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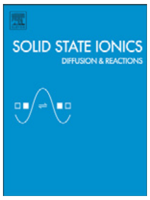

Effect of acceptor size and hole degeneracy on oxygen nonstoichiometry of $La_2NiO_{4+\delta}$

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ABSTRACT

It is conjectured that ever-hyperstoichiometric $La_2NiO_{4+\delta}$ tends to incorporate oxygen interstitials in the rocksalt layers to mitigate the tensile/compressive stress at the LaO–rocksalt/$LaNiO_3$–perovskilte layer interface due to their lattice mismatch, and the unusual positive deviation from ideal of its defect structure is due to the degeneracy pressure of charge compensating holes. In order to confirm these conjectures, oxygen nonstoichiometry (δ) has been measured, by coulometric titrometry, on the systems of $La_{1.9}A_{0.1}NiO_{3.95+\delta}$, doped with the same-valence, but different-size acceptor impurities $A = Ca^{2+}$ and Sr^{2+}, against oxygen activity across their entire stability ranges at 800°, 900°, and 1000 °C, respectively. It is found that the smaller Ca^{2+} enhances oxidation leading to larger oxygen excess over the larger Sr^{2+}, confirming the tensile stress effect on δ-increase. The positive deviation of δ and defect structure is quantitatively attributed to the hole degeneracy, confirming it to be the entire culprit for the positive deviation. Defect chemical parameters, partial molar quantities of component oxygen and phase-stability limits of $La_{1.9}A_{0.1}NiO_{3.95+\delta}$ are documented in comparison with the undoped host.

1. Introduction

Ever-hyperstoichiometric ($\delta > 0$) $La_2NiO_{4+\delta}$ is an excellent p-type electronic conductor with an oxide ionic conductivity comparable or even higher than that of stabilized zirconia [1–6]. It is, thus, considered to be a promising candidate for solid-oxide-fuel-cell cathode and oxygen separation membrane materials to name only a few.

The oxide comprises the alternating LaO–rocksalt (R) and $LaNiO_3$–perovskite layers (P). As the theoretical lattice parameter of the R-layer is smaller than that of the P-layer, it is expected that the R-layer should be subjected to a tensile stress and hence, to relieve the tensile stress, the structure tends to accommodate excess oxygen at tetrahedral interstices in the R-layers [7–9]. The presence of O_i'' has subsequently been confirmed by neutron diffraction analyses [8,9]. One may then readily envisage that the extent of oxygen nonstoichiometry may be varied by varying the interlayer stress e.g., by doping or substituting the host cation with different-size cations. It is known [4,7,10] that $Pr_2NiO_{4+\delta}$ and $Nd_2NiO_{4+\delta}$ have larger oxygen excess (δ) than $La_2NiO_{4+\delta}$ in the same thermodynamic conditions. This suggests that replacement of La^{3+} (ionic radius [11] $r = 0.1216$ nm) with the smaller size ions Pr^{3+} ($r = 0.1179$ nm) or Nd^{3+} ($r = 0.1163$ nm) has increased the tensile stress in the R-layers, thus enhancing the oxygen excess. If it is the case, the smaller one will enhance the oxidation reaction more than the larger one when doped with impurities with the same valence but with different sizes. We will confirm this expectation experimentally.

Furthermore, the defect-structure-sensitive properties, e.g., nonstoichiometry, electrical conductivity and thermopower, of this ever-hyperstoichiometric oxide always deviate positively from the ideal dilute solution behavior of the majority disorder, oxygen interstitials O_i'' and holes $h^\bullet$ [12–14]. This is quite unusual because charge-compensating defects are usually negatively deviated due to coulombic attractive interaction among them [15]. The positive deviation used to be interpreted as being due to the repulsion-induced site exclusion effect for O_i'' and $h^\bullet$, respectively [12] or due to the excess enthalpy of O_i'' [13]. Recently we have found that the positive deviation may be attributed to the hole degeneracy pressure effect [14]. We now wish to reconfirm the validity of this new interpretation by changing the defect structure of the oxide.

To these ends, we doped $La_2NiO_{4+\delta}$ with acceptor impurities of the same valence but with different sizes, Ca^{2+} ($r = 0.1180$ nm) and Sr^{2+} ($r = 0.1310$ nm), respectively, and measured oxygen nonstoichiometry on them across their entire stability ranges at elevated temperatures, expecting the nonstoichiometry to be larger for the Ca-doped. By analyzing defect-chemically the as-measured nonstoichiometries, we will confirm both the strain effect and hole degeneracy effect. The defect chemical parameters thereby and the stability limits of the doped systems are documented in comparison with those of the undoped system [14].

