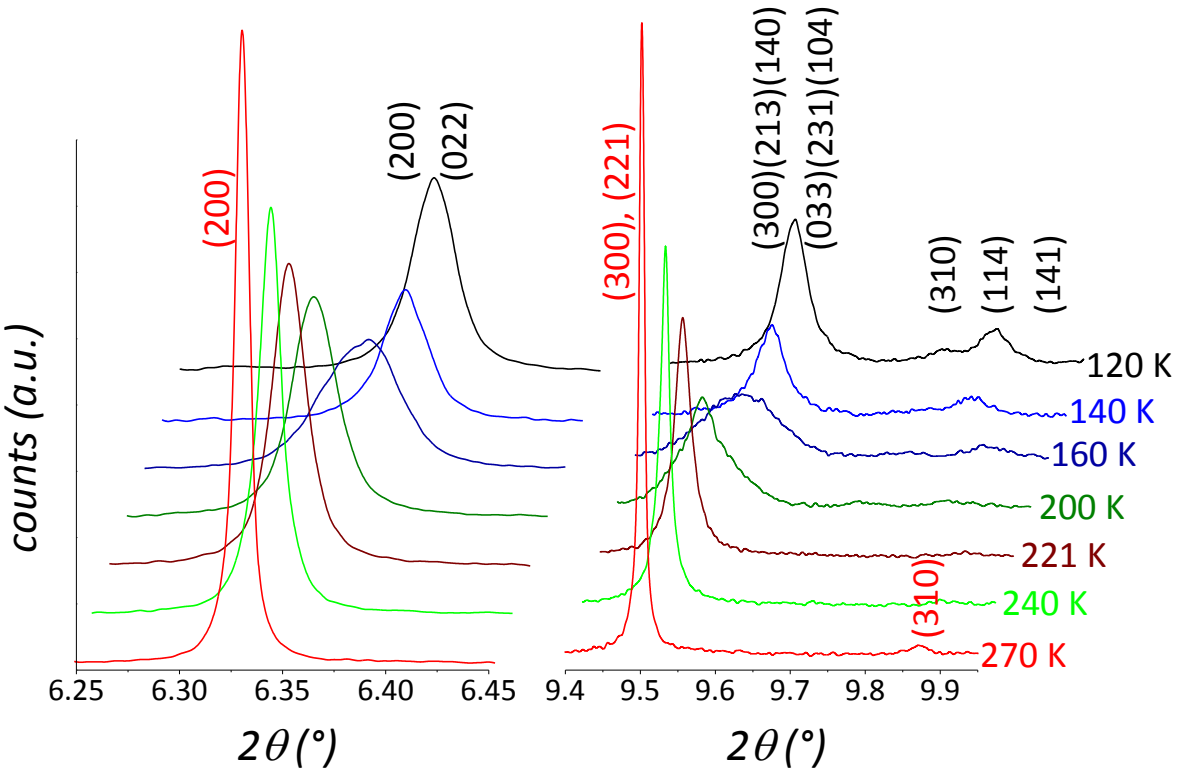


Figure S3: Thermal evolution of (200), (300) and (221) cubic lines from synchrotron diffraction. The Miller indices indicated in black correspond to the orthorhombic $Pcm2_1$ space group.

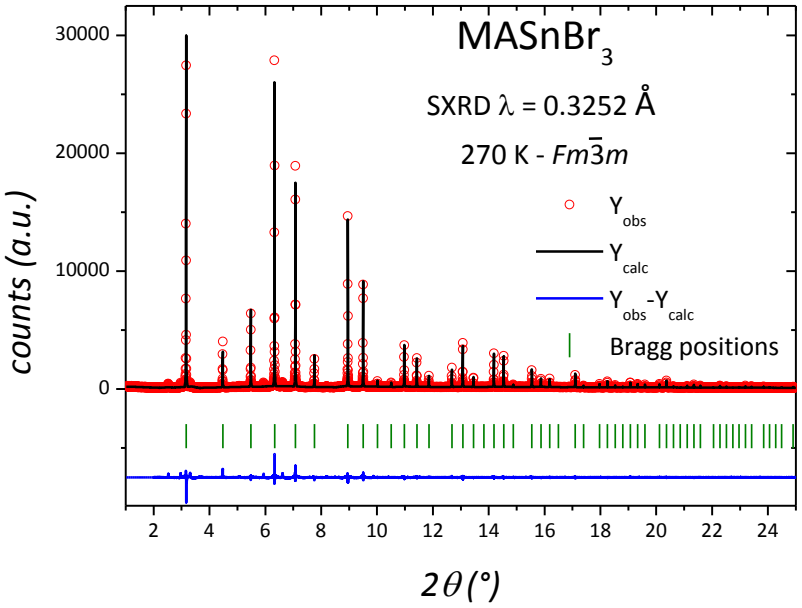


Figure S4: Rietveld refinement of synchrotron X-ray diffraction pattern at 270 K.

