Electronically Supporting Information for

Crystal and Magnetic Structures and Properties of $BiMnO_{3+\delta}$

Alexei A. Belik,[*a] Katsuaki Kodama,[b] Naoki Igawa,[b] Shinichi Shamoto,[b] Kosuke Kosuda,[c] Eiji Takayama-Muromachi [a]

International Center for Materials Nanoarchitectonics (MANA) and Materials Analysis Station (MAS), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan and Quantum Beam Science Directorate, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan

[a] MANA, NIMS
[b] Japan Atomic Energy Agency
[c] MAS, NIMS

* Author to whom correspondence should be addressed.
International Center for Materials Nanoarchitectonics, National Institute for Materials Science, Namiki 1-1, Tsukuba, Ibaraki, 305-0044, Japan. E-mail: Alexei.BELIK@nims.go.jp

Full reference 6c:

6c. Claridge, J. B.; Hughes, H.; Bridges, C. A.; Allix, M.; Suchomel, M. R.; Niu, H.; Kuang, X.; Rosseinsky, M. J.; Bellido, N.; Grebille, D.; Perez, O.; Simon, C.; Pelloquin, D.; Blundell, S. J.; Lancaster, T.; Baker, P. J.; Pratt, F. L.; Halasyamani, P. S. *J. Am. Chem. Soc.* **2009**, *131*, 14000.

Table S1. Selected Bond Lengths, *l* (Å), Bond Valence Sums, BVS, and Distortion Parameters of MnO_6, Δ, in $BiMnO_3$[1] at 300 and 550 K and in $BiMnO_{3.03}$ at 290 K[a]

	$BiMnO_3$		$BiMnO_{3.03}$
	300 K	550 K	290 K
Bi – O2	2.218(2)	2.213(3)	2.211(2)
Bi – O1	2.239(2)	2.304(3)	2.276(2)
Bi – O3	2.246(2)	2.248(3)	2.245(3)
Bi – O1a	2.466(2)	2.484(3)	2.461(3)
Bi – O3a	2.710(2)	2.751(3)	2.744(2)
Bi – O2a	2.837(2)	2.864(4)	2.874(3)
Bi – O3b	3.003(2)	2.956(3)	2.930(2)
Bi – O2b	3.077(2)	2.999(4)	2.987(3)
Bi – O1b	3.148(2)	3.209(3)	3.196(3)
Bi – O3c	3.265(2)	3.199(3)	3.191(3)
BVS(Bi)	3.00	2.88	2.97
Mn1 – O1 (×2)	2.199(2)	2.032(3)	2.044(2)
Mn1 – O2 (×2)	1.906(3)	2.011(4)	1.975(3)
Mn1 – O3 (×2)	1.986(3)	2.112(4)	2.059(3)
BVS(Mn1)	3.05	2.75	2.94
Δ(Mn1–O)	37.2×10^{-4}	4.5×10^{-4}	3.2×10^{-4}
Mn2 – O1 (×2)	1.924(2)	2.024(3)	2.009(2)
Mn2 – O2 (×2)	2.242(2)	2.106(3)	2.137(2)
Mn2 – O3 (×2)	1.941(2)	1.913(3)	1.916(2)
BVS(Mn2)	3.05	3.09	3.05
Δ(Mn2–O)	51.3×10^{-4}	15.4×10^{-4}	20.0×10^{-4}

[a] BVS = $\sum_{i=1}^{N} v_i$, $v_i = \exp[(R_0 - l_i)/B]$, N is the coordination number, $B = 0.37$, $R_0(Bi^{3+}) = 2.094$, and $R_0(Mn^{3+}) = 1.76$;[2] $\Delta = (1/N)\sum_{i=1}^{N} [(l_i - l_{av})/l_{av}]^2$, where $l_{av} = (1/N)\sum_{i=1}^{N} l_i$ is the average Mn-O distance.[3]

[1] Belik, A. A.; Iikubo, S.; Yokosawa, T.; Kodama, K.; Igawa, N.; Shamoto, S.; Azuma, M.; Takano, M.; Kimoto, K.; Matsui, Y.; Takayama-Muromachi, E. *J. Am. Chem. Soc.* **2007**, *129*, 971.
[2] Brese, R. E.; O'Keeffe, M. *Acta Crystallogr., Sec. B* **1991**, *47*, 192.
[3] Rodríguez-Carvajal, J.; Hennion, M.; Moussa, F.; Moudden, A. H.; Pinsard L.; Revcolevschi, A. *Phys. Rev. B* **1998**, *57*, 3189(R).

The refinement of occupation factors (together with (*x*, *y*, *z*) and other non-structural parameters) results in:
g(Mn1) = 0.980(16) with *B*(Mn1) = 0.03(15) Å^2 and *g*(Mn2) = 0.985(16) with *B*(Mn2) = 0.32(16) Å^2 and fixed *g*(Bi) = 0.99, and *g*(O1) = *g*(O2) = *g*(O3) = 1 (*B*(Bi), *B*(O1), *B*(O2), and *B*(O3) were refined). The refined *g* values are close to 0.99 within standard deviations.

Table S2. Selected Bond Lengths, *l* (Å), Bond Valence Sums, BVS, and Distortion Parameters of MnO_6, Δ, in $BiMnO_{3.08}$ at 290 K[a]

Bi1 – O5	2.248(6)	Bi2 – O4	2.281(7)
Bi1 – O3	2.420(7)	Bi2 – O2	2.291(8)
Bi1 – O1	2.439(6)	Bi2 – O1	2.328(6)
Bi1 – O5	2.485(6)	Bi2 – O6	2.339(6)
Bi1 – O3	2.544(7)	Bi2 – O4	2.642(6)
Bi1 – O6	2.642(7)	Bi2 – O6	2.951(6)
Bi1 – O2	2.653(7)	Bi2 – O2	3.001(7)
Bi1 – O4	3.167(7)	Bi2 – O6	3.089(6)
Bi1 – O3	3.181(7)	Bi2 – O4	3.155(6)
Bi1 – O1	3.213(6)	Bi2 – O5	3.155(6)
Bi1 – O1	3.228(6)	Bi2 – O3	3.238(6)
Bi1 – O5	3.296(6)	Bi2 – O2	3.259(8)
BVS(Bi1)	2.80	BVS(Bi2)	2.92
Mn1 – O3	1.916(10)	Mn2 – O5 (×2)	1.943(5)
Mn1 – O6	1.973(9)	Mn2 – O1 (×2)	1.952(5)
Mn1 – O2	1.999(10)	Mn2 – O3 (×2)	2.180(6)
Mn1 – O4	2.000(10)	BVS(Mn2)	3.05
Mn1 – O1	2.062(10)	**Δ(Mn2–O)**	**29.2×10^{-4}**
Mn1 – O5	2.071(9)		
BVS(Mn1)	3.14	Mn3 – O6 (×2)	1.924(5)
Δ(Mn1–O)	9.3×10^{-4}	Mn3 – O4 (×2)	2.038(6)
		Mn3 – O2 (×2)	2.062(6)
		BVS(Mn3)	3.11
		Δ(Mn3–O)	9.0×10^{-4}

[a] BVS = $\sum_{i=1}^{N} v_i$, $v_i = \exp[(R_0 - l_i)/B]$, N is the coordination number, $B = 0.37$, $R_0(Bi^{3+}) = 2.094$, and $R_0(Mn^{3+}) = 1.76$; $\Delta = (1/N)\sum_{i=1}^{N} [(l_i - l_{av})/l_{av}]^2$, where $l_{av} = (1/N)\sum_{i=1}^{N} l_i$ is the average Mn-O distance.

