

BRIEF COMMUNICATION

A New Family of Protonated Oxides $HLnTiO_4$ ($Ln = La, Nd, Sm, \text{ and } Gd$)

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A new series of well crystallized $HLnTiO_4$ ($Ln = La, Nd, Sm, \text{ and } Gd$) and hydrated $HLaTiO_4 \cdot xH_2O$ were synthesized by Na^+/H^+ exchange of $NaLnTiO_4$ in 0.1 *N* HNO_3 solutions. This protonated oxide retains the parent layered structure (*P4/nmm*), the layers being separated by H^+ ions occupying nine-coordinated Na^+ sites and adjacent blocks having the staggered conformation. Due to the relative displacements of proton layers on hydration, on the contrary, a doubling of *c* axis was observed in hydrated type $HLaTiO_4 \cdot xH_2O$ ($x \sim 0.4$). Thermal behaviors examined by thermogravimetric analyses showed that the interlayer protons are lost below 600°C as water. Further heating above the dehydration temperature led to $LnTiO_{3.5}$ which still contained perovskite layers. They transformed into corresponding pyrochlores $Ln_2Ti_2O_7$ from around 950°C. © 1996

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A number of layered perovskite-type oxides such as the Aurivillius phases (1), the Ruddlesden–Popper phases (2), and the Dion–Jacobson phases (3, 4) are known. These materials contain two-dimensional perovskite slabs of composition $[A_{n-1}B_nO_{3n+1}]$ as one of the units building the layered structure. Many of these layered oxide phases have sufficiently high ionic conductivity to undergo ion exchange reactions in molten salts and aqueous acid solutions. The ion exchange reaction of alkali cations with protons in aqueous acids is of particular interest for the synthesis of new materials; fully exchanged protonic or hydronium forms of the layered oxides are convenient starting materials for the study of both aqueous ion exchange and dehydration reactions. These protonated species also form intercalation compounds with a range of organic bases (5). Moreover proton exchange reaction is used to synthesize metastable forms of metal oxyhydroxide presenting potential interest for proton conduction and electrochromic

properties. Many series of layered oxides have been extensively studied in this way.

If we compare the Ruddlesden–Popper phases with the Dion–Jacobson phases, the interlayer cation density of the latter is only 50% of that in the former. The latter series having a lower layer charge density undergo ion exchange reaction with higher reactivity (4, 6, 7). Recently, Rietveld refinement for $NaLnTiO_4$ ($Ln = La, Nd, Sm, \text{ and } Gd$) confirmed that the structure is based on perovskite-like layers, alternate sodium and lanthanide bilayers perpendicular to the *c* axis giving *P4/nmm* space group (8). This structure is similar in arrangement to *n* = 1 member of Ruddlesden–Popper series such as Sr_2TiO_4 but differ in that the $LnTiO_4$ layers possess only a single negative charge per formula unit. As a consequence of low layer charge density in $NaLnTiO_4$, it could be anticipated that the interlayer sodium cations can be readily exchanged in mild acidic medium to form protonated derivatives. Particularly, if protonated types are prepared, it was expected that some new metastable oxides could be obtained by dehydration of them. In this communication, we describe the formation of new protonated oxide $HLnTiO_4$ by typical topotactic ion exchange reaction in aqueous acid and propose possible metastable structure for its hydrated type from comparison of experimental and simulated X-ray diffraction patterns.

The starting material $NaLnTiO_4$ was prepared by previously described procedures (8). This sodium phase was converted to the hydrogen analog by ion exchange in aqueous acid. $NaLnTiO_4$ was stirred in 0.1 *N* HNO_3 for 24 h at room temperature. Treatment of $NaLnTiO_4$ with HNO_3 solution higher than 1 *N* resulted in collapse of the structure. The product was filtered, washed with distilled water, and dried at 120°C for 1 h. The analysis using ICP (inductively coupled plasma) showed that the residual sodium in the proton exchanged product is negligible within experimental error. The exchange was also found to be complete

