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The oxygen deficient Ruddlesden–Popper $La_3Ni_2O_{7-\delta}$ ($\delta = 0.65$) phase: Structure and properties

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Abstract

$La_3Ni_2O_{7-\delta}$ ($\delta = 0.65$) was synthesized by hydrogen reduction of the parent $La_3Ni_2O_7$ Ruddlesden–Popper nickelate. The crystal structure of $La_3Ni_2O_{6.35}$ (space group: *I4/mmm*, $a = 3.8742$ (1) Å and $c = 20.055$ (1) Å) has been determined from powder neutron diffraction data by the Rietveld method for the first time. The oxygen vacancies are located in the LaO_x planes between two of the NiO_2 layers. Removal of these oxygen atoms from the parent phase results in a significant (∼0.4 Å) shrinkage of the perovskite block along *c*-direction and splitting of the Ni position. The major part of Ni cations is surrounded by five oxygen atoms forming square pyramids, while the rest are coordinated to six octahedrally arranged oxygen atoms. Over the 170–400 K temperature range, the conductivity of $La_3Ni_2O_{6.35}$ follows Mott's variable range hopping model modified for a 2D case.

Keywords: A. Oxides; B. Chemical synthesis; C. Neutron scattering; C. Thermogravimetric analysis; D. Crystal structure

1. Introduction

There has been an interest in layered mixed valence nickelates due to their crystal and electronic structural similarity to superconducting cuprates. Especially interesting are the Ni^+/Ni^{2+} phases, with the same electronic configuration ($3d^9/3d^8$) as the Cu^{2+}/Cu^{3+} complex oxides that show high temperature superconductivity. Phases, of the Ruddlesden–Popper (RP) series, $A_{(n+1)}B_nO_{3n+1-\delta}$, containing Ni^+/Ni^{2+} cations have been investigated by several groups [1–3]. Several phases, for example $LaSrNiO_{3.1}$ [1], $La_3Ni_2O_{6.35}$ [2] and $La_4Ni_3O_8$ [3], are oxygen deficient and were prepared by a low temperature topotactic reduction of parent nickelates. Structural data, which are crucial for properties understanding, have been reported only for RP phases with $n = 1$, $La_2NiO_{4-\sigma}$ and $LaSrNiO_{3.1}$ [1], and $n = 3$, $La_4Ni_3O_8$ [3]. For $La_3Ni_2O_{6.35}$, the most reduced phase of the $n = 2$ homologue known up to now, neither structural data nor a facile preparation method are reported.

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A controlled reduction of $La_3Ni_2O_7$ in a thermogravimetric instrument was employed to isolate the $La_3Ni_2O_{6.35}$ phase [2,3]. It was found that the *c* unit cell parameter of the tetragonal reduced phase is approximately 0.46 Å smaller than that for the parent rhombohedral RP $La_3Ni_2O_7$ phase [2]. However, detailed structural information for the reduced phase, reflecting coordination of Ni cations, was missing. In this article, we present syntheses and a crystal structure study by powder neutron diffraction of the oxygen deficient RP phase, $La_3Ni_2O_{6.35}$. Magnetic and electrical properties are also briefly reported.

2. Experimental

$La_3Ni_2O_7$ was synthesized by the sol–gel Pechini technique [4] with La_2O_3 and $Ni(OH)_2$ as source of metals. La_2O_3 was prepared by decomposition of $La(NO_3)_3{\cdot}6H_2O$ (Alfa, 99.9%) at 750 °C for 2 h in air. The precise composition of $Ni(OH)_2$ (Acros, 99.9%) was determined by TGA. Stoichiometric amounts of La_2O_3 and $Ni(OH)_2$ were dissolved in a solution of citric acid with several drops of concentrated nitric acid. When all the reactants had dissolved, an appropriate amount of ethylene glycol was added. The solution was stirred with moderate heating on a hot plate, resulting in the formation of a gel. The gel was dried at 300 °C and then heated at 600 °C overnight to remove organic matter. The resultant powder was pressed into pellets and annealed in oxygen flow at 1250 °C for 100 h with two intermittent grindings. Finally, treatment at 500 °C for 5 h in oxygen flow was performed as a final step to achieve oxygen stoichiometry. $La_3Ni_2O_{6.35}$ was prepared by the reduction of the $La_3Ni_2O_7$ powder in flowing 10% H_2 in Ar at 400 °C for 12 h in a tube furnace.

