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Alignment of Lone Pairs in a New Polar Material: Synthesis, Characterization, and Functional Properties of $Li_2Ti(IO_3)_6$

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The synthesis of new materials with advanced functional properties, e.g., piezoelectricity, battery applications, multiferroic behavior, etc. is of current and broad interest.[1] This is particularly true with polar materials, i.e., compounds exhibiting a macroscopic dipole moment. Polar materials are of great interest because of two technologically important properties: pyroelectricity and ferroelectricity.[2,3] In molecular compounds, such as NH_3, HCl, and H_2O, the concept of polarity is straightforward. For a solid-state material to be considered polar, the compound must crystallize in one of ten crystal classes: 1, 2, 3, 4, 6, *m*, *mm*2, 3*m*, 4*mm*, or 6*mm*.[4] Clearly, polarity and polar materials are important, yet the question of how to synthesize a new polar material remains. To address this question, we have synthesized several new polar oxides that contain cations susceptible to second-order Jahn−Teller (SOJT) effects:[5] octahedrally coordinated d^0 transition metals and lone-pair cations.[6] Because of SOJT effects, both groups of cations are in asymmetric coordination environments. With the d^0 cations, a displacement of the metal toward a corner, edge, or face of the oxide octahedron occurs,[7] whereas with the lone-pair cations, a nonbonded electron pair is observed.[8] For both types of cation, the local coordination is changed from nonpolar centrosymmetric to polar noncentrosymmetric. In fact, the lone-pair cation may be considered as predistorted,[9] since the cations are almost always found in asymmetric polar coordination environments. We have focused our attention on d^0 transition metal iodates.[10] We suggest that the local polar environments observed in the d^0 transition metals and the lone-pair cation I^{5+} are retained in the solid state, resulting in a macroscopically polar material. In this communication, we describe the synthesis, experimental and computational characterization, and functional properties of a new polar material, $Li_2Ti(IO_3)_6$. A novel and unique feature of this material that has profound implications for the functional properties is that the lone pairs on the iodate groups are aligned.

$Li_2Ti(IO_3)_6$ was synthesized by combining Li_2CO_3, TiO_2, HIO_3, and water in an autoclave at 230 °C for 4 days.[11] $Li_2Ti(IO_3)_6$ crystallizes in the polar noncentrosymmetric space group $P6_3$ (No. 173). The structure consists of a TiO_6 octahedron that is linked to six IO_3 polyhedra. It should be noted that the Ti^{4+} cation is disordered over two sites with 50% occupancy on each site. These groups of polyhedra are separated by the Li^+ cations. In connectivity terms, the structure can be written as $\{[TiO_{6/2}]^{2-}\cdot 6[IO_{1/2}O_{2/1}]^0\}^{2-}$, with charge balance maintained by the two Li^+ cations. Effectively, the structure may be considered as "zero-dimensional", with the large anionic polyhedra separated by Li^+ cations (see Figure 1).

The Ti−O and I−O bond distances range from 2.028(7) to 2.053(7) Å and from 1.791(5) to 1.871(6) Å, respectively. Bond valence calculations[12] resulted in values of 0.92, 4.18, and 4.94 for Li^+, Ti^{4+}, and I^{5+}, respectively. Both the Ti^{4+} and I^{5+} cations are in asymmetric coordination environments as a result of SOJT effects. The Ti^{4+} cation is slightly distorted toward a face of its octahedron (a C_3-type distortion), resulting in three "short" [2.028(7) Å] and three "long" [2.053(7) Å] Ti−O bonds. Each I^{5+} is bonded to three oxygen atoms, and because of its lone pair, a trigonal pyramidal coordination environment is observed. All of the lone pairs on the I^{5+} cations are aligned in a parallel manner (see Figure 2). This alignment of the lone pairs creates a macroscopic dipole moment, resulting in a polar material.

