JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
COMMUNICATION
pubs.acs.org/JACS

BiO(IO$_3$): A New Polar Iodate that Exhibits an Aurivillius-Type (Bi$_2$O$_2$)$^{2+}$ Layer and a Large SHG Response

Sau Doan Nguyen, Jeongho Yeon, Sang-Hwan Kim, and P. Shiv Halasyamani*

Department of Chemistry, University of Houston, 136 Fleming Building, Houston, Texas 77204-5003, United States

Supporting Information

ABSTRACT: A new noncentrosymmetric (NCS) and polar material containing two lone-pair cations, Bi^{3+} and I^{5+}, and exhibiting an Aurivillius-type $(Bi_2O_2)^{2+}$ layer has been synthesized and structurally characterized. The material, BiO(IO$_3$), exhibits strong second-harmonic generation (SHG), ~12.5 × KDP (or ~500 × α-SiO$_2$), using 1064 nm radiation, and is found in the NCS polar orthorhombic space group *Pca*2$_1$ (No. 29). The structure consists of $(Bi_2O_2)^{2+}$ cationic layers that are connected to $(IO_3)^-$ anions. The macroscopic polarity, observed along the *c*-axis direction, may be attributed to the alignment of the IO$_3$ polyhedra. In addition to the crystal structure and SHG measurements, polarization and piezoelectric measurements were performed, as well as electronic structure analysis.

The synthesis and characterization of new materials with functional applications, e.g., piezoelectricity, battery materials, multiferroics, etc. is of topical and technological interest.[1] This is clearly the situation with polar compounds, i.e, materials that exhibit a macroscopic dipole moment. Functional properties such as pyroelectricity, ferroelectricity, and multiferroic behavior are restricted to polar materials. Although the crystallographic symmetry requirements for polarity have been extensively discussed,[2] it remains an ongoing challenge to synthesize new polar compounds. A variety of strategies have been suggested toward the design and synthesis of new polar oxide materials.[3] We have focused on synthesizing new oxide materials[4] that contain cations susceptible to second-order Jahn–Teller (SOJT) distortions,[5] i.e., octahedrally coordinated d^0 cations (Ti^{4+}, Nb^{5+}, W^{6+}, etc.) and cations with a nonbonded electron pair (Se^{4+}, Te^{4+}, I^{5+}, etc.). With both families, the cation is in a locally polar coordination environment. When the local polar environments are aligned in the crystal structure, a macroscopically polar material is observed.

A class of materials that has not been explored extensively, are oxides that contain two lone-pair cations. Relatively few of these types of materials are known, and of these only TeSeO$_4$,[6] Pb$_3$SeO$_5$,[4k] Ln$_3$Pb$_3$(IO$_3$)$_{13}$ (μ^3-O) (Ln = La – Nd),[7] Bi$_2$SeO$_5$,[8] Bi(SeO$_3$)Cl,[9] and Bi$_2$TeO$_5$[10] are noncentrosymmetric. Interestingly, all of the aforementioned NCS materials are also polar. A lone-pair cation that has received considerable interest is I^{5+}. A variety of asymmetric coordination environments are found with I^{5+}, such as IO$_3$, IO$_4$, and IO$_5$.[11] Of these, the former is the most common. With respect to bismuth(III) iodates, two materials have been reported, Bi(IO$_3$)$_3$ (space group P-1) and Bi(IO$_3$)$_3$. 2H$_2$O (space group P2$_1$/n).[12] As seen from the respective space groups, both compounds are centrosymmetric. Bi^{3+} cations are also found in Aurivillius phases,[13] many of which are polar. The Aurivillius structure is built up from alternate layers of $(Bi_2O_2)^{2+}$ cations and perovskite-like $(A_{m-1}B_mO_{3\ m+1})^{2-}$ anionic blocks, with m being an integer corresponding to the number of corner-shared octahedra forming the perovskite blocks. The macroscopic polarity observed in some Aurivillius phases is attributable structurally to the $(Bi_2O_2)^{2+}$ layer, as well as the perovskite block. In this communication, we report on a new polar material, BiO(IO$_3$), that not only contains two lone-pair cations, Bi^{3+} and I^{5+}, but also exhibits an Aurivillius type $(Bi_2O_2)^{2+}$ layer. Instead of a perovskite-like block between the $(Bi_2O_2)^{2+}$ layer, polar IO$_3$ polyhedra are observed.

