11496 *J. Am. Chem. Soc.* **2001,** *123,* 11496−11497

# Bridging the Ruddlesden−Popper and the Aurivillius Phases: Synthesis and Structure of a Novel Series of Layered Perovskite Oxides, $(BiO)LnTiO_4$ (Ln = La, Nd, Sm)

Thathan Sivakumar, Ram Seshadri, and
Jagannatha Gopalakrishnan*

*Solid State and Structural Chemistry Unit*
*Indian Institute of Science, Bangalore 560 012, India*

*Received August 10, 2001*

Two series of layered perovskite oxides continue to attract research attention. One series is the Ruddlesden−Popper (R−P) oxides,[1] $A_2[A_{n-1}B_nO_{3n+1}]$, whose members such as[2−4] $K_2La_2Ti_3O_{10}$, $K_2SrTa_2O_7$, and $NaLnTiO_4$ (Ln = La or rare earth) have been investigated for a wide variety of properties, which include ion-exchange,[2,3] intercalation,[5] exfoliation,[5] topochemical dehydration,[6,7] reductive transformation to higher members,[8,9] and photocatalytic activity for decomposition of water.[10] The other series is the Aurivillius (A) phases,[11] $(Bi_2O_2)[A_{n-1}B_nO_{3n+1}]$, which are well-known high-temperature ferroelectric materials. In recent times, members of this series, for example, $Bi_2SrTa_2O_9$ and La-substituted $Bi_4Ti_3O_{12}$ in thin-film geometry, have been shown to possess nonvolatile ferroelectric memory characteristics that are promising for computer memory applications.[12,13] Considering that the 2D-perovskite unit, viz., $[A_{n-1}B_nO_{3n+1}]$, is common for both of the series of oxides, one could envisage the following from a crystal-chemistry standpoint: *Transformation* of R−P to A series and vice versa by exchanging the interlayer entities between the perovskite sheets, and *bridging* of the two series by sequentially arranging the interlayer entities between the perovskite sheets. The R−P → A and A → R−P transformations have recently been achieved[14,15] by innovative chemical reactions involving metathesis/selective acid leaching. Bridging of the two series of layered perovskites wherein structural units of R−P and A phases are stacked one over the other to give the layer sequence, $[Bi_2O_2][A_{n-1}B_nO_{3n+1}]A_2[A_{n-1}B_nO_{3n+1}]$, has, however, not been reported so far. We report in this Communication the synthesis and structure of new layered perovskite oxides of the formula, $(BiO)LnTiO_4$ (Ln = La, Nd, Sm), which could be regarded as $n = 1$ members of this series, $A(BiO)[A_{n-1}B_nO_{3n+1}]$, bridging the R−P and A layered perovskites for the first time.

**Table 1.** Crystallographic Data for $(BiO)LaTiO_4$[a]

| atom | Wyckoff position | *x* | *y* | *z* | occupancy |
|---|---|---|---|---|---|
| Bi1 | 2*c* | 0.25 | 0.25 | 0.9044(4) | 0.67(2) |
| La1 | 2*c* | 0.25 | 0.25 | 0.9044(4) | 0.33(2) |
| Bi2 | 2*c* | 0.25 | 0.25 | 0.5961(4) | 0.33(2) |
| La2 | 2*c* | 0.25 | 0.25 | 0.5961(4) | 0.67(2) |
| Ti | 2*c* | 0.25 | 0.25 | 0.257(2) | 1 |
| O1 | 4*f* | 0.25 | 0.75 | 0.236(2) | 1 |
| O2 | 2*c* | 0.25 | 0.25 | 0.367(3)[0.41][b] | 1 |
| O3 | 2*c* | 0.25 | 0.25 | 0.027(3)[0.08][b] | 1 |
| O4 | 2*a* | 0.25 | 0.75 | 0 | 1 |

[a] Space group *P*4/*nmm* (No. 129) with origin at (000). $a = 3.8907(2)$ Å; $c = 12.161(1)$ Å. $R_{wp} = 14.0\%$; $R_{Bragg} = 11.3\%$. All isotropic thermal parameters were constrained at $B = 1$ Å$^2$. [b] Numbers in parentheses are errors, and numbers in square brackets are the physically reasonable positions used to make the structure plot.