Table S3. Structure Parameters of $BiMnO_{3.14}$ at 8 and 290 K[a]

Site	Wyckoff position	*x*	*y*	*z*	*B* (Å^2)
Bi	4*c*	0.0002(12)	0.25	0.9970(12)	3.19(8)
		0.0026(16)	0.25	0.9994(13)	3.59(8)
Mn	4*b*	0.0	0.0	0.5	0.02(8)
		0	0	0.5	0.35(8)
O1	4*c*	0.4776(17)	0.25	0.0608(12)	3.10(17)
		0.481(2)	0.25	0.0603(13)	3.5(2)
O2	8*d*	0.250(3)	0.0441(6)	0.745(2)	4.45(12)
		0.256(3)	0.0436(6)	0.7399(17)	4.50(13)

[a] Space group *Pnma* (No 62); $Z = 4$. The first (*x*, *y*, *z*, and *B*) line of each site is for 8 K, the second one is for 290 K. *g*(Bi) = 0.955, *g*(Mn) = 0.955, and *g*(O1) = *g*(O2) = 1, where *g* is the occupation factor.

At 8 K, $a = 5.5039(4)$ Å, $b = 7.7984(7)$ Å, $c = 5.5388(5)$ Å, and $V = 237.73(4)$ Å^3, $R_{wp} = 9.81$ % ($S = 2.06$), $R_p = 7.34$ %, $R_B = 6.71$ %, and $R_F = 5.76$ %.

At 290 K, $a = 5.5136(4)$ Å, $b = 7.8069(8)$ Å, $c = 5.5454(5)$ Å, and $V = 238.70(4)$ Å^3, $R_{wp} = 9.32$ % ($S = 1.95$), $R_p = 6.90$ %, $R_B = 6.33$ %, and $R_F = 5.63$ %.

The refinement of occupation factors (together with (*x*, *y*, *z*) and other non-structural parameters) results in:

g(Bi) = 0.970(10) with *B*(Bi) = 3.68(9) Å^2 and fixed *g*(Mn) = 0.955, and *g*(O1) = *g*(O2) = 1 (*B*(Mn), *B*(O1), and *B*(O2) were refined);

g(O1) = 1.00(2) with *B*(O1) = 3.5(2) Å^2 and fixed *g*(Bi) = *g*(Mn) = 0.955, and *g*(O2) = 1 (*B*(Bi), *B*(Mn), and *B*(O2) were refined);

g(O2) = 1.027(10) with *B*(O2) = 4.74(16) Å^2 and fixed *g*(Bi) = *g*(Mn) = 0.955, and *g*(O1) = 1 (*B*(Bi), *B*(Mn), and *B*(O1) were refined);

These results show that the enlarged thermal parameters of Bi, O1, and O2 are probably due to the structural disorder induced by the presence of cation vacancies and not due to the (additional) site deficiency.

Model-independent Le Bail fits at 290 K resulted in $R_{wp} = 7.01$ % and $R_p = 5.06$ %.

Table S4. Selected Bond Lengths, *l* (Å), Bond Valence Sums, BVS, and Distortion Parameters of MnO_6, Δ, in $BiMnO_{3.14}$ at 290 K[a]

Bi – O1	2.444(9)	Mn – O2 (×2)	1.968(13)
Bi – O2 (×2)	2.492(10)	Mn – O1 (×2)	1.983(2)
Bi – O2 (×2)	2.572(10)	Mn – O2 (×2)	2.003(13)
Bi – O1	2.659(12)	BVS(Mn)	3.27
Bi – O1	2.896(12)	Δ(Mn–O)	0.51×10^{-4}
Bi – O2 (×2)	2.968(10)		
Bi – O2 (×2)	3.061(10)		
Bi – O1	3.106(12)		
BVS(Bi) with $R_0(Bi^{3+})$	2.35		
BVS(Bi) with $R_0(La^{3+})$	2.90		

[a] BVS = $\sum_{i=1}^{N} v_i$, $v_i = \exp[(R_0 - l_i)/B]$, N is the coordination number, $B = 0.37$, $R_0(Bi^{3+}) = 2.094$, $R_0(La^{3+}) = 2.172$, and $R_0(Mn^{3+}) = 1.76$; $\Delta = (1/N)\sum_{i=1}^{N} [(l_i - l_{av})/l_{av}]^2$, where $l_{av} = (1/N)\sum_{i=1}^{N} l_i$ is the average Mn-O distance.

Average oxidation state of Mn in $BiMnO_{3.14}$ is +3.28 being in good agreement with the calculated BVS value.
$BiMnO_{3.14} \equiv Bi_{0.9554}Mn_{0.9554}O_3 \equiv Bi_{0.9554}Mn^{3+}_{0.6879}Mn^{4+}_{0.2675}O_3$

Note that there are no short Bi-O bond lengths, and Bi^{3+} ions behave like La^{3+} ions which do not have the lone electron pair.

