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# **Thermochemistry of a new class of materials containing dinitrogen pairs in an oxide matrix.**

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## **ABSTRACT**

A series of N<sub>2</sub>-containing perovskite phases was prepared in the La–(Ba)–Ti–O system in order to study the dinitrogen retention phenomenon from a thermochemical viewpoint. High temperature oxide melt solution calorimetry was undertaken to determine the energetics of the corresponding starting oxynitrides, intermediate phases and oxides. Calorimetric results show that nitrogen is weakly bound within the oxide matrix and most of the enthalpy of oxidation of the intermediate phase is devoted to its structure change between the starting perovskite structure and the formation of a layered-perovskite La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> oxide.

## Introduction

Nitrides and oxynitrides represent a group of modern ceramic materials of increasing technological importance, with applications as hard materials, protective coatings, electronic and optical materials, refractories, and structural ceramics.

An important aspect of the use of nitride or oxynitride materials is their thermal oxidation behavior. Several investigations of nitride-type compounds have been made with the purpose of clarifying the oxidation mechanism during the transformation into oxide.<sup>1-3</sup> When heated in an oxygen atmosphere, a nitride or an oxynitride is systematically transformed at relatively high temperature into an oxide, or mixture of oxides, with nitrogen release as molecular dinitrogen. However, an intriguing family of oxynitrides shows a different behavior under similar conditions. As an example, different TGA profiles, under flowing oxygen, of the  $RTiO_2N$  perovskite series with  $R = La, Ce, Pr, Nd$  are given in Figure 1. An unexpected intermediate state, shown in Figure 2, appears between the starting oxynitride and final oxide, with an associated weight change surprisingly higher than that corresponding to the transformation into oxide. This behavior represents a dinitrogen retention phenomenon and the corresponding "intermediate phases" have been isolated and characterized as a new class of dinitrogen-containing inorganic compounds. This behavior has been frequently observed and many intermediate phases have been isolated and structurally characterized as indicated in Table 1.<sup>1-10</sup> While a significant number of organic dinitrogen-containing compounds, including conventional synthetic organometallic complexes,<sup>11</sup> as well as biological substances,<sup>12</sup> are known, the formation of such dinitrogen in inorganic materials is extremely rare. Actually,  $M \cdots N \equiv N$  or  $M \cdots N \equiv N \cdots M$  units have been only found in the following cases: in pernitrides or diazenides as  $BaN_2$  or  $SrN_2$ ,<sup>13,14</sup> prepared from the elements under high  $N_2$  pressure, in products obtained by cocondensation of metallic atoms with  $N_2$  at low temperature,<sup>15-28</sup> in surface layers of titanium dioxide films during their bombardment by  $N_2^+$  ions,<sup>29</sup> as molecular dinitrogen adsorbed on metallic or oxide substrates at low temperature,<sup>30-41</sup> and in partially oxidized (oxy)nitride materials, called "intermediate phases", the subject of this paper.

Their decomposition, studied by mass spectroscopy, takes place with a loss of dinitrogen, only, so

that their general formula can be written  $M^{n+}O_{n/2}(N_2)_x$ . Such an intermediate phase composition implies nitrogen atoms at a near zero oxidation state. By comparison to structures from organic chemistry, in particular of dinitrogen organometallic complexes, and also from XPS and Raman analysis,<sup>2,3</sup> it has been concluded that nitrogen is present as N–N pairs interacting with one or several cationic elements.

The basic thermodynamic properties of (oxy)nitride compounds and the relations among energetics, structure and bonding are generally far less well known than for oxides. We have performed a calorimetric study to evaluate the energetics of the specific interaction between  $N_2$  entities and the host structure. Intermediate phases have been prepared starting from  $LaTiO_2N$  and  $La_{0.7}Ba_{0.3}Ti(O,N)_3$  oxynitrides. High temperature oxidative drop solution calorimetry in a molten oxide solvent has been shown to be a general and convenient method to determine the heat of formation of nitrides and oxynitrides. Studies have already been successfully performed on the energetics of binary and ternary transition metal nitrides,  $Si_3N_4$  and sialon systems, GaN and nitridophosphate PON and "LiNaPON" glasses.<sup>42–46</sup>

## **Experimental**

### **Precursors**

$La_2Ti_2O_7$  precursor was prepared by molten salt synthesis.<sup>47</sup>  $La_2O_3$  and  $TiO_2$  were mixed in the appropriate stoichiometric ratio, and a salt consisting of 50 mol.% NaCl / 50 mol.% KCl was then added, constituting 50 wt.% of the total reaction mixture. The corresponding mixture was heated at 1273 K for 15 h. The resulting product was washed using distilled water, then dried at 423 K, and clearly identified as  $La_2Ti_2O_7$  (layered perovskite structure) by X-ray diffraction.

In the case of substituted oxynitrides  $La_{1-x}Ba_xTi(O,N)_3$ , the oxide precursor corresponds to a single perovskite phase for  $x > 0.5$ , while a mixture  $La_{2-p}Ba_pTi_2O_{7-p/2} + Ba_{1-q}La_qTiO_{3+q/2}$  results for  $0.1 < x < 0.5$ . The study was carried out with a precursor corresponding to  $x = 0.3$ .

