Inorganic Chemistry

Article

pubs.acs.org/IC

On the Structure of α-$BiFeO_3$

Hui Wang,[‡] Chengxu Yang,[†] Jun Lu,[§,∇] Meimei Wu,[∥] Jie Su,[⊥] Kuo Li,[†] Junrong Zhang,[#] Guobao Li,[*,†] Tounan Jin,[*,‡] Takashi Kamiyama,[#] Fuhui Liao,[†] Jianhua Lin,[*,†] and Yicheng Wu[§]

[†]Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China

[‡]College of Material Science and Engineering, Beijing University of Technology, Beijing 100022, P. R. China

[§]Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[∥]Neutron Scattering Laboratory, Department of Nuclear Physics, China Institute of Atomic Energy, Beijing 102413, China

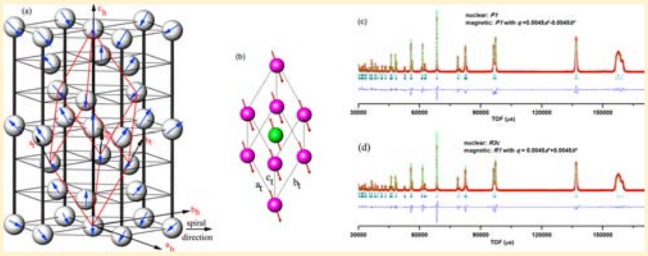
[⊥]Berzelii Centre EXSELENT on Porous Materials and Inorganic and Structural Chemistry, Department of Materials and Environmental Chemistry, Stockholm University, SE-106 91 Stockholm, Sweden

[#]Institute of Materials Structure Science, High Energy Accelerator, Research Organization (KEK), Tokai, Ibaraki 319-1106, Japan

[∇]State Key Laboratory of Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

Supporting Information

ABSTRACT: Polycrystalline and monocrystalline α-$BiFeO_3$ crystals have been synthesized by solid state reaction and flux growth method, respectively. X-ray, neutron, and electron diffraction techniques are used to study the crystallographic and magnetic structure of α-$BiFeO_3$. The present data show that α-$BiFeO_3$ crystallizes in space group *P*1 with $a = 0.563\,17(1)$ nm, $b = 0.563\,84(1)$ nm, $c = 0.563\,70(1)$ nm, $\alpha = 59.33(1)°$, $\beta = 59.35(1)°$, $\gamma = 59.38(1)°$, and the magnetic structure of α-$BiFeO_3$ can be described by space group *P*1 with magnetic modulation vector in reciprocal space $\mathbf{q} = 0.0045\mathbf{a}^* - 0.0045\mathbf{b}^*$, which is the magnetic structure model proposed by I. Sosnowska[1] applied to the new *P*1 crystal symmetry of α-$BiFeO_3$.



1. INTRODUCTION

$BiFeO_3$ has been extensively studied as a very promising multiferroic[2−5] with antiferromagnetic ordering at $T_N \approx 643$ K and ferroelectric dipole ordering at about 1100 K.[6−8] As reported, in bulk $BiFeO_3$ three phases are identified: namely α, β, and γ.[9−11] It is well accepted that at room temperature α-$BiFeO_3$ is thermodynamically stable, and crystallizes in the polar space group *R*3*c* ($a = 0.557\,88$ nm, $c = 1.386\,93$ nm)[12−15] with a G-type antiferromagnetic ordering.[16−21] In this case, there is only one crystallographic independent Fe atom in the unit cell, which disagrees with the Mössbauer spectra of α-$BiFeO_3$[8] showing two kinds of Fe atoms in the unit cell. Recently, with the help of high resolution synchrotron radiation, I. Sosnowska et al.[22] suggest a monoclinic space group *Cc* ($a = 0.9796$ nm, $b = 0.5580$ nm, $c = 1.3875$ nm, $\beta = 160.79°$) to describe the structure of α-$BiFeO_3$. These indicate that the structure of α-$BiFeO_3$ is complicated and more studies are needed. Below, our studies on the structure of α-$BiFeO_3$ are presented, which shows that α-$BiFeO_3$ crystallizes in *P*1 with two crystallographic independent Fe atoms in the unit cell.