Table S1: Crystallographic data for $MASnBr_3$ from the SXRD refinements at 270 K.

System: Cubic, Space group: $Fm\bar{3}m$, Z = 1. Unit-cell parameters: a = 5.89786(3) Å, and V = 205.16(1) Å^3.						
Atom		**x**	**y**	**z**	**U_{eq}**	**Occ**
Sn	1*a*	0	0	0	0.032(1)	1
Br	3*d*	0.5	0	0	0.104(1)	1
C	6*f*	0.639(2)	0.5	0.5	0.06(2)	0.166
N	6*f*	0.639(2)	0.5	0.5	0.06(2)	0.166
Anisotropic displacement parameters						
	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sn	0.032(1)	0.032(1)	0.032(1)	0	0	0
Br	0.051(1)	0.130(1)	0.130(1)	0	0	0
C/N	0.03(1)	0.08(2)	0.08(2)	0	0	0
R_p: 9.57%; R_{wp}: 12.6%; R_{exp}: 8.23%; χ^2: 2.34; R_{Bragg}: 5.13%						

Table S2: Crystallographic data for $MASnBr_3$ from the SXRD refinements at 160 K.

System: Cubic, Space group: *Pcm*2_1, Z = 2. Unit-cell parameters: *a* = 5.8893(4) Å, *b* = 8.3663(6) Å, *c* = 8.2491(6) Å and V = 406.44(5) Å^3.						
Atom		**x**	**y**	**z**	**U_{iso}**	**Occ**
Sn	2*a*	0	0.7532(8)	0	0.001	1
Br1	2*a*	0	0.577(1)	0.305(2)	0.071(2)	1
Br2	2*a*	0	1.029(1)	0.197(2)	0.071(2)	1
Br3	2*b*	0.5	0.767(1)	0.008(2)	0.071(2)	1
C	2*b*	0.5	0.318(3)	0.106(4)	0.001	1
N	2*b*	0.5	0.172(2)	0.015(3)	0.001	1
R_p: 8.23%; R_{wp}: 10.2%; R_{exp}: 8.02%; χ^2: 1.62; R_{Bragg}: 3.98%						

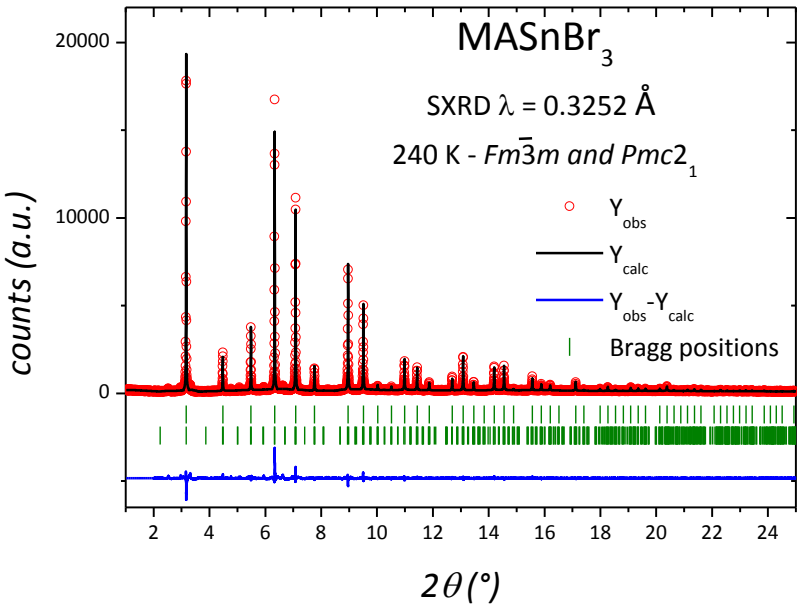


Figure S5: Rietveld refinement of synchrotron X-ray diffraction pattern at 240 K.