BiO(IO$_3$) was synthesized by combining Bi(NO$_3$)$_3$·5H$_2$O, HIO$_3$, and 1 M HNO$_3$ in an autoclave at 200 °C for 1 week.[14] BiO(IO$_3$) crystallizes in the polar NCS space group *Pca2$_1$* (No. 29), and exhibits a layered structural topology (see Figure 1a). The structure may be described as containing layers of $(Bi_2O_2)^{2+}$ cations that are connected to $(IO_3)^-$ anions. The $(Bi_2O_2)^{2+}$ cationic layer is structurally analogous to those observed in Aurivillius phases (see Figure 1b), however, instead of a perovskite-like anion block separating the layers, locally polar iodate anions are observed. The Bi–O and I–O distances range between 2.246(6) – 2.581(3) Å and 1.813(4) – 1.844(4) Å respectively. Both the Bi^{3+} and I^{5+} cations are in asymmetric and polar coordination environments attributable to their stereoactive lone-pairs. As we will demonstrate, it is the alignment of the I^{5+} lone-pair that results in the strong SHG response.

BiO(IO$_3$) is thermally stable up to ~400 °C. Above this temperature, the material decomposes to β-Bi$_2$O$_3$. The electronic structure of BiO(IO$_3$) provides insight into its structure–property relationships. The band structure (see Figure S10) reveals an energy gap of ~2.0 eV at the Fermi level, that is less than the measured value of 3.3 eV. It has been shown that these types of calculations underestimate the band gap.[15] The electron localization function (ELF)[16] isosurfaces for the pseudopotential calculations are also shown in Figure 2. Clearly, lobe-like isosurfaces are observed near both the Bi^{3+} and I^{5+} cations, and may be considered as stereoactive lone-pairs. Some caution needs to be taken with the ELF isosurface, as core electrons are excluded,[17] but the qualitative features are consistent with a lone-pair.[18]

Received: June 13, 2011
Published: July 21, 2011

dx.doi.org/10.1021/ja205456b | *J. Am. Chem. Soc.* 2011, 133, 12422–12425

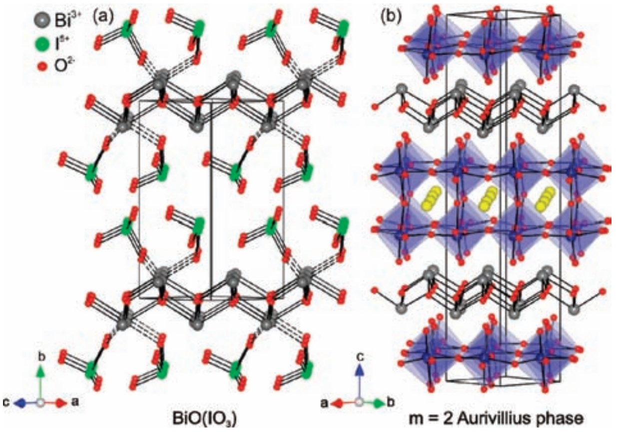

Figure 1. Ball-and-stick representation of $BiO(IO_3)$ (a) and polyhedral representation of the m = 2 Aurivillius phase (b). Note the similar $(Bi_2O_2)^{2+}$ cationic layer in each material.

