# Transformations of Ruddlesden−Popper Oxides to New Layered Perovskite Oxides by Metathesis Reactions

**J. Gopalakrishnan,*,† T. Sivakumar,† K. Ramesha,† V. Thangadurai,† and G. N. Subbanna‡**

*Contribution from the Solid State and Structural Chemistry Unit and Materials Research Centre, Indian Institute of Science, Bangalore-560 012, India*

*Received May 4, 1999. Revised Manuscript Received January 27, 2000*

**Abstract:** We report transformations of the Ruddlesden−Popper (R−P) oxide, $K_2La_2Ti_3O_{10}$, to layered perovskite oxides, $(Bi_2O_2)La_2Ti_3O_{10}$, $MLa_2Ti_3O_{10}$ (M = Pb, Ba, Sr), and $(VO)La_2Ti_3O_{10}$, by a novel metathesis reaction with BiOCl, $MCl_2$, and $VOSO_4{\cdot}3H_2O$, respectively. The formation of $(VO)La_2Ti_3O_{10}$, which occurs in aqueous medium around 100 °C, suggests that the reaction is most likely topotactic, where the structural integrity of the perovskite sheet is preserved. We believe that the method described here provides a new general route for the synthesis/assembly of layered perovskite materials containing $MX/M_2X_2$ sheets, as indeed shown by the independent report of $(CuX)LaNb_2O_7$ synthesis by a similar reaction.

## Introduction

Among the several lamellar materials derived from the perovskite ($CaTiO_3$ = $ABO_3$) structure,[1] the Ruddlesden−Popper (R−P) phases,[2] $A_2[A'_{n-1}B_nO_{3n+1}]$, and the Aurivillius (A) phases,[3] $(Bi_2O_2)[A_{n-1}B_nO_{3n+1}]$, are widely investigated for several materials properties.[4] The perovskite sheet, $[A'_{n-1}B_nO_{3n+1}]$, which may be thought of as derived by slicing the three-dimensional (3-D) perovskite structure along one of the cubic directions, is common for both series of oxides. $Sr_2TiO_4$, $Sr_3Ti_2O_7$, and $Sr_4Ti_3O_{10}$ are representative members of the R−P series and $Bi_2WO_6$, $Bi_2SrTa_2O_9$, and $Bi_4Ti_3O_{12}$ are typical members of the A family. Members of the R−P family such as $K_2La_2Ti_3O_{10}$ ($n = 3$) and $K_2SrTa_2O_7$ ($n = 2$) containing alkali cations between perovskite sheets[5,6] exhibit an interlayer reactivity ($K^+/H^+$ exchange) that suggests that the alkali cations are weakly bound to the perovskite sheets in these materials. A similar reactivity is not exhibited by R−P phases such as $Sr_4Ti_3O_{10}$ and $Sr_3Ti_2O_7$ containing divalent ($Sr^{2+}$) cations between the perovskite sheets. Accordingly, we expected that R−P phases such as $K_2La_2Ti_3O_{10}$ and $K_2SrTa_2O_7$ could be transformed to other layered perovskites such as the A phases in metathetical reactions of the kind

$$K_2[A_{n-1}B_nO_{3n+1}] + 2BiOCl \rightarrow (Bi_2O_2)[A_{n-1}B_nO_{3n+1}] + 2KCl \quad (1)$$

Indeed the reaction occurs around 800−900 °C transforming both R−P phases to the corresponding A phases, $Bi_2La_2Ti_3O_{12}$ and $Bi_2SrTa_2O_9$, in near-quantitative yields.

Having succeeded in the R−P → A transformation, we explored the synthesis of new layered perovskites by this strategy. We could prepare several $MLa_2Ti_3O_{10}$ (M = Pb, Ba, Sr) and, more importantly, a novel layered perovskite $(VO)La_2Ti_3O_{10}$ in similar metathetical reactions with $MCl_2$ and $VOSO_4{\cdot}3H_2O$, respectively. While the formation of $MLn_2Ti_3O_{10}$ phases ($A$ = alkali, Ln = rare earth) has been reported already,[7,8] a layered perovskite containing interlayer $(VO)^{2+}$ cation has not been reported. The facile formation of $(VO)La_2Ti_3O_{10}$ in aqueous medium around 100 °C suggests that the transformation, $K_2La_2Ti_3O_{10} \rightarrow (VO)La_2Ti_3O_{10}$, is most likely topotactic, replacing the weakly bound interlayer $K^+$ ions in the R−P phase by the $(VO)^{2+}$ oxocation. We believe that the metathesis reactions reported here provide a novel route for the assembly of new layered perovskites containing $MX/M_2X_2$ sheets, including the technologically important A phases, which find application in ferroelectric nonvolatile memory devices.[4f,9] Indeed after the present work was submitted for publication, Kodenkandath et al.[10] reported the synthesis of $(CuX)LaNb_2O_7$ in a similar reaction between $KLaNb_2O_7$ and $CuX_2$ (X = Cl, Br).

