

# $\text{Ln}_2\text{Ti}_2\text{O}_7$ (Ln = La, Nd, Sm, Gd): a novel series of defective Ruddlesden–Popper phases formed by topotactic dehydration of $\text{HLnTiO}_4$

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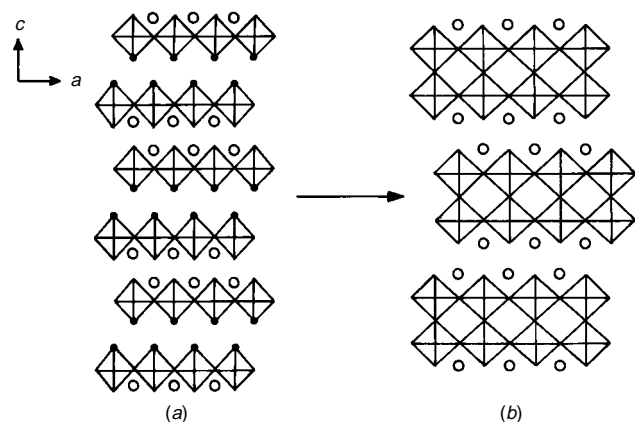
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Topotactic dehydration of  $\text{HLnTiO}_4$  (Ln = La, Nd, Sm or Gd) around 480–500 °C yields a new series of metastable layered perovskite oxides,  $\text{Ln}_2\text{Ti}_2\text{O}_7$ , that possess a defective  $\text{Sr}_3\text{Ti}_2\text{O}_7$  structure, where the cubooctahedral sites within the double-perovskite layers are most likely vacant.

Several layered oxides consisting of metal–oxygen ( $\text{MO}_6$ ) octahedra are regarded as derivatives of the three-dimensional perovskite ( $\text{CaTiO}_3 \equiv \text{ABO}_3$ ) structure.<sup>1</sup> Of these, the Ruddlesden–Popper (R–P) phases,  $\text{A}_2[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$ , originally discovered in the Sr–Ti–O system,<sup>2</sup> are the most widely known, because members/derivatives of this family exhibit several important physical properties of current interest. Thus,  $\text{La}_2\text{CuO}_4$ , an  $n = 1$  member of this family, is the parent material for the Bednorz–Müller discovery<sup>3</sup> of superconducting layered cuprates,  $\text{Sr}_{2-x}\text{Ln}_{1+x}\text{Mn}_2\text{O}_7$  (Ln = La or rare earth),  $n = 2$  members of this series, exhibit ferromagnetic and magnetoresistive properties<sup>4</sup> and  $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ , an  $n = 3$  member,<sup>5</sup> exhibits ion-exchange and hydration behaviour appropriate for photocatalytic decomposition of water.<sup>6</sup>

Oxides of the formula  $\text{NaLnTiO}_4$  (Ln = La, Nd, Sm, Gd), originally synthesized by Blasse,<sup>7</sup> are novel  $n = 1$  members of the R–P family exhibiting a unique ordering of Na and La atoms at the alternate interlayer sites between the single perovskite sheets in the sequence  $-\text{Ln}_2-\text{TiO}_{4/2}\text{O}_2-\text{Na}_2-\text{TiO}_{4/2}\text{O}_2-\text{Ln}_2-$  along the  $c$ -axis.<sup>8</sup> Clearly, the ordering seems to be dictated by the off-centre distortion of  $3d^0$ :  $\text{TiO}_6$  octahedra<sup>9</sup> giving rise to short and long axial Ti–O bonds, the oxygen to the short Ti–O bonds pointing towards the Na layer. Recently, protonated derivatives,  $\text{HLnTiO}_4$ , have been prepared<sup>10</sup> from  $\text{NaLnTiO}_4$  by  $\text{Na}^+/\text{H}^+$  exchange in dilute  $\text{HNO}_3$ .

Considering the topotactic nature of this ion-exchange which preserves the structural features of the parent  $\text{NaLnTiO}_4$ ,  $\text{HLnTiO}_4$  would consist of the layer sequence  $-\text{Ln}_2-\text{OTiO}_{4/2}(\text{OH})-(\text{OH})\text{TiO}_{4/2}\text{O}-\text{Ln}_2-$  along the  $c$ -direction (Fig. 1). Accordingly, we visualized that a topotactic dehydration

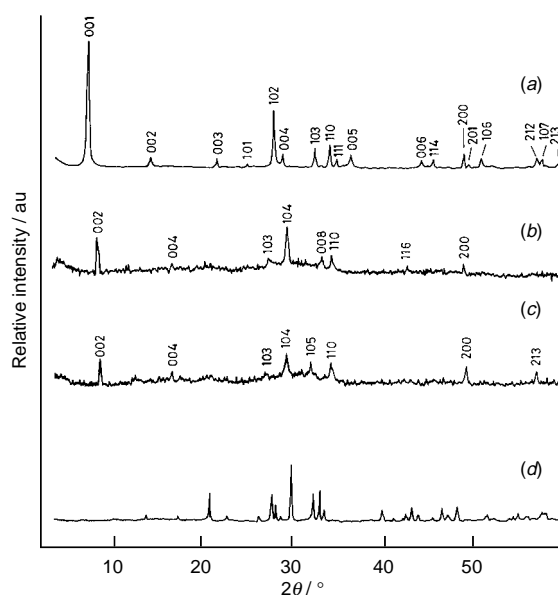
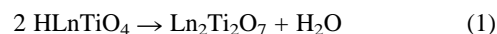