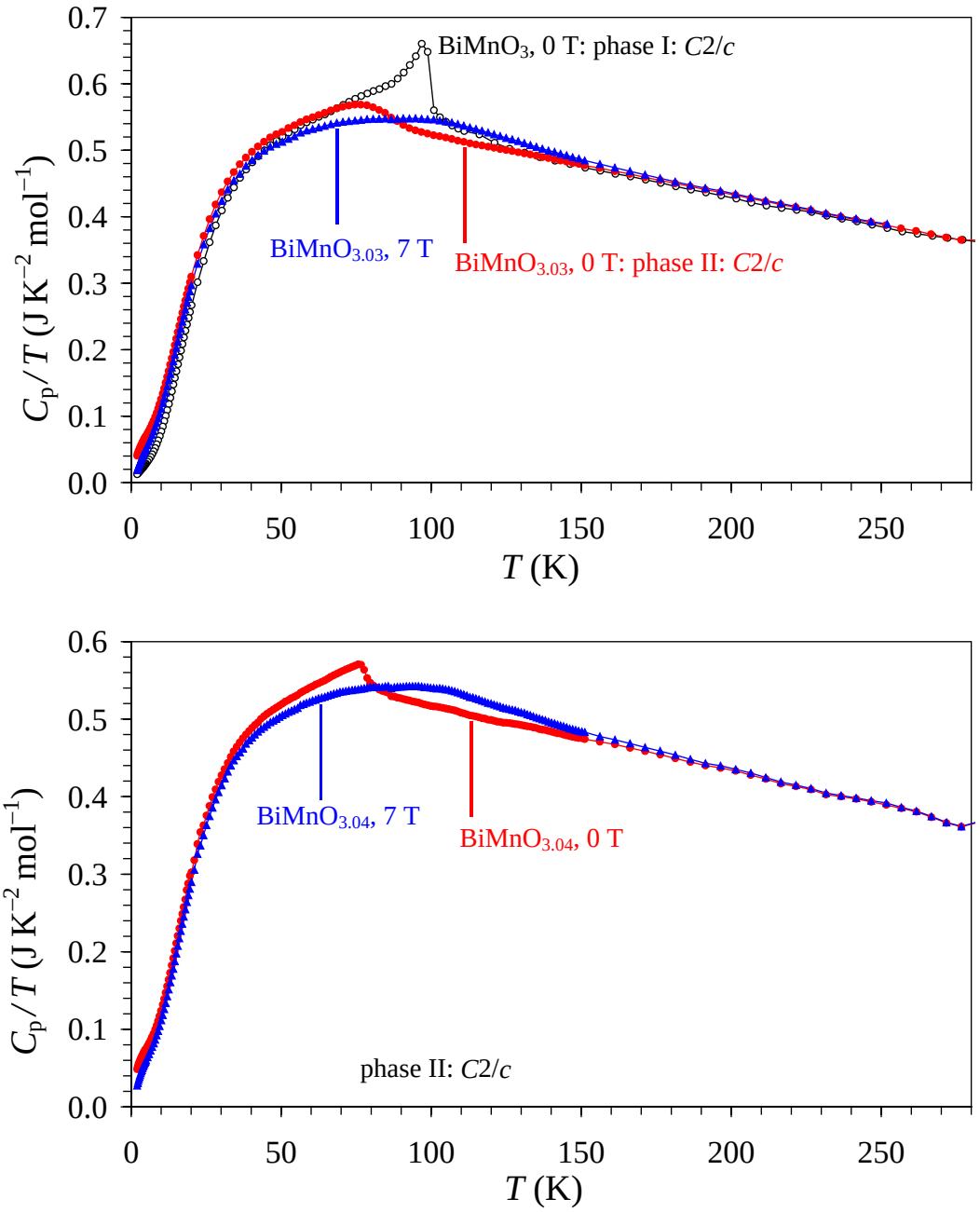

Fig. S1. The C_p/T vs T curves between 2 and 300 K for $BiMnO_3$ at 0 Oe, $BiMnO_{3.03}$ at 0 and 70 kOe, and $BiMnO_{3.04}$ at 0 and 70 kOe,. Measurements were performed on cooling. Note that the molecular weight is calculated for $Bi_{1-x}Mn_{1-x}O_3$.

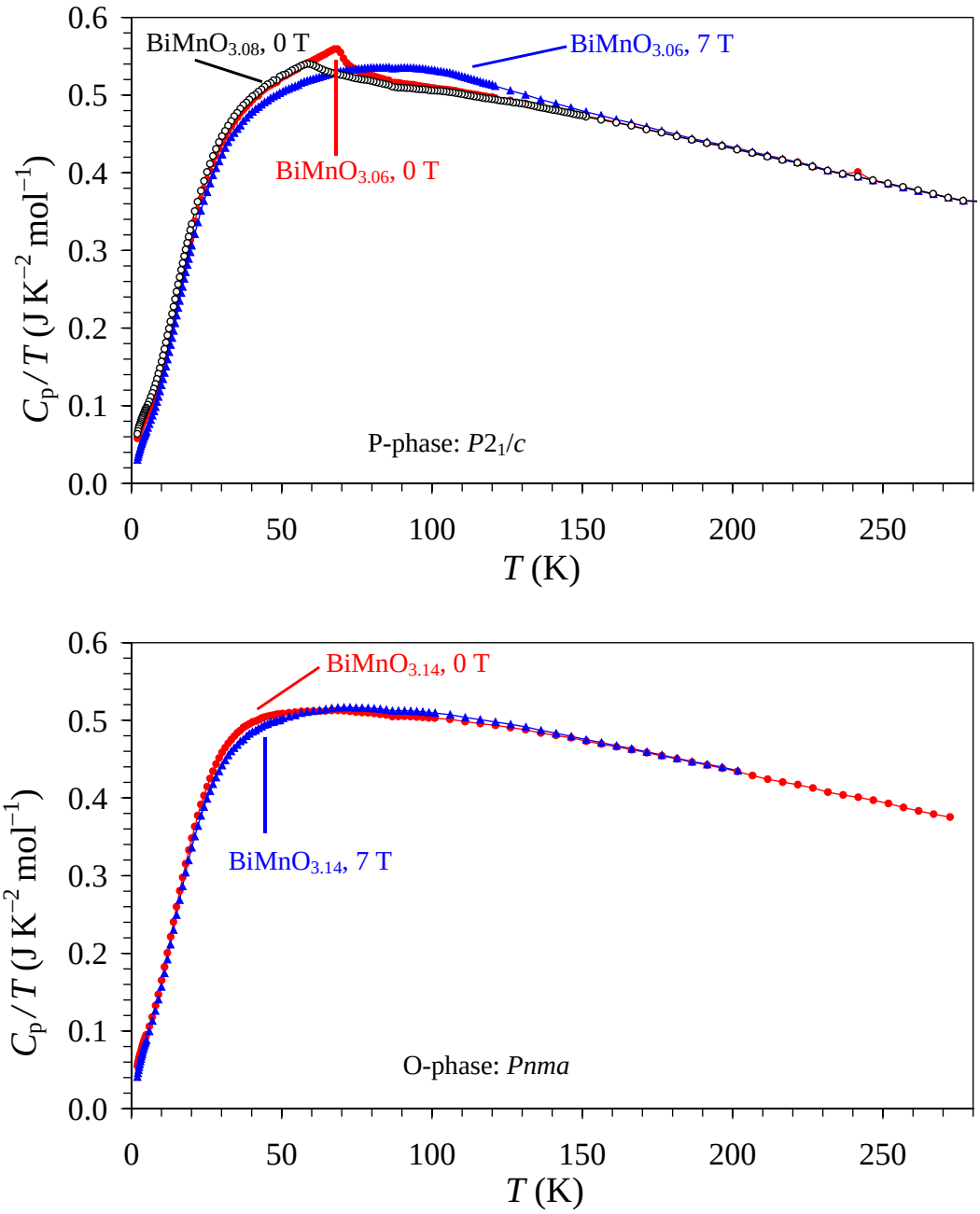

Fig. S2. The C_p/T vs T curves between 2 and 300 K for $BiMnO_{3.06}$ at 0 and 70 kOe, $BiMnO_{3.08}$ at 0 Oe, and $BiMnO_{3.14}$ at 0 and 70 kOe,. Measurements were performed on cooling. Note that the molecular weight is calculated for $Bi_{1-x}Mn_{1-x}O_3$.