Nitridation reactions were carried out in alumina boats placed inside an electric furnace through which ammonia gas flowed at 40–50 L h<sup>-1</sup>. The temperature was raised to the 1223–1273 K range with a heating rate of 10 K min<sup>-1</sup>. After a reaction time of 15 h, the furnace was switched off and the nitrided

powders were allowed to cool to room temperature under a pure nitrogen atmosphere. Oxynitride perovskites  $\text{LaTiO}_2\text{N}$  and  $\text{La}_{0.7}\text{Ba}_{0.3}\text{TiO}_{2.3}\text{N}_{0.7}$  were prepared and oxidized at 873 K to form intermediate phases listed in Table 1.<sup>3</sup>

## **Characterizations**

### **X-ray diffraction.**

XRD powder patterns were recorded using a Philips PW3710 diffractometer operating with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). X'PERT softwares – Data Collector and Graphics and Identify – were used, respectively, for recording, analysis and phase matching of the patterns. The intermediate phase crystallizes, as previously observed,<sup>1–3</sup> in the same structure type as its oxynitride precursor with a diffraction profile typical of a poorly crystallized material.

### **Elemental analysis.**

Nitrogen and oxygen contents were determined with a LECO TC–436 analyzer using the inert gas fusion method. Nitrogen was detected as  $\text{N}_2$  by thermal conductivity and oxygen as  $\text{CO}_2$  by infrared detection. The apparatus was calibrated using  $\text{N}_2$  and  $\text{CO}_2$  gas (purity  $\geq 99.95 \%$ ) as well as  $\epsilon\text{-TaN}$  as a nitrogen standard.<sup>48</sup>

### **Thermogravimetric analysis (TGA)**

The oxidation behavior of the different oxynitride phases was investigated with a thermobalance Setaram TGDTA 92 in the 298–1673 K temperature range. The samples were tested in static air ( $P = 1 \text{ atm}$ ) with constant heating rates always lower than  $1 \text{ K min}^{-1}$ . The phases present after oxidation were identified by powder X-ray diffraction. Thermograms are similar to those previously obtained with other systems (Figures 1 and 2).<sup>1–10</sup>

## **X-ray photoelectron (XPS) and Raman spectroscopies.**

XPS measurements were performed on a SSI model 206 spectrometer (Surface Science Instrument) equipped with a monochromatic Al  $K_{\alpha}$  X-ray source (1486.6 eV). More experimental details are given elsewhere.<sup>2,3,49</sup> XPS analysis show a single peak N1s close to 402 eV characteristic of  $N_2$ .

Room temperature Raman spectra were obtained with a Spectra Physics argon ion laser (Model 2000) excitation. The experimental setup was described earlier<sup>2</sup> and Raman spectroscopy confirms the previous XPS results: a single peak close to  $2328\text{ cm}^{-1}$  reveals that the retained nitrogen exists as  $N_2$  entities within a symmetric environment. The Raman peak position compares to that of  $2330\text{ cm}^{-1}$  in  $N_2$  gas,  $1380\text{ cm}^{-1}$  in SrN and  $1307\text{ cm}^{-1}$  in SrN<sub>2</sub> ( $(N_2)^{2-}$  pairs).<sup>50</sup>

## **Calorimetry**

High temperature oxidative drop solution calorimetry into a  $3Na_2O-4MoO_3$  molten solvent was performed in a Calvet type twin calorimeter described in detail by Navrotsky.<sup>51,52</sup> The solvent was prepared from  $Na_2MoO_4 \cdot 2H_2O$  and  $MoO_3$ , dehydrated and liquefied at 975 K, and quenched to room temperature by pouring into a graphite dish. The melt does not quench to a glass, so the entire batch was ground to a powder to homogenize it before it was loaded into the calorimetric crucibles. Oxygen gas was used only for bubbling through the solvent (at  $\sim 5\text{ cm}^3\text{ min}^{-1}$ ) to stir the melt and oxidize the oxynitride sample once it reached the solvent. When a stable baseline signal was achieved, a sample pellet was dropped from room temperature into liquid  $3Na_2O-4MoO_3$  at 975 K in the calorimeter. When  $N^{3-}$  is present, the calorimetry utilizes a redox reaction between  $MoO_3$  in the melt and  $N^{3-}$ , which supplies a rapid pathway for elimination of  $N^{3-}$  as  $N_2$  gas. The reaction includes the oxidation and the dissolution of the oxynitride, and represents the heat effect measured through oxidative drop solution calorimetry ( $\Delta H_{ds}$ ). Further details of the experimental procedure are provided in previous papers.<sup>53-55</sup>

## **Results and discussion**

Drop solution calorimetry has been performed on oxynitride perovskites  $\text{LaTiO}_2\text{N}$  and  $\text{La}_{0.7}\text{Ba}_{0.3}\text{TiO}_{2.20}\text{N}_{0.77}$ , as well as on intermediate phases  $\text{LaTiO}_{3.5}\text{N}_x$  ( $x = 0.54$  and  $0.64$ ) and  $\text{La}_{0.7}\text{Ba}_{0.3}\text{TiO}_{3.5}\text{N}_x$  ( $x = 0.57, 0.59$  and  $0.62$ ). Experimental enthalpies of drop solution are gathered in Table 2. Resulting enthalpies of formation and oxidation have been determined from these data (Table 2 and 3) and appropriate thermodynamic cycles detailed in Tables 4 to 10. The enthalpy of formation of  $\text{La}_2\text{Ti}_2\text{O}_7$  was determined from the cycle given in Table 6. The accuracy of the enthalpy of drop solution of  $\text{La}_2\text{O}_3$  ( $\Delta H_1$ ) was recently checked with a non hydrated sample and corrected to the value  $-225.10 \pm 3.16 \text{ kJ mol}^{-1}$ .<sup>56</sup> Using the experimental drop solution enthalpy value  $\Delta H_5 = 98.52 \pm 0.95 \text{ kJ mol}^{-1}$  determined by Helean *et al.*,<sup>57</sup> we establish the enthalpy of formation  $\Delta H^\circ_f$  ( $\text{La}_2\text{Ti}_2\text{O}_7$ ) to  $-3890.92 \pm 4.67 \text{ kJ mol}^{-1}$  and not  $-3855.5 \pm 3.5 \text{ kJ mol}^{-1}$  as initially reported by these authors.