We prepared $(BiO)LnTiO_4$ (Ln = La, Nd, Sm) starting from $NaLnTiO_4$, which are $n = 1$ members of the R−P series exhibiting a unique ordering of Na and Ln atoms at the alternate interlayer sites between single perovskite sheets in the sequence $Ln_2-TiO_{4/2}O_2-Na_2-TiO_{4/2}O_2-Ln_2$, along the *c*-axis.[4] We transformed $NaLnTiO_4$ into $(BiO)LnTiO_4$ in the following metathesis reaction[16] with BiOCl.

$$NaLnTiO_4 + BiOCl \rightarrow (BiO)LnTiO_4 + NaCl \qquad (1)$$

We found that the transformation occurs smoothly at 600 °C/6 h. The product oxides, after washing and drying to remove NaCl, are single-phase materials, as revealed by EDAX analysis and powder X-ray diffraction (XRD). EDAX analysis showed the expected 1:1:1 stoichiometry for Bi:La:Ti without chlorine impurity. Laboratory XRD patterns of the products are indexable on tetragonal cells with $a = 3.892(2)$ Å, 3.891(2) Å, 3.890(3) Å; $c = 12.16(1)$ Å, 12.15(1) Å, 12.14(1) Å for Ln = La, Nd, Sm phases, respectively. Significantly, we could not synthesize these oxides by direct solid-state reaction of $La_2O_3$, $Bi_2O_3$, and $TiO_2$ at elevated temperatures.

Considering that the $NaLnTiO_4 \rightarrow (BiO)LnTiO_4$ conversion in reaction 1 is similar to the conversion, $K_2La_2Ti_3O_{10} \rightarrow (Bi_2O_2)La_2Ti_3O_{10}$, in the metathesis reaction[14] with BiOCl, wherein interlayer K atoms are replaced by $(Bi_2O_2)$ sheets, we expected that the structure of $(BiO)LnTiO_4$ would consist of the layer sequence $Ln_2-TiO_{4/2}O_2-(Bi_2O_2)-TiO_{4/2}O_2-Ln_2$.

We determined the crystal structure of $(BiO)LaTiO_4$ by Rietveld refinement of powder XRD data.[17] The refinements employed XND code[18] and used as starting models the *P*4/*nmm* structure

---

* Author for correspondence. E-mail: gopal@sscu.iisc.ernet.in.

[1] Ruddlesden, S. N.; Popper, P. *Acta Crystallogr.* **1957**, *10*, 538−539. Ruddlesden, S. N.; Popper, P. *Acta Crystallogr.* **1958**, *11*, 54−55.

[2] Gopalakrishnan, J.; Bhat, V. *Inorg. Chem.* **1987**, *26*, 4299−4301.

[3] Ollivier, P. J.; Mallouk, T. E. *Chem. Mater.* **1998**, *10*, 2585−2587.

[4] (a) Byeon, S.-H.; Park, K.; Itoh, M. *J. Solid State Chem.* **1996**, *121*, 430−436. (b) Toda, K.; Kameo, Y.; Kurita, S.; Sato, M. *J. Alloys Cmpd.* **1996**, *234*, 19−25.

[5] Schaak, R. E.; Mallouk, T. E. *Chem. Mater.* **2000**, *12*, 3427−3434.

[6] Thangadurai, V.; Subbanna, G. N.; Gopalakrishnan, J. *Chem. Commun.* **1998**, 1299−1300.

[7] Schaak, R. E.; Mallouk, T. E. *J. Solid State Chem.* **2000**, *155*, 46−54.

[8] Schaak, R. E.; Mallouk, T. E. *J. Am. Chem. Soc.* **2000**, *122*, 2798−2803.

[9] Schaak, R. E.; Guidry, E. N.; Mallouk, T. E. *Chem. Commun.* **2001**, 853−854.

[10] (a) Takata, T.; Furumi, Y.; Shinohara, K.; Tanaka, A.; Hara, M.; Kondo, J. N.; Domen, K. *Chem. Mater.* **1997**, *9*, 1063−1064. (b) Ikeda, S.; Hara, M.; Kondo, J. N.; Domen, K.; Takahashi, H.; Okubo, T.; Kakihana, M. *Chem. Mater.* **1998**, *10*, 72−77.