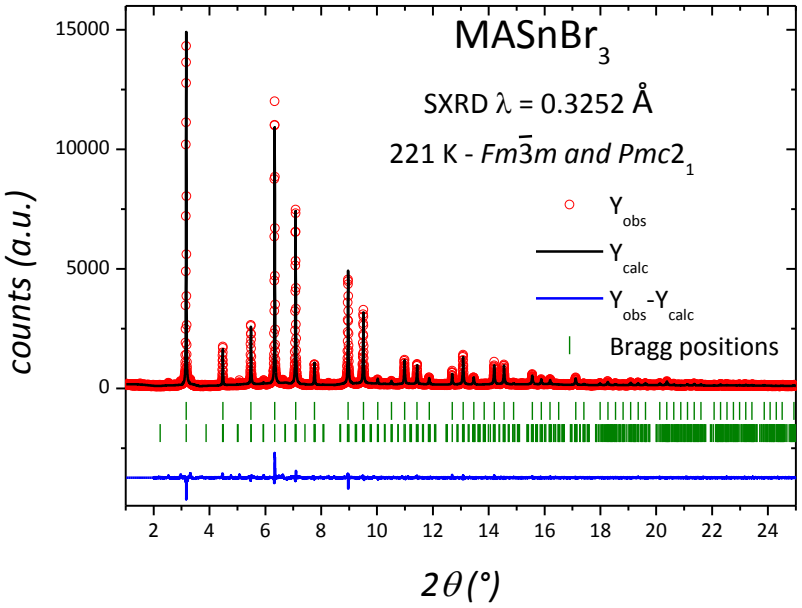


Figure S6: Rietveld refinement of synchrotron X-ray diffraction pattern at 221 K.

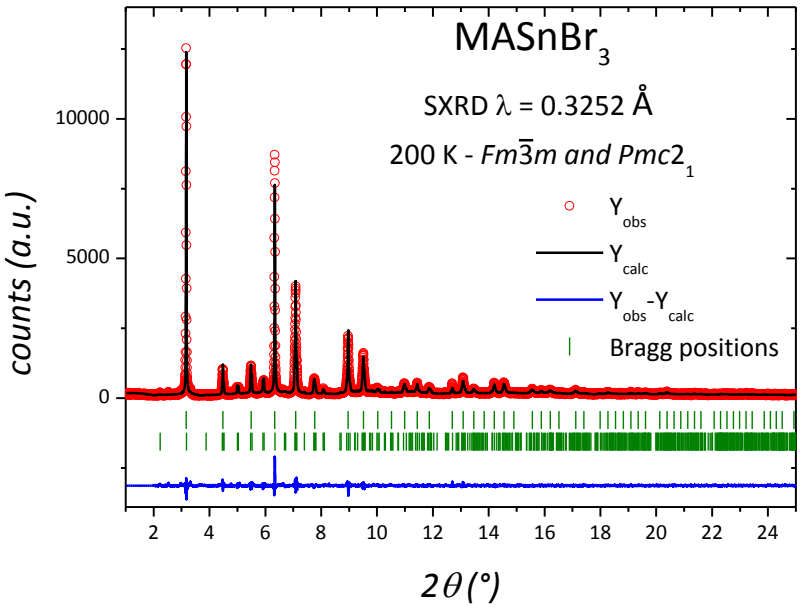


Figure S7: Rietveld refinement of synchrotron X-ray diffraction pattern at 200 K.

Table S3: Crystallographic data for $MASnBr_3$ from the SXRD refinements at 240 K.