---

* To whom correspondence should be addressed.

† Solid State and Structural Chemistry Unit.

‡ Materials Research Centre.

(1) (a) Tilley, R. J. D. In *Chemical Physics of Solids and Their Surfaces*; The Royal Society of Chemistry: London, 1980; Vol. 8, pp 149−160. (b) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, 1984.

(2) Ruddlesden, S. N.; Popper, P. *Acta Crystallogr.* **1957**, *10*, 538−539. Ruddlesden, S. N.; Popper, P. *Acta Crystallogr.* **1958**, *11*, 54−55.

(3) Aurivillius, B. *Ark. Kemi* **1949**, *1*, 463−480. Aurivillius, B. *Ark. Kemi* **1950**, *2*, 519−527.

(4) (a) Metallicity and superconductivity: Bednorz, J. G.; Müller, K. A. *Z. Phys. B.* **1986**, *64*, 189−193. Fukuoka, H.; Isami, T.; Yamanaka, S. *Chem. Lett.* **1997**, *8*, 703−704. Armstrong, A. R.; Anderson, P. A. *Inorg. Chem.* **1994**, *33*, 4366−4369. (b) Magnetism and colossal magnetoresistance: Moritomo, Y.; Asamitsu, A.; Kuwahara, H.; Tokura, Y. *Nature* **1996**, *380*, 141−144. (c) Photocatalytic activity: Takata, T.; Furumi, Y.; Shinohara, K.; Tanaka, A.; Hara, M.; Kondo, J. N.; Domen, K. *Chem. Mater.* **1997**, *9*, 1063−1064. (d) Dielectric properties, see: Frit, B.; Mercurio, J. P. *J. Alloys and Compounds* **1992**, *188*, 27−35. (e) Ionic conductivity: Kendall, K. R.; Navas, C.; Thomas, J. K.; zur Loye, H.-C. *Chem. Mater.* **1996**, *8*, 642−649. (f) Ferroelectric memory device: Paz de Araujo, C. A.; Cuchiaro, J. D.; McMillan, L. D.; Scott, M. C.; Scott, J. F. *Nature* **1995**, *374*, 627−629.

(5) Gopalakrishnan, J.; Bhat, V. *Inorg. Chem.* **1987**, *26*, 4299−4301.

(6) Ollivier, P. J.; Mallouk, T. E. *Chem. Mater.* **1998**, *10*, 2585−2587.

(7) Gondrand, M.; Joubert, J.-C. *Rev. Chem. Miner.* **1987**, *24*, 33−41.

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

(9) Park, B. H.; Kang, B. S.; Bu, S. D.; Noh, T. W.; Lee, J.; Jo, W. *Nature* **1999**, *401*, 682−684.

(10) Kodenkandath, T. A.; Lalena, J. N.; Zhou, W. L.; Carpenter, E. E.; Sangregorio, C.; Falster, A. U.; Simmons, W. B., Jr.; O'Connor, C. J.; Wiley, J. B. *J. Am. Chem. Soc.* **1999**, *121*, 10743−10746.

10.1021/ja9914644 CCC: $19.00

## Experimental Section

**Synthesis.** $K_2La_2Ti_3O_{10}$, $K_2SrTa_2O_7$, and $KLaNb_2O_7$ were prepared as reported in the literature.[5,6,11] $K_2La_2Ti_3O_{10}$ (10 mmol) was prepared by reacting stoichiometric quantities of $KNO_3$, $La_2O_3$ (predried at 900 °C), and $TiO_2$ at 1000 °C for 2 days with one intermediate grinding. Excess $KNO_3$ (25 mol %) was added to compensate for the loss due to volatilization. After the reaction, the product was washed with distilled water and dried in air at 200 °C. $KLaNb_2O_7$ was prepared similarly at 1100 °C and the washed product was dried at 110 °C in air. $K_2SrTa_2O_7$ was obtained from reaction of stoichiometric quantities of $KNO_3$, $SrCO_3$, and $Ta_2O_5$ with a 200% molar excess of $KNO_3$ at 1050 °C for 12 h and 1150 °C for 24 h in air with intermediate grindings. The washed product was dried in air at 450 °C. BiOCl was obtained by reacting $Bi_2O_3$ with hot 3 N HCl followed by hydrolysis with excess water.[12] $PbBiO_2Cl$ was prepared by reacting BiOCl and red PbO at 670 °C for 36 h in air.[13] Blue crystals of $VOSO_4 \cdot 3H_2O$ were obtained by passing $SO_2$ into a suspension of $V_2O_5$ in concentrated $H_2SO_4$ as described in the literature.[14]