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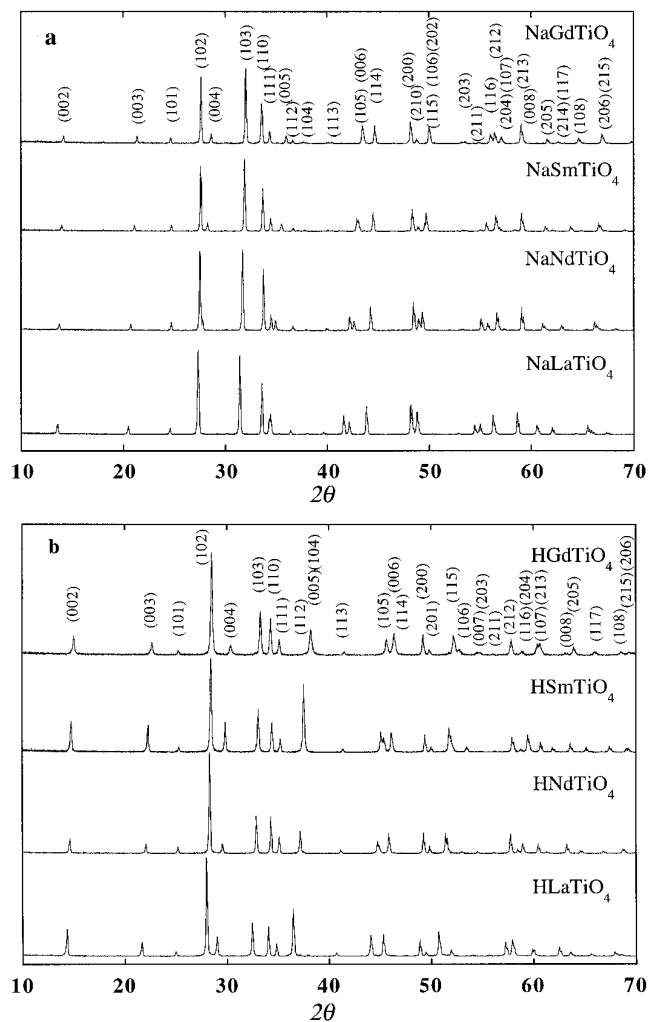


FIG. 1. X-ray powder diffraction patterns of (a) NaLnTiO_4 and (b) HLnTiO_4 ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{and Gd}$).

by measuring the amount of evolved H_2O upon heating the obtained products.

A comparison of the X-ray powder diffraction patterns for the parent and proton exchanged phases is shown in Fig. 1. X-ray diffraction data of HLnTiO_4 , closely related to those of NaLnTiO_4 , reveal that the protonated oxide retains the parent structure of NaLnTiO_4 except relative shift of diffraction angles as observed in similar layered perovskite oxides such as $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ (9) and $\text{K}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$ (7). The diffraction patterns for the protonated forms were therefore indexed by isostructural type ($P4/nmm$) with the sodium analogs. The lattice parameters refined by using least-square method are listed in Table 1. The presence of strong (00l) lines and comparable c parameters with those for the parent compounds would indicate that the sodium ions are exchanged by protons in a topochemical reaction. By analogy with the structures of

NaLnTiO_4 , therefore, that of HLnTiO_4 may be visualized as consisting of alternate HO and LnO double layers which are arranged with a sequence of $-(\text{HO})_2-\text{TiO}_2-(\text{LnO})_2-\text{TiO}_2-$ along the c axis. A schematic representation of the structure of HLnTiO_4 is illustrated in Fig. 2b.

The hydrated form of HLaTiO_4 was obtained when the sample was dried at room temperature after exchange rather than at 120°C . X-ray powder diffraction pattern of hydrated form is shown in Fig. 3 (top). This phase also crystallizes in tetragonal structure, the c parameter is however doubled by hydration ($a = 3.7535(1) \text{ \AA}$, $c = 28.1403(7) \text{ \AA}$). As proposed in Fig. 2c, such a c axis doubling indicates that perovskite slabs separated by a proton layer are displaced toward eclipsed conformation of each other on hydration. Such a displacement relative to the adjacent slab was observed for $\text{K}_2\text{Ln}_2\text{Ti}_3\text{O}_{10} \cdot \text{H}_2\text{O}$ (7) and $\text{NaEuTiO}_4 \cdot 0.5\text{H}_2\text{O}$ (10). A systematic absence of reflections with $h + k + l = \text{odd}$ would result from the formation of body-centered lattice. Thus, if we suppose that both La and Ti are located on the sites $4e$, and the oxygens occupy the $4e$, $4e$, and $8g$ sites of $I4/mmm$ space group, a simulated X-ray diffraction pattern is given as Fig. 3 (bottom) (11). This figure is quite similar to the experimental pattern.