a) System: Cubic, Space group: $Fm\bar{3}m$, Z = 1. Unit-cell parameters: *a* = 5.89244(7) Å, and V = 204.59(1) Å^3. Amount: 85(2) %w/w						
Atom		**x**	**y**	**z**	**U_{eq}**	**Occ**
Sn	1*a*	0	0	0	0.028(1)	1
Br	3*d*	0.5	0	0	0.098(2)	1
C	6*f*	0.631(3)	0.5	0.5	0.04(1)	0.166
N	6*f*	0.631(3)	0.5	0.5	0.04(1)	0.166
Anisotropic displacement parameters						
	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sn	0.028(1)	0.028(1)	0.028(1)	0	0	0
Br	0.040(2)	0.127(2)	0.127(2)	0	0	0
C/N	0.03(1)	0.05(1)	0.05(1)	0	0	0
b) System: Cubic, Space group: $Pcm2_1$, Z = 2. Unit-cell parameters: *a* = 5.9011(4) Å, *b* = 8.3567(6) Å, *c* = 8.3125(6) Å and V = 409.92(5) Å^3. Amount: 15(1) %w/w						
Atom		**x**	**y**	**z**	**U_{iso}**	**Occ**
Sn	2*a*	0	0.748(4)	0	0.049(7)	1
Br1	2*a*	0	0.547(7)	0.280(3)	0.10(1)	1
Br2	2*a*	0	0.971(6)	0.255(3)	0.10(1)	1
Br3	2*b*	0.5	0.753(7)	–0.041(2)	0.10(1)	1
C	2*b*	0.5	0.377(3)	0.09(1)	0.006	1
N	2*b*	0.5	0.206(2)	0.06(1)	0.006	1
R_p: 8.28%; R_{wp}: 10.7%; R_{exp}: 8.10%; χ^2: 1.74; R_{Bragg}: a) 4.48%; b) 20.4%						

Table S4: Crystallographic data for $MASnBr_3$ from the SXRD refinements at 221 K.

a) System: Cubic, Space group: $Fm\bar{3}m$, Z = 1. Unit-cell parameters: *a* = 5.8933(1) Å, and V = 204.68(1) Å^3. Amount: 69(2) %w/w						
Atom		**x**	**y**	**z**	**U_{eq}**	**Occ**
Sn	1*a*	0	0	0	0.019(1)	1
Br	3*d*	0.5	0	0	0.092(2)	1
C	6*f*	0.633(4)	0.5	0.5	0.03(2)	0.166
N	6*f*	0.633(4)	0.5	0.5	0.03(2)	0.166
Anisotropic displacement parameters						
	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sn	0.019(1)	0.019(1)	0.019(1)	0	0	0
Br	0.028(2)	0.124(2)	0.124(2)	0	0	0
C/N	0.02(2)	0.04(2)	0.04(2)	0	0	0
b) System: Cubic, Space group: $Pcm2_1$, Z = 2. Unit-cell parameters: *a* = 5.8910(7) Å, *b* = 8.3552(8) Å, *c* = 8.3100(7) Å and V = 409.02(7) Å^3. Amount: 31(2) %w/w						
Atom		**x**	**y**	**z**	**U_{iso}**	**Occ**
Sn	2*a*	0	0.750(4)	0	0.049(7)	1
Br1	2*a*	0	0.531(6)	0.274(4)	0.091(6)	1
Br2	2*a*	0	0.981(6)	0.250(5)	0.091(6)	1
Br3	2*b*	0.5	0.755(7)	–0.027(3)	0.091(6)	1
C	2*b*	0.5	0.378(5)	0.088(13)	0.006	1
N	2*b*	0.5	0.215(5)	0.028(13)	0.006	1
R_p: 7.41%; R_{wp}: 9.42%; R_{exp}: 8.04%; χ^2: 1.37; R_{Bragg}: a) 4.40%; b) 18.8%						

Table S5: Crystallographic data for $MASnBr_3$ from the SXRD refinements at 200 K.

a) System: Cubic, Space group: $Fm\bar{3}m$, Z = 1. Unit-cell parameters: *a* = 5.8937(3) Å, and V = 204.72(2) Å^3. Amount: 34(1) %w/w						
Atom		**x**	**y**	**Z**	**U_{iso}**	**Occ**
Sn	1*a*	0	0	0	0.001(2)	1
Br	3*d*	0.5	0	0	0.074(3)	1
C	6*f*	0.637(5)	0.5	0.5	0.01(2)	0.166
N	6*f*	0.637(5)	0.5	0.5	0.01(2)	0.166
b) System: Cubic, Space group: *Pcm*2$_1$, Z = 2. Unit-cell parameters: *a* = 5.8911(3) Å, *b* = 8.3819(3) Å, *c* = 8.2720(3) Å and V = 408.46(3) Å^3. Amount: 66(1) %w/w						
Atom		**x**	**y**	**z**	**U_{iso}**	**Occ**
Sn	2*a*	0	0.7508(9)	0	0.018(2)	1
Br1	2*a*	0	0.567(1)	0.322(2)	0.095(3)	1
Br2	2*a*	0	1.012(1)	0.238(2)	0.095(3)	1
Br3	2*b*	0.5	0.758(1)	–0.0080(2)	0.095(3)	1
C	2*b*	0.5	0.345(5)	0.151(5)	0.006	1
N	2*b*	0.5	0.224(4)	0.026(4)	0.006	1
R_p: 7.63%; R_{wp}: 9.59%; R_{exp}: 8.03%; χ^2: 1.43; R_{Bragg}: a) 2.86%; b) 4.9%						

