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$BiScO_3$: Centrosymmetric $BiMnO_3$-type Oxide

Alexei A. Belik,*[,†] Satoshi Iikubo,[‡] Katsuaki Kodama,[‡] Naoki Igawa,[‡] Shin-ichi Shamoto,[‡]
Makoto Maie,[§] Takuro Nagai,[¶] Yoshio Matsui,[§] Sergey Yu. Stefanovich,[#] Bogdan I. Lazoryak,[#] and
Eiji Takayama-Muromachi[§]

International Center for Young Scientists (ICYS), High Voltage Electron Microscopy Station (HVEMS), and
Advanced Materials Laboratory (AML), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba,
Ibaraki 305-0044, Japan, Neutron Science Research Center, Japan Atomic Energy Research Institute (JAERI),
Tokai, Ibaraki 319-1195, Japan, and Department of Chemistry, Moscow State University, Moscow 119992, Russia

Received November 6, 2005; E-mail: Alexei.Belik@nims.go.jp

Bi- and Pb-containing perovskites with transition metals have received much attention in recent years due to the renewed great interest in multiferroic materials.[1−4] In multiferroic systems, two or all three of (anti)ferroelectricity, (anti)ferromagnetism, and ferroelasticity occur in the same phase. Such systems are rare in nature[5] but have potentially wide technological applications.[1−4] The most attractive possible application is in multiple state memory elements.[2]

$BiMnO_3$[6−12] and $BiFeO_3$[13] are the most studied multiferroic systems among $BiMO_3$ with magnetic M ions. $BiMnO_3$ is believed to crystallize in the noncentrosymmetric space group $C2$ to fulfill the requirement of ferroelectricity.[10,11] This structural model is generally accepted for $BiMnO_3$ and related compounds, $BiCrO_3$[14] and Bi_2MnNiO_6.[3] Despite some efforts to understand the origin of ferroelectricity in $BiMnO_3$,[6,7] it is not yet completely understood.[8,12] On the other hand, little is known about simple Bi-containing compounds $BiM'O_3$ with nonmagnetic M′ ions (M′ = Al, Sc, Ga, and In). Recent theoretical studies of $BiAlO_3$ and $BiGaO_3$ predicted that they should be high-performance piezoelectrics and ferroelectrics with very large spontaneous polarization.[15] Solid solutions including $BiM'O_3$ as the end members, for example, $PbTiO_3-BiScO_3$ and $PbTiO_3-BiGaO_3$,[16] were extensively studied recently in the attempt to improve ferroelectric properties of $PbTiO_3$ and to reduce the amount of lead. In addition, $BiM'O_3$ can be model systems for theoretical understanding of the origin of ferroelectricity in multiferroic $BiMO_3$ because no additional complication of magnetic behavior exists in $BiM'O_3$.[15]

$BiScO_3$[16,17] was prepared at 6 GPa in a belt-type high-pressure apparatus at 1413 K for 40 min. Neutron powder diffraction (NPD) data of $BiScO_3$ were collected at room temperature with a high-resolution powder diffractometer (the JRR-3M rector in JAERI, Tokai, $\lambda = 1.8233(10)$ Å). Diffraction data were analyzed by the Rietveld method with RIETAN-2000. Indexing Bragg reflections in the X-ray powder diffraction and NPD of $BiScO_3$ revealed it to crystallize in the monoclinic system with lattice parameters of $a = 9.8899(5)$ Å, $b = 5.8221(3)$ Å, $c = 10.0462(5)$ Å, and $\beta = 108.300(3)°$. These lattice parameters are similar to those of $BiMnO_3$ ($a = 9.5323$ Å, $b = 5.6064$ Å, $c = 9.8535$ Å, and $\beta = 110.667°$),[10] $BiCrO_3$,[14] and Bi_2MnNiO_6,[3] indicating that $BiScO_3$ should have a very similar structure. Reflection conditions derived from the indexed reflections of $BiScO_3$ were $h + k = 2n$ for hkl, and $h = 2n$ and $l = 2n$ for $h0l$, affording possible space groups Cc (No. 9) and $C2/c$ (No. 15). The reflection conditions were checked and confirmed using electron diffraction. No reflections with $l = 2n+1$ were observed for $h0l$ and $00l$ (Figure 1). These data unambiguously confirmed that the space group of $BiScO_3$ cannot be $C2$ (or Cm or $C2/m$) such as in $BiMnO_3$.[10] No signal of second-harmonic generation was observed for $BiScO_3$, which shows it to be centrosymmetric. All these facts leave one possibility for $BiScO_3$, that is, space group $C2/c$.

