Chem. Mater. **2005,** *17,* 3570−3574

Thermochemistry of a New Class of Materials Containing Dinitrogen Pairs in an Oxide Matrix

Franck Tessier,*[,†] Laurent Le Gendre,[‡] François Cheviré,[†] Roger Marchand,[†] and Alexandra Navrotsky[§]

UMR CNRS 6512 "Verres et Céramiques", Institut de Chimie de Rennes, Université de Rennes 1, F-35042 Rennes Cedex, France, IUT de St-Brieuc, IETR, UMR CNRS 6164, Université de Rennes 1, F-22004 St-Brieuc Cedex 01, France, and Thermochemistry Facility, University of California at Davis, Davis, California 95616-8779

Received February 22, 2005. Revised Manuscript Received May 4, 2005

A series of N_2-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 $La_2Ti_2O_7$ 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.[1−3] 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.[1−10] While a significant number of organic dinitrogen-containing compounds, including conventional synthetic organometallic complexes,[11] as well as biological substances,[12] are known, the formation of such dinitrogen in inorganic materials is

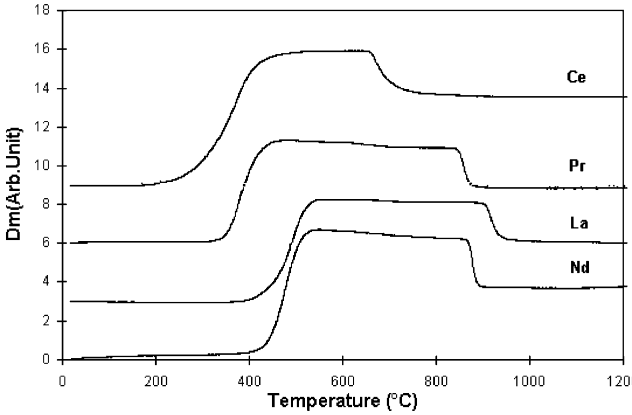

Figure 1. TGA under O_2 of $RTiO_2N$ phases (R = Ce, Pr, La, and Nd) (1 °C·min^{-1}).

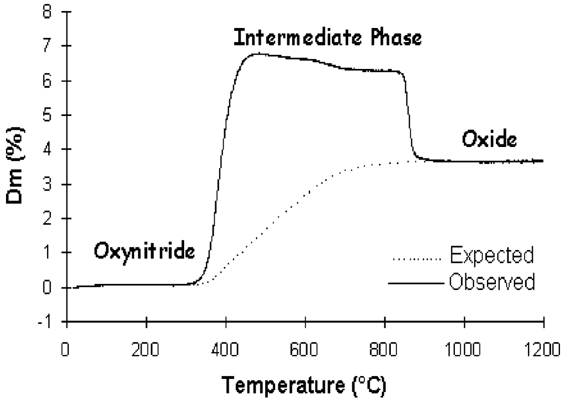

Figure 2. TGA analysis of an oxynitride manifesting the "intermediate phase" phenomenon.

---

* To whom correspondence should be addressed. E-mail: Franck.Tessier@univ-rennes1.fr.

[†] UMR CNRS 6512 "Verres et Céramiques", Institut de Chimie de Rennes, Université de Rennes 1.

[‡] IUT de St-Brieuc, IETR, UMR CNRS 6164, Université de Rennes 1.

[§] Thermochemistry Facility, University of California at Davis.

(1) Le Gendre, L. Thesis n°1907, Université de Rennes, France, 1997.

(2) Le Gendre, L.; Marchand, R.; Laurent, Y. *J. Eur. Ceram. Soc.* **1997**, *17*, 1813.

(3) Le Gendre, L.; Marchand, R.; Piriou B. Eur. *J. Solid State Inorg. Chem.* **1997**, *34*, 973.

