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# Defect formation and transport in $La_{0.95}Ni_{0.5}Ti_{0.5}O_{3-\delta}$

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**Abstract**

Deficiency in the A sublattice of orthorhombic perovskite-type $La_{1-x}Ni_{0.5}Ti_{0.5}O_{3-\delta}$, with maximum at $x = 0.07$–$0.08$, is compensated by the formation of trivalent nickel and oxygen vacancies. The atomistic computer simulations showed that these defects are trapped near the A-site cation vacancies, resulting in the stabilization of $Ni^{3+}$ cations and low electronic and oxygen-ionic transport. The average thermal expansion coefficient of $La_{0.95}Ni_{0.5}Ti_{0.5}O_{3-\delta}$ ceramics, calculated from dilatometric data in air, increases from $8.6 \times 10^{-6}$ $K^{-1}$ at 300–800 K to $12.0 \times 10^{-6}$ $K^{-1}$ at 1300–1500 K. The data on Seebeck coefficient and total conductivity, predominantly *p*-type electronic, suggest a broadband mechanism of hole transport. The activation energies for the hole and ionic conductivities are 89 and 430 kJ/mol, respectively. The oxygen ion transference numbers determined by the faradaic efficiency measurements in air, vary in the range $9.5 \times 10^{-5}$–$8.1 \times 10^{-4}$ at 1173–1248 K, increasing with temperature. Reducing oxygen partial pressure leads to a moderate decrease of the conductivity, followed by phase decomposition in the $p(O_2)$ range $9 \times 10^{-11}$ to $8 \times 10^{-9}$ atm at 1073–1223 K. The low-$p(O_2)$ stability limit of $La_{0.95}Ni_{0.5}Ti_{0.5}O_{3-\delta}$ perovskite was found between that of $La_3Ni_2O_7$ and Ni/NiO boundary.


*Keywords:* Lanthanum nickelate-titanate; A-site deficiency; Defect association; Oxygen ionic conductivity; Hole transport; Atomistic modelling; Thermal expansion

## 1. Introduction

Nickel-containing mixed conductors with perovskite-related structures are of great interest as the materials of oxygen-permeable ceramic membranes and as precursors of highly-active catalysts for the natural gas conversion in synthesis gas (syngas), the most important feedstock for commercial Fischer–Tropsch synthesis [1–9]. To date, industrial route for syngas production is based on steam reforming of $CH_4$ [5,6,9]; alternative processes include the catalytic partial oxidation of methane (POM), and the use of membrane reactors with $CH_4$ conversion by oxygen permeating through dense mixed-conducting ceramics [3–6,9,10]. Despite the reactor type, all these processes require catalysts active towards $CH_4$ reforming and/or POM. Typically, such catalysts represent highly dispersed metals, such as Ni, Ru or Pt, supported on porous oxide ceramics; the support is extremely important to suppress carbon deposition and to stabilize metal particles [5–9]. For Ni-based catalysts, the supporting material should preferably provide an oxidative character of metal particles neighborhood, a significant oxygen storage capacity and ionic transport, and an exchange of nickel species between the bulk and the surface. To a considerable extent these requirements are met by multiphase systems obtained on reduction of perovskite-related lanthanum nickelates and their derivatives, including $La_2NiO_{4+\delta}$, $LaNiO_{3-\delta}$ and $La(Ni,Fe)O_{3-\delta}$ [3,6–9,11].

Perovskite-type $LaNiO_{3-\delta}$ has a low thermodynamic stability and decomposes on heating and/or on reducing oxygen partial pressure, forming NiO and Ruddlesden–Popper $La_{1+n}Ni_nO_{3n+1}$ phases [12,13]. Extensive substitution of nickel makes it possible to stabilize perovskite lattice under oxidizing

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conditions. The maximum nickel content in $LaM_{1-y}Ni_yO_{3-\delta}$ ($M$ = Cr, Mn, Fe, Co, Ga) solid solutions stable at elevated temperatures corresponds to $y = 0.4$–$0.6$ [12,14,15]. For the heavily doped systems, reducing $p(O_2)$ leads to the co-existence of metallic Ni and perovskite, which contributes to catalytic performance due to interaction with metal and carbon oxidation by oxygen migrating from the lattice [6,7]. The tendency to metal phase separation in reducing atmospheres can be increased creating A-site cation deficiency in the perovskite solid solutions.

The present work was focused on the studies of defect chemistry, stability and transport properties of A-site deficient $La_{0.95}Ni_{0.5}Ti_{0.5}O_{3-\delta}$. This model perovskite was selected, in particular, to assess the effects of A-site vacancies on the nickel oxidation states and defect migration mechanisms. With respect to the parent compound, $LaNi_{0.5}Ti_{0.5}O_{3-\delta}$, where all Ni cations are divalent and the electronic transport occurs presumably via hopping of $p$-type charge carriers [16], $La_{0.95}Ni_{0.5}Ti_{0.5}O_{3-\delta}$ is expected to contain a greater amount of oxygen vacancies and/or holes formed according to the crystal electroneutrality condition. The information on behavior of such defects in the A-site deficient perovskite lattices is, however, very scarce. For instance, oxygen ionic conduction may increase with A-site deficiency due to charge compensation via the oxygen vacancy formation and to random distribution of the vacant cation sites suppressing long-range ordering in the oxygen sublattice [17,18]; opposite effects, which are also well known in literature [17,19,20], can be qualitatively explained in terms of local structural distortions and association of the oxygen and A-site cation vacancies. In order to identify the defect interaction mechanisms, atomistic computer simulations were performed.