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2. Experimental

Different-size acceptor Ca- or Sr-doped specimens of nominal composition $La_{1.9}Ca_{0.1}NiO_{3.95+\delta}$ and $La_{1.9}Sr_{0.1}NiO_{3.95+\delta}$ were prepared from the starting powders of $La(OH)_3$ (99.9%, Aldrich, USA), $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ (99.9%, Junsei, Japan), $SrCO_3$ (99.9 %, Aldrich, USA), and $CaCO_3$ (99.995 %, Aldrich, USA) by the polyaminocarboxylate complex method [16]. Briefly, the starting powders were dissolved into deionized water together with diethylene-triamine-penta-acetic acid (H_5DTPA, 98%, Aldrich, USA) in a molar ratio of component cations (La^{3+}, Ni^{2+}, Sr^{2+} or Ca^{2+}) to H_5DTPA, 3.0/1.7. The liquid mixture was kept at ca. 90 °C sufficiently long and subsequently dried out at 100 °C to obtain a solid polyaminocarboxylate complex. The solid complex was then pulverized, calcined at 900 °C for 2 h, and pressed uniaxially under the pressure of 3 MPa, followed by a cold isostatic pressing under 200 MPa and sintering at 1350 °C in air for 4 h. All the sintered pellets were found to be 97 ± 1% dense (by an Archimedes method) with an average grain size of 2.3 ± 0.2 μm. The final compositions of the Sr-doped and Ca-doped samples were confirmed to be of Sr/Ni and Ca/Ni ratio 0.102 ± 0.002 and 0.101 ± 0.002, respectively, via induction coupled plasma analyses (ICP-AES, Optima 4300DV, USA).

Phase purity and lattice parameters of the as-sintered specimens were examined by means of X-ray powder diffractometry (Bruker D5005, Germany) employing the NIST-SRM 640d, Si powder as the standard reference material. Fig. 1 shows all the diffractograms thereby in comparison with that of the undoped [14], indicating all the specimens being phase-pure. The peak profiles were fitted and refined by using the TOPAZ software to evaluate the lattice parameters as listed in Table 1. The lattice parameters for the Ca-doped are indeed smaller than those for the Sr-doped, supporting the expectation of the former being subjected to a larger tensile stress than the latter.

Oxygen nonstoichiometry changes relative to the initial nonstoichiometry $\Delta\delta(=\delta-\delta_o)$ of $La_{1.9}A_{0.1}NiO_{3.95+\delta}$ (A = Ca, Sr) were measured at 800°, 900° and 1000 °C, respectively, by a coulometric titration technique from a titration cell with the configuration,

$$\mathrm{Pt}, a_{O_2}|La_{2-x}A_xNiO_{3.95+\delta}|\mathrm{YSZ}|a_{O_2}^{ref}, \mathrm{Pt} \qquad (I)$$

as detailed elsewhere [17].

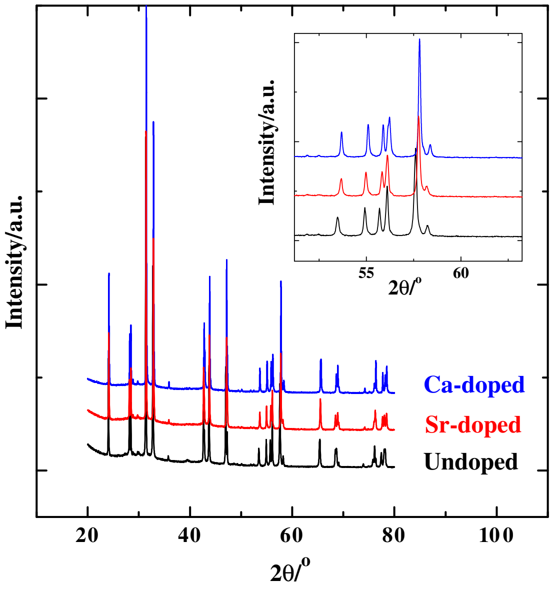

Fig. 1. (Color online). XRD patterns of $La_{1.9}Ca_{0.1}NiO_{3.95+\delta}$, and $La_{1.9}Sr_{0.1}NiO_{3.95+\delta}$ together with that of the host $La_2NiO_{4+\delta}$ [14]. Insets, the exploded view in the vicinity of 2θ = 55°.