10.1021/cm050402b CCC: $30.25

Table 1. Evidence of Intermediate Phases in Several Structure Types

oxynitride	structural type	intermediate phase formula[a]	ref
$BaTaO_2N$	perovskite	$BaTaO_{3.5}(N_2)_{0.15}$	2
$La_{0.91}W_{0.91}\square_{0.18}O_{1.37}N_{1.63}$	perovskite	$LaWO_{4.5}(N_2)_{0.23}$	2
$LaTiO_2N$	perovskite	$LaTiO_{3.5}(N_2)_{0.32}$	2
$Al_{2.85}\square_{0.15}O_{3.45}N_{0.55}$	spinelle	$Al_2O_3(N_2)_{0.095}$	2, 9
$Y_{2.67}W_{1.33}(O_{3.79}N_{2.80}\square_{1.41})$	fluorite	$Y_2WO_6(N_2)_{0.20}$	2
$Cr_{0.77}\square_{0.23}O_{0.69}N_{0.31}$	NaCl	$Cr_2O_3(N_2)_{0.15}$	2
$Ti_{0.67}\square_{0.33}O_{0.42}N_{0.58}$	NaCl	$TiO_2(N_2)_{0.06}$	2
$Nb_{0.54}\square_{0.46}O_{0.40}N_{0.60}$	NaCl	$Nb_2O_5(N_2)_{0.43}$	2
TaON	baddeleyite	$TaO_2(N_2)_{0.10}$	4
Zr_2N_2O	bixbyite	$ZrO_2(N_2)_{0.028}$	5
$Y_4Si_2O_7N_2$	cuspidine	$Y_4Si_2O_{10}(N_2)_{0.75}$	6
$LaAl_{12}O_{18}N$	magnetoplumbite	$LnAl_{12}O_{19.5}(N_2)_{0.17}$	7
$Y_5(SiO_4)_3N$	apatite	$Y_{10}Si_7O_{29}(N_2)_{0.335}$	8
$Sr_2NbO_{2.8}N$	K_2NiF_4	$Sr_2NbO_{4.5}(N_2)_{0.20}$	10
$La_{0.9}Ba_{0.1}TiO_{2.1}N_{0.9}$	perovskite	$La_{0.9}Ba_{0.1}TiO_{3.45}(N_2)_{0.31}$	1
$La_{0.7}Ba_{0.3}TiO_{2.3}N_{0.7}$	perovskite	$La_{0.7}Ba_{0.3}TiO_{3.35}(N_2)_{0.26}$	1
$La_{0.5}Ba_{0.5}TiO_{2.5}N_{0.5}$	perovskite	$La_{0.5}Ba_{0.5}TiO_{3.25}(N_2)_{0.23}$	1
$CeTiO_2N$	perovskite	$CeTiO_4(N_2)_{0.24}$	1
$PrTiO_2N$	perovskite	$PrTiO_{3.5}(N_2)_{0.25}$	1
$NdTiO_2N$	perovskite	$NdTiO_{3.5}(N_2)_{0.26}$	1

[a] Composition obtained with the highest nitrogen content.

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,[13,14] prepared from the elements under high N_2 pressure, in products obtained by co-condensation of metallic atoms with N_2 at low temperature,[15−28] in surface layers of titanium dioxide films during their bombardment by N_2^+ ions,[29] as molecular dinitrogen adsorbed on metallic or oxide substrates at low temperature,[30−41] 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,[2,3] 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.[42−46]

Experimental Section

Precursors. $La_2Ti_2O_7$ precursor was prepared by molten salt synthesis.[47] 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.