Reaction between $K_2La_2Ti_3O_{10}/K_2SrTa_2O_7$ and BiOCl in the solid state was investigated by heating stoichiometric mixtures of the reactants at various temperatures and duration in air. Examination of the products by powder X-ray diffraction (XRD) revealed that the reaction occurred according to eq 1 around 800−900 °C forming A-type phases and KCl as products. With $K_2La_2Ti_3O_{10}$, the reaction was complete at 810 °C after 9 h, while with $K_2SrTa_2O_7$, the reaction required higher temperatures (900 °C for 6 h).

Reaction of $K_2La_2Ti_3O_{10}$ with $MCl_2$ (M = Pb, Ba, Sr) was found to occur at 600 °C for M = Pb (flowing nitrogen, 48 h) and 750 °C (air, 12 h) for M = Ba, Sr. The reaction between $K_2La_2Ti_3O_{10}$ and $VOSO_4 \cdot 3H_2O$ readily occurred in aqueous medium. A sample of 1 mmol of $K_2La_2Ti_3O_{10}$ and 1.5 mmol of $VOSO_4 \cdot 3H_2O$ in 100 mL of distilled water was refluxed. The reaction was found to be complete in 5 days as judged by EDS analysis and XRD of the product. The solid products in all cases were washed with distilled water and dried in air at 100 °C (at room temperature and 150 °C for $(VO)La_2Ti_3O_{10}$).

**Characterization.** Analyses of chemical composition were carried out by energy-dispersive X-ray spectroscopy (EDS) using a JEOL JSM 840-A scanning electron microscope equipped with an EDAX microanalytical system. Structural characterization was made by powder XRD using a Siemens D-5005 powder diffractometer (Cu Kα radiation). Unit cell parameters were least-squares refined by the PROSZKI[15] program. Powder XRD intensities were calculated in select cases using the LAZY PULVERIX[15] program. Electron diffraction (ED) patterns of $Bi_2La_2Ti_3O_{12}$ were recorded using a JEOL JEM 200-CX transmission electron microscope, and infrared spectra were recorded in KBr pellets using a Perkin-Elmer FTIR spectrometer, model 1000 D.

## Results and Discussion

The XRD pattern (Figure 1) of product **1** obtained from the reaction between $K_2La_2Ti_3O_{10}$ and BiOCl is closely similar to that of $Bi_4Ti_3O_{12}$[16] and is indexable on an orthorhombic cell with $a = 5.441(1)$ Å, $b = 5.399(1)$ Å, and $c = 32.944(4)$ Å. Similarly, the XRD pattern of product **2** obtained from the reaction between $K_2SrTa_2O_7$ and BiOCl could be indexed on an orthorhombic cell with $a = 5.531(1)$ Å, $b = 5.535(1)$ Å, and $c = 24.965(5)$ Å, the data being in close agreement with the values reported for $Bi_2SrTa_2O_9$ in the literature.[17] In both cases, the $c$ axis expands by ca. 3.2 Å in going from the R−P phase to the A phase, corresponding to the replacement of interlayer $K^+$ ions by $[Bi_2O_2]^{2+}$ units. EDS analyses of both products show the expected metal atom ratios and the absence of K. For product **1**, we have calculated powder XRD intensities assuming the structure of $Bi_4Ti_3O_{12}$ (space group $B2cb$),[18] where Bi(1) are replaced by La. A comparison of the calculated and observed XRD intensities (Table 1) reveals that the structure of product **1** is indeed similar to that of $Bi_4Ti_3O_{12}$, where Bi atoms in the perovskite sheets are replaced by La. Electron diffraction (ED) and lattice images provide further support to the formation of A phases; for product **1** (Figure 2), we see clearly a ca. 5.5 × 5.5 Å cell in the $a-b$ plane with a repeat of ca. 16.4 Å in the $c$ direction, which is consistent with the powder XRD data. Accordingly, we formulate reaction products **1** and