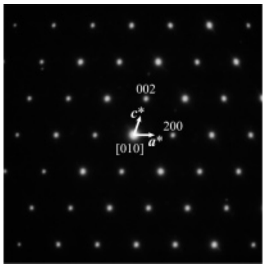
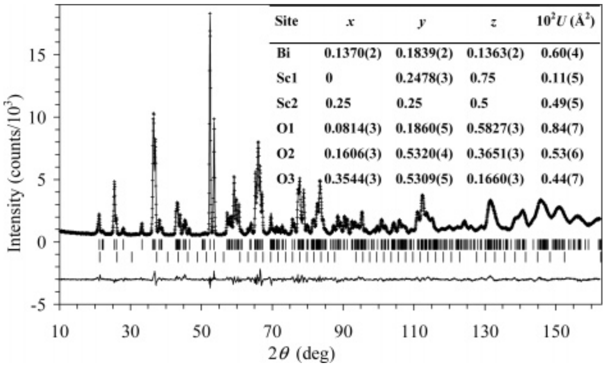


Figure 1. Electron diffraction pattern of $BiScO_3$ along the [010] zone axis.



Site	x	y	z	10^2U (Å^2)
Bi	0.1370(2)	0.1839(2)	0.1363(2)	0.60(4)
Sc1	0	0.2478(3)	0.75	0.11(5)
Sc2	0.25	0.25	0.5	0.49(5)
O1	0.0814(3)	0.1860(5)	0.5827(3)	0.84(7)
O2	0.1606(3)	0.5320(4)	0.3651(3)	0.53(6)
O3	0.3544(3)	0.5309(5)	0.1660(3)	0.44(7)

Figure 2. Observed (crosses), calculated (solid line), and difference patterns resulting from the Rietveld analysis of the neutron powder diffraction data for $BiScO_3$ at room temperature in space group $C2/c$. Bragg reflections are indicated by tick marks. The lower tick marks are given for the impurity phase, Sc_2O_3 (0.3 mass %). Final fractional coordinates and thermal parameters are listed.

Structure parameters of $BiScO_3$ were successfully refined from NPD in space group $C2/c$ using the fractional coordinates of $BiMnO_3$[10] transformed to space group $C2/c$ as the initial ones. R factors were $R_{wp} = 5.38\%$ ($S = 2.07$), $R_p = 3.98\%$, $R_B = 1.70\%$, and $R_F = 0.83\%$. Thermal parameters for all the sites were typical and positive, and estimated standard deviations (esd's) of fractional atomic coordinates and thermal parameters were small (for example, $3-5 \times 10^{-4}$ for oxygen coordinates and 7×10^{-2} for oxygen thermal parameters; Figure 2). Figure 2 displays observed, calculated, and difference NPD patterns for $BiScO_3$.

The bond valence sum calculations resulted in the values of 2.89 for Bi, 2.91 for Sc1, and 2.92 for Sc2, confirming the formal

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[†] ICYS.
[‡] JAERI.
[§] AML.
[¶] HVEMS.
[#] Moscow State University.

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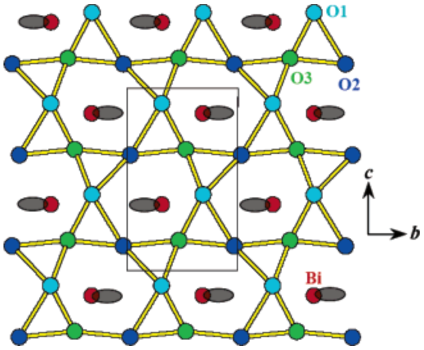

Figure 3. Projection of the structure of $BiScO_3$ along the *a* axis. One layer of O atoms (with bonds) and Bi atoms (with lone electron pair) is shown. Thin lines give a unit cell.

oxidation state +3 for Bi and Sc ions. Three Bi−O distances were short (2.15−2.25 Å), and other Bi−O distances were long (2.55−3.26 Å). Therefore, the lone electron pair of a Bi^{3+} ion is active in $BiScO_3$ (Figure 3), resulting in the antiparallel displacement of Bi^{3+} ions in the *b* direction from the centroids of their O coordination environments in the same manner as in $BiMnO_3$ with the *C*2 model.