2. EXPERIMENTAL SECTION

Powder α-$BiFeO_3$ has been synthesized using the method similar to that suggested by G. D. Achenbach:[23] the Bi_2O_3 (A. R.) and Fe_2O_3 (A. R.) were mixed in a 2: 1 molecular ratio and pressed into pellets to heat at 800 °C for 2 h in an alumina crucible, and then the product was crushed and washed with dilute HNO_3 until only peaks corresponding to α-$BiFeO_3$ were found in the X-ray diffraction patterns of the sample. The composition of the sample were confirmed by chemical titration as Bi:Fe:O = 1:1:3 (the details were presented in Supporting Information (SI)). Single crystals of α-$BiFeO_3$ were grown using flux method.[24]

Single-crystal X-ray diffraction data for α-$BiFeO_3$ were carried out at room temperature on a STOE IPDS diffractometer, equipped with an imaging plate system, using graphite-monochromatic Mo Kα radiation ($\lambda = 0.071\,073$ nm) from a rotating anode generator. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance diffractometer with Cu Kα1 ($\lambda = 0.154\,056$ nm) radiation (2θ range, 10−120°; step, 0.0197°; scan speed, 30 s/step) at 50 kV and 40 mA. High resolution synchrotron powder diffraction data were collected using beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory, using an average wavelength of 0.041 95 nm, with data points collected every 0.001° 2θ and scan speed of 0.01°/s.

Neutron powder diffraction (NPD) data were collected on the instrument Echidna at the OPAL reactor (Lucas Heights, Australia) in Australian Nuclear Science and Technology Organisation (ANSTO) at