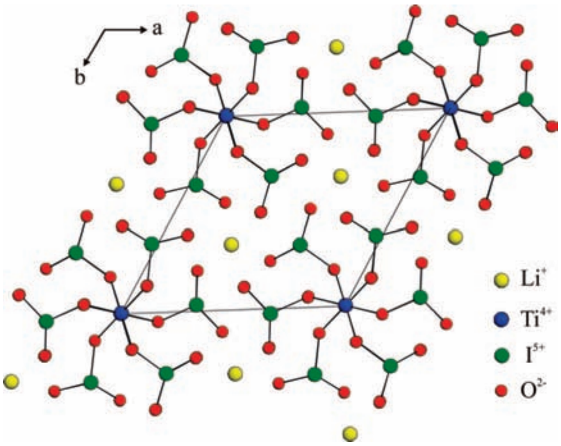

Figure 1. Ball-and-stick diagram of $Li_2Ti(IO_3)_6$ in the *ab* plane. It should be noted that the groups of metal oxide polyhedra are separated by Li^+ cations.

The IO_3 polyhedra strongly influence the structure as well as the functional properties of $Li_2Ti(IO_3)_6$. As Figure 1 shows, the TiO_6 octahedron is surrounded by six IO_3 groups. As we noted earlier,[9] when octahedrally coordinated d^0 cations are linked to lone-pair polyhedra, the SOJT distortion associated with the d^0 cation is in a direction away from the oxide ligand that bridges the two metals. In $Li_2Ti(IO_3)_6$, the Ti^{4+} cation is completely surrounded by six IO_3 groups, effectively "trapping" the Ti^{4+} cation in the center of its oxide octahedron. Because of this trapping, a very weak distortion (3.8×10^{-4} Å^2) is observed,[13] which is substantially smaller than the average for Ti^{4+} (∼0.056 Å^2).[9]

$Li_2Ti(IO_3)_6$ is thermally stable up to ∼400 °C. Above this temperature, the material decomposes to Li_2TiO_3.The electronic structure of $Li_2Ti(IO_3)_6$ provides insight into its structure−property relationships.[14] The band structure (see Figure S8 in the Supporting Information) reveals an energy gap of ∼1.6 eV at the Fermi level, which is less than the measured value of 3.0 eV. It has been shown that these types of calculations underestimate the band gap.[15] The top of the valence band (O 2p) and the bottom of the conduction

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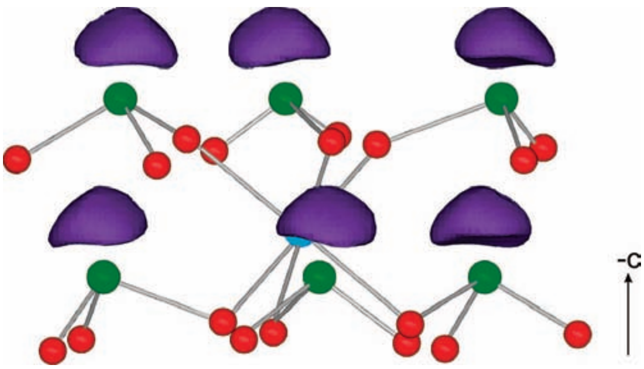

Figure 2. Visualization of the stereoactive lone pairs (purple) through the ELF for $Li_2Ti(IO_3)_6$ with $\eta = 0.9$, as obtained from pseudopotential calculations. Ti, light-blue; I, green; O, red.

band (Ti 3d) indicate that the optical band gap is attributable to ligand-to-metal (O-to-Ti) charge transfer. The electron localization function (ELF)[16] isosurfaces from the pseudopotential calculations are shown in Figure 2. Clearly, a lobelike isosurface near each I^{5+} cation is observed and may be considered as the stereoactive lone pair. The ELF isosurface needs to be regarded with some caution since core electrons are excluded,[17] but the qualitative features are consistent with a lone pair.[18] All of the lone pairs are aligned (see Figure 2), resulting in a net dipole moment approximately along the [001] direction.