---

(4) Ohran, E.; Tessier, F.; Marchand, R. *Solid State Sci.* **2002**, *4*, 1071.
(5) Clarke, S. J.; Michie, C. W.; Rosseinsky, M. J. *J. Solid State Chem.* **1999**, *146*, 309.
(6) Van Krevel, J. W. H.; Hintzen, H. T.; Metselaar, R.; Le Gendre, L.; Marchand, R. *Solid State Sci.* **2001**, *3*, 49.
(7) Wang, X. H.; Lejus, A.-M.; Vivien, D. *J. Am. Ceram. Soc.* **1999**, *73* (3), 770.
(8) Veyret, J.-B.; Van de Voorde, M.; Billy, M. *J. Am. Ceram. Soc.* **1992**, *75*, 3289.
(9) Goursat, P.; Billy, M.; Goeuriot, P.; Labbe, J. C.; Villechenoux, J. M.; Roult, G.; Bardolle, *J. Mater. Chem.* **1981**, *6*, 81.
(10) Tobias, G.; Oro-Sole, J.; Beltran-Porter, D.; Fuertes, A. *Cryst. Eng.* **2002**, 5, 479.
(11) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115.
(12) Reis, V. M.; Baldani, J. I.; Divan Baldani, V. L.; Dobereiner, *J. Crit. Rev. Plant. Sci.* **2000**, *19* (3), 227.
(13) Auffermann, G.; Prots, Y.; Kniep, R. Angew. *Chem. Int. Ed.* **2001**, *40* (3), 547. Prots, Y.; Auffermann, G.; Tovar, M.; Kniep, R. *Angew. Chem., Int. Ed.* **2002**, *41* (13), 2288.
(14) Vajenine, G. V.; Auffermann, G.; Prots, Y.; Schnelle, W.; Kremer, R. K.; Simon, A.; Kniep, R. *Inorg. Chem.* **2001**, *40*, 4866.
(15) Ozin, G. A.; Van der Voet, A. Can. *J. Chem.* **1973**, *51*, 3332.
(16) Burdett, J. K.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1971**, *16*, 885.
(17) Ozin, G. A.; Klotzbucher, W. *J. Am. Chem. Soc.* **1975**, *97*, 3965.
(18) Huber, E.; Kundig, E. P.; Moskovitz, M.; Ozin, G. A. *J. Am. Chem. Soc.* **1973**, *95*, 332.
(19) Crichton, O.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1977**, *6*, 536.
(20) De Vore, T. C. *Inorg. Chem.* **1976**, *15*, 1315.
(21) Huber, H.; Ford, T. A.; Klotzbucher, W.; Ozin, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 3176.
(22) Busby, R.; Klotzbucher, W.; Ozin, G. A. *Inorg. Chem.* **1977**, *16*, 822.
(23) Green, D. W.; Hodges, R. V.; Gruen, D. M. *Inorg. Chem.* **1976**, *15*, 971.
(24) Burdett, J. K.; Graham, M. A.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1620.
(25) Rest, A. J. *J. Organomet. Chem.* **1972**, *C76*, 40.
(26) Moskovits, M.; Ozin, G. A. *J. Chem. Phys.* **1973**, *58*, 1251.
(27) Andrews, L.; Citra, A.; Chertihin, G. V.; Bare, W. D.; Neurock, M. *J. Phys. Chem. A* **1998**, *102*, 2561.
(28) Manceron, L.; Alikhani, M. E.; Joly, H. A. *Chem. Phys.* **1998**, *228*, 73.
(29) Wolff, M.; Schultze, J. W.; Strehblow, H. H. *Surf. Interface Anal.* **1991**, *17*, 726.
(30) Shinn, N. D.; Tsang, K. L. *J. Vac. Sci. Technol.* **1991**, *A9* (3), 1558.
(31) Fuggle, J. C.; Menzel, D. *Vakuum Tech.* **1977**, *27* (5), 130.
(32) Johnson, D. W.; Roberts, M. W. *Surf. Sci.* **1979**, *87*, L255.
(33) Nilsson, A.; Tillborg, H.; Martensson, N. *Phys. Rev. Lett.* **1991**, *67* (8), 1015.
(34) Wakabayashi, F.; Kondo, J.; Wada, A.; Domen, K.; Hirose, C. *J. Phys. Chem.* **1993**, *97*, 10761.
(35) Kameoka, S.; Kuroda, M.; Uetsuka, H.; Hito, S.; Kunimori,. K. *J. Chem. Soc., Faraday Trans.* **1996**, *92* (9), 1643.
(36) Atzei, D.; De Filipo, D.; Rossi, A. *Spectrochim. Acta* **1993**, *49* (A)-12, 1779.
(37) Birchem, T.; Muhler, M. *Surf. Sci.* **1995**, *334*, L701.
(38) Wang, H. P.; Yates, J. T., Jr. *J. Phys. Chem.* **1984**, *88*, 852.
(39) Arumainayagam, C. R.; Tripa, C. E.; Xu, J.; Yates Jr., J. T. *Surf. Sci.* **1996**, *360*, 121.
(40) Vettraino, M.; Trudeau, M.; Lo, A. Y. H.; Schurko, R. W.; Antonelli, D. *J. Am. Chem. Soc.* **2002**, *124* (32), 9567.
(41) Recchia, S.; Dossi, C.; Psaro, R.; Fusi, A.; Ugo, R.; Moretti, G. *J. Phys. Chem. B* **2002**, *106* (51), 13326.
(42) Navrotsky, A. *J. Alloys Compd.* **2001**, *321*, 300.
(43) Tessier, F.; Navrotsky, A.; Le Sauze, A.; Marchand, R. *Chem. Mater.* **2000**, *12*, 148.
(44) Tessier, F.; Navrotsky, A.; Niewa, R.; Leineweber, A.; Jacobs, H.; Kikkawa, S.; Takahashi, M.; Kanamaru, F.; DiSalvo, F. J. *Solid State Sci.* **2000**, *2*, 457.
(45) Ranade, M. R.; Tessier, F.; Navrotsky, A.; Leppert, V. J.; Risbud, S. H.; DiSalvo, F. J.; Balkas, C. M. *J. Phys. Chem. B* **2000**, *104* (17), 4060.
(46) Ranade, M. R.; Tessier, F.; Navrotsky, A.; Marchand, R. *J. Mater. Res.* **2000**, *16* (10), 2824.
(47) Fuierer, P. A.; Newnham, R. E. *J. Am. Ceram. Soc.* **1991**, *74*, 2876.