The amounts of exchanged proton and intercalated water were estimated by heating ($2^\circ\text{C}/\text{min}$) the samples in air to 800°C . Thermal analysis experiments for HLnTiO_4 ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Gd}$) dried at 120°C showed only a small amount of water (less than $0.01 \text{ H}_2\text{O}$ per formula unit) continuously lost with increasing temperature to 200°C , which is associated with the surface of the samples. The weight loss from above 200°C up to 600°C corresponded to $0.5 \text{ H}_2\text{O}$ per formula unit. This result shows that the interlayer protons are lost as water according to the reaction $\text{HLnTiO}_4 \rightarrow \text{LnTiO}_{3.5} + 1/2 \text{ H}_2\text{O}$. Figure 4 shows the thermal behavior of $\text{HLaTiO}_4 \cdot x\text{H}_2\text{O}$ dried at room temperature. The interlayer water molecules are lost by two steps below 120°C . A phase (close to $\text{HLaTiO}_4 \cdot 0.1\text{H}_2\text{O}$) formed after the first step weight loss could not be identified probably because structural rearrangement

TABLE 1
Tetragonal Unit Cell Parameters of NaLnTiO_4 and HLnTiO_4
($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{and Gd}$)

| Compound | $a(\text{\AA})$ | $c(\text{\AA})$ |
|----------------------|-----------------|-----------------|
| NaLaTiO ₄ | 3.77343(4) | 13.0178(1) |
| HLaTiO ₄ | 3.7200(1) | 12.3012(2) |
| NaNdTiO ₄ | 3.75055(4) | 12.8242(1) |
| HNdTiO ₄ | 3.6971(1) | 12.0928(1) |
| NaSmTiO ₄ | 3.76127(4) | 12.6335(2) |
| HSmTiO ₄ | 3.6882(1) | 11.9863(2) |
| NaGdTiO ₄ | 3.77085(7) | 12.4644(2) |
| HGdTiO ₄ | 3.7000(1) | 11.7750(3) |

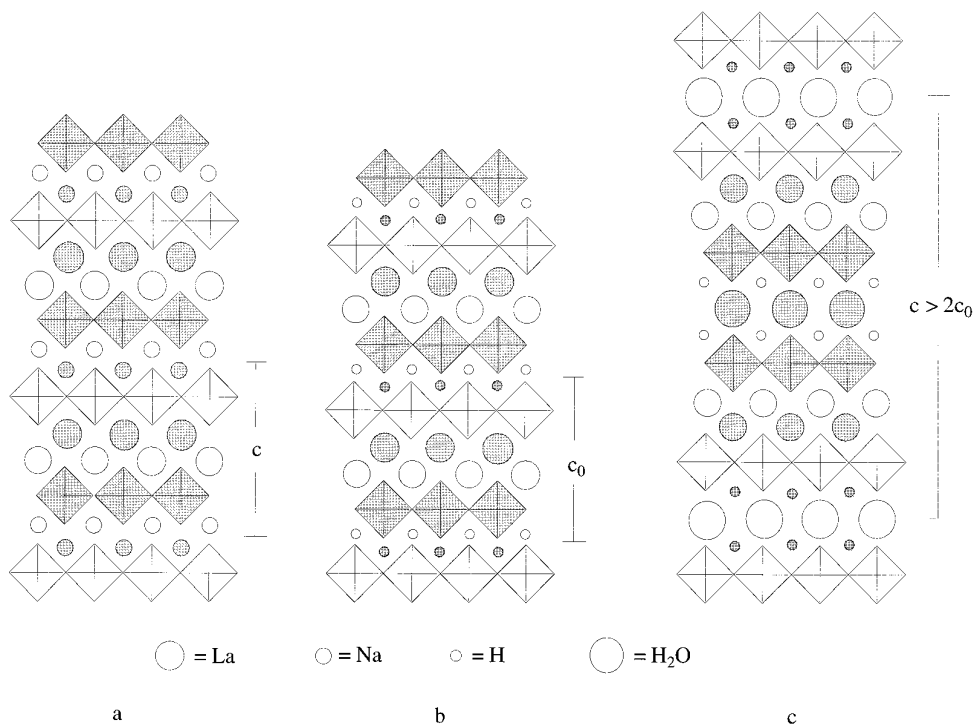


FIG. 2. Schematic representation of the structures of (a) NaLnTiO_4 , (b) HLnTiO_4 ($Ln = \text{La, Nd, Sm, and Gd}$), and (c) $\text{HLaTiO}_4 \cdot 0.4 \text{H}_2\text{O}$. Shaded circles are corresponding atoms at $b = 1/2$.