Received: September 21, 2012
Published: February 21, 2013

dx.doi.org/10.1021/ic302047z | Inorg. Chem. 2013, 52, 2388−2392

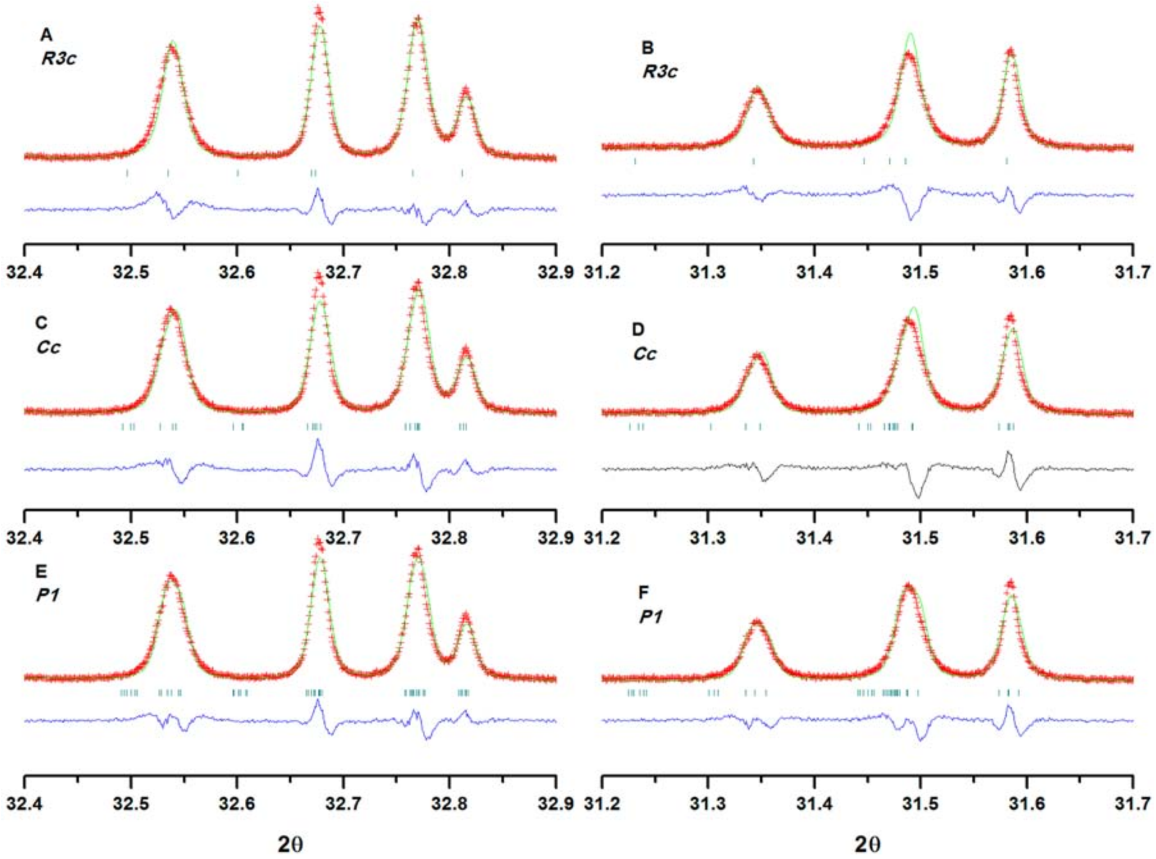


Figure 1. Rietveld plots of the powder X-ray diffraction pattern collected from beamline 11-BM at the Advanced Photon Source (APS) (λ = 0.041 395 nm) for α-BiFeO$_3$ in space group $R3c$ (A, B), Cc (C, D), and $P1$ (E, F). The symbol + represents the observed value, solid line represents the calculated value; the marks below the diffraction patterns are the calculated reflection positions, and the difference curve is shown at the bottom of the figure.

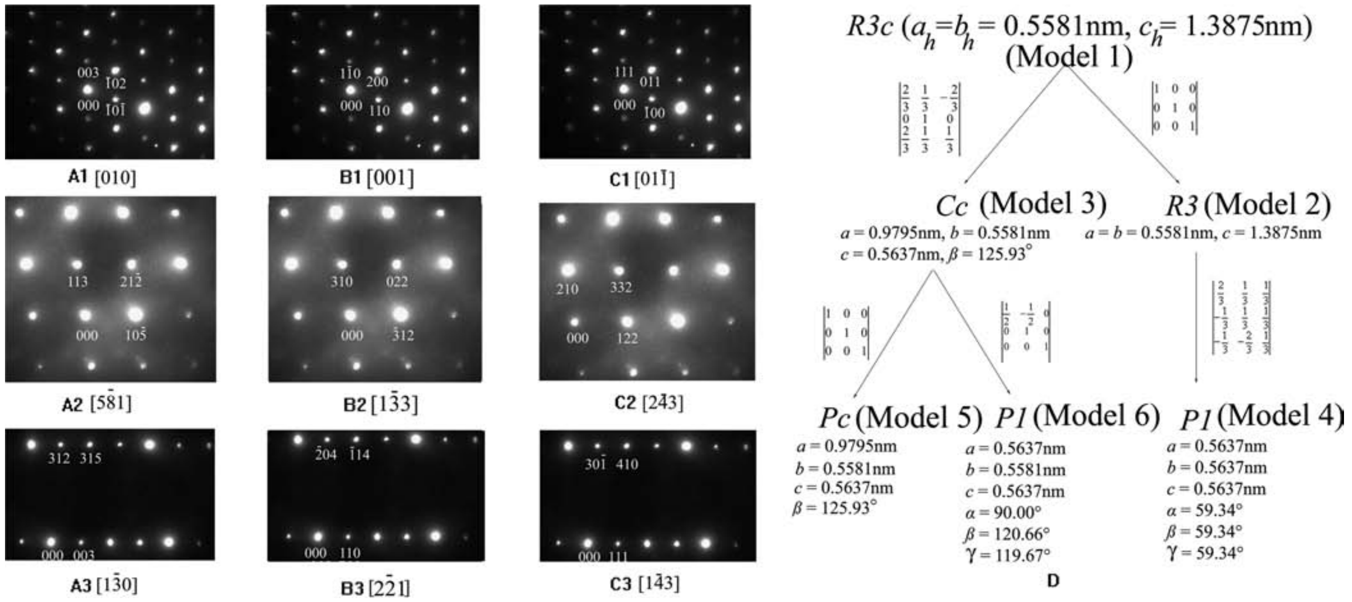


Figure 2. SAED patterns of α-BiFeO$_3$ along three different directions with interpretations in three different settings of space groups: A1, A2, A3, $R3$, a = 0.558 07(1) nm, c = 1.387 54(2) nm; B1, B2, B3, Cc, a = 0.979 83(1) nm, b = 0.557 92(1) nm, c = 0.563 49(1) nm, β = 125.91(1)°; C1, C2, C3, $P1$, a = 0.56350(1) nm, b = 0.563 84(1) nm, c = 0.563 68(1) nm, α = 59.32(1)°, β = 59.37(1)°, γ = 59.34(1)°; D, the scheme for the transition from $R3c$ to $R3$, Cc, Pc, or $P1$.