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 the 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^{-1}. The temperature was raised to the 1223−1273 K range with a heating rate of 10 K min^{-1}. 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 $LaTiO_2N$ and $La_{0.7}Ba_{0.3}TiO_{2.3}N_{0.7}$ were prepared and oxidized at 873 K to form intermediate phases listed in Table 1.[3]

Characterizations. *X-ray diffraction.* XRD powder patterns were recorded using a Philips PW3710 diffractometer operating with Cu Kα radiation ($\lambda = 1.5418$ Å). 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,[1−3] 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 N_2 by thermal conductivity and oxygen as CO_2 by infrared detection. The apparatus was calibrated using N_2 and CO_2 gas (purity ≥ 99.95%) as well as ϵ−TaN as a nitrogen standard.[48]

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 ($P = 1$ atm) with constant heating rates always lower than 1 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).[1−10]

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 Kα X-ray source (1486.6 eV). More experimental details are given elsewhere.[2,3,49] XPS analysis shows a single-peak N 1s 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[2] and Raman spectroscopy confirms the previous XPS results: a single peak close to 2328 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 cm^{-1} in N_2 gas, 1380 cm^{-1} in SrN, and 1307 cm^{-1} in SrN_2 ($(N_2)^{2-}$ pairs).[50]

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.[51,52] 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 ~5 cm^3 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 (ΔH_{ds}). Further details of the experimental procedure are provided in previous papers.[53−55]

Table 2. Enthalpies of Drop Solution, Decomposition, and Formation from the Elements at 298 K (kJ mol^{-1}) Determined in This Study[a]

	ΔH drop solution	ΔH decomposition (per mole of La)	ΔH° formation
$LaTiO_{3.5}$	49.26 ± 0.47		−1944.41 ± 2.41
$LaTiO_2N$	−485.16 ± 4.65		−1417.10 ± 5.18
$La_{0.7}Ba_{0.3}TiO_{2.3}N_{0.7}$	−311.53 ± 1.14		−1506.43 ± 2.03
$LaTiO_{3.5}N_{0.64}$	29.68 ± 1.41	−26.19 ± 1.43	−1919.27 ± 2.69
$LaTiO_{3.5}N_{0.54}$	28.67 ± 1.39	−26.17 ± 1.41	−1919.29 ± 2.68
$La_{0.7}Ba_{0.3}TiO_{3.35}N_{0.62}$	35.56 ± 0.55	−24.12 ± 1.04	−1842.88 ± 1.77
$La_{0.7}Ba_{0.3}TiO_{3.35}N_{0.59}$	38.85 ± 0.53	−18.98 ± 1.01	−1846.48 ± 1.76
$La_{0.7}Ba_{0.3}TiO_{3.35}N_{0.57}$	38.39 ± 0.49	−19.34 ± 0.97	−1846.22 ± 1.75

[a] 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^{-1} [a]

	ΔH drop solution	ΔH° formation	ref
La_2O_3	$\Delta H_1 = -225.10 \pm 3.16$	$\Delta H_2 = -1793.7 \pm 1.6$	59
TiO_2	$\Delta H_3 = 57.95 \pm 0.71$	$\Delta H_4 = -944.75 \pm 1.26$	60
$La_2Ti_2O_7$	$\Delta H_5 = 98.52 \pm 0.95$	$\Delta H_6 = -3890.92 \pm 4.67$	this work
$BaTiO_3$	$\Delta H_9 = 38.53 \pm 0.63$	$\Delta H_{10} = -1659.797$	61

[a] Uncertainty is two standard deviations of the mean.