Heats of drop solution of nitrogen-containing intermediate phases are endothermic and within  $20 \text{ kJ mol}^{-1}$  of those of the nitrogen-free products. Thus, no major oxidation phenomenon, with associated strong exothermic effect, is occurring. The enthalpies of formation of  $\text{LaTiO}_{3.5}\text{N}_x$  phases are close to each other and less exothermic than that of  $\text{LaTiO}_{3.5}$  oxide, as expected. The heat of drop solution of intermediate phases does not depend much on nitrogen content, though there is not much variation in nitrogen content. The small difference in enthalpy suggests that nitrogen is weakly bound to the oxide network.

We have devised cycles (Tables 4 and 5) representing the oxidation of the intermediate phases as an approach to determine the energetic contribution of  $\text{N}_2$  pairs within the oxide matrix. The intermediate phases  $\text{La}_{0.7}\text{Ba}_{0.3}\text{TiO}_{3.5}\text{N}_x$  are not well crystallized but represent perovskite derived structures. They decompose to crystalline  $\text{BaTiO}_3$  (perovskite) and  $\text{La}_2\text{Ti}_2\text{O}_7$  (layered perovskite). We suggest that the observed enthalpy associated with release of  $\text{N}_2$  gas contains two contributions, that from any oxidation or bonding change of the dinitrogen and, that arising from the transformation of the  $\text{LaTiO}_{3.5}$  component from the perovskite to the stable layered structure. However, only 0.7 mole of  $\text{LaTiO}_{3.5}$  is formed as compared to one mole for the non barium-substituted La–Ti system. Thus, for the La–Ba–Ti system, it

is necessary to divide the mixed system (La–Ba–Ti) by 0.7 to get the same number of moles of  $\text{LaTiO}_{3.5}$ . Then, interestingly, we obtain a very similar heat effect to the pure La–Ti system. The measured enthalpies of decomposition, between  $-19$  and  $-26$   $\text{kJ mol}^{-1}$ , are relatively constant, suggesting that the phase transition dominates the energetics. Thus, most of the energetics is tied up with the structure change, from a perovskite to a layered-perovskite structure, and not with the  $\text{N}_2$  bonding. The release of nitrogen may have an effect on the  $5\text{--}10$   $\text{kJ mol}^{-1}$  level and the energetics of the phase transition may release  $20\text{--}25$   $\text{kJ mol}^{-1}$ .

It is also possible to determine the energetics of formation of the oxynitride perovskite  $\text{LaTiO}_2\text{N}$  from the cycle in Table 7. Heat contents  $H_{975}\text{--}H_{298}$  of  $\text{N}_2$  and  $\text{O}_2$  are respectively  $\Delta H_7 = 20.65$  and  $\Delta H_8 = 21.84$   $\text{kJ mol}^{-1}$ .<sup>58</sup> From the enthalpy of drop solution  $\Delta H_{\text{ds}} = -485.16 \pm 4.65$   $\text{kJ mol}^{-1}$ , we calculate the enthalpy of formation  $\Delta H^\circ_f (\text{LaTiO}_2\text{N}) = -1417.10 \pm 5.18$   $\text{kJ mol}^{-1}$ . A similar approach allows us to determine the enthalpy of the barium-containing oxynitride perovskite  $\text{La}_{0.7}\text{Ba}_{0.3}\text{TiO}_{2.20}\text{N}_{0.77}$ . From the thermochemical cycle given in Table 8 an enthalpy of formation  $\Delta H^\circ_f (\text{La}_{0.7}\text{Ba}_{0.3}\text{TiO}_{2.3}\text{N}_{0.7}) = -1506.43 \pm 2.03$   $\text{kJ mol}^{-1}$  is obtained. Compared to the enthalpy of formation of  $\text{LaTiO}_2\text{N}$ , this value is more exothermic. Barium has a stabilizing effect through the concept of the well known inductive effect in solid state chemistry,<sup>58</sup> but the trend is not totally explained because nitrogen contents are different and the differences in the standard enthalpies of  $\text{BaO}$  ( $-548.10$   $\text{kJ mol}^{-1}$ ) and  $\text{La}_2\text{O}_3$  ( $-1793.7$   $\text{kJ mol}^{-1}$ ) contribute as major factors.