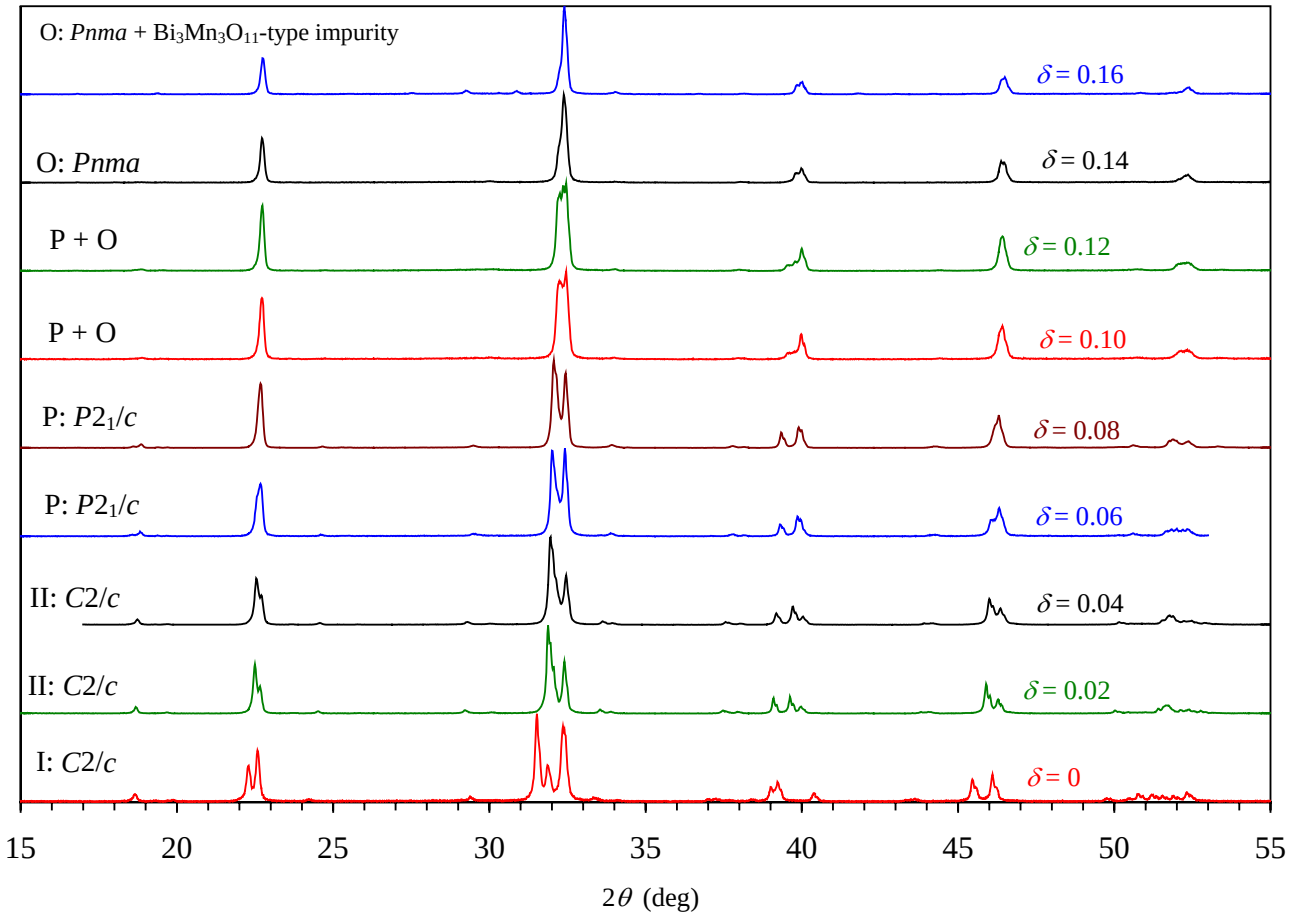

Fig. S3. X-ray powder diffraction patterns of $BiMnO_{3+\delta}$ ($0.0 \le \delta \le 0.16$) measured with CuKα radiation at room temperature. 'I' means the composition with the phase I structure; 'II' means the composition with the phase II structure; 'P' means the composition with the P-phase structure; 'O' means the composition with the orthorhombic O structure.