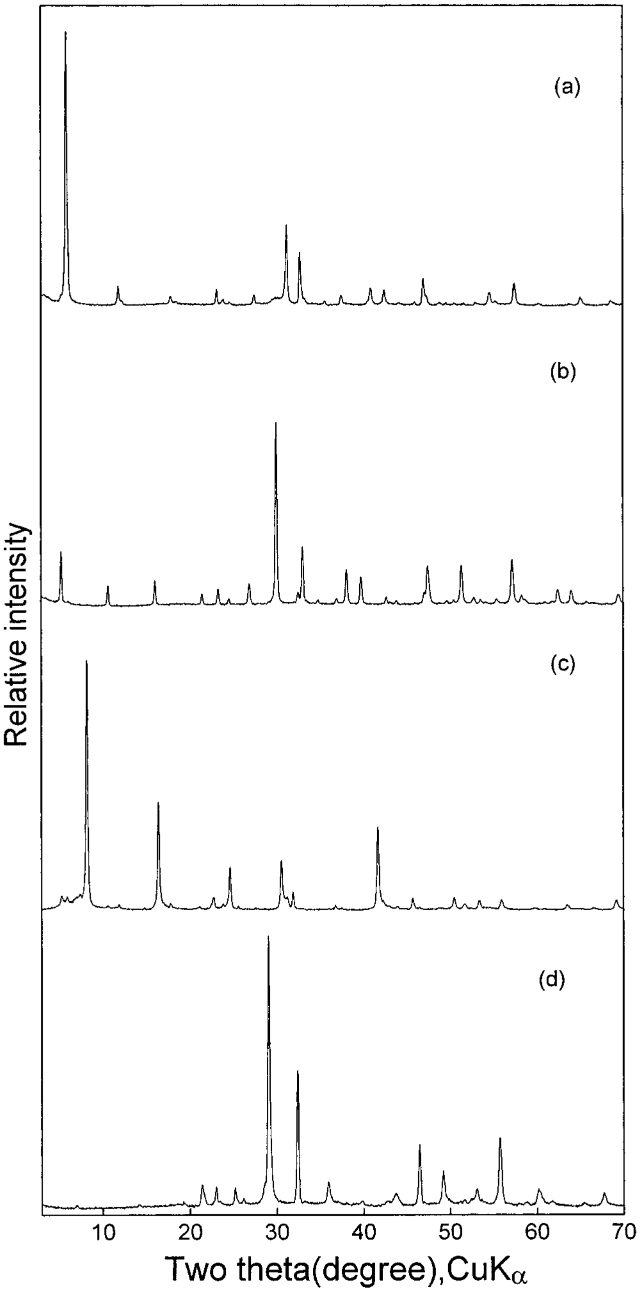

**Figure 1.** Powder XRD patterns of (a) $K_2La_2Ti_3O_{10}$, (b) $Bi_2La_2Ti_3O_{12}$ obtained from part a, (c) $K_2SrTa_2O_7$, and (d) $Bi_2SrTa_2O_9$ obtained from part c.

---

[11] Gopalakrishnan, J.; Bhat, V.; Raveau, B. *Mater. Res. Bull.* **1987**, *22*, 413−417.

[12] Brauer, G. *Handbook of Preparative Inorganic Chemistry*; Academic Press: New York, 1963; Vol. 1, pp 622−623.

[13] Ketteres, J.; Kramer, V. *Mater. Res. Bull.* **1985**, *20*, 1031−1036.

[14] Brauer, G. *Handbook of Preparative Inorganic Chemistry*; Academic Press: New York, 1965; Vol. 2, pp 1285−1286.

[15] Losocha, W.; Lewinski, K. *J. Appl. Crystallogr.* **1994**, *27*, 437−438.

[16] JCPDS File No. 35-0795.

[17] Rae, A. D.; Thompson, J. G.; Withers, R. L. *Acta Crystallogr.* **1992**, *B48*, 418−428.

[18] Dorrian, J. F.; Newnham, R. E.; Smith, D. K.; Kay, M. I. *Ferroelectrics* **1971**, *3*, 17−27.