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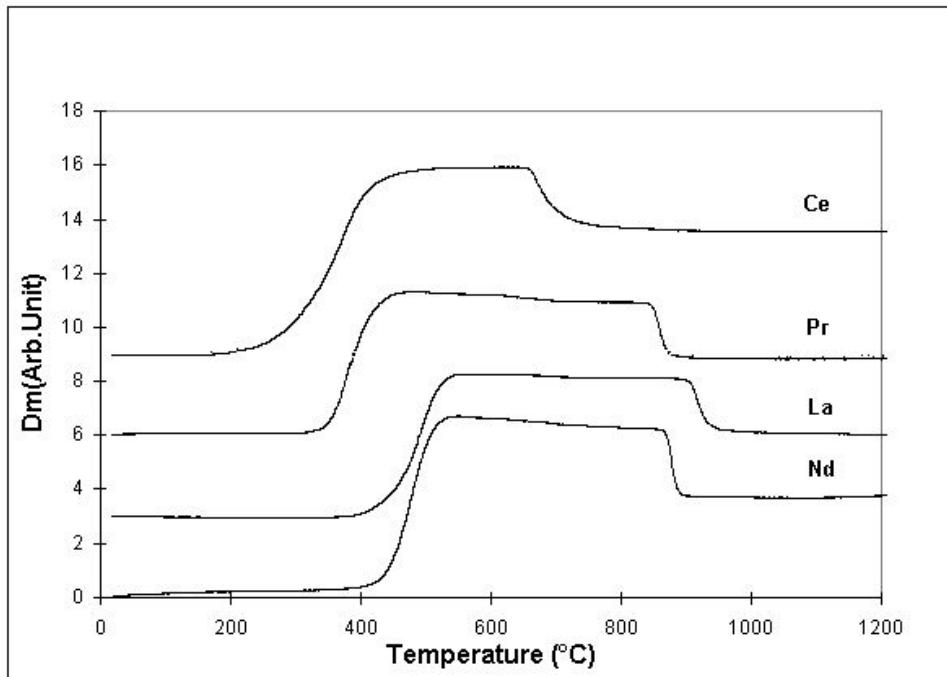


Figure 1. TGA under O<sub>2</sub> of RTiO<sub>2</sub>N phases (R = Ce, Pr, La and Nd) (1°C.min<sup>-1</sup>)

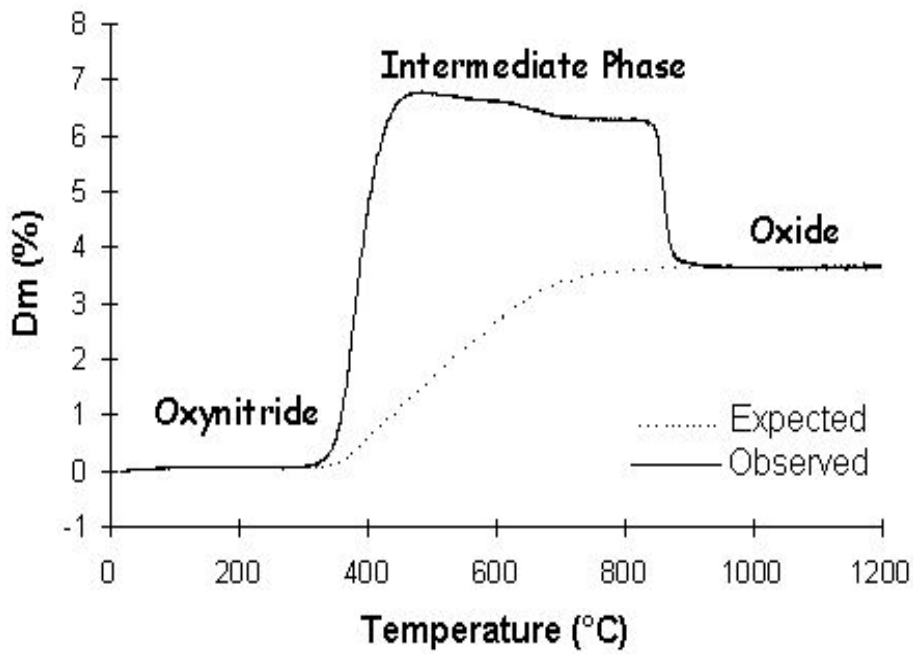


Figure 2. TGA analysis of an oxynitride manifesting the "intermediate phase" phenomenon.