λ = 0.243 95 nm. Sample was placed in 9 mm diameter vanadium can, and data were collected over 4 h per sample. High resolution neutron powder diffraction (NPD) data were collected on a super high resolution powder diffractometer (SuperHRPD) in time-of-flight

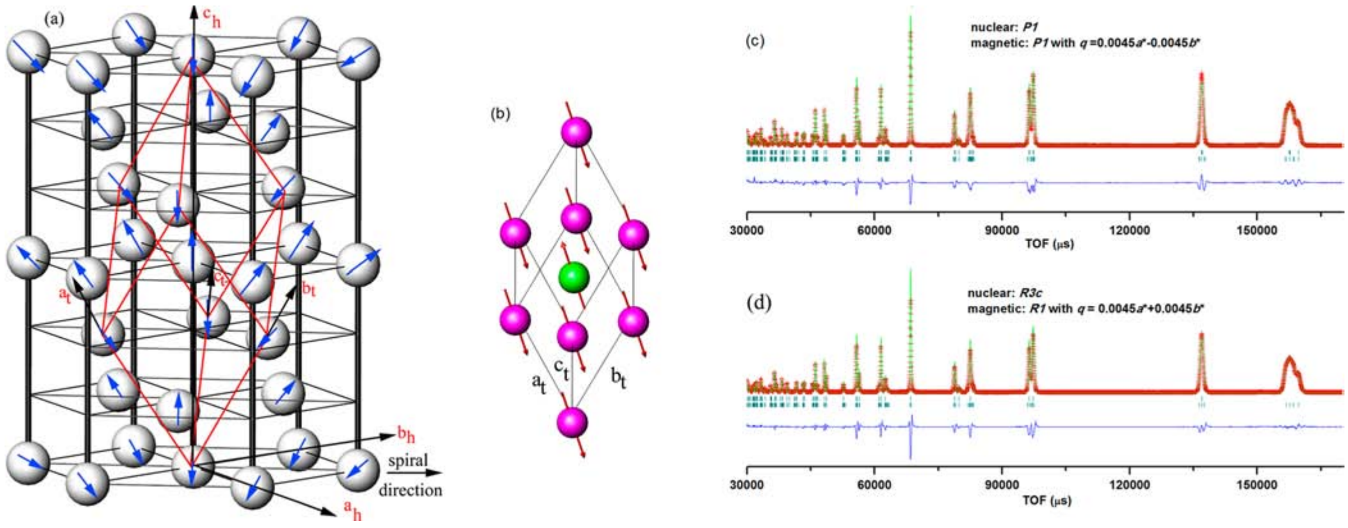


Figure 3. Hexagonal and triclinic lattices for α-BiFeO$_3$ (a), the arrangement of magnetic moment ofα-BiFeO$_3$ in space group *P*1 (b), and Rietveld plot of the powder neutron diffraction pattern collected from on super high resolution powder diffractometer (SuperHRPD) in time-of-flight mode at the Materials and Life Science Experimental Facility in the Japan Proton Accelerator Research Complex for α-BiFeO$_3$ in nuclear space group *R*3*c* and magnetic space group *R*1 (c), and nuclear space group *P*1 and magnetic space group *P*1 (d). The symbol + represents the observed value, solid line represents the calculated value; the marks below the diffraction patterns are the calculated reflection positions (up for nuclear diffraction, down for magnetic diffraction), and the difference curve is shown at the bottom of the figure.

mode with the highest possible resolution of 0.03%, which is located at about 100 m from a thin side of a decoupled poisoned moderator at the Materials and Life Science Experimental Facility in the Japan Proton Accelerator Research Complex (J-PARC).

The powder X-ray and neutron diffraction data were analyzed by using GSAS software[25,26] or Fullprof software[27] (only in the case related to modulated magnetic structure).

Selected area electron diffractions (SAED) were carried out on JEM2100F with an accelerating voltage of 200 KV.