We also tried to apply the *C*2 model as in the case of $BiMnO_3$, $BiCrO_3$, and Bi_2NiMnO_6 using the atomic coordinates of $BiMnO_3$[10] as the initial ones in the structure analysis of $BiScO_3$. The *R* factors in the *C*2 model ($R_{wp} = 5.14\%$ ($S = 1.99$), $R_p = 3.82\%$, $R_B = 1.50\%$, and $R_F = 0.72\%$) were slightly smaller than those of the *C*2/*c* model because of the larger number of the refined structural parameters (39 vs 19). However, thermal parameters of two O atoms were negative. The esd's of fractional atomic coordinates (for example, $8{-}24 \times 10^{-4}$ for O) and thermal parameters (for example, 0.2−0.3 for O) of all the atoms were about 1 order of magnitude larger than one may expect from NPD data.

The esd's of fractional atomic coordinates and thermal parameters in the *Cc* model (the number of refined structural parameters was 38) were almost the same as those of the *C*2 model with slightly smaller *R* factors in the *Cc* model: $R_{wp} = 5.02\%$ ($S = 1.94$), $R_p = 3.70\%$, $R_B = 1.33\%$, and $R_F = 0.56\%$. Two O atoms also had negative thermal parameters in the *Cc* model. The negative thermal parameters for O atoms and large esd's for all the sites obtained from NPD data are good indicators that the symmetry of $BiScO_3$ is higher than *C*2 or *Cc* and a center of symmetry is missed.[18] It is known that disregarding a center of symmetry results in errors in the atomic coordinates that are large compared with normal esd's.[18]

Checking the available structural data for $BiMnO_3$ and related compounds revealed the same problem, which was systematically ignored, with the *C*2 model. In the first paper reporting the crystal structure of $BiMnO_3$ from NPD at room temperature, esd's for O coordinates were $1{-}5 \times 10^{-3}$.[10] In ref 11, using NPD at 20 K, the thermal parameters for all the sites were fixed, and esd's for O coordinates were $2{-}9 \times 10^{-3}$. These esd's of O coordinates are very large for NPD data. In the structural analysis of Bi_2NiMnO_6 from high-quality synchrotron XRD, the authors had to refine the common thermal parameters for all Bi sites, all Ni/Mn sites, and all O sites.[3] The esd's of Bi coordinates were $1{-}12 \times 10^{-3}$, which are extremely large for heavy Bi atoms.

All of the above facts and structural information obtained for $BiScO_3$ in this work indicate that the structural model for $BiMnO_3$ and related compounds should be revised. There is good indication that the atomic arrangements in the bulk $BiMnO_3$ are very close to centrosymmetric, if not centrosymmetric at all. Therefore, it seems that the structural distortion cannot be the origin of ferroelectricity in bulk $BiMnO_3$ as generally accepted. In ref 6, it was noted that noncentrosymmetric distortion in $BiMnO_3$ is most unusual for the d^4 Mn^{3+} Jahn−Teller ion. In refs 7 and 12, it was suggested that ferroelectricity in $BiMnO_3$ may originate from an electronic phase transition (electronic ferroelectricity)[19] in contrast to the conventional displacive ferroelectricity caused by a lattice distortion. In ref 20, a very small polarization was obtained for $BiMnO_3$ in the *C*2 model from first-principles calculations. $BiScO_3$ may serve as a model system to understand a role of Mn^{3+} ions in ferroelectricity of $BiMnO_3$. We hope that the results of this work will stimulate further research activities in studying the intriguing question about the origin of ferroelectricity in $BiMnO_3$.

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Supporting Information Available: Details of experiments; selected interatomic distances in the *C*2/*c* model; observed, calculated, and difference NPD patterns and structure parameters for $BiScO_3$ refined in space groups *C*2 and *Cc* (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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