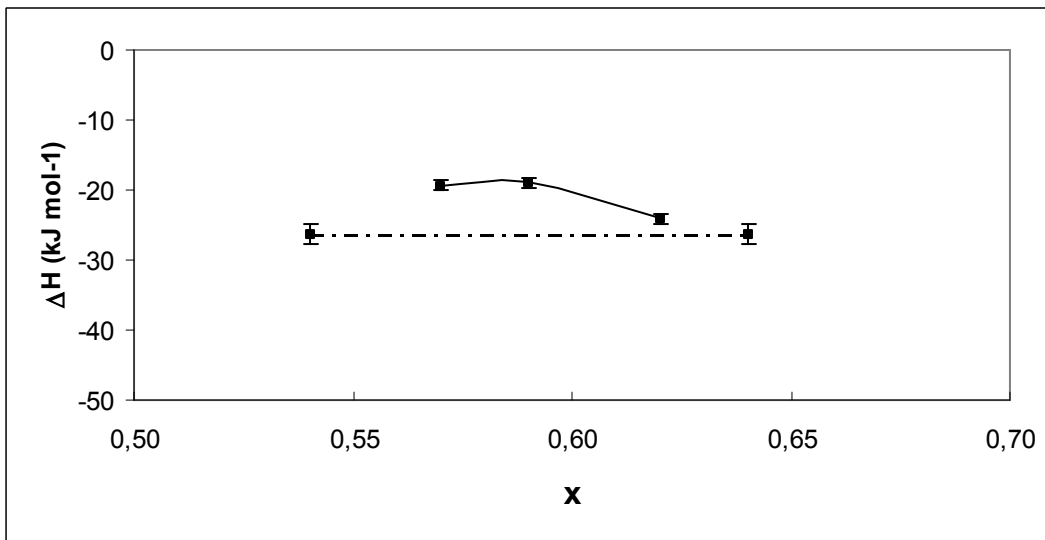


Figure 3. Enthalpies of oxidation (per mole of lanthanum) versus nitrogen content within  $\text{LaTiO}_{3.5}\text{N}_x$  (dashed line) and  $\text{La}_{0.7}\text{Ba}_{0.3}\text{TiO}_{3.35}\text{N}_x$  (solid curve) intermediate phases.

Table 1. Evidence of intermediate phases in several structure types

Oxynitride	Structural type	Intermediate phase formula <sup>1</sup>	Ref.
BaTaO <sub>2</sub> N	perovskite	BaTaO <sub>3.5</sub> (N <sub>2</sub> ) <sub>0.15</sub>	2
La <sub>0.91</sub> W <sub>0.91</sub> O <sub>1.18</sub> N <sub>1.63</sub>	perovskite	LaWO <sub>4.5</sub> (N <sub>2</sub> ) <sub>0.23</sub>	2
LaTiO <sub>2</sub> N	perovskite	LaTiO <sub>3.5</sub> (N <sub>2</sub> ) <sub>0.32</sub>	2
Al <sub>2.85</sub> O <sub>3.45</sub> N <sub>0.55</sub>	spinnelle	Al <sub>2</sub> O <sub>3</sub> (N <sub>2</sub> ) <sub>0.095</sub>	2, 9
Y <sub>2.67</sub> W <sub>1.33</sub> (O <sub>3.79</sub> N <sub>2.80</sub> ) <sub>1.41</sub>	fluorite	Y <sub>2</sub> WO <sub>6</sub> (N <sub>2</sub> ) <sub>0.20</sub>	2
Cr <sub>0.77</sub> O <sub>0.23</sub> N <sub>0.31</sub>	NaCl	Cr <sub>2</sub> O <sub>3</sub> (N <sub>2</sub> ) <sub>0.15</sub>	2
Ti <sub>0.67</sub> O <sub>0.33</sub> N <sub>0.58</sub>	NaCl	TiO <sub>2</sub> (N <sub>2</sub> ) <sub>0.06</sub>	2
Nb <sub>0.54</sub> O <sub>0.46</sub> N <sub>0.60</sub>	NaCl	Nb <sub>2</sub> O <sub>5</sub> (N <sub>2</sub> ) <sub>0.43</sub>	2
TaON	baddeleyite	TaO <sub>2</sub> (N <sub>2</sub> ) <sub>0.10</sub>	4
Zr <sub>2</sub> N <sub>2</sub> O	bixbyite	ZrO <sub>2</sub> (N <sub>2</sub> ) <sub>0.028</sub>	5
Y <sub>4</sub> Si <sub>2</sub> O <sub>7</sub> N <sub>2</sub>	cuspidine	Y <sub>4</sub> Si <sub>2</sub> O <sub>10</sub> (N <sub>2</sub> ) <sub>0.75</sub>	6
LaAl <sub>12</sub> O <sub>18</sub> N	magnetoplumbite	LnAl <sub>12</sub> O <sub>19.5</sub> (N <sub>2</sub> ) <sub>0.17</sub>	7
Y <sub>5</sub> (SiO <sub>4</sub> ) <sub>3</sub> N	Apatite	Y <sub>10</sub> Si <sub>7</sub> O <sub>29</sub> (N <sub>2</sub> ) <sub>0.335</sub>	8
Sr <sub>2</sub> NbO <sub>2.8</sub> N	K <sub>2</sub> NiF <sub>4</sub>	Sr <sub>2</sub> NbO <sub>4.5</sub> (N <sub>2</sub> ) <sub>0.20</sub>	10
La <sub>0.9</sub> Ba <sub>0.1</sub> TiO <sub>2.1</sub> N <sub>0.9</sub> La <sub>0.7</sub> Ba <sub>0.3</sub> TiO <sub>2.3</sub> N <sub>0.7</sub> La <sub>0.5</sub> Ba <sub>0.5</sub> TiO <sub>2.5</sub> N <sub>0.5</sub> CeTiO <sub>2</sub> N PrTiO <sub>2</sub> N NdTiO <sub>2</sub> N	perovskite	La <sub>0.9</sub> Ba <sub>0.1</sub> TiO <sub>3.45</sub> (N <sub>2</sub> ) <sub>0.31</sub> La <sub>0.7</sub> Ba <sub>0.3</sub> TiO <sub>3.35</sub> (N <sub>2</sub> ) <sub>0.26</sub> La <sub>0.5</sub> Ba <sub>0.5</sub> TiO <sub>3.25</sub> (N <sub>2</sub> ) <sub>0.23</sub> CeTiO <sub>4</sub> (N <sub>2</sub> ) <sub>0.24</sub> PrTiO <sub>3.5</sub> (N <sub>2</sub> ) <sub>0.25</sub> NdTiO <sub>3.5</sub> (N <sub>2</sub> ) <sub>0.26</sub>	1

<sup>1</sup>composition obtained with the highest nitrogen content

Table 2. Enthalpies of drop solution, decomposition and formation from the elements at 298 K (kJ mol<sup>-1</sup>) determined in this study.