3. RESULTS AND DISCUSSION

It is well accepted that at room temperature the space group for the nuclear structure of α-BiFeO$_3$ is *R*3*c* (a = 0.557 88 nm, c = 1.386 93 nm),[12−15] which was noted as model 1. The X-ray diffraction data of the sample α-BiFeO$_3$ from a Bruker D8 Advance diffractometer with Cu Kα1 (λ = 0.154 056 nm) radiation can be fitted well with model 1 (see Figure S2 and Table S2 in SI); however, the high resolution synchrotron powder diffraction data from beamline 11-BM at the Advanced Photon Source (APS) are not fitted well as indicated in Figure 1A with some peaks misfit. For example, the peaks around the 2θ range about 32.5° were not fit well as shown in Figure 1A: there are two or three peaks around 32.5° but only one peak is expected by the space group *R*3*c*. It is obvious that the symmetry of the lattice structure for α-BiFeO$_3$ may be different from *R*3*c*, which is mentioned by I. Sosnowska et al.[22]

It is known that the selected area electron diffraction (SAED) patterns are very useful to determine the structure of solids.[28,29] Figure 2 shows the SAED patterns of α-BiFeO$_3$. The spots corresponding to the $d \approx 0.45$ nm are obtained, which could not be indexed by the *R*3*c* with a = 0.557 88 nm, c = 1.386 93 nm. The subgroups of *R*3*c*, such as *R*3 (a = 0.557 88 nm, c = 1.386 93 nm), *P*3*c*1 (a = 0.557 88 nm, c = 1.386 93 nm), and *Cc* [a = 0.979 83(1) nm, b = 0.557 92(1) nm, c = 0.563 49(1) nm, β = 125.91(1)° (this is the same as that suggested by I. Sosnowska et al.[22])] have been tried. The transition of *R*3*c* to *R*3 or *Cc* is performed by the matrix shown in Figure 2d. *R*3 and *Cc* can permit the presence of the spots corresponding to the $d \approx 0.45$ nm. As shown in Figure 2, the SAED patterns can be indexed by *R*3 and *Cc*. However, the spots of $d \approx 0.69$ and 0.48 nm expected by the space group *P*3*c*1 (a = 0.557 88 nm, c = 1.386 93 nm) are not found in the SAED patterns. Therefore, the space groups *R*3 (model 2) and *Cc* (model 3) are suggested for further analysis.

It is found that the high resolution synchrotron powder diffraction data are also not fitted well with model 2: two or more peaks are found around 32.5°, but only one peak is expected by the space group *R*3 (see Figure S4B in SI). The synchrotron data are fitted better with model 3 than model 2. Figure 1C shows that the peaks around 32.5° can be fitted well by model 3, but there are about three peaks around 31.35° with only two peaks expected by model 3 as shown in Figure 1D. Then, the subgroups of *R*3 or *Cc*, *P*1 (a = 0.563 50 nm, b = 0.563 84 nm, c = 0.563 68 nm, α = 59.32°, β = 59.37°, γ = 59.34°, model 4), *Pc* (a = 0.979 83 nm, b = 0.557 92 nm, c = 0.563 49 nm, β = 125.91°, model 5), and *P*1 (a = 0.5637 nm, b = 0.5581 nm, c = 0.5637 nm, α = 90.00°, β = 120.66°, γ = 119.67°, model 6), are suggested to describe the structure of α-BiFeO$_3$. The matrix for the corresponding transition is shown in Figure 2D. The expected spots of d = 0.793 nm and d = 0.558 nm for model 5 could not be found in SAED patterns of α-BiFeO$_3$. So, model 5 is not used for further analysis. Model 6 and model 4 are the same. We prefer model 4 because it is similar to a rhombohedra cell. The synchrotron data can be fitted well with model 4 as shown in Figure 1E,F. That is to say, the symmetry of α-BiFeO$_3$ at room temperature may be *P*1. It is lucky that in this case there are two crystallographic independent Fe atoms in the unit cell (see Table S2 in SI), which agrees well with the Mössbauer spectra of α-BiFeO$_3$[8] and the ^{209}Bi NMR spectrum of BiFeO$_3$ observed by A. A. Bush et al.[30] In addition, the single crystal data obtained for α-BiFeO$_3$ can also be explained by the space group *P*1 (the corresponding CIF file is presented in SI).