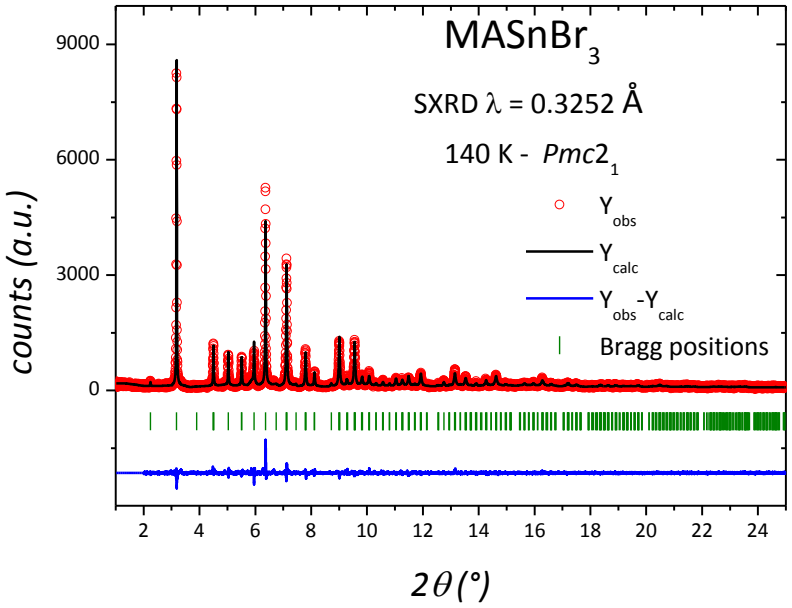


Figure S8: Rietveld refinement of synchrotron X-ray diffraction pattern at 140 K.

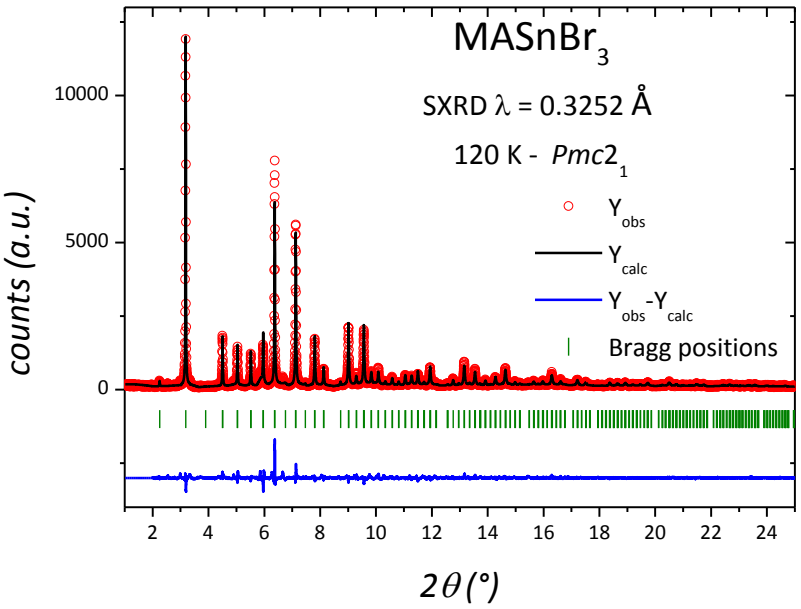


Figure S9: Rietveld refinement of synchrotron X-ray diffraction pattern at 120 K.

Table S6: Crystallographic data for $MASnBr_3$ from the SXRD refinements at 140 K.