	$\Delta H$ drop solution	$\Delta H$ decomposition (per mole of La)	$\Delta H^\circ$ formation
LaTiO <sub>3.5</sub>	49.26 ± 0.47	-	-1944.41 ± 2.41
LaTiO <sub>2</sub> N	-485.16 ± 4.65	-	-1417.10 ± 5.18
La <sub>0.7</sub> Ba <sub>0.3</sub> TiO <sub>2.3</sub> N <sub>0.7</sub>	-311.53 ± 1.14	-	-1506.43 ± 2.03
LaTiO <sub>3.5</sub> N <sub>0.64</sub>	29.68 ± 1.41	-26.19 ± 1.43	-1919.27 ± 2.69
LaTiO <sub>3.5</sub> N <sub>0.54</sub>	28.67 ± 1.39	-26.17 ± 1.41	-1919.29 ± 2.68
La <sub>0.7</sub> Ba <sub>0.3</sub> TiO <sub>3.35</sub> N <sub>0.62</sub>	35.56 ± 0.55	-24.12 ± 1.04	-1842.88 ± 1.77
La <sub>0.7</sub> Ba <sub>0.3</sub> TiO <sub>3.35</sub> N <sub>0.59</sub>	38.85 ± 0.53	-18.98 ± 1.01	-1846.48 ± 1.76
La <sub>0.7</sub> Ba <sub>0.3</sub> TiO <sub>3.35</sub> N <sub>0.57</sub>	38.39 ± 0.49	-19.34 ± 0.97	-1846.22 ± 1.75

uncertainty is two standard deviations of the mean.

Table 3. Data used in thermodynamic cycles to determine the enthalpy of formation from drop solution calorimetry. All values are in kJ mol<sup>-1</sup>.

	$\Delta H$ drop solution	$\Delta H^\circ$ formation	Reference
La <sub>2</sub> O <sub>3</sub>	$\Delta H_1 = -225.10 \pm 3.16$	$\Delta H_2 = -1793.7 \pm 1.6$	[59]
TiO <sub>2</sub>	$\Delta H_3 = 57.95 \pm 0.71$	$\Delta H_4 = -944.75 \pm 1.26$	[60]
La <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>	$\Delta H_5 = 98.52 \pm 0.95$	$\Delta H_6 = -3890.92 \pm 4.67$	this work
BaTiO <sub>3</sub>	$\Delta H_9 = 38.53 \pm 0.63$	$\Delta H_{10} = -1659.797$	[61]

uncertainty is two standard deviations of the mean.

Table 4. Thermochemical cycle for calculation of the enthalpy of decomposition of  $\text{LaTiO}_{3.5}\text{N}_x$

Reaction	$\Delta H$
$\text{LaTiO}_{3.5}\text{N}_x (\text{s}, 298) \rightarrow \text{LaTiO}_{3.5} (\text{s}, 298) + x/2 \text{N}_2 (\text{g}, 298)$	$\Delta H$
$\text{LaTiO}_{3.5}\text{N}_x (\text{s}, 298) \rightarrow \text{LaTiO}_{3.5} (\text{soln}, 975) + x/2 \text{N}_2 (\text{g}, 975)$	$\Delta H_{\text{ds}}$
$\text{LaTiO}_{3.5} (\text{s}, 298) \rightarrow \text{LaTiO}_{3.5} (\text{soln}, 975)$	$1/2 \Delta H_5$
$\text{N}_2 (\text{g}, 298) \rightarrow \text{N}_2 (\text{g}, 975)$	$\Delta H_7$
$\Delta H = \Delta H_{\text{ds}} - 1/2 \Delta H_5 - x/2 \Delta H_7$	

Table 5. Thermochemical cycle for calculation of the enthalpy of decomposition of  $\text{La}_{0.7}\text{Ba}_{0.3}\text{TiO}_{3.35}\text{N}_x$ .

Reaction	$\Delta H$
$\text{La}_{0.7}\text{Ba}_{0.3}\text{TiO}_{3.35}\text{N}_x (\text{s}, 298) \rightarrow 0.7 \text{LaTiO}_{3.5} (\text{s}, 298) + 0.3 \text{BaTiO}_3 (\text{s}, 298) + x/2 \text{N}_2 (\text{g}, 298)$	$\Delta H$
$\text{La}_{0.7}\text{Ba}_{0.3}\text{TiO}_{3.35}\text{N}_x (\text{s}, 298) \rightarrow \text{LaTiO}_{3.5} (\text{soln}, 975) + 0.3 \text{BaTiO}_3 (\text{s}, 975) + x/2 \text{N}_2 (\text{g}, 975)$	$\Delta H_{\text{ds}}$
$\text{LaTiO}_{3.5} (\text{s}, 298) \rightarrow \text{LaTiO}_{3.5} (\text{soln}, 975)$	$1/2 \Delta H_5$
$\text{BaTiO}_3 (\text{s}, 298) \rightarrow \text{BaTiO}_3 (\text{soln}, 975)$	$\Delta H_9$
$\text{N}_2 (\text{g}, 298) \rightarrow \text{N}_2 (\text{g}, 975)$	$\Delta H_7$
$\Delta H = \Delta H_{\text{ds}} - 0.35 \Delta H_5 - x/2 \Delta H_7 - 0.3 x \Delta H_9$	



Table 6. Thermochemical cycle for calculation of the enthalpy of formation of La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>.