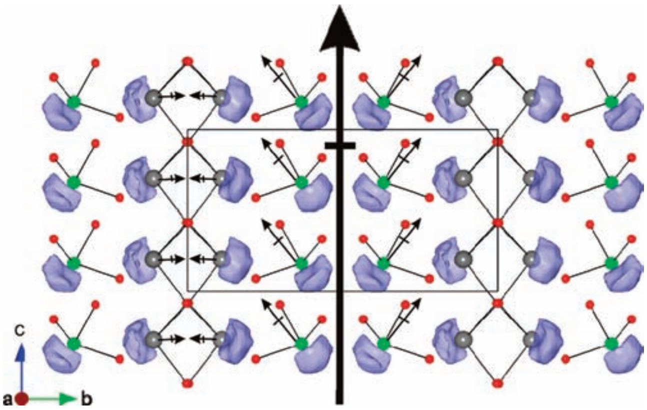

Figure 2. Ball-and-stick representation of $BiO(IO_3)$ in the bc-plane. The partially parallel and antiparallel alignments of the polarization attributable to the IO_3 and BiO_6 polyhedra respectively are shown. A net macroscopic polarization directed toward the *c*-axis is represented by the large black arrow. Note that the lobe-like isosurfaces were calculated through electron localization function with η=0.9 utilizing pseudopotential calculations.

The occurrence and alignment of the lone-pair profoundly impact the functional properties of $BiO(IO_3)$. As seen in Figure 2 and Table S4, the polarization attributable to the Bi^{3+} polyhedra is negligible – the local dipole moments are directed nearly in an antiparallel manner. With the IO_3 polyhedra, however, the local dipole moment is additive and results in a macroscopic polarization along the *c*-axis direction. Powder SHG measurements, using 1064 nm radiation, indicated that $BiO(IO_3)$ is a strong frequency-doubler with an efficiency of ~12.5 × KDP (or ~500 × α-SiO_2). This efficiency compares well to $BaTiO_3$ (400 × α-SiO_2) and $LiNbO_3$ (600 × α-SiO_2).[19] Particle size vs SHG efficiency data indicate that $BiO(IO_3)$ is type 1 phase-matchable with a calculated $\langle d_{eff} \rangle$ of ~26 pm/V (see Figure 3). As with $Li_2Ti(IO_3)_6$ and $Na_2Ti(IO_3)_6$,[4i,j] the alignment of the iodate lone-pair is, structurally, wholly responsible for the large SHG efficiency. In addition, the SHG efficiency of $BiO(IO_3)$ is similar to $A_2Ti(IO_3)_6$ (A = Li^+ or Na^+), i.e., $\langle d_{eff} \rangle$ of 23 – 26 pm/V.

In addition to investigating the SHG phenomena, piezoelectric and polarization properties were also examined. With the piezoelectricity, a d_{33} charge constant of ~26 pm/V was measured (see Figure S6). This value compares well with those of other iodates, namely $LiIO_3$ (d_{33} = 92 pm/V) and KIO_3 (d_{33} = 39 pm/V), as well as $Li_2Ti(IO_3)_6$ (d_{33} = 81 pm/V).[4i,20] As noted, $BiO(IO_3)$ is polar and may exhibit pyroelectric and ferroelectric phenomena. Pyroelectric measurements revealed a pyroelectric coefficient, p, of $-0.26\,\mu C\,m^{-2}\,K^{-1}$ at 50 °C. Variable frequency ferroelectric measurements were also performed. 'Hysteresis loops' were observed, however $BiO(IO_3)$ is ***not ferroelectric*** (see Figures S7 and S8).[21] Ferroelectricity indicates macroscopic polarization reversal, that in turn implies microscopic (local) polarization reversibility. There are two oxide polyhedra that exhibit local polarity – the asymmetric BiO_6 and IO_3 polyhedra. With the Bi^{3+} oxide polyhedra, polarization reversal has been observed, for example in $BiFeO_3$ as well as the m = 2 Aurivillius phase $SrBi_2Ta_2O_9$.[22] With the IO_3 group, we have demonstrated earlier that the energy barrier to inversion is ~8.5 eV.[4j] This value in comparison to well-known ferroelectrics such as $BaTiO_3$ (~1.8 × 10^{-2} eV) and $PbTiO_3$ (2.0 × 10^{-1} eV)[23] clearly demonstrates why $BiO(IO_3)$ is not ferroelectric - polarization reversal for the IO_3 polyhedra is energetically very unfavorable. It could be argued that the polarization with the IO_3 remains frozen, whereas the dipole moment associated with the BiO_6 polyhedra invert. This is unlikely for two reasons. First, recall that the polarization associated with the BiO_6 groups is directed in an antiparallel manner (see Figure 2). Any inversion in one polyhedron would be canceled by its opposite neighbors. This type of 'reversal' has been described as an antipolar ferroelectric.[24] Second, invoking an antipolar ferroelectric mechanism would still require an antidistortive displacement of the Bi^{3+} cations. That displacement coupled with the frozen polarization of the IO_3 polyhedra would suggest any ferroelectric hysteresis loop would be displaced. As this is not observed, and antipolar antidisortive displacements are rather rare, we suggest that the data are consistent with $BiO(IO_3)$ being a nonferroelectric pyroelectric.