The alignment of the lone pairs profoundly influences three functional properties associated with $Li_2Ti(IO_3)_6$: second-harmonic generation (SHG), piezoelectricity, and pyroelectricity (see Figures S4−S6 in the Supporting Information).[19] The SHG efficiency using 1064 nm radiation for $Li_2Ti(IO_3)_6$ is very strong ($\sim$500× α-SiO_2) and compares well to those of $BaTiO_3$ (400× α-SiO_2) and $LiNbO_3$ (600× α-SiO_2).[20] Additional SHG experiments indicate that the material is type-1 phase-matchable, with a calculated $\langle d_{\mathrm{eff}}\rangle_{\mathrm{exp}}$ of $\sim$26 pm/V. The alignment of the iodate lone pairs is directly responsible for the large SHG efficiency. All SHG-active materials are, by symmetry, piezoelectric.[21] Converse piezoelectric measurements on bulk $Li_2Ti(IO_3)_6$ revealed a d_{33} charge constant of $\sim$81 pm/V. This charge constant compares well to those of other iodates, namely, $LiIO_3$ ($d_{33} = 92$ pm/V) and KIO_3 ($d_{33} = 39$ pm/V).[22,23] As previously stated, $Li_2Ti(IO_3)_6$ is polar and has the proper symmetry for pyroelectric and ferroelectric behavior. Pyroelectric measurements revealed a pyroelectric coefficient, p, of approximately $-2.4\ \mu C\ m^{-2}\ K^{-1}$ at 55 °C. Ferroelectric measurements were also performed. Although hysteresis “loops” were measured, $Li_2Ti(IO_3)_6$ is *not* ferroelectric. Ferroelectric behavior indicates that the polarization must be reversible. Macroscopic polarization reversibility implies microscopic (local) polarization reversibility, i.e., the dipole moments associated with the IO_3 polyhedra must be reversible. Since the distortion associated with Ti^{4+} is extremely small, the associated polarization may be neglected. Hypothetical polarization reversal of an IO_3 polyhedron is shown in Figure S11 in the Supporting Information. Clearly, this reversal is energetically very unfavorable, as large structural rearrangements would have to occur. Thus, the polar IO_3 polyhedra are “frozen”, i.e., unable to undergo dipole-moment reversibility. This frozen nature is observed in other lone-pair cations, specifically those of elements in the fourth and fifth periods: Se^{4+}, Sn^{2+}, Te^{4+}, etc. In oxides, ferroelectricity with the polarization in these cations being switched has never been observed. Ferroelectric behavior with lone-pair cations has only been observed in the sixth-period cations Tl^{+}, Pb^{2+}, and Bi^{3+}.[24] This is likely attributable to the less stereoactive nature of their lone pairs, rendering them more switchable.

In summary, a new polar material, $Li_2Ti(IO_3)_6$, has been synthesized and characterized. The functional properties are directly attributable to the parallel alignment of the lone pairs on the I^{5+} cations. We are continuing our efforts to synthesize new polar materials in order to understand the structural nature of their polarity and characterize their functional properties.