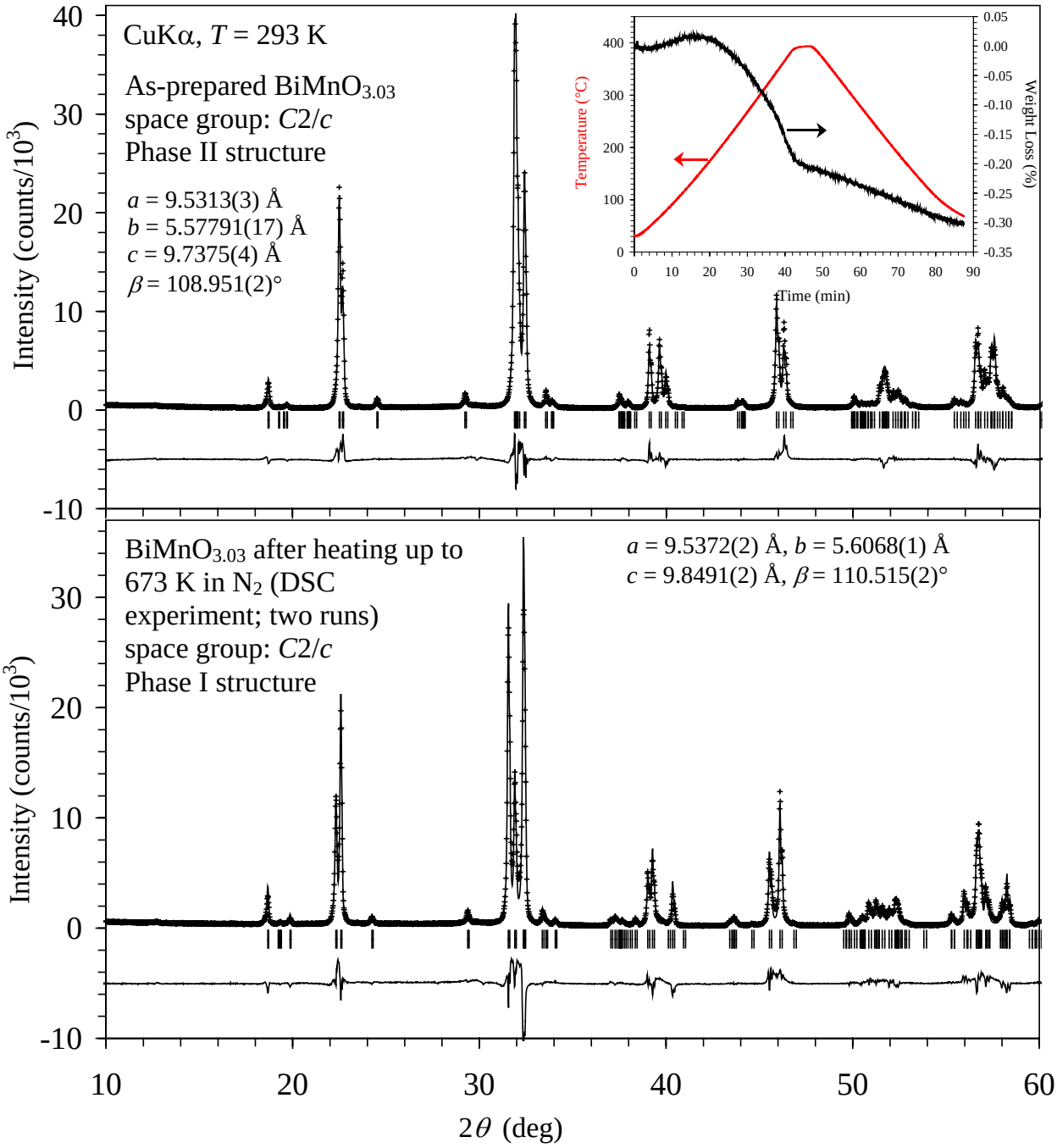

Fig. S4. X-ray powder diffraction patterns (CuKα radiation) of the as-prepared $BiMnO_{3.03}$ (up) and after a DSC experiment (heated up to 673 K and cooled to RT at 20 K/min in N_2 two times, see Figure S7) (bottom). The refined lattice parameters are given. Bragg reflections are indicated by tick marks. The insert shows the thermogravimetry curve of $BiMnO_{3.03}$ in high purity Ar.

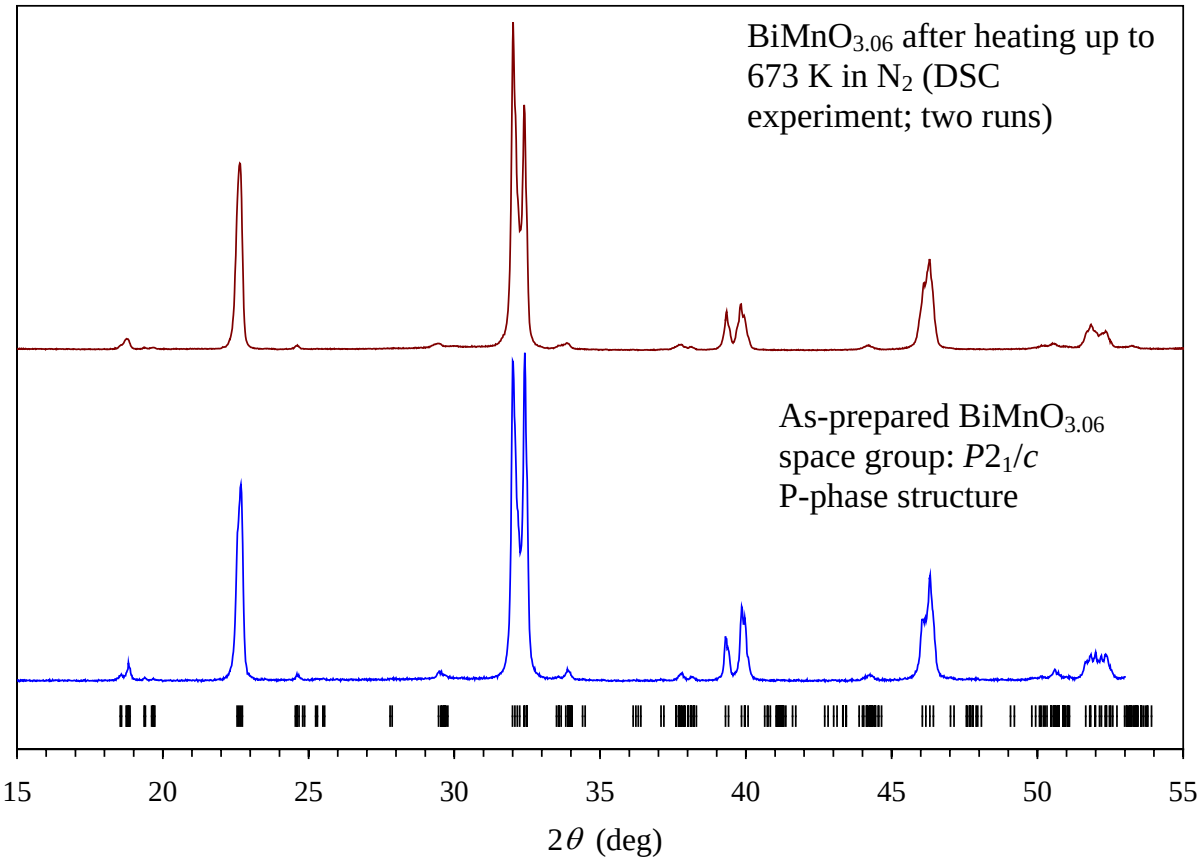

Fig. S5 X-ray powder diffraction patterns (CuKα radiation) of the as-prepared $BiMnO_{3.06}$ (bottom) and after a DSC experiment (heated up to 673 K and cooled to RT at 20 K/min in N_2 two times; see Figure S7) (up). Bragg reflections for $BiMnO_{3.06}$ are indicated by tick marks.