**Fig. 1** Schematic representation of dehydration of (a)  $\text{HLnTiO}_4$  to give (b) layered  $\text{Ln}_2\text{Ti}_2\text{O}_7$ . The open circles represent Ln atoms and the closed dots in (a) denote OH.

would result in a condensation of the adjacent single-perovskite  $\text{TiO}_{4/2}\text{O}(\text{OH})$  sheets to give double-perovskite  $\text{Ti}_2\text{O}_{10/2}\text{O}_2$  ( $\equiv \text{Ti}_2\text{O}_7$ ) sheets on elimination of a water molecule (Fig. 1). The dehydration product,  $\text{Ln}_2\text{Ti}_2\text{O}_7$ , would be a novel  $n = 2$  member of the R–P series similar to  $\text{Sr}_3\text{Ti}_2\text{O}_7$ ,<sup>2</sup> where the interlayer cubooctahedral Sr-sites in the ( $\text{SrTi}_2\text{O}_7$ ) perovskite sheets would be vacant. Here we show that indeed dehydration of  $\text{HLnTiO}_4$  (Ln = La, Nd, Sm, Gd) proceeds by this mechanism yielding a new series of  $\text{Ln}_2\text{Ti}_2\text{O}_7$  that are related to  $\text{Sr}_3\text{Ti}_2\text{O}_7$ . It must be mentioned that these layered titanates are truly metastable phases stabilized by the topotactic nature of the dehydration reaction under the mild conditions; the stable titanates of this composition adopt either the  $\langle 110 \rangle$  terminated layered perovskite structure<sup>11</sup> for  $\text{La}_2\text{Ti}_2\text{O}_7$  and  $\text{Nd}_2\text{Ti}_2\text{O}_7$  or the pyrochlore structure<sup>12</sup> for the other titanates.

$\text{NaLnTiO}_4$  (Ln = La, Nd, Sm, Gd) were prepared as reported in the literature<sup>8</sup> by reacting  $\text{Na}_2\text{CO}_3$ ,  $\text{Ln}_2\text{O}_3$  and  $\text{TiO}_2$  at 900 °C for 2 days with intermittent grinding.  $\text{HLnTiO}_4$  were prepared by ion-exchange in 0.1 M  $\text{HNO}_3$  as reported in the literature,<sup>10</sup> followed by drying in the air at ambient condition. Powder X-ray diffraction (XRD) patterns (JEOL JDX-8P X-ray powder diffractometer using  $\text{Cu-K}\alpha$  radiation) (Fig. 2) and the unit cell parameters (Table 1) obtained by least-squares refinement of the powder XRD data indicated the formation of  $\text{HLnTiO}_4$ .

We investigated the dehydration of  $\text{HLnTiO}_4$  by thermogravimetry (TG) in air (Cahn TG-131 system, heating rate 1 °C  $\text{min}^{-1}$ ). All the samples showed a single-step mass loss in the region 250–500 °C corresponding to the dehydration reaction



**Fig. 2** Powder XRD patterns ( $\text{Cu-K}\alpha$ ) of (a)  $\text{HLaTiO}_4$ , (b)  $\text{La}_2\text{Ti}_2\text{O}_7$ , (c)  $\text{Nd}_2\text{Ti}_2\text{O}_7$  and (d) sample (b) heated at 900 °C; stable  $\text{La}_2\text{Ti}_2\text{O}_7$

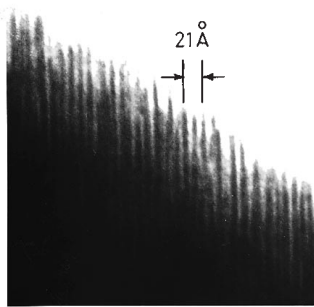
**Table 1** Synthesis conditions and lattice parameters of the parent (HLnTiO<sub>4</sub>) and product (Ln<sub>2</sub>□Ti<sub>2</sub>O<sub>7</sub>) oxides

Parent	Lattice parameters/Å		Synthesis conditions	Product	Lattice parameters/Å	
	<i>a</i>	<i>c</i>			<i>a</i>	<i>c</i>
HLaTiO <sub>4</sub>	3.722(2)	12.303(6)	500 °C; 15 min	La <sub>2</sub> □Ti <sub>2</sub> O <sub>7</sub>	3.725(3)	21.68(5)
HNdTiO <sub>4</sub>	3.694(2)	12.099(6)	500 °C; 15 min	Nd <sub>2</sub> □Ti <sub>2</sub> O <sub>7</sub>	3.705(6)	21.15(8)
HSmTiO <sub>4</sub>	3.689(1)	11.995(5)	500 °C; 12 min	Sm <sub>2</sub> □Ti <sub>2</sub> O <sub>7</sub>	3.679(2)	21.14(6)
HGdTlO <sub>4</sub>	3.698(3)	11.769(9)	480 °C; 15 min	Gd <sub>2</sub> □Ti <sub>2</sub> O <sub>7</sub>	3.679(3)	20.81(6)

The mass% losses observed in this temperature range are in agreement with the expected mass losses within ±0.1% error.