System: Cubic, Space group: *Pcm*2_1, Z = 2. Unit-cell parameters: *a* = 5.8644(6) Å, *b* = 8.3027(8) Å, *c* = 8.2780(8) Å and V = 403.06(7) Å^3.						
Atom		**x**	**y**	**z**	**U_{iso}**	**Occ**
Sn	2*a*	0	0.7522(9)	0	0.007(1)	1
Br1	2*a*	0	0.562(2)	0.294(2)	0.075(3)	1
Br2	2*a*	0	1.034(2)	0.190(2)	0.075(3)	1
Br3	2*b*	0.5	0.777(2)	0.046(2)	0.075(3)	1
C	2*b*	0.5	0.332(5)	0.105(9)	0.001	1
N	2*b*	0.5	0.176(2)	0.030(4)	0.001	1
R_p: 11.3%; R_{wp}: 14.5%; R_{exp}: 13.4%; χ^2: 1.17; R_{Bragg}: 7.88%						

Table S7: Crystallographic data for $MASnBr_3$ from the SXRD refinements at 120 K.

System: Cubic, Space group: *Pcm*2_1, Z = 2. Unit-cell parameters: *a* = 5.8601(4) Å, *b* = 8.2904(6) Å, *c* = 8.2755(6) Å and V = 402.05(5) Å^3.						
Atom		**x**	**y**	**z**	**U_{iso}**	**Occ**
Sn	2*a*	0	0.7541(7)	0	0.007(1)	1
Br1	2*a*	0	0.565(2)	0.293(2)	0.070(2)	1
Br2	2*a*	0	1.037(2)	0.190(2)	0.070(2)	1
Br3	2*b*	0.5	0.774(2)	0.057(1)	0.070(2)	1
C	2*b*	0.5	0.323(4)	0.103(7)	0.001	1
N	2*b*	0.5	0.168(2)	0.028(3)	0.001	1
R_p: 9.16%; R_{wp}: 11.8%; R_{exp}: 8.02%; χ^2: 2.15; R_{Bragg}: 6.17%						

Table S8: Angles and interatomic distances of orthorhombic phases.

	120 K	140 K	160 K	200 K	221 K	240 K
Sn–Br3 (Å)	2.972(2)	2.964(3)	2.948(1)	2.947(1)	2.954(3)	2.970(3)
Sn–Br2a (Å)	2.82(2)	2.82(2)	2.82(1)	2.94(2)	2.84(6)	2.82(5)
Sn–Br1a (Å)	2.89(1)	2.90(2)	2.92(2)	3.05(1)	2.92(5)	2.87(5)
Sn–Br2b (Å)	3.10(1)	3.12(2)	3.10(2)	2.95(2)	3.03(6)	3.11(5)
Sn–Br1b (Å)	3.15(1)	3.12(2)	3.20(1)	3.07(1)	3.01(6)	3.07(5)
Br3–Sn–Br3 (°)	160.7(4)	163.1(7)	174.8(6)	176.5(6)	171(1)	166.7(8)
Sn–Br3–Sn (°)	160.7(4)	163.1(7)	174.8(6)	176.5(6)	171(1)	166.7(8)
Sn–Br2–Sn (°)	157.9(6)	158.6(7)	161.3(5)	174.5(6)	176(2)	172(2)
Sn–Br1–Sn (°)	155.9(5)	156.2(7)	150.6(5)	149.0(5)	167(2)	162(2)
MA angle (°)	19(3)	19(4)	16 (2)	-1(3)	25(6)	35(6)