Reaction	$\Delta H$
La <sub>2</sub> O <sub>3</sub> (s, 298) → La <sub>2</sub> O <sub>3</sub> (soln, 975)	$\Delta H_1$
2 La (s, 298) + 3/2 O <sub>2</sub> (g, 298) → La <sub>2</sub> O <sub>3</sub> (s, 298)	$\Delta H_2$
TiO <sub>2</sub> (s, 298) → TiO <sub>2</sub> (soln, 975)	$\Delta H_3$
Ti (s, 298) + O <sub>2</sub> (g, 298) → TiO <sub>2</sub> (s, 298)	$\Delta H_4$
La <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub> (s, 298) → La <sub>2</sub> O <sub>3</sub> (soln, 975) + 2 TiO <sub>2</sub> (soln, 975)	$\Delta H_5$
2 La (s, 298) + 2 Ti (s, 298) + 7/2 O <sub>2</sub> (g, 298) → La <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub> (s, 298)	$\Delta H_6$
$\Delta H^\circ_f (\text{La}_2\text{Ti}_2\text{O}_7) = \Delta H_6 = -\Delta H_5 + \Delta H_1 + \Delta H_2 + 2(\Delta H_3 + \Delta H_4)$	

Table 7. Thermochemical cycle for calculation of the enthalpy of formation of LaTiO<sub>2</sub>N.

Reaction	$\Delta H$
La <sub>2</sub> O <sub>3</sub> (s, 298) → La <sub>2</sub> O <sub>3</sub> (soln, 975)	$\Delta H_1$
2 La (s, 298) + 3/2 O <sub>2</sub> (g, 298) → La <sub>2</sub> O <sub>3</sub> (s, 298)	$\Delta H_2$
TiO <sub>2</sub> (s, 298) → TiO <sub>2</sub> (soln, 975)	$\Delta H_3$
Ti (s, 298) + O <sub>2</sub> (g, 298) → TiO <sub>2</sub> (s, 298)	$\Delta H_4$
LaTiO <sub>2</sub> N (s, 298) + 3/4 O <sub>2</sub> (g, 975) → 1/2 La <sub>2</sub> O <sub>3</sub> (soln, 975) + TiO <sub>2</sub> (soln, 975) + 1/2 N <sub>2</sub> (g, 975)	$\Delta H_{ds}$
La (s, 298) + Ti (s, 298) + O <sub>2</sub> (g, 298) + 1/2 N <sub>2</sub> (g, 298) → LaTiO <sub>2</sub> N (s, 298)	$\Delta H^\circ_f$
N <sub>2</sub> (g, 298) → N <sub>2</sub> (g, 975)	$\Delta H_7$
O <sub>2</sub> (g, 298) → O <sub>2</sub> (g, 975)	$\Delta H_8$
$\Delta H^\circ_f (\text{LaTiO}_2\text{N}) = \Delta H^\circ_f = -\Delta H_{ds} + 1/2 (\Delta H_1 + \Delta H_2) + \Delta H_3 + \Delta H_4 + 1/2 \Delta H_7 - 3/4 \Delta H_8$	

Table 8. Thermochemical cycle for calculation of the enthalpy of formation of  $\text{La}_{0.7}\text{Ba}_{0.3}\text{TiO}_{2.3}\text{N}_{0.7}$ .

Reaction	$\Delta H$
$\text{La}_2\text{Ti}_2\text{O}_7 (\text{s}, 298) \rightarrow \text{La}_2\text{Ti}_2\text{O}_7 (\text{soln}, 975)$	$\Delta H_5$
$2 \text{La} (\text{s}, 298) + 2 \text{Ti} (\text{s}, 298) + 7/2 \text{O}_2 (\text{g}, 298) \rightarrow \text{La}_2\text{Ti}_2\text{O}_7 (\text{s}, 298)$	$\Delta H_6$
$\text{N}_2 (\text{g}, 298) \rightarrow \text{N}_2 (\text{g}, 975)$	$\Delta H_7$
$\text{O}_2 (\text{g}, 298) \rightarrow \text{O}_2 (\text{g}, 975)$	$\Delta H_8$
$\text{BaTiO}_3 (\text{s}, 298) \rightarrow \text{BaTiO}_3 (\text{soln}, 975)$	$\Delta H_9$
$\text{Ba} (\text{s}, 298) + \text{Ti} (\text{s}, 298) + 3/2 \text{O}_2 (\text{g}, 298) \rightarrow \text{BaTiO}_3 (\text{s}, 298)$	$\Delta H_{10}$
$\text{La}_{0.7}\text{Ba}_{0.3}\text{TiO}_{2.3}\text{N}_{0.7} (\text{s}, 298) + 0.525 \text{O}_2 (\text{g}, 975) \rightarrow 0.35 \text{La}_2\text{Ti}_2\text{O}_7 (\text{soln}, 975) + 0.3 \text{BaTiO}_3 (\text{soln}, 975) + 0.35 \text{N}_2 (\text{g}, 975)$	$\Delta H_{\text{ds}}$
$0.7 \text{La} (\text{s}, 298) + 0.3 \text{Ba} (\text{s}, 298) + 1.15 \text{O}_2 (\text{g}, 298) + 0.35 \text{N}_2 (\text{g}, 298) \rightarrow \text{La}_{0.7}\text{Ba}_{0.3}\text{TiO}_{2.3}\text{N}_{0.7} (\text{s}, 298)$	$\Delta H^\circ_f$
$\Delta H^\circ_f (\text{La}_{0.7}\text{Ba}_{0.3}\text{TiO}_{2.3}\text{N}_{0.7}) = \Delta H^\circ_f = -\Delta H_{\text{ds}} + 0.35 (\Delta H_5 + \Delta H_6) + 0.3 (\Delta H_9 + \Delta H_{10}) + 0.35 \Delta H_7 - 0.525 \Delta H_8$	