Table 1
X-ray determined lattice parameters of $La_2NiO_{4+\delta}$, $La_{1.9}Ca_{0.1}NiO_{3.95+\delta}$, and $La_{1.9}Sr_{0.1}NiO_{3.95+\delta}$.

	a/Å	c/Å
$La_2NiO_{4+\delta}$	3.8632 ± 0.0001	12.6641 ± 0.0002
$La_{1.9}Ca_{0.1}NiO_{3.95+\delta}$	3.8507 ± 0.0001	12.6395 ± 0.0002
$La_{1.9}Sr_{0.1}NiO_{3.95+\delta}$	3.8522 ± 0.0001	12.6741 ± 0.0002

The absolute value for the nonstoichiometry was determined by thermogravimetrically measuring the overall mass loss relative to the reference state $\delta^*\left(a_{O_2}^*, T\right)$, upon decomposition of the oxide systems in H_2 atmosphere via the following reaction [12,13,18]

$$La_{2-x}A_xNiO_{4-x/2+\delta^*} \overset{H_2}{\rightarrow} (1-0.5x)La_2O_3 + xAO + Ni + \frac{(1+\delta^*)}{2}O_2 \qquad (1)$$

at 800°, 900° and 1000 °C, respectively. The reference oxygen content δ^* was previously fixed by equilibrating the specimen oxide in a fixed oxygen activity atmosphere in the range of $\log a_{O_2}^* = -4.06 \sim -3.10$ (actually in Ar atmosphere but with different oxygen activity depending on gas tanks) at each T.

3. Results and discussion

3.1. Hole degeneracy effect

Fig. 2(a) and (b) shows the oxygen nonstoichiometry (δ) variations as measured against oxygen activity a_{O_2} on the systems of $La_{1.9}Ca_{0.1}NiO_{3.95+\delta}$ and $La_{1.9}Sr_{0.1}NiO_{3.95+\delta}$, respectively, at three different temperatures. (How to determine the absolute values for δ will be described later and the values for the initial nonstoichiometry δ^* given in Table 3.) A rather flat inflection point on each δ-isotherm already indicates that a stoichiometric composition falls there and that must be the ionic one, viz., $3.95+\delta=4.00$ in the present doped cases.

It has been repeatedly observed [10,12–14] that defect structures of hyperstoichiometric La_2NiO_4-based systems deviate positively from the ideal behavior. The present results are no exception either: the value for the oxygen exponent "m" such that $\delta \propto \log a_{O_2}^m$ in Fig. 2 grows ever smaller than the ideal value as a_{O_2} increases (see below). For the undoped case, the positive deviation has been attributed entirely to the hole degeneracy [14]. It is because the quantum concentrations for the ionic structure elements, whether regular or irregular, are orders of magnitude larger than that of holes, thus the former may be regarded as ideal following the Boltzmann statistics, but the latter as nonideal following Fermi–Dirac statistics [19]. If it is the case, the same should remain true for the doped systems. We will examine if this is indeed so.

As acceptor-doping normally enhances generation of holes and oxygen vacancies while suppressing electrons, one may, thus, consider the structure elements (SE) (in Kroger–Vink notations):

$$\left\{O_O^x, V_i^x; O_i^{''}, V_O^{\bullet\bullet}, h^{\bullet}, A'_{La}\right\}$$

for the present acceptor-doped systems $La_{2-x}A_xNiO_{4-x/2+\delta}$ (A = Ca, Sr), referring to the defect structure of the host $La_2NiO_{4+\delta}$ [13,14]. The defect structure of the doped should then be uniquely determined by the external and internal equilibria subjected to mass-, charge- and site-conservation constraints as:

$$\frac{1}{2}O_{2(g)} + V_i^x \rightleftharpoons O_i^{''} + 2h^{\bullet}: \quad K_{Ox} = \frac{\left[O_i^{''}\right](\gamma_h p/N_V)^2}{a_{O_2}^{1/2}\left[V_i^x\right]} \qquad (2)$$

$$O_O^x + V_i^x \rightleftharpoons V_O^{\bullet\bullet} + O_i^{''}: \quad K_F = \frac{\left[V_O^{\bullet\bullet}\right]\left[O^{''}\right]}{\left[O_O^x\right]\left[V_i^x\right]} \qquad (3)$$