Supporting Information in the manuscript

$BiScO_3$: centrosymmetric $BiMnO_3$-type oxide

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Synthesis. Stoichiometric mixtures of Bi_2O_3 and Sc_2O_3 were dried at 873 K for 8 h and then placed in Au capsules and treated at 6 G Pa in a belt-type high pressure apparatus at 1413 K for 40 min. After heat treatment, the samples were quenched to room temperature (RT), and the pressure was slowly released. $BiScO_3$ was recovered from a Au capsule in the form of powder. $BiScO_3$ was white. $BiScO_3$ contained small amount of Sc_2O_3 according to X-ray powder diffraction data.

X-ray Powder Diffraction (XRD) Experiments. XRD data of $BiScO_3$ were collected at room temperature on a RIGAKU Ultima III diffractometer using CuK_α radiation (2θ range of 4–100°, a step width of 0.02°, and a counting time of 10 s/step).

Neutron Powder Diffraction Experiments and Structure Refinements. Neutron powder diffraction data of $BiScO_3$ were collected at room temperature with the high-resolution powder diffractometer (HRPD) installed at the JRR-3M rector in JAERI, Tokai. The incident neutron wavelength was 1.8233(10) Å. About 4.66 g of the sample was contained in a V holder (diameter: 6.0 mm). The holder was slowly oscillated during the measurement. The data were taken with a step of ca. 0.05° in a 2θ range between 2.5 and 162° with 64 ^{3}He detectors. The measurement time was 18 h.

Neutron powder diffraction data were analyzed by the Rietveld method with RIETAN-2000.[1] The background was represented by a 9th-order Legendre polynomial. The split pseudo-Voigt function of Toraya[2] was used as a profile function. Isotropic atomic displacement parameters, U, with the isotropic Debye–Waller factor represented as $\exp(-8\pi^2 U \sin^2\theta / \lambda^2)$ were assigned to all the sites. Bound coherent scattering lengths, b_c, used for the structure refinement were 8.532 fm (Bi), 12.290 fm (Sc), and 5.803 fm (O).[3]

For the impurity of Sc_2O_3, we refined only a scale factor and the a lattice parameter, fixing its structure parameters. The mass percentage of Sc_2O_3 in $BiScO_3$ was calculated at 0.3 % from the refined scale factors.

Electron Diffraction. The electron diffraction patterns were obtained using an ultra-high-voltage transmission electron microscope (Hitachi H-1500) operated at an accelerating voltage of 820 kV. The TEM specimens were prepared by crushing the synthesized samples into fine fragments, which were ultrasonically dispersed in CCl_4 and transferred to carbon microgrids.

Second-Harmonic Generation (SHG) Experiments. SHG responses of powder samples were measured in a reflection scheme. A Q-switch pulsed Nd:YAG laser operated at λ_{ω} = 1064 nm was used as a radiation source with a repetition rate of 4 impulses/s and a duration of impulses of about 12 ns. The laser beam was split into two beams to excite the radiation at a doubled frequency, $\lambda_{2\omega}$, of 532 nm simultaneously in samples to be measured and a reference sample: polycrystalline α-SiO_2. The incident-beam peak power was about 0.1 MW on a spot 3 mm in diameter on the surface of the sample.

Table S1. Selected Bond Lengths, *l* (Å), and Bond Valence Sums, *BVS*,[4] in $BiScO_3$ in space group *C*2/*c*

Bonds	*l* and *BVS*
Bi – O3	2.154(3)
Bi – O2	2.193(3)
Bi – O1	2.246(3)
Bi – O1a	2.553(3)
Bi – O3a	2.897(3)
Bi – O2a	3.019(3)
Bi – O3b	3.036(3)
Bi – O2b	3.257(3)
BVS(Bi)	2.89
Sc1 – O2 (×2)	2.086(3)
Sc1 – O1 (×2)	2.110(3)
Sc1 – O3 (×2)	2.157(3)
BVS(Sc1)	2.91
Sc2 – O3 (×2)	2.096(3)
Sc2 – O1 (×2)	2.117(3)
Sc2 – O2 (×2)	2.136(3)
BVS(Sc2)	2.92

