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$La_3Ni_2O_6$: A New Double T′-type Nickelate with Infinite $Ni^{1+/2+}O_2$ Layers

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The Ni^{1+}/Ni^{2+} mixed-valent nickelates received much attention due to the same ($3d^9/3d^8$) electronic configuration of Ni^{1+}/Ni^{2+} as that of Cu^{2+}/Cu^{3+} in the high-temperature superconductors. The common structural feature of the superconducting cuprates is the presence of CuO_2 layers formed from corner-sharing square planar CuO_4, square pyramidal CuO_5, or octahedral CuO_6 units. In all these environments, Cu^{3+} (d^8) is in a low-spin configuration, while a square-planar coordination of oxygen atoms is needed to force Ni^{2+} in the low-spin configuration.[1] Therefore Ni^{1+}/Ni^{2+} compounds containing NiO_2 infinite layers are of special interest.

The only known examples of such nickelates are $RNiO_2$ and $R_4Ni_3O_8$ (R = La, Nd, and Pr).[2−6] These phases, except $NdNiO_2$, were synthesized by hydrogen reduction of the parent perovskite $LaNiO_3$ or $n = 3$ Ruddlesden−Popper (RP) $La_4Ni_3O_{10}$ phases at low temperature. Numerous attempts to prepare $La_3Ni_2O_6$ in a similar way were unsuccessful, leading to $La_3Ni_2O_{6.4}$ as the most reduced phase.[3,7,8] Recently, metal hydrides were introduced as powerful low-temperature agents for topotactic oxygen deintercalation.[5,9] In this communication, we report the low-temperature synthesis and structure of a new Ni^{1+}/Ni^{2+} nickelate, $La_3Ni_2O_6$, with infinite NiO_2 layers. Moreover, the phase crystallizes in a unique double T′-type structure, which has not been observed earlier.

$La_3Ni_2O_6$ was prepared by the reaction of $La_3Ni_2O_7$ with calcium hydride (CaH_2) at 350 °C in a sealed Pyrex ampule for 4 days. At higher temperatures (above 375 °C), a complete decomposition to La_2O_3 and Ni metal was observed. Thus, the reduced nickelate phase is metastable with respect to reduction to elemental nickel. Most of the CaO formed as a byproduct during the reaction was removed by washing in a 0.1 M solution of NH_4Cl in degassed methanol under argon. After being filtered, the black $La_3Ni_2O_6$ was dried under vacuum. The X-ray diffraction pattern of the reduced nickelate can be indexed in the tetragonal system with lattice constants of $a \sim 3.968$ Å and $c \sim 19.32$ Å. It should be noted that this is the shortest c-parameter in $La_3Ni_2O_{7-x}$ nickelates; for comparison, $c \sim 20.52$ Å for $La_3Ni_2O_7$ and 20.06 Å for $La_3Ni_2O_{6.4}$.[7]

Table 1. Crystallographic Data for $La_3Ni_2O_6$ [a]

atom	Wyckoff position	*x*	*y*	*z*	10^2 *U* (Å)	occ.
La1	2b	0	0	0.5	0.50(3)	1
La2	4e	0	0	0.3170(1)	0.72(2)	1
Ni	4e	0	0	0.0826(1)	0.69(1)	1
O1	4d	0	0.5	0.25	1.04(3)	1
O2	8g	0	0.5	0.0838(1)	0.97(2)	1

[a] Space group: *I*4/*mmm* (No. 139); $a = 3.9686(1)$ Å, $c = 19.3154(6)$ Å; $\chi^2 = 2.3\%$, $wRp = 3.2\%$, $Rp = 1.3\%$.

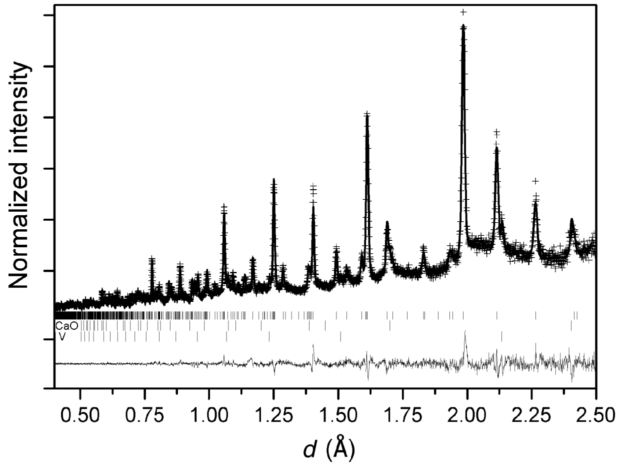

Figure 1. Rietveld refinement profiles for the PND data of $La_3Ni_2O_6$: observed intensities (crosses), calculated pattern (solid line), difference curve (bottom solid line), and Bragg positions (tick marks).