Table 4. Thermochemical Cycle for Calculation of the Enthalpy of Decomposition of $LaTiO_{3.5}N_x$

reaction	ΔH
$LaTiO_{3.5}N_x$ (s, 298) → $LaTiO_{3.5}$ (s, 298) + $x/2$ N_2 (g, 298)	ΔH
$LaTiO_{3.5}N_x$ (s, 298) → $LaTiO_{3.5}$ (soln, 975) + $x/2$ N_2 (g, 975)	ΔH_{ds}
$LaTiO_{3.5}$ (s, 298) → $LaTiO_{3.5}$ (soln, 975)	$^1/_2\Delta H_5$
N_2 (g, 298) → N_2 (g, 975)	ΔH_7

$\Delta H = \Delta H_{ds} - 1/2\ \Delta H_5 - x/2\ \Delta H_7$

Results and Discussion

Drop solution calorimetry has been performed on oxynitride perovskites $LaTiO_2N$ and $La_{0.7}Ba_{0.3}TiO_{2.20}N_{0.77}$, as well as on intermediate phases $LaTiO_{3.5}N_x$ ($x = 0.54$ and 0.64) and $La_{0.7}Ba_{0.3}TiO_{3.5}N_x$ ($x = 0.57$, 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 (Tables 2 and 3) and appropriate thermodynamic cycles detailed in Tables 4−10. The enthalpy of formation of $La_2Ti_2O_7$ was determined from the cycle given in Table 6. The accuracy of the enthalpy of drop solution of La_2O_3 (ΔH_1) was recently checked with a

---

(48) Dopita, M.; Wollein, B.; Rafaja, D.; Gruner, W.; Lengauer, W. *Defect Diffus. Forum, Diffus. Mater. DIMAT-2000* **2001**, *194−199*, 1613.

(49) Wiame, H.; Centeno, M.-A.; Picard, S.; Bastians, P.; Grange, P. *J. Eur. Ceram. Soc.* **1998**, *18* (9), 1293.

(50) Auffermann, G.; Prots, Y.; Kniep, R.; Parker, S. F.; Bennington, S. M.; *ChemPhysChem.* **2000**, *3*, 815.

(51) Navrotsky, A. *Phys. Chem. Miner.* **1977**, *2*, 89.

(52) Navrotsky, A. *Phys. Chem. Miner.* **1997**, *24*, 222.

(53) McHale, J. M.; Kowach, G. R.; Navrotsky, A.; DiSalvo, F. J. *Chem. Eur. J.* **1996**, *2* (12), 1514.

(54) McHale, J. M.; Navrotsky, A.; Kowach, G. R.; Balbarin, V. E.; DiSalvo, F. J. *Chem. Mater.* **1997**, *9*, 1538.

(55) McHale, J. M.; Navrotsky, A.; DiSalvo, F. J. *Chem. Mater.* **1999**, *11* (4), 1148.

Table 5. Thermochemical Cycle for Calculation of the Enthalpy of Decomposition of $La_{0.7}Ba_{0.3}TiO_{3.35}N_x$

reaction	ΔH
$La_{0.7}Ba_{0.3}TiO_{3.35}N_x$ (s, 298) → 0.7 $LaTiO_{3.5}$ (s, 298) + 0.3 $BaTiO_3$ (s, 298) + $x/2$ N_2 (g, 298)	ΔH
$La_{0.7}Ba_{0.3}TiO_{3.35}N_x$ (s, 298) → $LaTiO_{3.5}$ (soln, 975) + 0.3 $BaTiO_3$ (s, 975) + $x/2$ N_2 (g, 975)	ΔH_{ds}
$LaTiO_{3.5}$ (s, 298) → $LaTiO_{3.5}$ (soln, 975)	$^1/_2\Delta H_5$
$BaTiO_3$ (s, 298) → $BaTiO_3$ (soln, 975)	ΔH_9
N_2 (g, 298) → N_2 (g, 975)	ΔH_7

$\Delta H = \Delta H_{ds} - 0.35\ \Delta H_5 - x/2\ \Delta H_7 - 0.3x\ \Delta H_9$