Table S2. Structure Parameters Determined for $BiScO_3$ at Room Temperature from Neutron Powder Diffraction Data in Space Group *C*2 [a]

Site	Wyckoff position	*x*	*y*	*z*	10^2U (Å^2)
Bi1	4*c*	0.1405(8)	–0.0470(19)	0.3913(6)	0.86(16)
Bi2	4*c*	0.3683(8)	0.0824(18)	0.1205(8)	0.28(15)
Sc1 [b]	2*a*	0.0	0.0	0.0	0.42(18)
Sc2	4*c*	0.2469(7)	0.0036(24)	0.7484(7)	0.80(6)
Sc3	2*b*	0.5	0.0043(9)	0.5	0.34(18)
O1	4*c*	0.0874(9)	–0.0518(24)	0.8376(11)	0.8(3)
O2	4*c*	0.4261(10)	0.0758(24)	0.6719(12)	1.4(3)
O3	4*c*	0.1647(10)	0.3041(20)	0.6255(10)	1.0(2)
O4	4*c*	0.3642(8)	0.2998(18)	0.4137(8)	–0.7(2)
O5	4*c*	0.3431(10)	0.2440(20)	0.9171(10)	1.4(3)
O6	4*c*	0.1546(8)	0.2414(19)	0.1041(8)	–0.3(2)

[a] Space group *C*2 (No 5); $Z = 8$; $a = 9.8906(5)$ Å, $b = 5.8222(3)$ Å, $c = 10.0467(5)$ Å, and $\beta = 108.303(3)°$; $V = 549.26(4)$ Å^3. $R_{wp} = 5.14$ % ($S = R_{wp}/R_e = 1.99$), $R_p = 3.82$ %, $R_B = 1.50$ %, and $R_F = 0.72$ %. The occupation of all the sites is unity.

[b] The Sc1 site was placed at the origin ($y = 0$) owing to the arbitrariness of setting the origin in the non-centrosymmetric space group of *C*2.

Table S3. Structure Parameters Determined for $BiScO_3$ at Room Temperature from Neutron Powder Diffraction Data in Space Group *Cc* [a]

Site	Wyckoff position	*x*	*y*	*z*	10^2U (Å^2)
Bi1	4*a*	0.1287(10)	0.1779(12)	0.1318(11)	1.0(2)
Bi2	4*a*	0.8568(8)	0.1898(10)	0.3630(10)	0.1(2)
Sc1	4*a*	–0.0037(11)	0.2478(3)	0.7489(10)	0.49(7)
Sc2 [b]	4*a*	1/4	0.2508(12)	1/2	0.36(7)
O1	4*a*	0.0702(11)	0.1786(15)	0.5787(14)	0.0(2)
O2	4*a*	0.9084(13)	0.1998(20)	0.9124(15)	2.0(3)
O3	4*a*	0.1507(15)	0.5356(20)	0.3767(13)	1.9(3)
O4	4*a*	0.8302(12)	0.5263(14)	0.1436(10)	–0.9(2)
O5	4*a*	0.3403(11)	0.5173(16)	0.1696(13)	0.8(3)
O6	4*a*	0.6298(11)	0.5420(13)	0.3373(12)	–0.5(2)

[a] Space group *Cc* (No 9); $Z = 8$; $a = 9.8905(5)$ Å, $b = 5.8222(3)$ Å, $c = 10.0471(5)$ Å, and $\beta = 108.299(3)°$; $V = 549.30(4)$ Å^3. $R_{wp} = 5.02$ % ($S = 1.94$), $R_p = 3.70$ %, $R_B = 1.33$ %, and $R_F = 0.56$ %. The occupation of all the sites is unity.

[b] The Sc2 site was placed at (1/4, *y*, 1/2) owing to the arbitrariness of setting the origin in the non-centrosymmetric space group of *Cc*.

The lower values of *R* factors of the *Cc* model (38 refined structure parameters) compared with those of *C*2 model (39 refined structure parameters) can be explained by the fact that space group *Cc* is 'closer' to the real space group (*C*2/*c*) from the view point of reflection conditions. The lower values of *R* factors of the *Cc* model (38 refined structure parameters) compared with those of *C*2/*c* model (19 refined structure parameters) can be explained by the larger number of the refined structure parameters in the *Cc* model.

