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Mixed conductivity, thermal expansion and defect chemistry of A-site deficient $LaNi_{0.5}Ti_{0.5}O_{3-\delta}$

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Abstract

This work is focused on the analysis of defect chemistry and partial electronic and oxygen ionic conductivities of A-site deficient $La_{1-x}Ni_{0.5}Ti_{0.5}O_{3-\delta}$ ($x = 0.05$ and 0.10). The orthorhombic-to-rhombohedral phase transition was monitored by means of dilatometry and high-temperature X-ray diffractometry. The average thermal expansion coefficients vary in the range $(8.5–13.0) \times 10^{-6}\,K^{-1}$, increasing with temperature and A-site deficiency. The ion transference numbers determined by the Faradaic efficiency measurements are lower than 0.1% at 900–975 °C in air. Activation energies of the oxygen ionic conductivity at 897–977 °C are 430 and 220 kJ/mol for $x = 0.05$ and 0.10, respectively. Atomistic simulation demonstrated high stability of ternary defect clusters formed by the vacant sites in the A-sublattice, oxygen vacancies and Ni^{3+} cations, which leads to a very low level of mixed conductivity.

Keywords: Defects; Thermal expansion; Ionic conductivity; Perovskites; Membranes; Transition metal oxides

1. Introduction

Nickel-containing mixed oxygen-ionic and electronic conductors with perovskite-like structure are of interest as materials of oxygen-permeable ceramic membranes and as catalyst precursors for natural gas conversion processes.[1,2] Perovskite-type $LaNiO_{3-\delta}$ possesses a low thermodynamic stability and decomposes on heating or reducing oxygen partial pressure with formation of nickel oxide and Ruddlesden-Popper $La_{1+n}Ni_nO_{3n+1}$ phases. Co-existence of Ni and perovskite-type structure results in high catalytic activity of the system due to interaction with metal and oxidation of carbon by oxygen migrating from the lattice.[2] To some extent, stability of perovskite structure can be improved by the extensive substitution of nickel with other transition metal cations having lower reducibility (Cr, Mn, Ti, etc.).[3]

The present work was focused on the evaluation of the effect of A-site nonstoichiometry on thermal expansion, defect chemistry and transport properties of $La_{1-x}Ni_{0.5}Ti_{0.5}O_{3-\delta}$ ($x = 0.05$ and 0.1). In the parent compound, $LaNi_{0.5}Ti_{0.5}O_{3-\delta}$, all Ni cations are divalent and the electronic transport occurs presumably via hopping of p-type charge carriers.[4] Introducing A-site deficiency is expected to result in higher concentration of the oxygen vacancies and/or holes. The information on the behavior of such defects in the A-site nonstoichiometric compounds is, however, scarce and contradictory. The oxygen ionic transport may increase with A-site deficiency due to the increase of the oxygen vacancy concentration (according to the neutrality conditions) and due to random distribution of the vacant sites in the cation sub-lattice suppressing ordering in the oxygen sub-lattice.[5,6] On another hand, local structural distortions and association of the oxygen and cation vacancies can result in deterioration of transport properties of ceramics.[7] In the present work, atomistic computer simulations were carried out in order to clarify the defect interaction mechanisms.

2. Experimental

Powders of $La_{1-x}Ni_{0.5}Ti_{0.5}O_{3-\delta}$ ($x = 0.05$ and 0.10) were synthesized employing conventional solid state reaction technique. High-purity $La(NO_3)_3{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$ and TiO_2 were used as raw materials. The solid-state reactions were conducted in air at 1000–1100 °C for 6 h with multiple intervening grinding steps. Dense samples were uniaxially pressed and sintered at 1520–1540 °C in air for 15 h with slow cooling. Microstructure and phase composition of ceramic samples were investigated using scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis. Structural parameters were

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Table 1
Properties of $La_{1-x}Ni_{0.5}Ti_{0.5}O_{3-\delta}$ ceramics