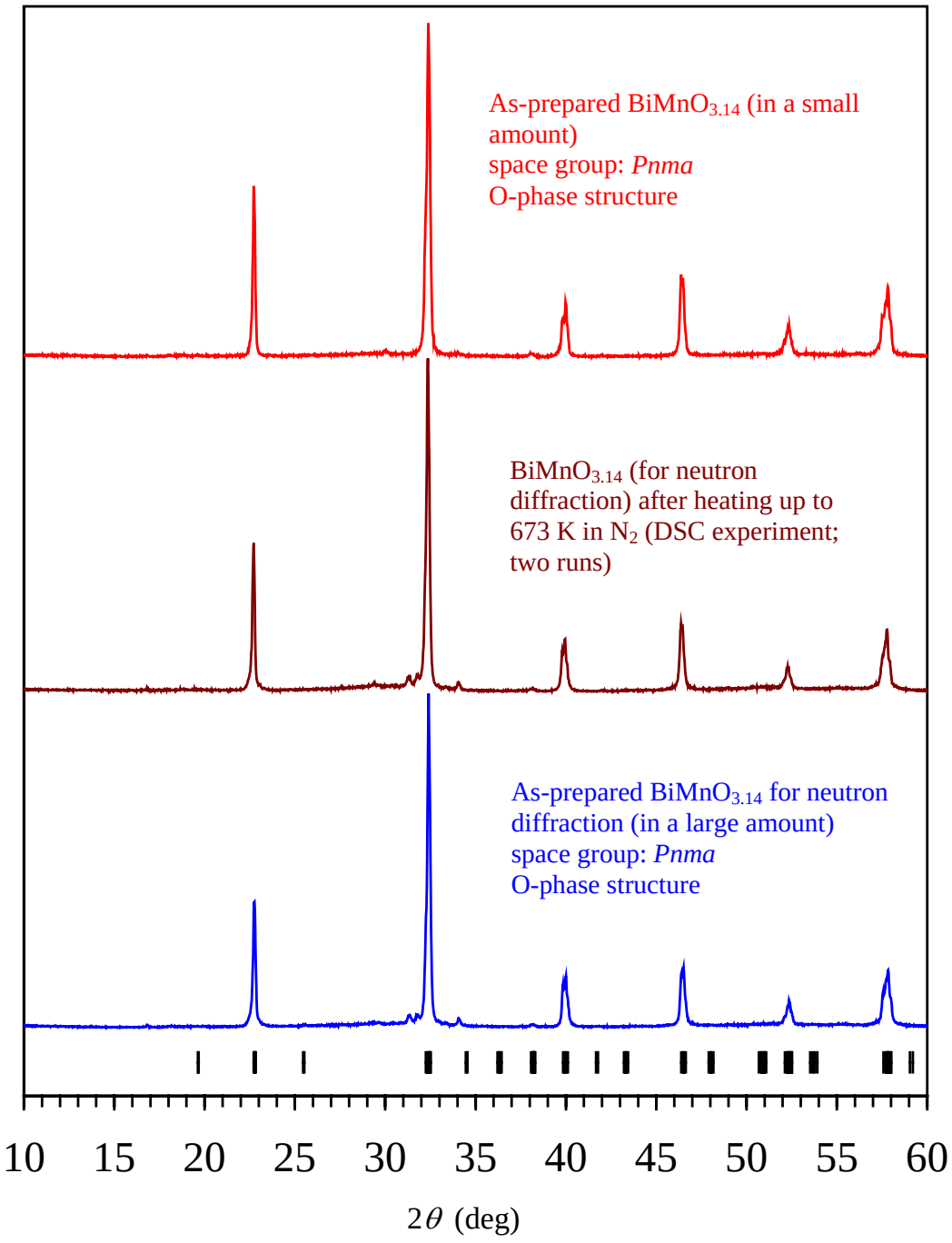

Fig. S6. X-ray powder diffraction patterns (CuKα radiation) of the as-prepared $BiMnO_{3.14}$ in a large amount for neutron diffraction (bottom), $BiMnO_{3.14}$ [for neutron diffraction] after a DSC experiment (heated up to 673 K and cooled to RT at 20 K/min in N_2 two times) (middle), and the as-prepared $BiMnO_{3.14}$ in a small amount (top). Bragg reflections for $BiMnO_{3.14}$ are indicated by tick marks.