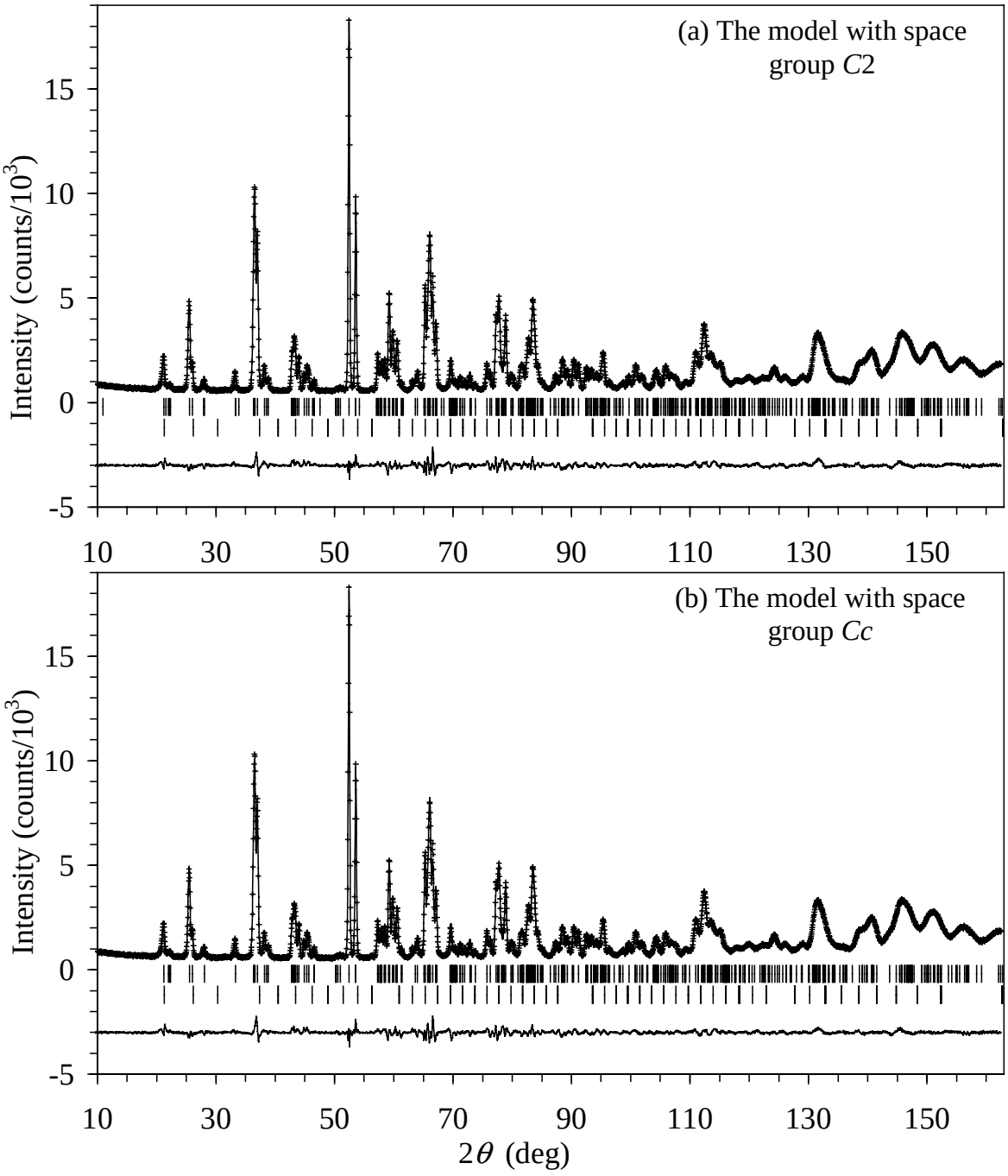

FIG. S1 Observed (crosses), calculated (solid line), and difference patterns resulting from the Rietveld analysis of the neutron powder diffraction data for $BiScO_3$ in space groups *C*2 and *Cc*. Bragg reflections are indicated by tick marks. The lower tick marks are given for the impurity phase, Sc_2O_3.