**Table 1.** X-ray Powder Diffraction Data for $Bi_2La_2Ti_3O_{12}$ (**1**)

| $h$ | $k$ | $l$ | $d_{obs}$(Å) | $d_{cal}{}^{a}$ (Å) | $I_{obs}$ | $I_{cal}{}^{b}$ |
|---|---|---|---|---|---|---|
| 0 | 0 | 2 | 16.532 | 16.472 | 31 | 30 |
| 0 | 0 | 4 | 8.239 | 8.236 | 11 | 10 |
| 0 | 0 | 6 | 5.487 | 5.491 | 14 | 7 |
| 0 | 0 | 8 | 4.119 | 4.118 | 6 | 4 |
| 1 | 1 | 1 | 3.794 | 3.806 | 10 | 13 |
| 1 | 1 | 3 | 3.610 | 3.618 | 4 | 7 |
| 0 | 0 | 10 | 3.302 | 3.294 | 14 | 15 |
| 1 | 1 | 7 | 2.967 | 2.972 | 100 | 100 |
| 0 | 0 | 12 | 2.746 | 2.745 | 6 | 4 |
| 0 | 2 | 0 | 2.702 | 2.700 | 35 | 39 |
| 0 | 2 | 4 | 2.567 | 2.565 | 3 | 3 |
| 0 | 2 | 6 | 2.422 | 2.422 | 4 | 4 |
| 1 | 11 | 1 |  | 2.359 |  | 4 |
|  |  |  | 2.352 |  | 19 |  |
| 0 | 0 | 14 |  | 2.353 |  | 12 |
| 0 | 2 | 8 | 2.259 | 2.258 | 17 | 17 |
| 1 | 1 | 13 | 2.113 | 2.114 | 4 | 2 |
| 0 | 2 | 10 | 2.088 | 2.088 | 1 | 1 |
| 0 | 0 | 16 | 2.059 | 2.058 | 2 | 1 |
| 0 | 2 | 12 | 1.926 | 1.925 | 7 | 7 |
| 2 | 2 | 0 | 1.912 | 1.916 | 22 | 21 |
| 2 | 2 | 4 | 1.863 | 1.866 | 2 | 2 |
| 0 | 0 | 18 | 1.830 | 1.830 | 2 | 1 |
| 2 | 2 | 6 | 1.805 | 1.809 | 2 | 2 |
| 2 | 0 | 14 |  | 1.779 |  | 10 |
|  |  |  | 1.777 |  | 22 |  |
| 0 | 2 | 14 |  | 1.774 |  | 10 |
| 1 | 1 | 17 | 1.729 | 1.729 | 3 | 3 |
| 1 | 1 | 3 | 1.706 | 1.706 | 2 | 2 |
| 2 | 1 | 14 | 1.691 | 1.690 | 1 | 1 |
| 2 | 2 | 10 | 1.654 | 1.656 | 4 | 3 |
| 1 | 3 | 7 | 1.607 | 1.606 | 26 | 34 |
| 1 | 1 | 19 | 1.579 | 1.580 | 5 | 5 |
| 2 | 2 | 12 | 1.570 | 1.571 | 3 | 3 |
| 0 | 2 | 18 | 1.515 | 1.515 | 1 | 1 |
| 0 | 0 | 22 | 1.496 | 1.497 | 1 | 1 |
| 2 | 2 | 14 | 1.484 | 1.485 | 9 | 11 |
| 1 | 1 | 21 | 1.453 | 1.452 | 8 | 9 |
| 1 | 3 | 13 | 1.417 | 1.417 | 2 | 1 |
| 2 | 2 | 16 | 1.402 | 1.402 | 1 | 1 |
| 0 | 4 | 0 | 1.350 | 1.350 | 6 | 7 |

[a] $a = 5.441(1)$ Å, $b = 5.399(1)$ Å, $c = 32.944(4)$ Å. [b] Intensities are calculated by LAZY PULVERIX using the atomic coordinates of $Bi_4Ti_3O_{12}$ where Bi(1) is replaced by La (ref 18).

**2** as $Bi_2La_2Ti_3O_{12}$ and $Bi_2SrTa_2O_9$, respectively, having been formed in the metathetical reactions 2 and 3.

$$K_2La_2Ti_3O_{10} + 2BiOCl \rightarrow (Bi_2O_2)La_2Ti_3O_{10} + 2KCl \quad (2)$$

$$K_2SrTa_2O_7 + 2BiOCl \rightarrow (Bi_2O_2)SrTa_2O_7 + 2KCl \quad (3)$$

In Figure 3, we show schematically the transformation of $K_2La_2Ti_3O_{10}$ to $Bi_2La_2Ti_3O_{12}$. In a similar reaction between $KLaNb_2O_7$ and $PbBiO_2Cl$ at 810 °C for 9 h, we could prepare another layered perovskite of the formula $(PbBiO_2)LaNb_2O_7$ indicating that $(PbBiO_2)^+$ could replace the $K^+$ in $KLaNb_2O_7$ in between the perovskite sheets.