[11] Aurivillius, B. *Ark. Kemi* **1949**, *1*, 463−480. Aurivillius, B. *Ark. Kemi* **1950**, *2*, 519−527.

[12] Paz de Araujo, C. A.; Cuchiaro, J. D.; McMillan, L. D.; Scott, M. C.; Scott, J. F. *Nature* **1995**, *374*, 627−629.

[13] Park, B. H.; Kang, B. S.; Bu, S. D.; Noh, T. W.; Lee, J.; Jo, W. *Nature* **1999**, *401*, 682−684.

[14] Gopalakrishnan, J.; Sivakumar, T.; Ramesha, K.; Thangadurai, V.; Subbanna, G. N. *J. Am. Chem. Soc.* **2000**, *122*, 6237−6241.

[15] Sugimoto, W.; Shirata, M.; Sugahara, Y.; Kuroda, K. *J. Am. Chem. Soc.* **1999**, *121*, 11601−11602.

[16] $NaLnTiO_4$ (Ln = La, Nd, Sm) were prepared, as reported in the literature,[4] by reacting stoichiometric amounts of the starting materials, $Na_2CO_3$, $Ln_2O_3$, and $TiO_2$ with 20% molar excess of $Na_2CO_3$ at 900 °C for 48 h with intermediate grindings. $(BiO)LnTiO_4$ were synthesized by reacting an intimate stoichiometric mixture of $NaLnTiO_4$ and BiOCl (Alfa, 99.99%) at 450 ° (12 h), 500 ° (6 h) and 600 °C (6 h), with intermediate grindings. The final product was washed with distilled water to remove NaCl and dried at 110 °C.

[17] XRD data for Rietveld refinement were collected on a Microcontrole diffractometer mounted on a Rigaku Geigerflex rotating anode operated at 15 kW. Graphite monochromatised Cu K$\beta$ radiation ($\lambda = 1.39223$ Å) was employed to increase the number of peaks in the pattern. The sample was mounted using silicone grease on a Si wafer to minimize background and preferred orientation. Data were scanned using a step size of 0.02° $2\theta$ with longer times at higher angles.

[18] Bérar, J.-F. *Program XND*; ESRF: Grenoble, France. More information under: http://www.ccp14.ac.uk; Bérar, J.-F.; *Proceedings of the IUCr Satellite Meeting on Powder Diffractometry*; Toulouse, France, July 1990; Bérar J.-F.; Garnier, P. II APD conference, NIST (U.S.A.): Gaithersburg, Maryland, May 1992; Bérar J.-F.; Garnier, P. *NIST Special Publication* **1992**, *846*, 212.

10.1021/ja011941u CCC: $20.00

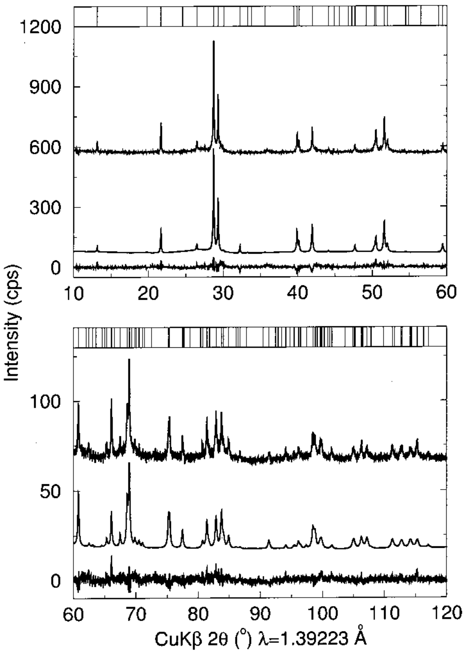

**Figure 1.** Experimental (top), Rietveld refined (middle), and difference (bottom) XRD profiles of (BiO)LaTiO$_4$. The vertical lines are expected peak positions in the space group *P*4/*nmm*. The data have been plotted separately at low and high angles in order to better visualize the fit.