Table 6. Thermochemical Cycle for Calculation of the Enthalpy of Formation of $La_2Ti_2O_7$

reaction	ΔH
La_2O_3 (s, 298) → La_2O_3 (soln, 975)	ΔH_1
2 La (s, 298) + 3/2 O_2 (g, 298) → La_2O_3 (s, 298)	ΔH_2
TiO_2 (s, 298) → TiO_2 (soln, 975)	ΔH_3
Ti (s, 298) + O_2 (g, 298) → TiO_2 (s, 298)	ΔH_4
$La_2Ti_2O_7$ (s, 298) → La_2O_3 (soln, 975) + 2 TiO_2 (soln, 975)	ΔH_5
2 La (s, 298) + 2 Ti (s, 298) + 7/2 O_2 (g, 298) → $La_2Ti_2O_7$ (s, 298)	ΔH_6

$\Delta H°_f\ (La_2Ti_2O_7) = \Delta H_6 = -\Delta H_5 + \Delta H_1 + \Delta H_2 + 2(\Delta H_3 + \Delta H_4)$

nonhydrated sample and corrected to the value -225.10 ± 3.16 kJ mol^{-1}.[56] Using the experimental drop solution enthalpy value $\Delta H_5 = 98.52 \pm 0.95$ kJ mol^{-1} determined by Helean et al.,[57] we establish the enthalpy of formation $\Delta H°_f$ ($La_2Ti_2O_7$) to -3890.92 ± 4.67 kJ mol^{-1} and not -3855.5 ± 3.5 kJ mol^{-1} as initially reported by these authors.

Heats of drop solution of nitrogen-containing intermediate phases are endothermic and within 20 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 $LaTiO_{3.5}N_x$ phases are close to each other and less exothermic than that of $LaTiO_{3.5}$ 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. (See Figure 3.)

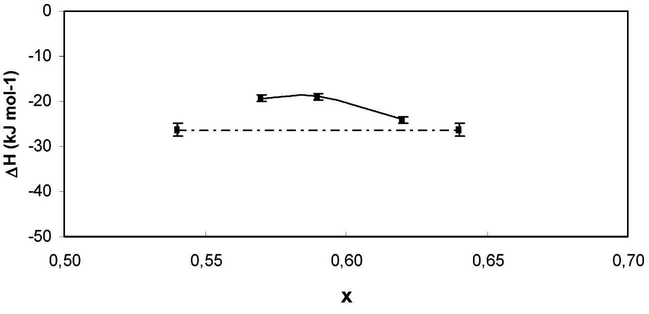

Figure 3. Enthalpies of oxidation (per mole of lanthanum) versus nitrogen content within $LaTiO_{3.5}N_x$ (dashed line) and $La_{0.7}Ba_{0.3}TiO_{3.35}N_x$ (solid curve) intermediate phases.

Table 7. Thermochemical Cycle for Calculation of the Enthalpy of Formation of $LaTiO_2N$

reaction	ΔH
La_2O_3 (s, 298) → La_2O_3 (soln, 975)	ΔH_1
2 La (s, 298) + 3/2 O_2 (g, 298) → La_2O_3 (s, 298)	ΔH_2
TiO_2 (s, 298) → TiO_2 (soln, 975)	ΔH_3
Ti (s, 298) + O_2 (g, 298) → TiO_2 (s, 298)	ΔH_4
$LaTiO_2N$ (s, 298) + 3/4 O_2 (g, 975) → 1/2 La_2O_3 (soln, 975) + TiO_2 (soln, 975) + 1/2 N_2 (g, 975)	ΔH_{ds}
La (s, 298) + Ti (s, 298) + O_2 (g, 298) + 1/2 N_2 (g, 298) → $LaTiO_2N$ (s, 298)	
N_2 (g, 298) → N_2 (g, 975)	$\Delta H°_f$
O_2 (g, 298) → O_2 (g, 975)	ΔH_7
$\Delta H°_f\ (LaTiO_2N) = \Delta H°_f = -\Delta H_{ds} + 1/2\ (\Delta H_1 + \Delta H_2) + \Delta H_3 + \Delta H_4 + 1/2\ \Delta H_7 - 3/4\ \Delta H_8$	ΔH_8