When the nuclear structure of α-BiFeO$_3$ is described by the space group *P*1, the magnetic structure of BiFeO$_3$ needs to be described on the basis of *P*1. As is well-known, the magnetic structure of α-BiFeO$_3$ has been studied extensively.[1,17−21] An

Table 1. Magnetic Phase Used to Fit the Neutron Diffraction Data of α-$BiFeO_3$ Obtained from J-Parc

	model 1m[a]	model 4m[a]
magnetic space group	*R*1	*P*1
lattice params	a = 0.558 00(1) nm, c = 1.386 86(2) nm	a = 0.563 17(1) nm, b = 0.563 84(1) nm, c = 0.563 70(1) nm, α = 59.33(1)°, β = 59.35(1)°, γ = 59.38(1)°
atom	$(x, y, z)/(R_x, R_y, R_z)^b/U_{iso}(Å^2 \times 100)$	$(x, y, z)/(R_x, R_y, R_z)^b/U_{iso}(Å^2 \times 100)$
Fe1	(0.0000, 0.0000, 0.2206(1))/(2.10(1), −2.10(1), 3.60(1))/0.49	(0.2213(1), 0.2209(1), 0.2202(1))/(4.39(1), 1.52(1), −1.62(1))/0.59
Fe2	(0.0000, 0.0000, 0.7206(1))/(−2.10(1), 2.10(1), −3.60(1))/0.49	(0.7187(1), 0.7241(1), 0.7196(1))/(−4.39(1), −1.52(1), 1.62(1))/0.59
q	$0.0042a^* + 0.0042b^*$	$0.0045a^* - 0.0045b^*$
R factor[c]	$R_F^m = 0.030$	$R_F^m = 0.023$

[a] The coordinations of other atoms are listed in Table S1 in SI. [b] R_x, R_y, R_z components along the crystallographic axis of the magnetic moments, in units of Bohr magnetons. *X*-axis coincides with the crystallographic *a*-axis, *Y*-axis belongs to the plane *a*−*b*, and *Z*-axis is perpendicular to the plane *a*−*b*. Therefore, it should be mentioned that the directions of R_x, R_y, R_z are different when the lattices used are different. [c] R_F^m, magnetic *R*-factor.

antiferromagnetic G-type spin configuration was first assigned by Kiselev et al.[17] in 1962, where each Fe^{3+} is surrounded by six antiparallel nearest neighbors. After that, I. Sosnowska et al.[1] in 1982 suggested a modified model: a spiral structure with a period of 62 nm to explain magnetic diffraction peaks obtained by high-resolution time-of-flight diffractometer, where the spins are cycloidal modulated along the $[110]_h$ direction under the hexagonal notation for α-$BiFeO_3$ (a = 0.557 88 nm and c = 1.386 93 nm) as shown in Figure 3a with $\mathbf{q}_h = 0.045\mathbf{a}_h^* + 0.045\mathbf{b}_h^*$ (noted as model 1m). Our model is very similar to the rhombohedral notation for α-$BiFeO_3$ ($a = b = c$ = 0.563 45 nm, $\alpha = \beta = \gamma$ = 59.347°) but $a \neq b \neq c$, and $\alpha \neq \beta \neq \gamma$. The lattice can be chosen as shown in Figure 3a, which permits the modulation along the $[-110]_t$ direction under the triclinic notation for α-$BiFeO_3$ with $\mathbf{q}_t = 0.045\mathbf{a}_t^* - 0.045\mathbf{b}_t^*$ (noted as model 4m). With the help of Fullprof, the high resolution neutron powder diffraction (NPD) data obtained from J-Parc for α-$BiFeO_3$ can be fitted well as shown in Figure 3d using model 4m with the magnetic parameters listed in Table 1(the nuclear structural parameters are listed in Table S3 in SI). The obtained magnetic moments $(4.39, 1.52, -1.62)_t$, $(-4.39, -1.52, 1.62)_t$ at the sites $(0.2213, 0.2209, 0.2202)_t$ and $(0.7187, 0.7241, 0.7196)_t$, respectively, by model 4m agree well with the *P*1 symmetry as shown in Figure 3b. The amplitude of this magnetic moment is about 4.92 μ_B, which is reasonable for Fe^{3+}. It should be mentioned that the high resolution neutron powder diffraction (NPD) data can be also fitted well with model 1m as shown in Figure 3c with the parameters listed in Table 1. For the reason that no full magnetic space group can be used well in software Fullprof,[27] the space group *R*1 is used to describe the magnetic structure of α-$BiFeO_3$ in model 1m, which should be *R*3 (or *R*3*c*). The amplitude of the magnetic moment is about 4.67 μ_B, which is reasonable for Fe^{3+}. However, the obtained magnetic moment $(2.1, -2.1, 3.6)_h$ at the site $(0, 0, 0.2217)_h$ (in the hexagonal note) does not agree with the 3-fold symmetry as mentioned by I. Sosnowska et al.[22] Therefore, it is reasonable to suggest model 4m describes the magnetic structure of α-$BiFeO_3$. The neutron diffraction data of α-$BiFeO_3$ collected on the instrument Echidna at the OPAL reactor (Lucas Heights, Australia) can also be fitted well with model 4m (the details are listed Table S4 in SI).