Composition	Density ($g\,cm^{-3}$)	Unit cell parameters	Average TEC	
			T (°C)	$\bar{\alpha}$ ($\times 10^{-6}\,K^{-1}$)
$La_{0.95}Ni_{0.5}Ti_{0.5}O_{3-\delta}$	5.94	$a = 5.5491 \pm 0.0004$ Å	17–527	8.55 ± 0.02
		$b = 5.5503 \pm 0.0004$ Å	527–927	9.99 ± 0.01
		$c = 7.8386 \pm 0.0005$ Å	1027–1227	11.96 ± 0.01
		$V = 241.423 \pm 0.031$ Å^3		
$La_{0.90}Ni_{0.5}Ti_{0.5}O_{3-\delta}$	6.18	$a = 5.5487 \pm 0.0002$ Å	27–527	9.30 ± 0.02
		$b = 5.5473 \pm 0.0002$ Å	527–827	10.00 ± 0.01
		$c = 7.8374 \pm 0.0002$ Å	927–1097	13.00 ± 0.01
		$V = 241.207 \pm 0.007$ Å^3		

	Total conductivity		Oxygen-ionic conductivity	
	T (°C)	E_a ($kJ\,mol^{-1}$)	T (°C)	E_a ($kJ\,mol^{-1}$)
$La_{0.95}Ni_{0.5}Ti_{0.5}O_{3-\delta}$	507–1017	89 ± 1	897–977	426 ± 5
$La_{0.90}Ni_{0.5}Ti_{0.5}O_{3-\delta}$	547–897	90 ± 1	897–977	222 ± 4

refined using the GSAS software.[8] Thermal expansion was studied by means of dilatometry at a heating rate of −270 °C/min. The oxygen nonstoichiometry variations were determined by thermogravimetric analysis (TGA), as described in.[9] Characterization of transport properties included measurements of the total conductivity (four-probe DC) and oxygen transference numbers (Faradaic efficiency method[10]). The GULP software[11] was used to perform the atomistic modeling of the structure. Detailed description of the method, successfully used earlier for atomistic computer simulation and analysis of experimental $p(O_2)$-T-δ diagrams of perovskite-type $La_{0.3}Sr_{0.7}Fe(M)O_{3-\delta}$ and $SrFe(M)O_{3-\delta}$ (M = Al and Ga), can be found elsewhere.[12]

3. Results and discussion

SEM analysis of prepared ceramics revealed no open porosity, cracks or any traces of liquid phase appearance during sintering. Room-temperature XRD analysis of $La_{0.95}Ni_{0.5}Ti_{0.5}O_{3-\delta}$ ceramics showed formation of single-phase material with orthorhombically distorted perovskite-type structure (space group *Pbnm*), in agreement with data on the parent composition.[4] The occupancy of the cation sites was calculated by the Rietveld refinement and is found to be very close to nominal; no indication of B-site ordering was revealed. The increase of A-site deficiency up to 10% resulted in the segregation of approx. 2 wt.% of NiO. The lattice parameters are listed in Table 1. Introducing A-site deficiency results in lattice expansion compared to parent compound, $LaNi_{0.5}Ti_{0.5}O_{3-\delta}$ ($a = 5.5171$ Å, $b = 5.5501$ Å, and $c = 7.8562$ Å),[4] as expected taking into account the higher anion repulsion in A-site deficient structure.

Fig. 1 shows the dilatomertic curves of $La_{1-x}Ni_{0.5}Ti_{0.5}O_{3-\delta}$ ($x = 0.05$ and 0.10); average thermal expansion coefficients (TECs) are given in Table 1. Increasing of the A-site deficiency leads to moderate increase of the TECs values. Thermal expansion is linear, with the exception of anomaly at approximately 977 and 887 °C for $La_{0.95}Ni_{0.5}Ti_{0.5}O_{3-\delta}$ and $La_{0.90}Ni_{0.5}Ti_{0.5}O_{3-\delta}$, respectively (Fig. 1). This effect is associated with the orthorhombic-to-rhombohedral phase transition on heating observed by high-temperature XRD analysis.

The average oxygen nonstoichiometry (δ) and fraction of Ni^{3+} cations ($[Ni^{3+}]/[Ni]_{total}$), calculated from TGA results, were found essentially temperature-independent in the entire temperature range studied (25–950 °C), and are equal to 0.04 and 0.13 for $La_{0.95}Ni_{0.5}Ti_{0.5}O_{3-\delta}$ and 0.11 and 0.14 for $La_{0.90}Ni_{0.5}Ti_{0.5}O_{3-\delta}$, respectively. Combining the results of TGA and Rietveld refinement, chemical formula for the latter material can be written as $La_{0.950}Ni^{2+}_{0.396}Ni^{3+}_{0.076}Ti_{0.528}O_{2.991}$.