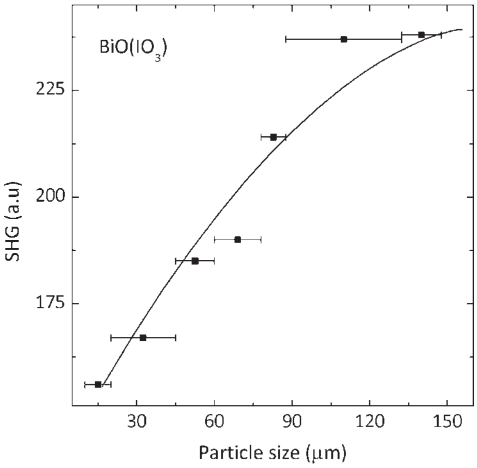

Figure 3. SHG intensity vs particle size data for $BiO(IO_3)$. The curve is drawn to guide the eye and is not a fit to the data.

In summary, we have synthesized and characterized a new polar material, with a large SHG response ~12.5 × KDP (or ~500 × α-SiO_2), that contains two lone-pair cations and exhibits an Aurivillius type $(Bi_2O_2)^{2+}$ layer. The observed functional properties are attributable to the stereoactive lone-pairs found on both the Bi^{3+} and I^{5+} cations. We are in the process of synthesizing other polar materials that contain two lone-pair cations and will be reporting on them in the near future.

■ ASSOCIATED CONTENT

Supporting Information. Detailed synthesis description, X-ray crystallographic data, experimental and calculated powder X-ray diffraction patterns, infrared and UV−vis spectra, thermogravimetric and differential thermal analysis data, piezoelectric and polarization data, density of states and analysis for $BiO(IO_3)$. The material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
psh@uh.edu.

■ ACKNOWLEDGMENT

We thank the Robert A. Welch Foundation (Grant E-1457), the Texas Center for Superconductivity, and the NSF (DMR-0652150) for support. S.N. thanks the Vietnam Government for an opportunity to study at the University of Houston.

■ REFERENCES

(1) (a) Lang, S. B. *Phys. Today* **2005**, *58*, 31. (b) Ok, K. M.; Chi, E. O.; Halasyamani, P. S. *Chem. Soc. Rev.* **2006**, *35*, 710. (c) Khomskii, D. I. *Physics* **2009**, *2*, 20.

(2) Space Group Symmetry. In *International Tables for Crystallography*; Hahn, Th., Ed.; Kluwer Academic: Dordrecht, Holland, 2006; Vol. A.