4. CONCLUSION

We claim that the space group *P*1 is more appropriate to describe the real structure of α-$BiFeO_3$. From the high resolution synchrotron powder diffraction data of α-$BiFeO_3$, we observe triple-splitting of the reflections belonging to the *P*1 group, which are single in the *R*3*c* group, or double-splitting in the *Cc* group. Single crystal diffraction data and the selected area electron diffraction (SAED) patterns agree well with the *P*1 group. With the help of the high resolution neutron powder diffraction (NPD) data obtained from J-PARC (obtained just before the 311 Earth quack) and the neutron diffraction data obtained from ANSTO, the magnetic structure of α-$BiFeO_3$ is solved in *P*1 group with $a \approx 0.56344$ nm, $b \approx 0.56370$ nm, $c \approx 0.56363$ nm, $\alpha \approx 59.32°$, $\beta \approx 59.36°$, $\gamma \approx 59.33°$, and $\mathbf{q} \approx 0.0045\mathbf{a}^* - 0.0045\mathbf{b}^*$. Two crystallographically independent Fe^{3+} ions are found in the unit cell, which make the understanding of the Mössbauer spectra[8] and the ^{209}Bi NMR spectrum[30] of α-$BiFeO_3$ more comfortable. The magnetic moments contributed by the two Fe^{3+} ions are $(4.29, 1.80, -1.68)_t$ and $(-4.29, -1.80, 1.68)_t$, respectively, which agree well with the *P*1 symmetry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional figures, tables, and details. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: liguobao@pku.edu.cn (G.L.), tnjinkim@bjut.edu.cn (T.J.), jhlin@pku.edu.cn (J.L.). Phone: (8610)62750342. Fax: (8610)62753541.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by a National Key Basic Research Project of China (2010CB833103), the National Natural Science Foundation of China (Grants 11075220 and 51102249), and Scientific Research Key Program of Beijing Municipal Commission of Education (KM201010005019). Use of the Advanced Photon Source at Argonne National Laboratory was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract DE-AC02-06CH11357. We thank Dr. M. Avdeev for assistance collecting the neutron power diffraction data at the OPAL facility. We thank Mr. Yan Wang and Mrs. Jinling Gen for help analyzing the composition of α-$BiFeO_3$ by chemical titration.

■ REFERENCES

(1) Sosnowska, I.; Peterlin-Neumaier, T.; Steichele, E. *J. Phys. C: Solid State Phys.* **1982**, *15*, 4835.

(2) Wang, J.; Neaton, J. B.; Zheng, H.; Nagarajan, V.; Ogale, S. B.; Liu, B.; Viehland, D.; Vaithyanathan, V.; Schlom, D. G.; Waghmare, U. V.; Spaldin, N. A.; Rabe, K. M.; Wuttig, M.; Ramesh, R. *Science* **2003**, *299*, 1719.

(3) Ramesh, R.; Spaldin, N. A. *Nat. Mater.* **2007**, *6*, 21.

(4) Choi, T.; Lee, S.; Choi, Y. J.; Kiryukhin, V.; Cheong, S. W. *Science* **2009**, *324*, 63.

(5) Lebeugle, D.; Mougin, A.; Viret, M.; Colson, D.; Ranno, L. *Phys. Rev. Lett.* **2009**, *103*, 257601.