In an attempt to characterize the dehydration products, we recorded the powder XRD patterns of the TG residues. The patterns however did not show the characteristic features expected for the formation of a layered Ln<sub>2</sub>□Ti<sub>2</sub>O<sub>7</sub>; instead the patterns showed broad features corresponding to the stable Ln<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> phases. Heating HLnTiO<sub>4</sub> separately in air around 750 °C and above clearly showed the formation of stable Ln<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (Fig. 2). We therefore believed that formation of layered Ln<sub>2</sub>□Ti<sub>2</sub>O<sub>7</sub> would perhaps occur at lower temperatures, immediately after the dehydration. Accordingly, we investigated the dehydration of HLnTiO<sub>4</sub> around 450–500 °C for various durations, monitoring the samples by both mass loss and powder XRD. We found that samples (*ca.* 1 g) heated at 480–500 °C for about 15 min in air showed XRD patterns (Fig. 2) characteristic of the desired layered structure. The reflections at *ca.* 10.8, 5.4, 2.6, 1.85 Å (for La<sub>2</sub>□Ti<sub>2</sub>O<sub>7</sub>) clearly indicated the formation of a phase similar to Sr<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub> with a tetragonal unit cell, *a* ≈ 3.725 and *c* ≈ 21.68 Å. The observation of a strong reflection at *ca.* 3.10 Å which could be indexed as (104) however indicated that the structure would not exactly be the same as Sr<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub> with *I4/mmm* space group. Moreover, many of the reflections in the pattern are broad, suggesting poor crystallinity/disorder of the samples. In Fig. 2, we show powder XRD patterns of two of the members (Ln = La, Nd) and in Table 1, we list the lattice parameters of the parent (HLnTiO<sub>4</sub>) and product (Ln<sub>2</sub>□Ti<sub>2</sub>O<sub>7</sub>) phases together with synthesis conditions.

In order to characterize the layered Ln<sub>2</sub>□Ti<sub>2</sub>O<sub>7</sub> further, we recorded the electron diffraction (ED) patterns (JEOL JEM 200-CX transmission electron microscope). All the samples are quite crystalline showing typical perovskite like  $\sqrt{2}a_c \times \sqrt{2}a_c$  patterns in the [001] direction. When the beam direction is along [010], we see clear evidence for a *ca.* 21 Å repeat in the *c*\* direction which is consistent with the *c* axis of the tetragonal cell found from XRD patterns (Table 1). We also see lattice fringes with a *ca.* 10 Å repeat (which would correspond to 0.5 *c*) in the lattice image (Fig. 3) recorded with the same [010]



**Fig. 3** Lattice image of La<sub>2</sub>□Ti<sub>2</sub>O<sub>7</sub> corresponding to the electron diffraction pattern recorded with the [010] beam direction, revealing the presence of *ca.* 10 Å fringes in the *c*-direction.

beam orientation. The ED patterns however show streaking both in the *a*\**b*\*-plane as well as along the *c*\*-direction, which indicate considerable disorder. Disorder in the *c*\* periodicity is also seen in the lattice images. The disorder could arise from a turbostratic stacking of the double-perovskite Ti<sub>2</sub>O<sub>7</sub> sheets in the dehydrated samples. Despite the disorder, the presence of a tetragonal or pseudotetragonal cell with  $\sqrt{2}(\approx 3.7) \times \sqrt{2}(\approx 3.7) \times \approx 21$  Å dimension is clear from the ED patterns for all the Ln<sub>2</sub>□Ti<sub>2</sub>O<sub>7</sub> members studied, showing that gentle dehydration of HLnTiO<sub>4</sub> indeed yields a layered Ln<sub>2</sub>□Ti<sub>2</sub>O<sub>7</sub> that is related to Sr<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub>.

We believe that the present work has shown for the first time the possibility of transforming *n* = 1 R–P members to *n* = 2 members (albeit defective) of the same series by a topotactic dehydration reaction. The key to the success of this *n* = 1 to *n* = 2 transformation lies in the 1 : 1 ordering of the Na and Ln atoms in the precursor NaLnTiO<sub>4</sub> oxides, which in turn is dictated by the distortion of d<sup>0</sup>: TiO<sub>6</sub> octahedra giving short and long axial Ti–O bonds.<sup>9</sup> We envisage that the method could be generalized and extended to the synthesis of metastable 2*n* R–P phases from appropriately tailored *n* R–P phases.

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## Notes and References

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