(3) (a) Heier, K. R.; Norquist, A. J.; Halasyamani, P. S.; Duarte, A.; Stern, C. L.; Poeppelmeier, K. R. *Inorg. Chem.* **1999**, *38*, 762. (b) Welk, M. E.; Norquist, A. J.; Stern, C. L.; Poeppelmeier, K. R. *Inorg. Chem.* **2000**, *39*, 3946. (c) Welk, M. E.; Norquist, A. J.; Stern, C. L.; Poeppelmeier, K. R. *Inorg. Chem.* **2001**, *40*, 5479. (d) Welk, M. E.; Norquist, A. J.; Arnold, F. P.; Stern, C. L.; Poeppelmeier, K. R. *Inorg. Chem.* **2002**, *41*, 5119. (e) Izumi, H. K.; Kirsch, J. E.; Stern, C. L.; Poeppelmeier, K. R. *Inorg. Chem.* **2005**, *44*, 884. (f) Marvel, M. R.; Lesage, J.; Baek, J.; Halasyamani, P. S.; Stern, C. L.; Poeppelmeier, K. R. *J. Am. Chem. Soc.* **2007**, *129*, 13963. (g) Marvel, M. R.; Pinlac, R. A. F.; Lesage, J.; Stern, C. L.; Poeppelmeier, K. R. *Z. Anorg. Allg. Chem.* **2009**, *635*, 869. (h) Kong, F.; Huang, S.-P.; Sun, Z.-M.; Mao, J.-G.; Cheng, W.-D. *J. Am. Chem. Soc.* **2006**, *128*, 7750. (i) Jiang, H.-L.; Huang, S.-P.; Fan, Y.; Mao, J.-G.; Cheng, W.-D. *Chem.—Eur. J.* **2008**, *14*, 1972. (j) Mao, J.-G.; Jiang, H.-L.; Kong, F. *Inorg. Chem.* **2008**, *47*, 8498. (k) Sun, C.-F.; Hu, C.-L.; Xu, X.; Ling, J.-B.; Hu, T.; Kong, F.; Long, X.-F.; Mao, J.-G. *J. Am. Chem. Soc.* **2009**, *131*, 9486. (l) Zhang, S.-Y.; Jiang, H.-L.; Sun, C.-F.; Mao, J.-G. *Inorg. Chem.* **2009**, *48*, 11809. (m) Kong, F.; Xu, X.; Mao, J.-G. *Inorg. Chem.* **2010**, *49*, 11573. (n) Yang, B.-P.; Hu, C.-L.; Xu, X.; Sun, C.-F.; Zhang, J.-H.; Mao, J.-G. *Chem. Mater.* **2010**, *22*, 1545. (o) Sun, C. F.; Hu, C.-L.; Xu, X.; Yang, B.-P.; Mao, J.-G. *J. Am. Chem. Soc.* **2011**, *133*, 5561. (p) Bera, T. K.; Jang, J. I.; Ketterson, J. B.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2008**, *131*, 75. (q) Chung, I.; Jang, J. I.; Malliakas, C. D.; Ketterson, J. B.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2009**, *132*, 384. (r) Chung, I.; Song, J.-H.; Jang, J. I.; Freeman, A. J.; Ketterson, J. B.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2009**, *131*, 2647. (s) Bera, T. K.; Jang, J. I.; Song, J.-H.; Malliakas, C. D.; Freeman, A. J.; Ketterson, J. B.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2010**, *132*, 3484. (t) Chung, I.; Jang, J.-I.; Malliakas, C. D.; Ketterson, J. B.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2010**, *132*, 384.

(4) (a) Goodey, J.; Broussard, J.; Halasyamani, P. S. *Chem. Mater.* **2002**, *14*, 3174. (b) Ra, H.-S.; Ok, K. M.; Halasyamani, P. S. *J. Am. Chem. Soc.* **2003**, *125*, 7764. (c) Ok, K. M.; Halasyamani, P. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 5489. (d) Chi, E. O.; Ok, K. M.; Porter, Y.; Halasyamani, P. S. *Chem. Mater.* **2006**, *18*, 2070. (e) Sivakumar, T.; Ok, K. M.; Halasyamani, P. S. *Inorg. Chem.* **2006**, *45*, 3602. (f) Kim, J.-H.; Baek, J.; Halasyamani, P. S. *Chem. Mater.* **2007**, *19*, 5637. (g) Chang, H. Y.; Sivakumar, T.; Ok, K. M.; Halasyamani, P. S. *Inorg. Chem.* **2008**, *47*, 8511. (h) Chang, H. Y.; Kim, S.-H.; Ok, K. M.; Halasyamani, P. S. *Chem. Mater.* **2009**, *21*, 1654. (i) Chang, H.-Y.; Kim, S.-H.; Halasyamani, P. S.; Ok, K. M. *J. Am. Chem. Soc.* **2009**, *131*, 2426. (j) Chang, H.-Y.; Kim, S.-H.; Ok, K. M.; Halasyamani, P. S. *J. Am. Chem. Soc.* **2009**, *131*, 6865. (k) Kim, S.-H.; Yeon, J.; Halasyamani, P. S. *Chem. Mater.* **2009**, *21*, 5335. (l) Chang, H. Y.; Kim, S. W.; Halasyamani, P. S. *Chem. Mater.* **2010**, *22*, 3241. (m) Yeon, J.; Kim, S.-H.; Halasyamani, P. S. *Inorg. Chem.* **2010**, *49*, 6986. (n) Zhang, W.; Li, F.; Kim, S.-H.; Halasyamani, P. S. *Cryst. Growth Des.* **2010**, *10*, 4091.