(6) Lu, J.; Guenther, A.; Schrettle, F.; Mayr, F.; Krohns, S.; Lunkenheimer, P.; Pimenov, A.; Travkin, V. D.; Mukhin, A. A.; Loidl, A. *Eur. Phys. J. B* **2010**, *75*, 451.

(7) Smith, R. T.; Achenbach, G. D.; Gerson, R.; James, W. J. *J. Appl. Phys.* **1968**, *39*, 70.

(8) Blaauw, C.; van der Woude, F. *J. Phys. C: Solid State Phys.* **1973**, *6*, 1422.

(9) Haumont, R.; Kornev, I. A.; Lisenkov, S.; Bellaiche, L.; Kreisel, J.; Dkhil, B. *Phys. Rev. B* **2008**, *78*, 134108.

(10) Selbach, S. M.; Tybell, T.; Einarsrud, M. A.; Grande, T. *Adv. Mater.* **2008**, *20*, 3692.

(11) Arnold, D. C.; Knight, K. S.; Morrison, F. D.; Lightfoot, P. *Phys. Rev. Lett.* **2009**, *102*, 027602.

(12) Michel, C.; Moreau, J.-M.; Achenbach, G. B.; Gerson, R.; James, W. J. *Solid State Commun.* **1969**, *7*, 701.

(13) Moreau, J. M.; Michel, C.; Gerson, R.; James, W. J. *J. Phys. Chem. Solids* **1971**, *32*, 1315.

(14) Kubel, F.; Schmid, H. *Acta Crystallogr., Sect. B* **1990**, *46*, 698.

(15) Palewicz, A.; Przenioslo, R.; Sosnowska, I.; Hewat, A. W. *Acta Crystallogr., Sect. B* **2007**, *63*, 537.

(16) Wollan, E. O.; Koehler, W. C. *Phys. Rev.* **1955**, *100*, 545.

(17) Kiselev, S. V.; Zhdanov, G. S.; Ozerov, R. P. *Doklady Akademii Nauk SSSR* **1962**, *145*, 1255.

(18) Kiselev, S. V.; Kshnyakina, A. N.; Ozerov, R. P.; Zhdanov, G. S. *Phys. Solid State* **1964**, *5*, 2425.

(19) Jacobson, A. J.; Fender, B. E. F. *J. Phys. C: Solid State Phys.* **1975**, *8*, 844.

(20) Fischer, P.; Polomska, M.; Sosnowska, I.; Szymanski, M. *J. Phys. C: Solid State Phys.* **1980**, *13*, 1931.

(21) Sosnowska, I.; Loewenhaupt, M.; David, W. I. F.; Ibberson, R. M. *Physica B* **1992**, *180−181*, 117.

(22) Sosnowska, I.; Przenioslo, R.; Palewicz, A.; Wardecki, D.; Fitch, A. *J. Phys. Soc. Jpn.* **2012**, *81*, 044604.

(23) Achenbach, G. D.; James, W. J.; Gerson, R. *J. Am. Ceram. Soc.* **1967**, *50*, 437.

(24) Lu, J.; Qiao, L. J.; Fu, P. Z.; Wu, Y. C. *J. Cryst. Growth* **2011**, *318*, 936.

(25) Rietveld, H. M. *J. Appl. Crystallogr.* **1969**, *2*, 65.

(26) Larson, A. C.; von Dreele, R. B. *Report LAUR 86-748*; Los Alamos National Laboratory: Los Alamos, NM, 1985.

(27) Rodriguez-Carvajal, J. *Phys. B* **1993**, *192*, 55.

(28) Li, G. B.; Liu, S. X.; Liao, F. H.; Tian, S. J.; Jing, X. P.; Lin, J. H.; Uesu, Y.; Kohn, K.; Saitoh, K.; Terauchi, M.; Di, N. L.; Cheng, Z. H. *J. Solid State Chem.* **2004**, *177*, 1695.

(29) Li, G. B.; You, L. P.; Wei, W. T.; Lu, Y.; Ju, J.; Wannberg, A.; Rundlof, H.; Zou, X. D.; Yang, T.; Tian, S. J.; Liao, F. H.; Toyota, N.; Lin, J. H. *J. Am. Chem. Soc.* **2005**, *127*, 14094.

(30) Bush, A. A.; Gippius, A. A.; Zalesskii, A. V.; Morozova, E. N. *JETP Lett.* **2003**, *78*, 389.