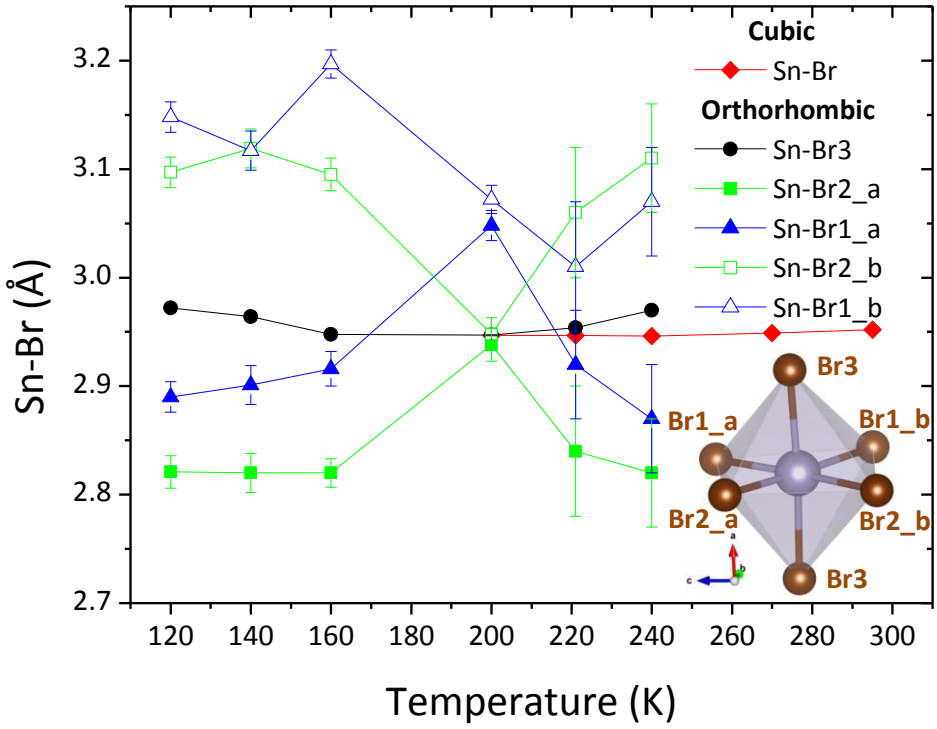


Figure S10: Sn–Br distances at different temperatures.

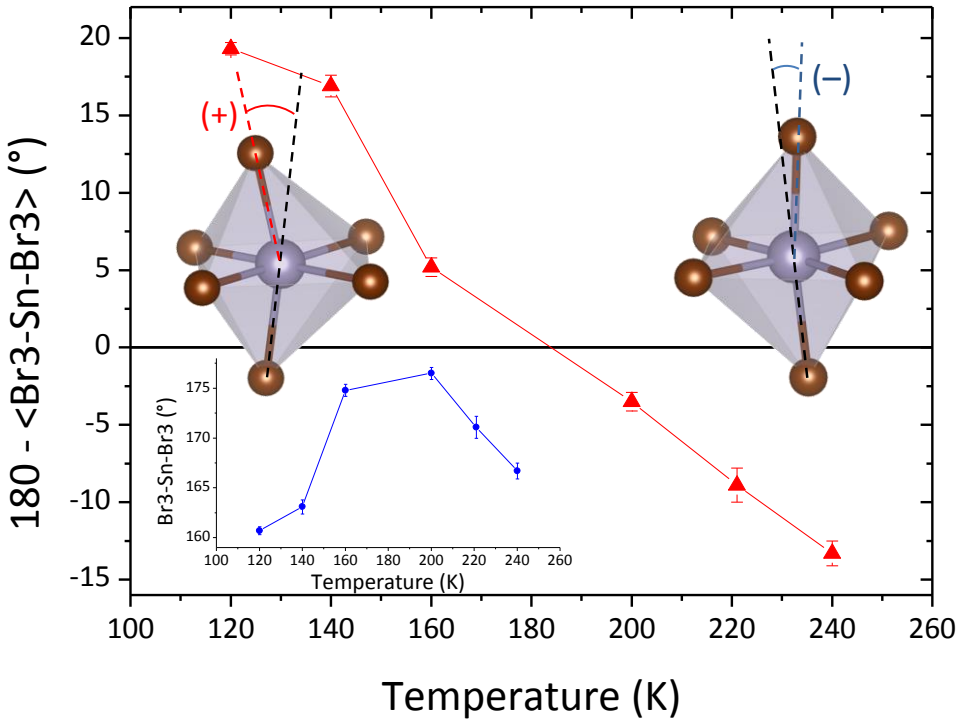


Figure S11: Angular deviation of Br3–Sn–Br3 respect to ideal 180°. Insets: Br3–Sn–Br3 angle at different temperatures and schematic view of plotted angular deviation.