Table 8. Thermochemical Cycle for Calculation of the Enthalpy of Formation of $La_{0.7}Ba_{0.3}TiO_{2.3}N_{0.7}$

reaction	ΔH
$La_2Ti_2O_7$ (s, 298) → $La_2Ti_2O_7$ (soln, 975)	ΔH_5
2 La (s, 298) + 2 Ti (s, 298) + 7/2 O_2 (g, 298) → $La_2Ti_2O_7$ (s, 298)	ΔH_6
N_2 (g, 298) → N_2 (g, 975)	ΔH_7
O_2 (g, 298) → O_2 (g, 975)	ΔH_8
$BaTiO_3$ (s, 298) → $BaTiO_3$ (soln, 975)	ΔH_9
Ba (s, 298) + Ti (s, 298) + 3/2 O_2 (g, 298) → $BaTiO_3$ (s, 298)	ΔH_{10}
$La_{0.7}Ba_{0.3}TiO_{2.3}N_{0.7}$ (s, 298) + 0.525 O_2 (g, 975) → 0.35 $La_2Ti_2O_7$ (soln, 975) + 0.3 $BaTiO_3$ (soln, 975) + 0.35 N_2 (g, 975)	ΔH_{ds}
0.7 La (s, 298) + 0.3 Ba (s, 298) + 1.15 O_2 (g, 298) + 0.35 N_2 (g, 298) → $La_{0.7}Ba_{0.3}TiO_{2.3}N_{0.7}$ (s, 298)	$\Delta H°_f$

$\Delta H°_f\ (La_{0.7}Ba_{0.3}TiO_{2.3}N_{0.7}) = \Delta H°_f = -\Delta H_{ds} + 0.35\ (\Delta H_5 + \Delta H_6) + 0.3\ (\Delta H_9 + \Delta H_{10}) + 0.35\ \Delta H_7 - 0.525\ \Delta H_8$

Table 9. Thermochemical Cycle for Calculation of the Enthalpy of Formation of $LaTiO_{3.5}N_x$

reaction	ΔH
La_2O_3 (s, 298) → La_2O_3 (soln, 975)	ΔH_1
2 La (s, 298) + 3/2 O_2 (g, 298) → La_2O_3 (s, 298)	ΔH_2
TiO_2 (s, 298) → TiO_2 (soln, 975)	ΔH_3
Ti (s, 298) + O_2 (g, 298) → TiO_2 (s, 298)	ΔH_4
$LaTiO_{3.5}N_x$ (s, 298) → 1/2 La_2O_3 (soln, 975) + TiO_2 (soln, 975) + $x/2$ N_2 (g, 975)	ΔH_{ds}
La (s, 298) + Ti (s, 298) + 7/4 O_2 (g, 298) + $x/2$ N_2 (g, 298) → $LaTiO_{3.5}N_x$ (s, 298)	$\Delta H°_f$
N_2 (g, 298) → N_2 (g, 975)	ΔH_7

$\Delta H°_f\ (LaTiO_{3.5}N_x) = \Delta H°_f = -\Delta H_{ds} + 1/2\ (\Delta H_1 + \Delta H_2) + (\Delta H_3 + \Delta H_4) + x/2\ \Delta H_7$

We have devised cycles (Tables 4 and 5) representing the oxidation of the intermediate phases as an approach to determine the energetic contribution of N_2 pairs within the oxide matrix. The intermediate phases $La_{0.7}Ba_{0.3}TiO_{3.5}N_x$ are not well-cystallized but represent perovskite-derived structures. They decompose to crystalline $BaTiO_3$ (perovskite) and $La_2Ti_2O_7$ (layered perovskite). We suggest that the observed enthalpy associated with release of N_2 gas contains two contributions, that from any oxidation or bonding change of the dinitrogen, and that arising from the transformation of the $LaTiO_{3.5}$ component from the perovskite to the stable layered structure. However, only 0.7 mol of $LaTiO_{3.5}$ is formed as compared to 1 mol 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 $LaTiO_{3.5}$. Then, interestingly, we obtain a very similar heat effect to the pure La−Ti system. The measured enthalpies of decomposition, between −19 and −26 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 N_2 bonding. The release of nitrogen may have an effect on the 5−10 kJ mol^{-1} level and the energetics of the phase transition may release 20−25 kJ mol^{-1}.

---

(56) Cheng, J.; Navrotsky, A. *J. Mater. Res.* **2003**, *18* (10), 2501.