(5) (a) Opik, U.; Pryce, M. H. L. *Proc. R. Soc. London, Ser. A* **1957**, *238*, 425. (b) Bader, R. F. W. *Mol. Phys.* **1960**, *3*, 137. (c) Bader, R. F. W. *Can. J. Chem.* **1962**, *40*, 1164. (d) Pearson, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 4947. (e) Pearson, R. G. *J. Mol. Struct. (THEOCHEM)* **1983**, *103*, 25. (f) Wheeler, R. A.; Whangbo, M. H.; Hughbanks, T.; Hoffmann, R.; Burdett, J. K.; Albright, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 2222. (g) Kunz, M.; Brown, I. D. *J. Solid State Chem.* **1995**, *115*, 395. (h) Goodenough, J. B. *Annu. Rev. Mater. Sci.* **1998**, *28*, 1. (i) Halasyamani, P. S.; Poeppelmeier, K. R. *Chem. Mater.* **1998**, *10*, 2753.

(6) (a) Porter, Y.; Bhuvanesh, N. S. P.; Halasyamani, P. S. *Inorg. Chem.* **2001**, *40*, 1172. (b) Porter, Y.; Ok, K. M.; Bhuvanesh, N. S. P.; Halasyamani, P. S. *Chem. Mater.* **2001**, *13*, 1910.

(7) Hu, T.; Qin, L.; Kong, F.; Zhou, Y.; Mao, J.-G. *Inorg. Chem.* **2009**, *48*, 2193.

(8) (a) Rademacher, O.; Göbel, H.; Ruck, M.; Oppermann, H. *Z. Kristallogr. - New Cryst. Struct.* **2001**, *216*, 29. (b) Dityatyev, O. A.; Smidt, P.; Stefanovich, S. Y.; Lightfoot, P.; Dolgikh, V. A.; Opperman, H. *Solid State Sci.* **2004**, *6*, 915.

(9) Berdonosov, P. S.; Stefanovitch, S. Y.; Dolgikh, V. A. *J. Solid State Chem.* **2000**, *149*, 236.

(10) Ok, K. M.; Bhuvanesh, N. S. P.; Halasyamani, P. S. *Inorg. Chem.* **2001**, *40*, 1978.

(11) (a) Bean, A. C.; Campana, C. F.; Kwon, O.; Albrecht-Schmitt, T. E. *J. Am. Chem. Soc.* **2001**, *123*, 8806. (b) Sykora, R. E.; Wells, D. M.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2002**, *41*, 2697. (c) Sykora, R. E.; Deakin, L.; Mar, A.; Skanthakumar, S.; Soderholm, L.; Albrecht-Schmitt, T. E. *Chem. Mater.* **2004**, *16*, 1343. (d) Bray, T. H.; Beitz, J. V.; Bean, A. C.; Yu, Y.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2006**, *45*, 8251. (e) Sullens, T. A.; Almond, P. M.; Byrd, J. A.; Beitz, J. V.; Bray, T. H.; Albrecht-Schmitt, T. E. *J. Solid State Chem.* **2006**, *179*, 1192. (f) Phanon, D.; Gautier-Luneau, I. *Angew. Chem., Int. Ed.* **2007**, *46*, 8488. (g) Chai, W.; Lin, J.; Song, L.; Shu, K.; Qin, L.; Shi, H.; Guo, J. *Solid State Sci.* **2010**, *12*, 2100.