Powder neutron diffraction (PND) data were collected on 2.5 g sample at 300 K on the NPDF time-of-flight neutron diffractometer at the Lujan Neutron Science Center of the Los Alamos National Laboratory. Two-phase Rietveld refinement of the obtained data [5] was performed with GSAS [6] program with EXPGUI [7] interface. Vanadium was introduced as a second phase to the refinement, since small peaks from the vanadium sample container ware observed in the PND pattern. In the final runs, the scale factor, unit-cell parameters, peak profile parameters, background coefficients, absorption coefficient, atomic coordinates, isotropic atomic displacement parameters and fractional occupancy for oxygen atoms were simultaneously refined. The quality of agreement between the observed and calculated profiles was monitored by a set of conventional *R* factors, as described by Young [8].

The powder X-ray diffraction (PXD) patterns were recorded at room temperature over an angular range $5^\circ \leq 2\theta \leq 90^\circ$ with a step of 0.02° (2θ) on a Bruker D8 Advance diffractometer (Bragg-Brentano geometry, Cu Kα radiation). Thermogravimetric analysis (TGA) was performed with a TA Instrument 2050 thermal analyzer. Samples were ramped at 2 °C/min to a final temperature of 900 °C. The dc magnetic susceptibility measurements were carried out on powder samples with a commercial SQUID magnetometer (Quantum Design, MPMS-*XL*). All measurements were performed by warming the samples in the applied field after cooling to 5 K in zero field (ZFC, zero field cooling) and by cooling the samples in the applied measuring field of 0.01, 0.1 or 1 T (FC, field cooling). Resistivity measurements were performed on the same machine with Keithley equipment and with a standard four-probe technique.

3. Results and discussion

The purity of the parent $La_3Ni_2O_7$ phase was confirmed by the indexing of all of the observed reflections of the PXD pattern. The refined unit cell parameters of the orthorhombic $La_3Ni_2O_7$ phase, $a = 5.395$ (1) Å, $b = 5.448$ (1) Å and $c = 20.517$ (3) Å, are in good agreement with previously reported data [2,9,10]. The oxygen stoichiometry of this phase was determined as $La_3Ni_2O_{7.04}$ by TGA in a 10% H_2/Ar flow (Fig. 1). The reduction of $La_3Ni_2O_7$ during the TGA measurement occurs in two steps with a final formation of a mixture of La_2O_3 and Ni (confirmed by PXD). A plateau in the TGA curve corresponds to the stabilization of oxygen deficient RP $La_3Ni_2O_{6.35}$ phase that was already noted in the literature [1,2]. However, attempts to prepare a large (several grams) sample of $La_3Ni_2O_{6.35}$ by the reduction of $La_3Ni_2O_7$ at 450 °C for 12 h in a 10% H_2/Ar flow led to complete decomposition, unlike the controlled reduction in TGA [2].

A pure bulk 2.5 g powder sample of $La_3Ni_2O_{6.35}$ was prepared by annealing of the $La_3Ni_2O_7$ powder at 400 °C for 12 h in a tubular furnace in a 10% H_2/Ar flow. It should be noted, that $La_3Ni_2O_{6.35}$ is metastable at the preparation condition. Namely, prolonged (60 h) annealing at the above specified conditions resulted in admixture of La_2O_3 and Ni. The oxygen stoichiometry of the sample was derived as $La_3Ni_2O_{6.38(2)}$ by TGA, which is in the range of the