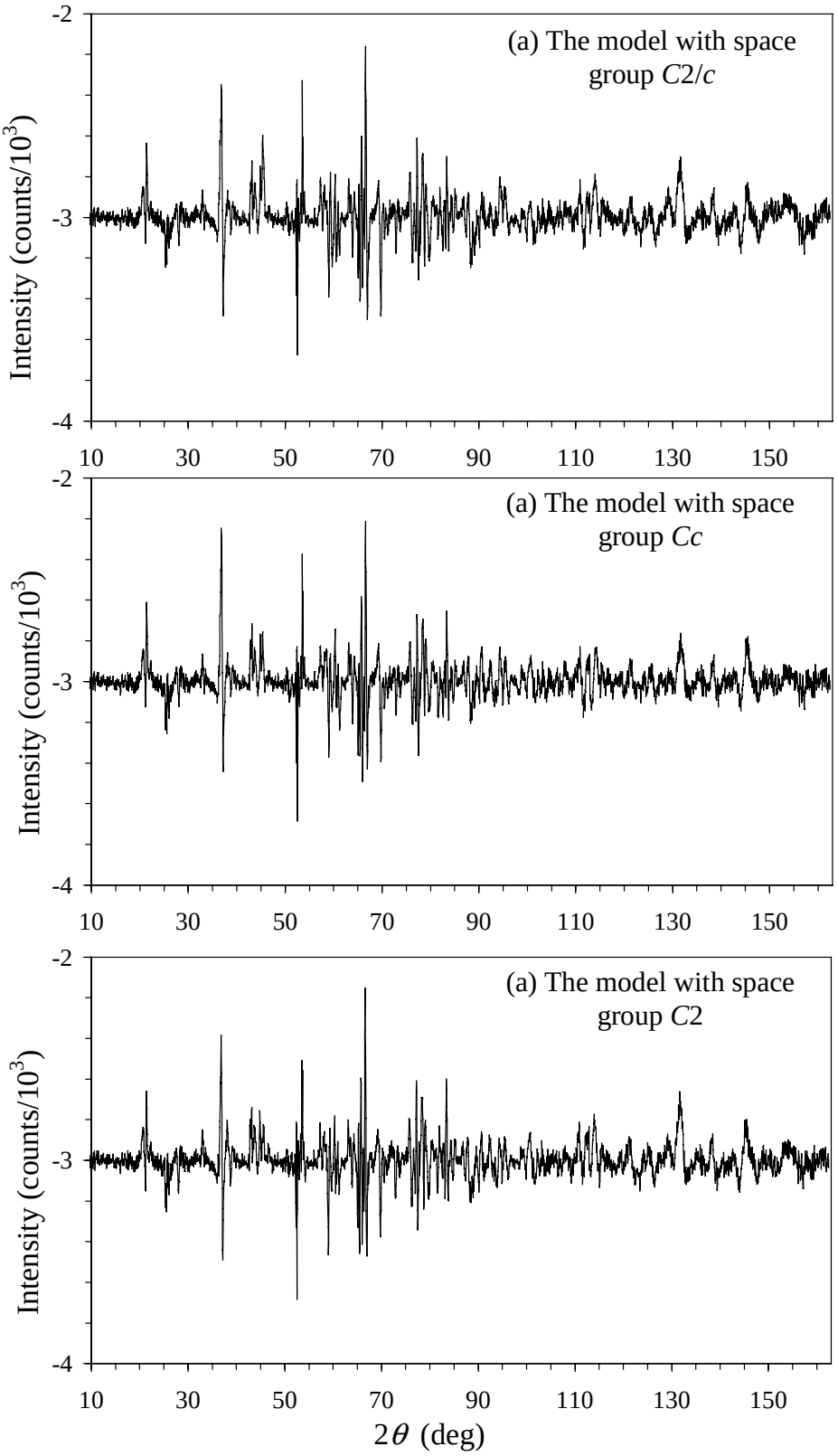

FIG. S2 Enlarged difference patterns resulting from the Rietveld analysis of the neutron powder diffraction data for $BiScO_3$ in space groups *C*2/*c*, *Cc*, and *C*2.

References

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