Table 10. Thermochemical Cycle for Calculation of the Enthalpy of Formation of $La_{0.7}Ba_{0.3}TiO_{3.35}N_x$

reaction	ΔH
$La_2Ti_2O_7$ (s, 298) → $La_2Ti_2O_7$ (soln, 975)	ΔH_5
2 La (s, 298) + 2 Ti (s, 298) + 7/2 O_2 (g, 298) → $La_2Ti_2O_7$ (s, 298)	ΔH_6
N_2 (g, 298) → N_2 (g, 975)	ΔH_7
O_2 (g, 298) → O_2 (g, 975)	ΔH_8
$BaTiO_3$ (s, 298) → $BaTiO_3$ (soln, 975)	ΔH_9
Ba (s, 298) + Ti (s, 298) + 3/2 O_2 (g, 298) → $BaTiO_3$ (s, 298)	ΔH_{10}
$La_{0.7}Ba_{0.3}TiO_{3.35}N_x$ (s, 298) → 0.35 $La_2Ti_2O_7$ (soln, 975) + 0.3 $BaTiO_3$ (soln, 975) + x/2 N_2 (g, 975)	ΔH_{ds}
0.7 La (s, 298) + 0.3 Ba (s, 298) + Ti (s, 298) + 1.675 O_2 (g, 298) + x/2 N_2 (g, 298) → $La_{0.7}Ba_{0.3}TiO_{3.35}N_x$ (s, 298)	ΔH°_f

$$\Delta H^\circ_f (La_{0.7}Ba_{0.3}TiO_{3.35}N_x) = \Delta H^\circ_f = -\Delta H_{ds} + 0.35 (\Delta H_5 + \Delta H_6) + 0.3 (\Delta H_9 + \Delta H_{10}) + x/2\ \Delta H_7$$

It is also possible to determine the energetics of formation of the oxynitride perovskite $LaTiO_2N$ from the cycle in Table 7. Heat contents $H_{975}-H_{298}$ of N_2 and O_2 are respectively $\Delta H_7 = 20.65$ and $\Delta H_8 = 21.84$ kJ mol^{-1} .[58] From the enthalpy of drop solution $\Delta H_{ds} = -485.16 \pm 4.65$ kJ mol^{-1}, we calculate the enthalpy of formation ΔH°_f ($LaTiO_2N$) $= -1417.10 \pm 5.18$ kJ mol^{-1}. A similar approach allows us to determine the enthalpy of the barium-containing oxynitride perovskite $La_{0.7}Ba_{0.3}TiO_{2.20}N_{0.77}$. From the thermochemical cycle given in Table 8 an enthalpy of formation ΔH°_f ($La_{0.7}Ba_{0.3}TiO_{2.3}N_{0.7}$) $= -1506.43 \pm 2.03$ kJ mol^{-1} is obtained. Compared to the enthalpy of formation of $LaTiO_2N$, this value is more exothermic. Barium has a stabilizing effect through the concept of the well-known inductive effect in solid-state chemistry,[58] but the trend is not totally explained because nitrogen contents are different and the differences in the standard enthalpies of BaO (-548.10 kJ mol^{-1}) and La_2O_3 (-1793.7 kJ mol^{-1}) contribute as major factors.

Acknowledgment. The authors are grateful for financial support from the France-Berkeley Fund and from the U.S. Department of Energy (Grant DE-FG0397SF14749).

CM050402B

---

(57) Helean, K. B.; Ushakov, S. V.; Brown, C. E.; Navrotsky, A.; Liang, J.; Ewing, R. C.; Farmer, J. M.; Boatner, L. A. *J. Solid State Chem.* **2004**, *177* (6), 1858.

(58) Chase, M. W.; et al. *JANAF Thermochemical Tables*, 3rd ed.; Journal of Physical and Chemical Reference Data; American Chemical Society: Washington, DC, 1985; Vol. 14, Suppl. no. 1.

(59) Robie, R. A.; Hemingway, B. S. *Thermodynamic Properties of Minerals and related Substances at 295.15K and 1 Bar (10^5 Pa) Pressure and at Higher Temperatures*; U.S. Geological Survey Bulletin 2131; U.S. Geological Survey: Washington, DC, 1995.

(60) Ranade, M. R.; Navrotsky, A.; Zhang, H. Z.; Banfield, J. F.; Elder, S. H.; Zaban, A.; Borse, P. H.; Kulkarni, S. K.; Doran, G. S.; Whitfield, H. J. *Proc. Natl. Acad. Sci.* **2002**, *99* (Suppl. 2), 6476.

(61) Barin, I. *Thermochemical Data of Pure Substances*; VCH: New York, 1989.