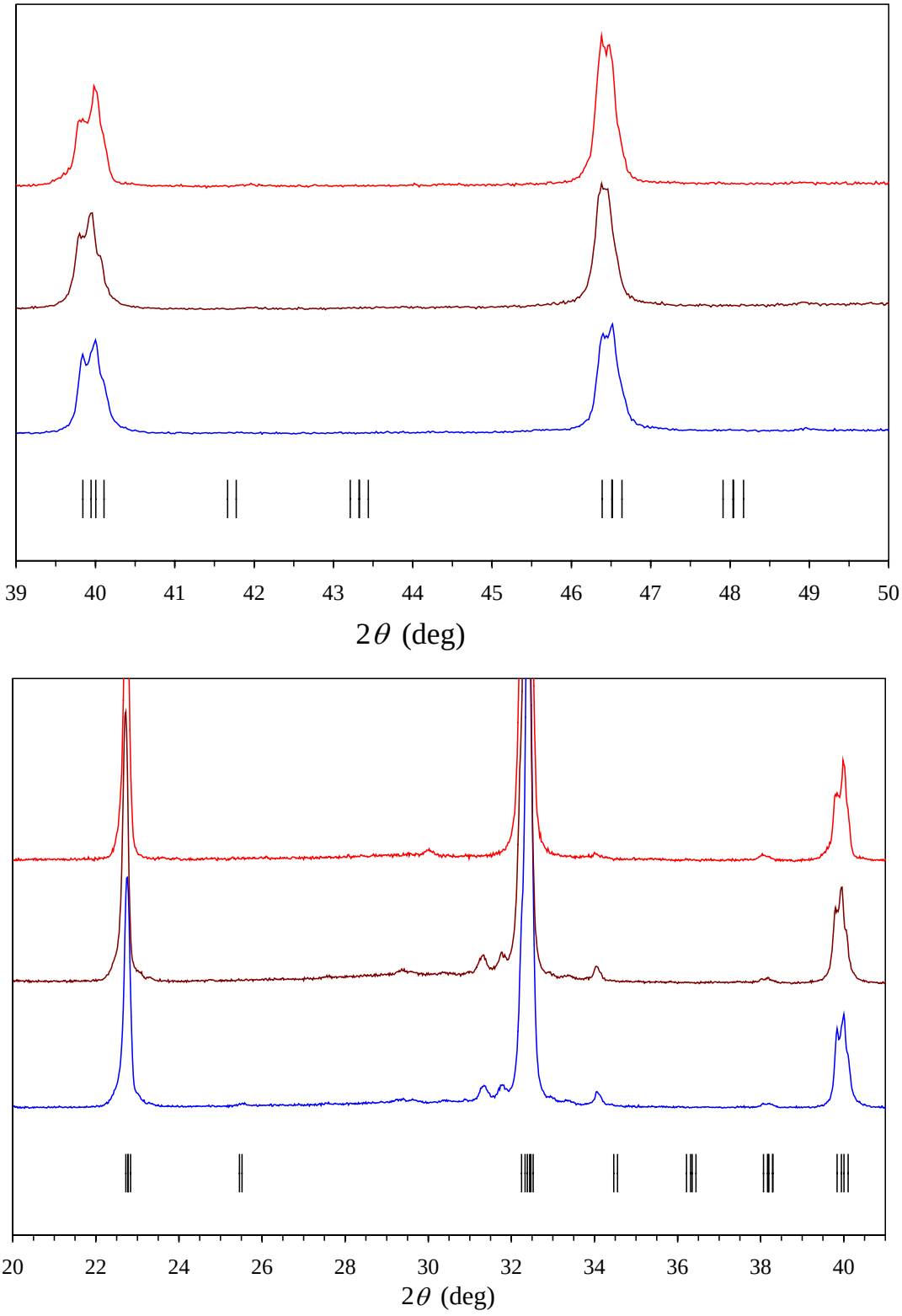

Fig. S6a. Enlarged fragments of Fig. S6

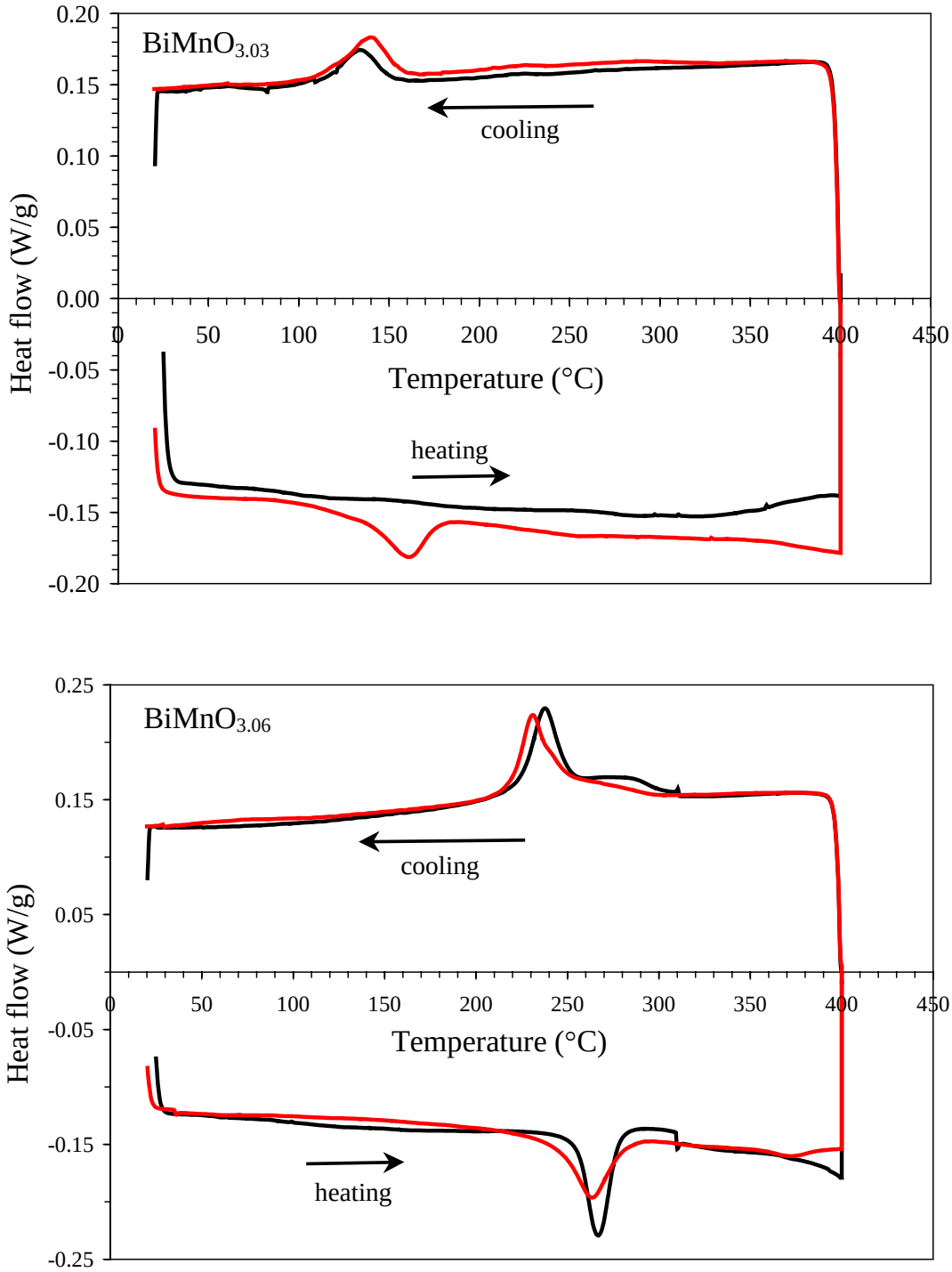

Fig. S7. Differential scanning calorimetry curves of $BiMnO_{3.03}$ (up) and $BiMnO_{3.06}$ (bottom) in N_2 with heating/cooling rate of 20 K/min. The black curves are the first run, and the red curves are the second run.