Table 9. Thermochemical cycle for calculation of the enthalpy of formation of  $\text{LaTiO}_{3.5}\text{N}_x$

Reaction	$\Delta H$
$\text{La}_2\text{O}_3 (\text{s}, 298) \rightarrow \text{La}_2\text{O}_3 (\text{soln}, 975)$	$\Delta H_1$
$2 \text{La} (\text{s}, 298) + 3/2 \text{O}_2 (\text{g}, 298) \rightarrow \text{La}_2\text{O}_3 (\text{s}, 298)$	$\Delta H_2$
$\text{TiO}_2 (\text{s}, 298) \rightarrow \text{TiO}_2 (\text{soln}, 975)$	$\Delta H_3$
$\text{Ti} (\text{s}, 298) + \text{O}_2 (\text{g}, 298) \rightarrow \text{TiO}_2 (\text{s}, 298)$	$\Delta H_4$
$\text{LaTiO}_{3.5}\text{N}_x (\text{s}, 298) \rightarrow 1/2 \text{La}_2\text{O}_3 (\text{soln}, 975) + \text{TiO}_2 (\text{soln}, 975) + x/2 \text{N}_2 (\text{g}, 975)$	$\Delta H_{\text{ds}}$
$\text{La} (\text{s}, 298) + \text{Ti} (\text{s}, 298) + 7/4 \text{O}_2 (\text{g}, 298) + x/2 \text{N}_2 (\text{g}, 298) \rightarrow \text{LaTiO}_{3.5}\text{N}_x (\text{s}, 298)$	$\Delta H^\circ_f$
$\text{N}_2 (\text{g}, 298) \rightarrow \text{N}_2 (\text{g}, 975)$	$\Delta H_7$
$\Delta H^\circ_f (\text{LaTiO}_{3.5}\text{N}_x) = \Delta H^\circ_f = -\Delta H_{\text{ds}} + 1/2 (\Delta H_1 + \Delta H_2) + (\Delta H_3 + \Delta H_4) + x/2 \Delta H_7$	

Table 10. Thermochemical cycle for calculation of the enthalpy of formation of  $\text{La}_{0.7}\text{Ba}_{0.3}\text{TiO}_{3.35}\text{N}_x$ .

Reaction	$\Delta H$
$\text{La}_2\text{Ti}_2\text{O}_7 (\text{s}, 298) \rightarrow \text{La}_2\text{Ti}_2\text{O}_7 (\text{soln}, 975)$	$\Delta H_5$
$2 \text{La} (\text{s}, 298) + 2 \text{Ti} (\text{s}, 298) + 7/2 \text{O}_2 (\text{g}, 298) \rightarrow \text{La}_2\text{Ti}_2\text{O}_7 (\text{s}, 298)$	$\Delta H_6$
$\text{N}_2 (\text{g}, 298) \rightarrow \text{N}_2 (\text{g}, 975)$	$\Delta H_7$
$\text{O}_2 (\text{g}, 298) \rightarrow \text{O}_2 (\text{g}, 975)$	$\Delta H_8$
$\text{BaTiO}_3 (\text{s}, 298) \rightarrow \text{BaTiO}_3 (\text{soln}, 975)$	$\Delta H_9$
$\text{Ba} (\text{s}, 298) + \text{Ti} (\text{s}, 298) + 3/2 \text{O}_2 (\text{g}, 298) \rightarrow \text{BaTiO}_3 (\text{s}, 298)$	$\Delta H_{10}$
$\text{La}_{0.7}\text{Ba}_{0.3}\text{TiO}_{3.35}\text{N}_x (\text{s}, 298) \rightarrow 0.35 \text{La}_2\text{Ti}_2\text{O}_7 (\text{soln}, 975) + 0.3 \text{BaTiO}_3 (\text{soln}, 975) + x/2 \text{N}_2 (\text{g}, 975)$	$\Delta H_{\text{ds}}$
$0.7 \text{La} (\text{s}, 298) + 0.3 \text{Ba} (\text{s}, 298) + \text{Ti} (\text{s}, 298) + 1.675 \text{O}_2 (\text{g}, 298) + x/2 \text{N}_2 (\text{g}, 298) \rightarrow \text{La}_{0.7}\text{Ba}_{0.3}\text{TiO}_{3.35}\text{N}_x (\text{s}, 298)$	$\Delta H^\circ_f$
$\Delta H^\circ_f (\text{La}_{0.7}\text{Ba}_{0.3}\text{TiO}_{3.35}\text{N}_x) = \Delta H^\circ_f = -\Delta H_{\text{ds}} + 0.35 (\Delta H_5 + \Delta H_6) + 0.3 (\Delta H_9 + \Delta H_{10}) + x/2 \Delta H_7$	