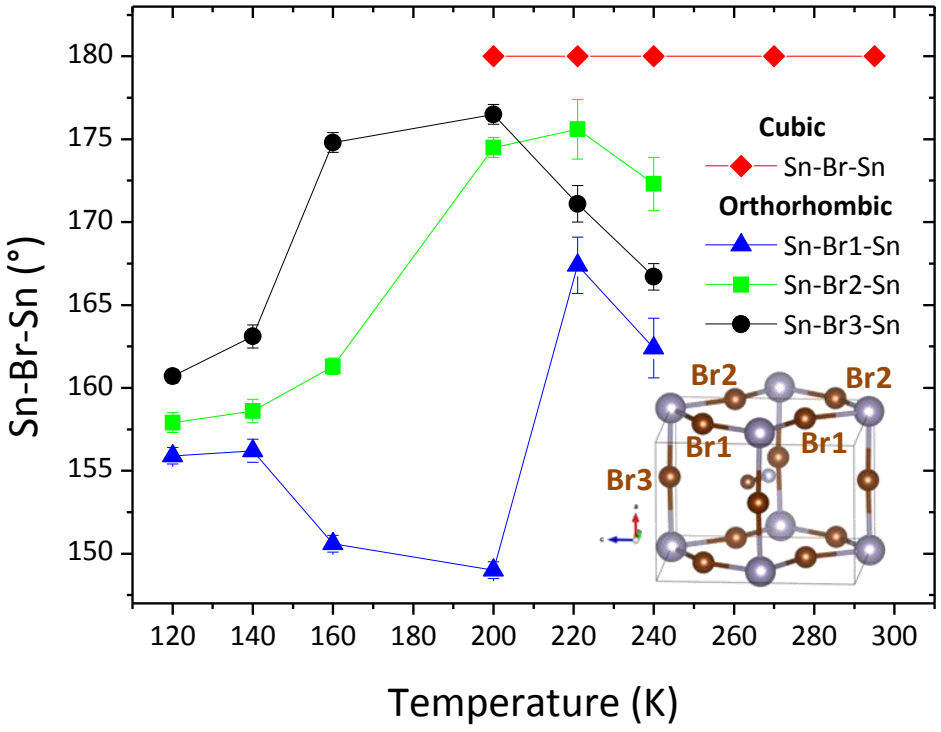


Figure S12: Sn–Br–Sn angles at different temperatures, describing the octahedral tilting angles.

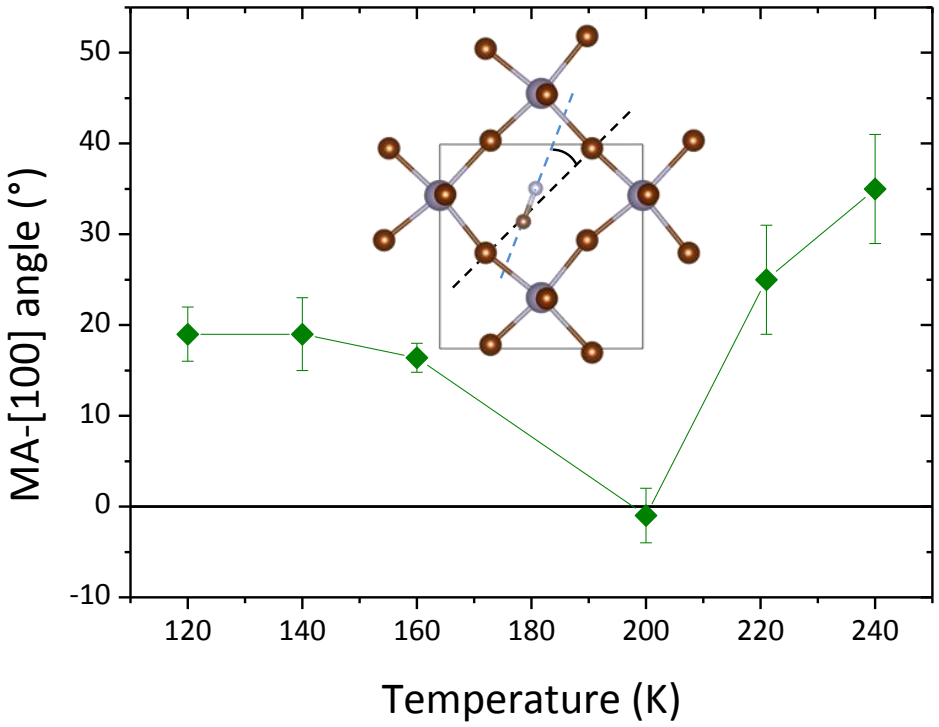


Figure S13: Deflection angle of MA at different temperatures. Inset shows a scheme of the plotted angle.