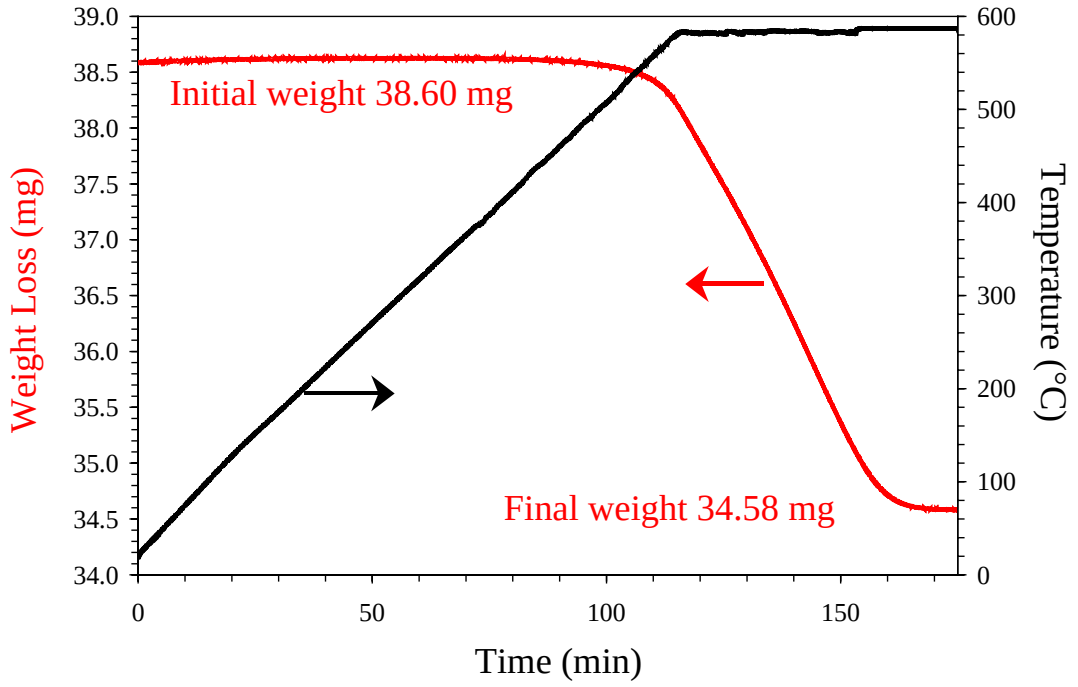

Fig. S8. Thermogravimetric curve of $BiMnO_{3.03}$ performed in a mixture of 3% H_2 + 97% Ar using a Perkin Elmer Pyris 1 TGA system in Al_2O_3 holders (the sample was heated up to 870 K at a heating rate of 5 K/min and soaked there for 1 h). The calculated oxygen content is $BiMnO_{3.03(1)}$ assuming the reduction reaction: $BiMnO_{3.03}$ > Bi + MnO.

Table S5. Structure Parameters Determined for $BiMnO_{3.03}$ at Room Temperature from Neutron Powder Diffraction Data in Space Group *C*2

Rwp = 5.18 Rp = 4.08 RR = 8.04 Re = 5.07 S = 1.0203 d1 = 0.9454 d2 = 0.6316

BiMnO3.03
RI = 1.78 RF = 0.96 E(SCIO) = 1155.45

0 Lattice parameters (Angstrom or degree) and unit-cell volume (Angstrom**3) in BiMnO3.03

a	b	c	alpha	beta	gamma	V
9.53135	5.57803	9.73793	90.0000	108.9514	90.0000	489.6646
0.00024	0.00012	0.00026	-	0.0018	-	0.0208

Structure parameters, g, x, y, z, B/Angstrom**2, and U/Angstrom**2, in BiMnO3.03

	neq	*	g	=	n	x	y	z	B	U
Bi1a	4		1.0000		4.0000	0.13148	0.22346	0.37598	0.356	0.00451
	-		-		-	0.00061	0.00332	0.00055	0.099	0.00125
Bi1b	4		1.0000		4.0000	0.86418	0.79256	0.11965	1.897	0.02402
	-		-		-	0.00079	0.00338	0.00068	0.149	0.00188
Mn1a	2		1.0000		2.0000	0.00000	0.21492	0.00000	-0.113	-0.00143
				-	-	-	-	0.00416	-	0.117	0.00149
Mn1b	2		1.0000		2.0000	0.00000	0.76470	0.50000	-0.113	-0.00143
				-	-	-	-	0.00376	-	-	-
Mn2	4		1.0000		4.0000	0.25078	0.25000	0.75193	0.652	0.00826
	-		-		-	0.00172	-	0.00136	0.121	0.00153
O1a	4		1.0000		4.0000	0.08409	0.19100	0.84058	1.111	0.01407
	-		-		-	0.00081	0.00388	0.00082	0.049	0.00062
O1b	4		1.0000		4.0000	0.90397	0.82221	0.66525	1.111	0.01407
	-		-		-	0.00089	0.00396	0.00087	-	-
O2a	4		1.0000		4.0000	0.15895	0.56083	0.62989	1.553	0.01967
	-		-		-	0.00086	0.00386	0.00079	0.059	0.00075
O2b	4		1.0000		4.0000	0.85167	0.45125	0.88944	1.553	0.01967
	-		-		-	0.00093	0.00395	0.00082	-	-
O3a	4		1.0000		4.0000	0.35833	0.56545	0.41083	1.184	0.01499
	-		-		-	0.00093	0.00373	0.00085	0.058	0.00073
O3b	4		1.0000		4.0000	0.64959	0.47149	0.09365	1.184	0.01499
	-		-		-	0.00087	0.00389	0.00086	-	-

Table S6. Structure Parameters Determined for $BiMnO_{3.03}$ at Room Temperature from Neutron Powder Diffraction Data in Space Group *Cc*

Rwp = 5.22 Rp = 4.13 RR = 8.18 Re = 5.07 S = 1.0296 d1 = 0.9295 d2 = 0.6306

BiMnO3.03
RI = 1.78 RF = 0.93 E(SCIO) = 1153.96

0 Lattice parameters (Angstrom or degree) and unit-cell volume (Angstrom**3) in BiMnO3.03

a	b	c	alpha	beta	gamma	V
9.53128	5.57802	9.73783	90.0000	108.9511	90.0000	489.6559
0.00025	0.00012	0.00026	-	0.0019	-	0.0210

Structure parameters, g, x, y, z, B/Angstrom**2, and U/Angstrom**2, in BiMnO3.03

									100*B/nm**2	100*U/nm**2
	neq	*	g	=	n	x	y	z	B	U
Bi1a	4		1.0000		4.0000	0.13615	0.21487	0.12432	1.636	0.02072
	-		-		-	0.00214	0.00134	0.00193	0.157	0.00199
Bi1b	4		1.0000		4.0000	0.86925	0.21540	0.36816	0.566	0.00717
	-		-		-	0.00216	0.00124	0.00189	0.127	0.00160
Mn1	4		1.0000		4.0000	0.00008	0.22632	0.74996	0.107	0.00136
	-		-		-	0.00263	0.00069	0.00256	0.119	0.00151
Mn2	4		1.0000		4.0000	0.25000	0.25000	0.50000	0.439	0.00556
	-		-		-	-	-	-	0.132	0.00168
O1a	4		1.0000		4.0000	0.09563	0.18619	0.57978	1.344	0.01702
	-		-		-	0.00247	0.00229	0.00206	0.214	0.00271
O1b	4		1.0000		4.0000	0.91541	0.18165	0.90482	0.832	0.01054
	-		-		-	0.00240	0.00212	0.00211	0.204	0.00258
O2a	4		1.0000		4.0000	0.15840	0.55682	0.35454	1.511	0.01914
	-		-		-	0.00228	0.00175	0.00200	0.219	0.00278
O2b	4		1.0000		4.0000	0.85111	0.55116	0.11287	1.463	0.01853
	-		-		-	0.00232	0.00183	0.00200	0.210	0.00266
O3a	4		1.0000		4.0000	0.36679	0.55437	0.15206	1.265	0.01603
	-		-		-	0.00224	0.00146	0.00208	0.174	0.00220
O3b	4		1.0000		4.0000	0.65787	0.54055	0.33421	1.153	0.01461
	-		-		-	0.00221	0.00150	0.00204	0.184	0.00233