(12) (a) Bentria, B.; Benbertal, D.; Bagieu-Beucher, M.; Masse, R.; Mosset, A. *J. Chem. Crystallogr.* **2003**, *33*, 867. (b) Phanon, D.; Gautier-Luneau, I. *Z. Kristallogr.* **2006**, 243.

(13) (a) Aurivillius, B. *Ark. Kemi* **1949**, *1*, 499. (b) Aurivillius, B. *Ark. Kemi* **1949**, *1*, 463. (c) Aurivillius, B. *Ark. Kemi* **1950**, *2*, 519.

(14) $BiO(IO_3)$ was synthesized by hydrothermal methods: 0.485 g (1.00 mmol) of $Bi(NO_3)_3 \cdot 5H_2O$, 0.176 g (1.00 mmol) of HIO_3, and 3 mL of 1 M HNO_3 were placed in a 23-mL Teflon-lined autoclave. The autoclave was closed, heated to 200 °C, held for 1 week, and cooled slowly, 6 °C h^{-1}, to room temperature. The product was recovered by filtration and washed with distilled water. Yellow, thin, plate-shaped crystals and white polycrystalline powder were recovered in near quantitative yield based on $Bi(NO_3)_3 \cdot 5H_2O$.

(15) (a) Eng, H. W.; Barnes, P. W.; Auer, B. M.; Woodward, P. M. *J. Solid State Chem.* **2003**, *175*, 94. (b) Mizoguchi, H.; Eng, H. W.; Woodward, P. M. *Inorg. Chem.* **2004**, *43*, 1667. (c) Mizoguchi, H.; Woodward, P. M. *Chem. Mater.* **2004**, *16*, 5233.

(16) (a) Becke, A. D.; Edgecombe, K. E. *J. Chem. Phys.* **1990**, *92*, 5397. (b) Seshadri, R.; Hill, N. A. *Chem. Mater.* **2001**, *13*, 2892. (c) Stoltzfus, M. W.; Woodward, P. M.; Seshadri, R.; Klepeis, J.-H.; Bursten, B. *Inorg. Chem.* **2007**, *46*, 3839.

(17) Kohout, M.; Savin, A. *J. Comput. Chem.* **1997**, *18*, 1431.

(18) Burdett, J. K.; McCormick, T. A. *J. Phys. Chem. A* **1998**, *102*, 6366.

(19) Kurtz, S. K.; Perry, T. T. *J. Appl. Phys.* **1968**, *39*, 3798.

(20) (a) Hamid, S. A. *Phys. Status Solidi A* **1977**, *43*, K29. (b) *Numerical Values and Functions from the Natural Sciences and Technology (New Series), Group 3: Crystal and Solid State Physics*; Landolt, H., Ed.; Springer Verlag: Berlin, 1979; Vol. 11.

(21) Scott, J. F. *J. Phys.: Condens. Matter* **2008**, *20*, 021001/1.

(22) (a) Shimakawa, Y.; Kubo, Y.; Nakagawa, Y.; Kamiyama, T.; Asano, H.; Izumi, F. *Appl. Phys. Lett.* **1999**, *74*, 1904. (b) Baek, S. H.; Jang, H. W.; Folkman, C. M.; Li, Y. L.; Winchester, B.; Zhang, J. X.; He, Q.; Chu, Y. H.; Nelson, C. T.; Rzchowski, M. S.; Pan, X. Q.; Ramesh, R.; Chen, L. Q.; Eom, C. B. *Nat. Mater.* **2010**, *9*, 309. (c) Hatt, A. J.; Spaldin, N. A.; Ederer, C. *Phys. Rev. B* **2010**, *81*, 054109/1.

(23) Cohen, R. E. *Nature* **1992**, *358*, 136.

(24) Lines, M. E.; Glass, A. M. *Principles and Applications of Ferroelectrics and Related Materials*; Oxford University Press: Oxford, 1991.