## 2. Experimental

### 2.1. Synthesis and characterization

Powders of $La_{1-x}Ni_{0.5}Ti_{0.5}O_{3-\delta}$ ($x = 0.05$ and 0.10) were prepared by the standard ceramic synthesis technique using high-purity $La(NO_3)_3{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$ and $TiO_2$ as starting materials. The solid state reactions were conducted in air at 1273–1373 K for 6 h with multiple intervening grinding steps. Dense ceramic samples were sintered at 1793–1813 K in air for 15 h, with subsequent slow cooling in order to retain equilibrium with atmospheric oxygen at low temperatures. The cation composition was verified by the inductively-coupled plasma (ICP) spectroscopy. Characterization of the ceramic materials included the scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM/EDS), X-ray diffraction analysis (XRD), dilatometry, measurements of total conductivity (4-probe DC) and Seebeck coefficient as function of the oxygen partial pressure and temperature, determination of ion transference numbers by the faradaic efficiency method; the experimental procedures and equipment were described elsewhere ([4,14,15,17,21] and references cited). X-ray photoelectron spectroscopy (XPS) was carried out using an Omicron Full Lab System for ceramic samples etched with $Ar^+$ (1 keV, ion current 100 nA); the charging effect was compensated using the position of C: 1s line as reference.

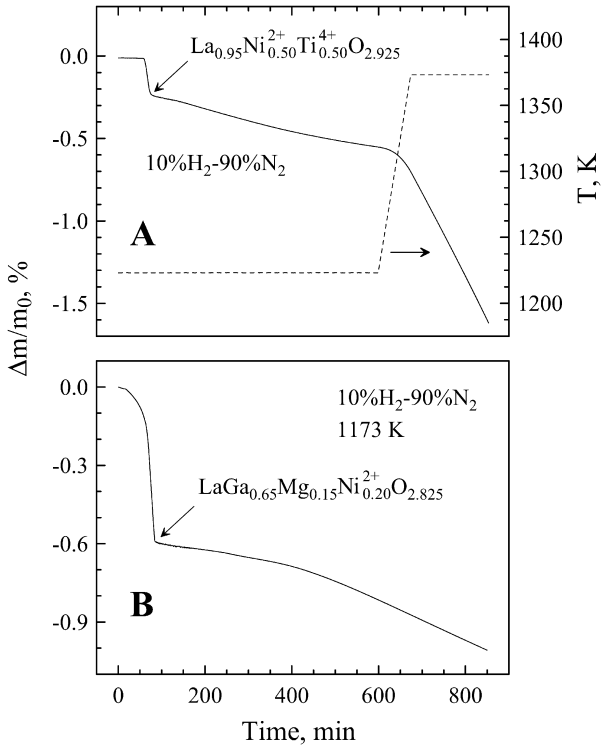


Fig. 1. Examples of reduction kinetics of $L_{0.95}Ni_{0.5}Ti_{0.5}O_{3-\delta}$ (A) and $LaGa_{0.65}Mg_{0.15}Ni_{0.20}O_{3-\delta}$ (B) in flowing 10% $H_2$ – 90% $N_2$ mixture (see text).

The oxygen stoichiometry variations were studied by thermogravimetric analysis (TGA, Setaram SetSys 16/18). Experimental procedure included heating (3 K/min) to 1223 K in a flow of dry air, temperature cycling in the range 923–1223 K with a step of 50 K and equilibration at each temperature during 2–3 h, and then reduction in flowing 10% $H_2$ – 90% $N_2$ mixture at 1223–1373 K. The absolute values of oxygen nonstoichiometry ($\delta$) in air were estimated with respect to the point of $La_{0.95}Ni_{0.50}Ti_{0.50}O_{2.925}$ decomposition determined from the relaxation curves (Fig. 1A), assuming that the Ni and Ti oxidation states in this point are 2+ and 4+, respectively. Further reduction is accompanied with extremely slow $Ti^{4+}$ reduction into $Ti^{3+}$, making it impossible to obtain the reference point based on thermodynamic equilibrium. As the $Ni^{3+} \rightarrow Ni^{2+}$ transition times are relatively short, possible reduction of $Ti^{4+}$ cations at the initial stage was neglected. Earlier this technique was successfully validated for another Ni-containing perovskite, $LaGa_{0.65}Mg_{0.15}Ni_{0.20}O_{3-\delta}$ [21], which also exhibits prolonged relaxation in reducing atmospheres due to gallium oxide volatilization (Fig. 1B). The reproducibility of weight changes in air is illustrated by Fig. 2.

### 2.2. Atomistic simulations

The atomistic modelling studies were carried out using the GULP software [22]. This simulation method [22,23] is based on the Born model for ionic solids, where the ion charges de-