of (NdCeSr)$_2$CuO$_4$[19] and LaSrMnO$_4$F.[20] During the refinement, it became clear that there is a mixing of La and Bi atoms in the two sites; therefore, keeping in mind the chemical composition of Bi:La:Ti = 1:1:1, the amount of La and Bi in their respective sites were allowed to refine, while ensuring that the total ratio was conserved. The atomic coordinates together with refinement parameters are given in Table 1, and the experimental, calculated, and difference profiles are shown in Figure 1. The refinement reveals that there is some disorder in the structure perhaps arising from its layered nature and the relatively low temperature of synthesis. The disorder manifests as a broad background near the stronger peaks. As a result of this, the final *R* factors remain rather high. In the presence of strong scatterers, La and Bi, as well as the disorder, two of the oxygen atoms refined to unphysical positions. Therefore, we have moved these oxygen atoms slightly (Table 1) to obtain a physically reasonable structural model (Figure 2). A neutron diffraction study would help determine the exact position of oxygen atoms in the structure.

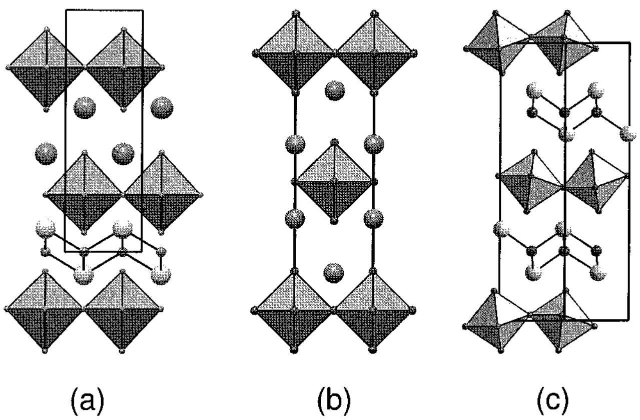

**Figure 2.** Proposed structure of (BiO)LaTiO$_4$ (a). The octahedra are around Ti. Large dark gray spheres are La, while large light gray spheres are Bi. For comparison, the structures of typical R−P phase, Sr$_2$TiO$_4$, and A phase, Bi$_2$WO$_6$, are shown in (b) and (c), respectively.

Despite these limitations, we find the gross structural features of (BiO)LaTiO$_4$ (Figure 2a), namely ReO$_3$-like TiO$_{4/2}$O$_2$ sheets flanked on one side by La atoms as in R−P phases and by (Bi$_2$O$_2$) sheets on the other side as in A phases, suggest that our expectations are indeed borne out. The coordinations of La (with La−O distances, 2.26−2.82 Å) and Ti (with Ti−O distances, 1.96−2.15 Å) are comparable to those[4] in NaLaTiO$_4$, while the [Bi$_2$O$_2$] unit (with Bi−O distances 2.27−2.59 Å) is similar to that in A phases.[21] Accordingly, the oxides (BiO)LnTiO$_4$ could be regarded as simplest ($n = 1$) members of a new series of layered perovskites, A(BiO)[A$_{n-1}$B$_n$O$_{3n+1}$], that bridge both the R−P and A series. We believe that the significance of the present work extends beyond the synthesis of a new series of layered perovskite titanates. Considering that several currently important materials properties (that include magnetoresistance, superconductivity, and ferroelectricity) are exhibited by layered perovskites belonging to R−P and A family of oxides, the present work suggests the possibility of synergistically combining these properties in new R−P/A family of layered perovskites.

**Acknowledgment.** We thank the Department of Science and Technology, Government of India, and the Council of Scientific and Industrial Research, New Delhi, for support of this work. We also thank G. Baldinozzi of the Ecole Centrale, Paris, for help in acquiring the high resolution powder XRD data and in the analysis.

JA011941U

---

[19] Izumi, F.; Takayama-Muromachi, E.; Fujimori, A.; Kamiyama, T.; Asano, H.; Akimitsu, J.; Sawa, H. *Physica C* **1989**, *158*, 440−448.

[20] Aikens, L. D.; Li, R. K.; Greaves, C. *Chem. Commun.* **2000**, 2129−2130.

[21] Newnham, R. E.; Wolfe, R. E.; Dorrian, J. F. *Mater. Res. Bull.* **1971**, *6*, 1029−1040.