The total conductivity of $La_{0.95}Ni_{0.5}Ti_{0.5}O_{3-\delta}$ in air exhibits a linear Arrhenius behavior in the entire temperature range, as illustrated in Fig. 2. Such dependence is rather atypical for nickel-containing perovskite materials.[13,14] In the most cases, the total conductivity of Ni-substituted perovskites decreases with increasing temperature due to progressive oxygen losses from the crystal lattice; in particular, $LaNi_{1-x}Ti_xO_{3-\delta}$ ($x < 0.4$) and $LaNi_{0.5}M_{0.5}O_{3-\delta}$ (M = Ga, Fe, and Co) ceramics exhibit a transition to pseudo-metallic behavior on heating above 327–527 °C.[4,13,14] Obviously, the difference in the conductivity behavior is associated with the temperature-independent oxygen nonstoichiometry of $La_{1-x}Ni_{0.5}Ti_{0.5}O_{3-\delta}$, as mentioned above.

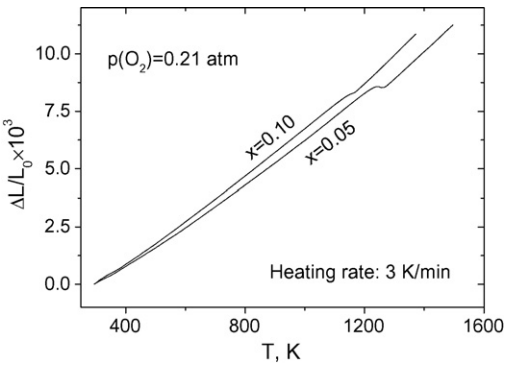

Fig. 1. Dilatomertic curves of $La_{1-x}Ni_{0.5}Ti_{0.5}O_{3-\delta}$ ceramics in air.

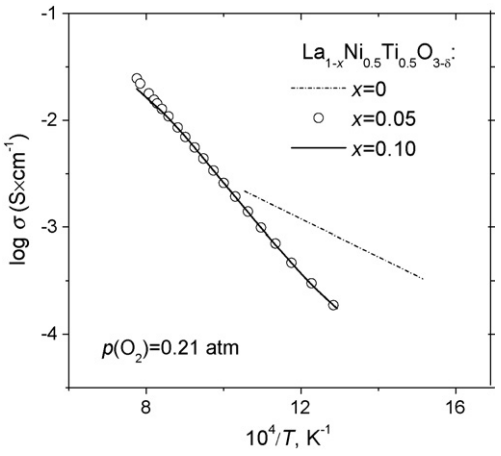

Fig. 2. Total conductivity of $La_{1-x}Ni_{0.5}Ti_{0.5}O_{3-\delta}$ ceramics in air. The data on $LaNi_{0.5}Ti_{0.5}O_{3-\delta}$[4] are shown for comparison.

An increase of the A-site deficiency (10% of vacancies in the nominal composition) promotes oxygen losses and results in a slight deviation from the Arrhenius plot at temperatures above 877 °C.

The total conductivity of both studied compositions is predominantly electronic; the oxygen ion transference numbers (t_O) in air are lower than 0.001. At 727 °C, the total conductivity of cation-deficient materials is similar to that of $LaNi_{0.5}Ti_{0.5}O_{3-\delta}$ (Fig. 2), but is characterized with significantly higher activation energy (E_a). Furthermore, the E_a values of $La_{1-x}Ni_{0.5}Ti_{0.5}O_{3-\delta}$ (Table 1) are higher than expected for a small-polaron mechanism. This may indicate either strong trapping of electronic charge carriers or a broadband conduction mechanism.