by the loss of water molecules was complicated. The weight loss of $0.5 \text{H}_2\text{O}$ per formula unit from 200°C and of $\sim 0.9 \text{H}_2\text{O}$ from room temperature, which is estimated from several measurements, indicates that an average composi-

tion of hydrated form is close to $\text{HLaTiO}_4 \cdot 0.4\text{H}_2\text{O}$. Heat treatment just above the dehydroxylation temperature led to the formation of disordered phases which still contain perovskite layer as evidenced by the presence of $hk0$ reflections. For several layered oxides, the proton exchanged forms dehydrate at temperatures above $300\text{--}350^\circ\text{C}$ to form metastable oxides in which some of the structural features of the starting oxide layers are preserved. One example for this behavior is a metastable form of $\text{TiO}_2(\text{B})$ obtained from the dehydration of layered $\text{H}_2\text{Ti}_4\text{O}_9$ (12). Another example is the formation of $\text{Nd}_{2/3}\text{TiO}_3$ with layered struc-

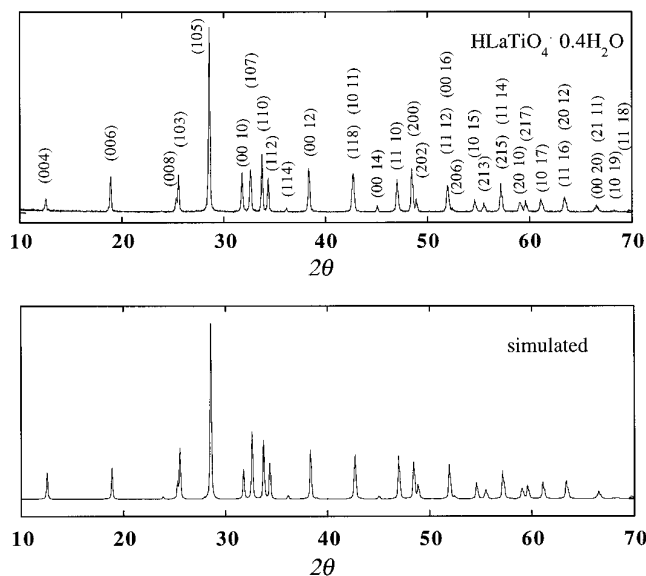


FIG. 3. Observed (top) and simulated (bottom) X-ray powder diffraction pattern of $\text{HLaTiO}_4 \cdot 0.4\text{H}_2\text{O}$.

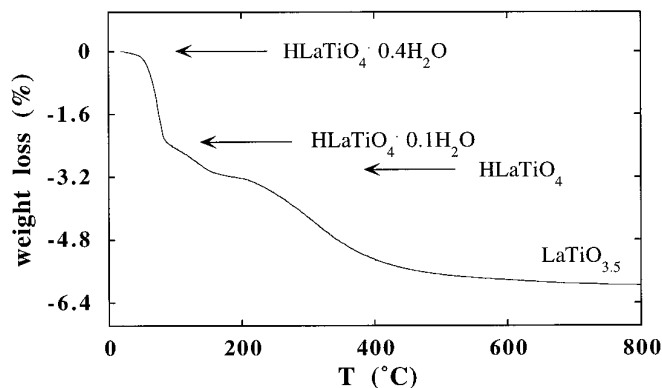


FIG. 4. Thermogravimetric analysis of $\text{HLaTiO}_4 \cdot 0.4\text{H}_2\text{O}$.

ture from $\text{H}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}$ (13). An investigation on the existence of a metastable form of layered $\text{LnTiO}_{3.5}$ (i.e., $\text{Ln}_2\text{Ti}_2\text{O}_7$) is in progress by using high temperature X-ray diffraction and Raman scattering techniques. In the temperature region 600–900°C, $\text{LnTiO}_{3.5}$ has a c parameter of ~ 12 Å, which may indicate that the layer-like features are retained. On heating above 950°C, however, they transformed to $\text{Ln}_2\text{Ti}_2\text{O}_7$ pyrochlore rather than to the perovskite.

In summary, we have synthesized a new series of protonated oxides HLnTiO_4 by Na^+/H^+ exchange from NaLnTiO_4 under mild conditions. Water intercalation into the proton layer of these oxides induced the c axis doubling by structural reorganization. These protonated oxides are expected to be used for the synthesis of metastable form with new layered structure.

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