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Supporting Information Available: Additional experimental and theoretical data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Halasyamani, P. S.; Poeppelmeier, K. R. *Inorg. Chem.* **2008**, *47*, 8427.
(2) Lang, S. B. *Phys. Today* **2005**, *58*, 31.
(3) Lines, M. E.; Glass, A. M. *Principles and Applications of Ferroelectrics and Related Materials*; Oxford University Press: Oxford, U.K., 1991.
(4) Hahn, T. *International Tables for Crystallography, Volume A: Space Group Symmetry*; Kluwer Academic: Dordrecht, The Netherlands, 2006.
(5) (a) Wheeler, R. A.; Whangbo, M.-H.; Hughbanks, T.; Hoffmann, R.; Burdett, J. K.; Albright, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 2222. (b) Kunz, M.; Brown, I. D. *J. Solid State Chem.* **1995**, *115*, 395. (c) Halasyamani, P. S.; Poeppelmeier, K. R. *Chem. Mater.* **1998**, *10*, 2753.
(6) (a) Ra, H.-S.; Ok, K. M.; Halasyamani, P. S. *J. Am.Chem. Soc.* **2003**, *125*, 7764. (b) Ok, K. M.; Halasyamani, P. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 5489. (c) Kim, J.-H.; Baek, J.; Halasyamani, P. S. *Chem. Mater.* **2007**, *19*, 5637.
(7) Goodenough, J. B. *Annu. Rev. Mater. Sci.* **1998**, *28*, 1.
(8) (a) Gillespie, R. J.; Nyholm, R. S. *Q. Rev., Chem. Soc.* **1957**, *11*, 339. (b) Orgel, L. E. *J. Chem. Soc.* **1959**, 3815. (c) Seshadri, R.; Hill, N. A. *Chem. Mater.* **2001**, *13*, 2892.
(9) Halasyamani, P. S. *Chem. Mater.* **2004**, *16*, 3586.
(10) (a) Larson, A. C.; Cromer, D. T. *Acta Crystallogr.* **1961**, *14*, 128. (b) Meschede, W.; Mattes, R. *Z. Anorg. Allg. Chem.* **1976**, *420*, 25. (c) Sykora, R. E.; Ok, K. M.; Halasyamani, P. S.; Albrecht-Schmitt, T. E. *J. Am. Chem. Soc.* **2002**, *124*, 1951.
(11) $Li_2Ti(IO_3)_6$ was synthesized by combining Li_2CO_3 (0.30 g, 4.06×10^{-3} mol), TiO_2 (0.300 g, 3.76×10^{-3} mol), HIO_3 (5.00 g, 2.84×10^{-2} mol), and water (10 mL) in a 23 mL Teflon-lined stainless steel autoclave and heating to 230 °C for 4 days followed by cooling to room temperature at 6 °C/h. The only product from the reaction, clear, colorless crystals of $Li_2Ti(IO_3)_6$, was washed with water and ethanol and recovered in 91% yield based on TiO_2.
(12) (a) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244. (b) Brese, N. E.; O’Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192.
(13) Llunell, M.; Casanova, D.; Cirera, J.; Bofill, J. M.; Alemany, P.; Alvarez, S.; Pinsky, M.; Avnir, D. *Shape*, version 1.1b; University of Barcelona: Barcelona, Spain, 2004.
(14) Baroni, S.; Dal Corso, A.; de Gironcoli, S.; Giannozzi, P.; Cavazzoni, C.; Ballabio, G.; Scandolo, S.; Chiarotti, G.; Focher, P.; Pasquarello, A.; Laasonen, K.; Trave, A.; Car, R.; Marzari, N.; Kokalj, A. PWscf Home Page. http://www.pwscf.org/ (accessed Jan 28, 2009).
(15) (a) Eng, H. W.; Barnes, P. W.; Auer, B. M.; Woodward, P. M. *J. Solid State Chem.* **2003**, *175*, 94. (b) Mizoguchi, H.; Woodward, P. M. *Chem. Mater.* **2004**, *16*, 5233. (c) Mizoguchi, H.; Eng, H. W.; Woodward, P. M. *Inorg. Chem.* **2004**, *43*, 1667.
(16) (a) Becke, A. D.; Edgecombe, K. E. *J. Chem. Phys.* **1990**, *92*, 5397. (b) Silvi, B.; Savin, A. *Nature* **1994**, *371*, 683. (c) Seshadri, R.; Hill, N. A. *Chem. Mater.* **2001**, *13*, 2892. (d) 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) Ok, K. M.; Chi, E. O.; Halasyamani, P. S. *Chem. Soc. Rev.* **2006**, *35*, 710.
(20) Kurtz, S. K.; Perry, T. T. *J. Appl. Phys.* **1968**, *39*, 3798.
(21) Nye, J. F. *Physical Properties of Crystals*; Oxford University Press: Oxford, U.K., 1957.
(22) Hamid, S. A. *Phys. Status Solidi A* **1977**, *43*, K29.
(23) Landolt, H. *Numerical Values and Functions from the Natural Sciences and Technology (New Series), Group 3: Crystal and Solid State Physics*; Springer-Verlag: Berlin, 1979; Vol. 11, p 317.
(24) Kubel, F.; Schmid, H. *Acta Crystallogr.* **1990**, *B46*, 698.

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