We investigated the applicability of the metathesis route for the synthesis of other layered perovskites. Thus we could synthesize $MLa_2Ti_3O_{10}$ Dion−Jacobson (D−J) phases[19] for M = Pb, Ba, Sr in a reaction between $K_2La_2Ti_3O_{10}$ and $MCl_2$. Similar transformations of R−P phases to D−J phases with other rare-earth and M cations have been reported in the literature.[7,8] Powder XRD patterns of $MLa_2Ti_3O_{10}$ could be indexed on orthorhombic (M = Ba) or monoclinic (M = Pb, Sr) systems. The lattice parameters are listed in Table 2. The orthorhombic lattice parameters of the M = Ba phase are in agreement with the values reported in the literature[20] for $BaLa_2Ti_3O_{10}$. The monoclinic M = Pb, Sr phases have not been reported to our knowledge. In view of the close similarity of the powder XRD patterns and lattice parameters of $MLa_2Ti_3O_{10}$ (M = Pb, Sr) to those of $BaNd_2Ti_3O_{10}$,[21] we believe that the $MLa_2Ti_3O_{10}$ members are isotypic with $BaNd_2Ti_3O_{10}$ consisting of triple perovskite sheets interleaved by large $M^{2+}$ ions.

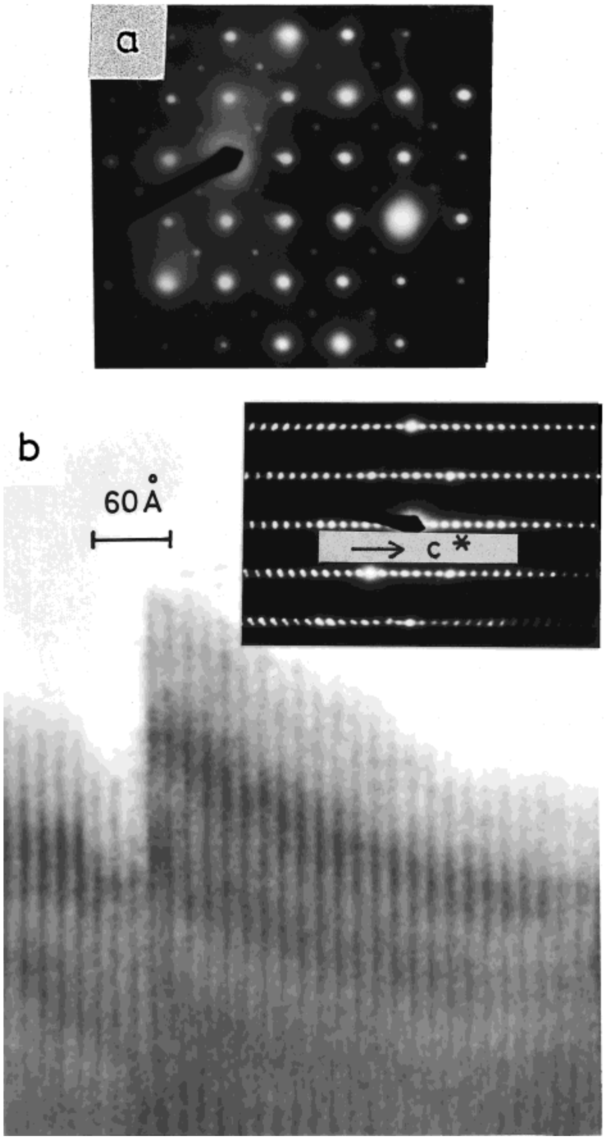

**Figure 2.** (a) Electron diffraction (ED) pattern of $Bi_2La_2Ti_3O_{12}$ showing an ca. 5.5 × 5.5 Å cell in the $a-b$ plane. (b) Lattice image of $Bi_2La_2Ti_3O_{12}$ showing an ca. 16.4 Å repeat along the $c$ direction. The inset shows the corresponding ED pattern.

We have prepared a novel layered perovskite $(VO)La_2Ti_3O_{10}$ in the following reaction.

$$K_2La_2Ti_3O_{10} + VOSO_4{\cdot}3H_2O \rightarrow (VO)La_2Ti_3O_{10} + K_2SO_4 + 3H_2O \quad (4)$$

Interestingly, the reaction occurs in aqueous medium under reflux (∼100 °C). As-prepared material (dried in air at room

---

[19] (a) Dion, M.; Ganne, M.; Tournoux, M. *Mater. Res. Bull.* **1981**, *16*, 1429−1435. (b) Dion, M.; Ganne, M.; Tournoux, M.; Ravez, J. *Rev. Chim. Miner.* **1984**, *21*, 92−103. (c) Jacobson, A. J.; Johnson, J. W.; Lewandowski, J. T. *Inorg. Chem.* **1985**, *24*, 3727−3729.

[20] Guha, J. P. *J. Am. Ceram. Soc.* **1991**, *74*, 878−880; JCPDS file No. 42-0418.

[21] Olsen, A.; Roth, R. S. *J. Solid State Chem.* **1985**, *60*, 347−357.