The oxygen ionic conductivities (σ_O), calculated from the results of Faradaic efficiency and total conductivity measurements, are shown in Fig. 3. For comparison, the data on $Gd_2Sn_2O_7$[15] and $(Sm_{0.9}Sr_{0.1})_2Ti_2O_7$[16] pyrochlores are also presented. Two latter materials are characterized with a very low concentration of ionic charge carriers formed due to intrinsic thermal disorder.[15,16] For $La_{1-x}Ni_{0.5}Ti_{0.5}O_{3-\delta}$, the oxygen deficiency results from the A-site vacancies charge compensation and is low, but still significant. Nevertheless, the level of ionic transport in $La_{1-x}Ni_{0.5}Ti_{0.5}O_{3-\delta}$ is lower compared

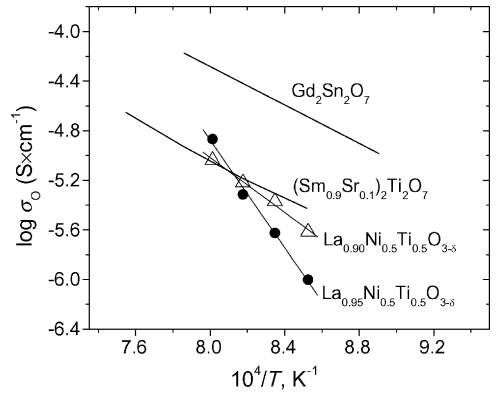

Fig. 3. Temperature dependencies of the oxygen-ionic conductivity of $La_{1-x}Ni_{0.5}Ti_{0.5}O_{3-\delta}$ ceramics in air. The data on $Gd_2Sn_2O_7$[15] and $(Sm_{0.9}Sr_{0.1})_2Ti_2O_7$[16] pyrochlores are shown for comparison.

to $Gd_2Sn_2O_7$ but compatible to $(Sm_{0.9}Sr_{0.1})_2Ti_2O_7$. One may conclude, therefore, that most oxygen vacancies in the lattice of lanthanum nickelate–titanate are in a trapped state, presumably due to point-defect cluster formation, and do not participate in ionic transport.

In agreement with the results of electronic and ionic transport characterization, the results of the static lattice simulation showed a strong tendency toward localization of the oxygen vacancies near vacant A-site. In most cases, the energetic effects of $V'''_A \cdots V''_O$ pair cluster formation vary in the range from −183 to −76 kJ/mol. The localization of electron holes at the nickel cations surrounding A-site vacancy is also energetically favorable; energy of the cluster formation varies in the narrow range −22 to −35 kJ/mol. For the ternary $V'''_A \ldots V''_O \ldots Ni^X_B$ clusters it was observed that their average energy of formation is substantially higher than the sum of corresponding pair-cluster energies and lies in the range −49 to −345 kJ/mol, suggesting a maximum stability of these elements in $La_{0.95}Ni_{0.5}Ti_{0.5}O_{3-\delta}$. Most likely, formation of such ternary clusters is responsible for the very low ionic and electronic conductivities (Figs. 2 and 3).

4. Conclusions

The charge compensation of A-site deficiency in $La_{1-x}Ni_{0.5}Ti_{0.5}O_{3-\delta}$ ($x = 0.05$ and 0.10) occurs via a mixed mechanism involving formation of Ni^{3+} cations and oxygen vacancies. The oxygen content variations with temperature are very low, indicating a stabilization of trivalent nickel in the lattice of A-site deficient lanthanum nickelate-titanate. $La_{1-x}Ni_{0.5}Ti_{0.5}O_{3-\delta}$ ceramics exhibit moderate thermal expansion with TECs values in the range $(8.6–9.3) \times 10^{-6}\,K^{-1}$ at 27–527 °C and $(12.0–13.0) \times 10^{-6}\,K^{-1}$ at 927–1227 °C. Dilatometric and high-temperature XRD studies revealed an orthorhombic-to-rhombohedral phase transition at 977 °C for $La_{0.95}Ni_{0.5}Ti_{0.5}O_{3-\delta}$ and 887 °C for $La_{0.90}Ni_{0.5}Ti_{0.5}O_{3-\delta}$.

The total conductivity of $La_{1-x}Ni_{0.5}Ti_{0.5}O_{3-\delta}$ is predominantly electronic with oxygen ionic contribution lower than 0.1% at 900–975 °C. The ionic conductivity of $La_{1-x}Ni_{0.5}Ti_{0.5}O_{3-\delta}$ is low and has extremely high activation energy, 430 kJ/mol ($x = 0.05$) and 222 kJ/mol ($x = 0.10$). The atomistic computer simulations showed energetic favorability of defect association, particularly the formation of ternary clusters involving lanthanum and oxygen vacancies and Ni^{3+}. This type of behavior seems responsible for the low ionic and electronic transport.

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