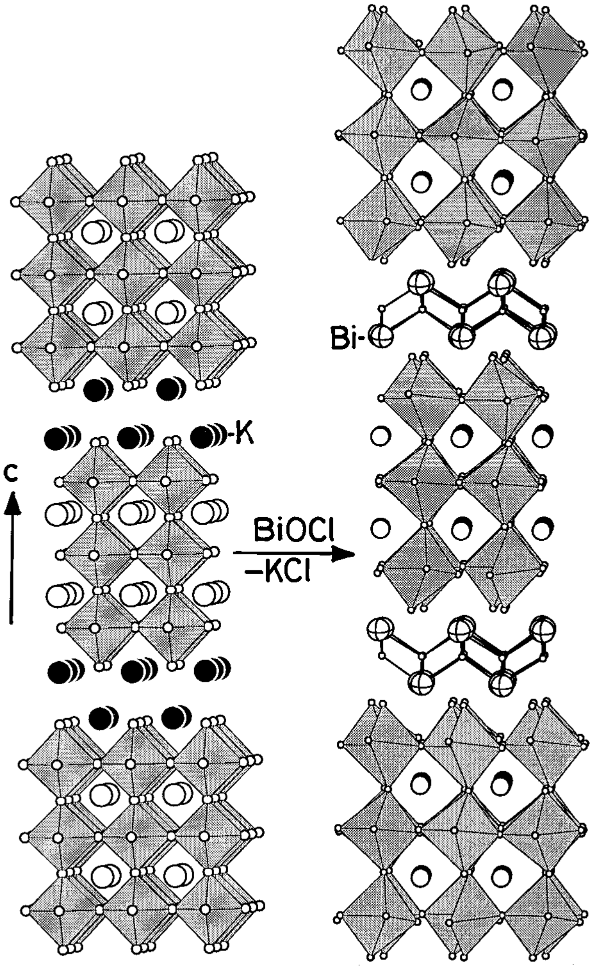

**Figure 3.** Schematic representation of the metathetical reaction between $K_2La_2Ti_3O_{10}$ (left) and BiOCl yielding $Bi_2La_2Ti_3O_{12}$ (right) showing replacement of interlayer $K^+$ by $(Bi_2O_2)^{2+}$ sheets.

**Table 2.** Lattice Parameters of Layered Perovskites

| compd | crystal system | unit cell parameters (Å) |
|---|---|---|
| $(Bi_2O_2)La_2Ti_3O_{10}$ | orthorhombic | $a = 5.441(1)$<br>$b = 5.399(1)$<br>$c = 32.944(4)$ |
| $(Bi_2O_2)SrTa_2O_7$ | orthorhombic | $a = 5.531(1)$<br>$b = 5.535(1)$<br>$c = 24.965(5)$ |
| $(PbBiO_2)LaNb_2O_7$ | tetragonal | $a = 3.896(1)$<br>$b = 25.54(1)$ |
| $PbLa_2Ti_3O_{10}$ | monoclinic | $a = 7.683(7)$<br>$b = 7.651(3)$<br>$c = 14.48(1)$<br>$\beta = 97.8(1)°$ |
| $BaLa_2Ti_3O_{10}$ | orthorhombic | $a = 7.669(1)$<br>$b = 28.616(3)$<br>$\mathrm{c} = 3.869(1)$ |
| $SrLa_2Ti_3O_{10}$ | monoclinic | $a = 7.841(2)$<br>$b = 7.641(2)$<br>$c = 14.171(9)$<br>$\beta = 100.8(1)°$ |
| $(VO)La_2Ti_3O_{10}$ | tetragonal | $a = 3.809(2)$<br>$c = 27.65(1)$ |

temperature) is monohydrate (as revealed by thermogravimetry). The water of hydration is lost around 150 °C giving a green crystalline product whose powder XRD pattern (Figure 4) could be indexed on a tetragonal cell with $a = 3.809(2)$ Å and $c = 27.65(1)$ Å. As compared to the anhydrous $(VO)La_2Ti_3O_{10}$, the hydrated material is rather poorly crystalline showing broad, mainly 00*l* reflections in the XRD pattern, which could also be indexed on a tetragonal cell of approximate lattice parameters $a = 3.82$ Å and $c = 29.46$ Å. As compared to the lattice parameters of the parent $K_2La_2Ti_3O_{10}$ [$a = 3.8769(1)$ Å and $c = 29.824(1)$ Å], there is a considerable decrease (~2.15 Å) in the *c* parameter of anhydrous $(VO)La_2Ti_3O_{10}$, which is consistent with the replacement of the two larger $K^+$ ions (ionic radius 1.55 Å in 9-coordination) by the smaller $(V{=}O)^{2+}$ cation (bond distance ~1.63 Å)[22] in the interlayer space. The presence of a strong infrared absorption around 1010 $cm^{-1}$ which is characteristic of the $(V{=}O)^{2+}$ stretch[23] both in the hydrated and anhydrous materials and the near absence of K in the EDS together with the V:La:Ti atomic ratio of 0.98:2:3 (expected ratio for stoichiometric $(VO)La_2Ti_3O_{10}$ is 1:2:3) clearly reveals that the metathesis reaction proceeds according to eq 4, yielding a new layered perovskite $(VO)La_2Ti_3O_{10}$.

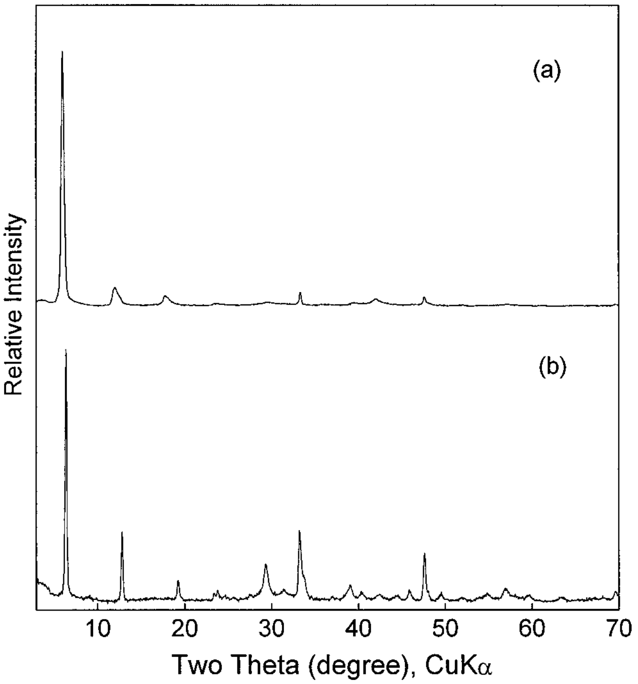

**Figure 4.** Powder XRD patterns of (a) $(VO)La_2Ti_3O_{10}{\cdot}H_2O$ and (b) $(VO)La_2Ti_3O_{10}$.

While the metathesis reactions with BiOCl, $PbBiO_2Cl$, and $MCl_2$ which occur at considerably high temperatures (600−900 °C) are not likely topotactic, the facile occurrence of reaction 4 in aqueous medium around ~100 °C suggests that it is most likely topotactic, where the integrity of the perovskite sheets is preserved during the chemical transformation. Further work is essential to establish the actual structure of $(VO)La_2Ti_3O_{10}$ and the topotactic nature of reaction 4.

## Conclusion

While metathesis reactions involving exchange of atomic/ionic species between the reactants are well-known in solid-state chemistry,[24] for example $MoCl_5 + {}^5/_2Na_2S \rightarrow MoS_2 + 5NaCl + {}^1/_2S$, the metathesis reported here is unique in that it involves replacement of interlayer alkali cations in R−P phases by structural entities such as $(Bi_2O_2)^{2+}$, $(PbBiO_2)^+$, and $(VO)^{2+}$. The formation of $(VO)La_2Ti_3O_{10}$ is particularly significant since

---

[22] Longo J. M.; Arnott, R. J. *J. Solid State Chem.* **1970**, *1*, 394−398.

[23] Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd ed.; Wiley-Interscience: New York, 1970; p 114.

[24] (a) Wiley, J. B.; Kaner, R. B. *Science* **1992**, *255*, 1093−1097. (b) Gillan, E. G.; Kaner, R. B. *Chem. Mater.* **1996**, *8*, 333−343.

it occurs at ∼100 °C in aqueous medium. We believe the significance of the present work goes beyond the transformation of R−P phases reported here; the strategy could in principle be extended to the synthesis/assembly of novel layered materials containing dimensionally compatible $[MX]^{n+}/[M_2X_2]^{n+}$ layered units, as indeed is shown by the recent synthesis of $(CuX)LaNb_2O_7$ by Kodenkandath et al.[10]

**Acknowledgment.** We thank the Department of Science and Technology, Government of India (Project No. SP/S1/H-17/97), for financial support. We also thank Professor K. Venkatesan for helpful discussions on the crystal structure of $Bi_4Ti_3O_{12}$.

**Supporting Information Available:** Powder XRD data for $(PbBiO_2)LaNb_2O_7$ and $MLa_2Ti_3O_{10}$ (M = Ba, Sr, Pb) (PDB). This material is available free of charge via the Internet at http://pubs.acs.org.

JA9914644