The crystal structure of $La_3Ni_2O_6$ was solved by the analysis of the powder neutron diffraction (PND) data collected at 300 K on the NPDF time-of-flight diffractometer at the Lujan Jr. Neutron Science Center of the Los Alamos National Laboratory. Rietveld refinement[10] of the PND data was performed with the GSAS[11,12] program. CaO and vanadium were added into the refinement since the peaks of ∼10% of unwashed CaO and ∼1% of vanadium from the sample container were observed in the PND pattern. The atomic coordinates of $La_3Ni_2O_{6.4}$ (space group *I*4/*mmm*)[13] were used as the starting model of the Rietveld refinement. $La_3Ni_2O_{6.4}$ is the most reduced $n = 2$ RP lanthanum nickelate known, and the oxygen vacancies are located solely in the $LaO_{0.4}$ planes between two of the NiO_2 layers. This refinement converged with bad fit parameters $\chi^2 = 12.7$. An attempt to introduce cation splitting due to oxygen vacancies[13] did not result in significant improvement of the profile fitting: $\chi^2 = 10.6$. A good fit of the pattern ($\chi^2 = 2.3$) was achieved only when the oxygen atom in the "rock salt" part of the structure was shifted into the position typical for the "fluorite" arrangement. It should be noted that a structural transformation of a rock salt block to a fluorite arrangement is known for Ln_2CuO_4 (Ln = lanthanides) as a T to T′ transition, where a stable structural type depends on a specific lanthanide element. The occupancies of the oxygen atom sites in the NiO_2 layers and in the fluorite block were set to unity since no statistically significant deviations were found

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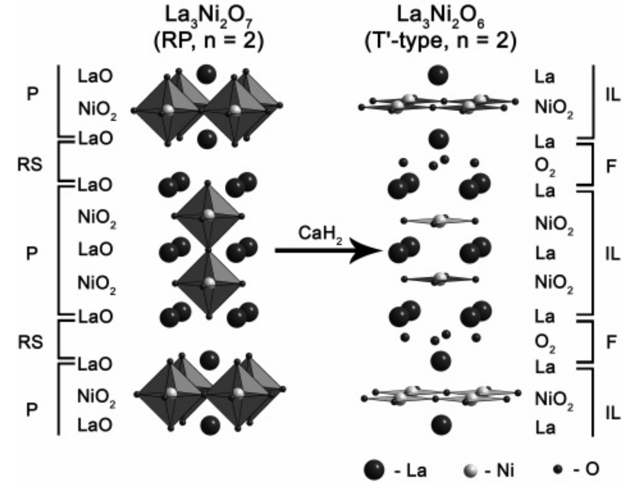

Figure 2. Structure models of $La_3Ni_2O_7$ and $La_3Ni_2O_6$ with denoted layers and structural blocks: P, perovskite; RS, rock salt; IL, infinite layer; F, fluorite.

by the refinement. The refined structural data for $La_3Ni_2O_6$ and goodness of fit parameters are listed in Table 1, and the experimental, calculated, and difference profiles are shown in Figure 1.

The structure of $La_3Ni_2O_6$ can be obtained by complete removal of the oxygen atoms from the LaO layers in the perovskite blocks of $La_3Ni_2O_7$ and rearrangement of oxygen atoms in $(LaO)_2$ blocks. A similar type of transformation was observed by Lacorre during the preparation of $Ln_4Ni_3O_8$ (Ln = La, Nd, Pr).[3] Such structural transformation leads to exclusively square-planar nickel coordination and to the appearance of infinite NiO_2 planes. Thus, the crystal structure of $La_3Ni_2O_6$ can be described as intergrowth of fluorite ($La/O_2/La$) blocks and double infinite layer ($La/NiO_2/La/NiO_2/La$) blocks. Figure 2 shows the structural relationship between the $La_3Ni_2O_6$ and $La_3Ni_2O_7$ RP phase.

Interestingly, all the known Ni^{1+}/Ni^{2+} compounds with infinite NiO_2 layers, namely, $RNiO_2$, $La_3Ni_2O_6$, and $R_4Ni_3O_8$ (R = La, Nd, Pr), can be considered as a T′-type homologous series $Ln_{n+1}Ni_nO_{2n+2}$. All these phases were prepared by "soft chemistry" methods, which emphasize the importance of synthesis in the design of inorganic materials. $La_3Ni_2O_6$ is the $n = 2$ member of this series with a crystal structure, which was not reported before.

Apparently, the Jahn−Teller distortion of the Ni^{1+} (d^9) coordination environment, preference for the Ni^{2+} (d^8) cation for square-planar coordination, and the increasing average ionic radii of the Ni cations during the reduction are driving the T to T′ structure transformation during the preparation of the $n = 2$ and 3 members of this series. The reductive structural transformation is reversible, and slow oxidation of $La_3Ni_2O_6$ in air at room temperatures results in the $La_3Ni_2O_{7-x}$ RP phase.

To confirm the systematic evolution of the Ni oxidation states in lanthanum nickelates, Ni K-edge X-ray absorption spectroscopy (XAS) measurements (see Figure 3) were performed at X19-A at the Brookhaven National Synchrotron Light Source. The Ni K-edge can be seen to exhibit a systematic chemical shift down in energy, with increasing O deficiency in the $La_3Ni_2O_{7-x}$ materials, clearly confirming the decreasing Ni valence. The $La_3Ni_2O_6$ spectrum, in particular, develops a dramatically down-shifted shoulder, in the 0−5 eV range, which is similar to the XAS shoulder, which develops with increasing Cu^{1+} admixture in the cuprates.[14,15] In the cuprates with structures where there has been apical O removal, such a strong low-energy feature is associated with $4p_\pi$ states along the missing O direction with d^{10} and $d^{10}\underline{L}$ character (where the L denotes an O ligand hole). By analogy, this Ni K-feature is associated with $4p_\pi$ d^{10} and $d^{10}\underline{L}$ states directed along the missing O sites in this O-deficient compound. Thus the Ni K-XAS results support both the expected Ni^{1+} admixture and the missing O coordination as demanded by the structure determination.

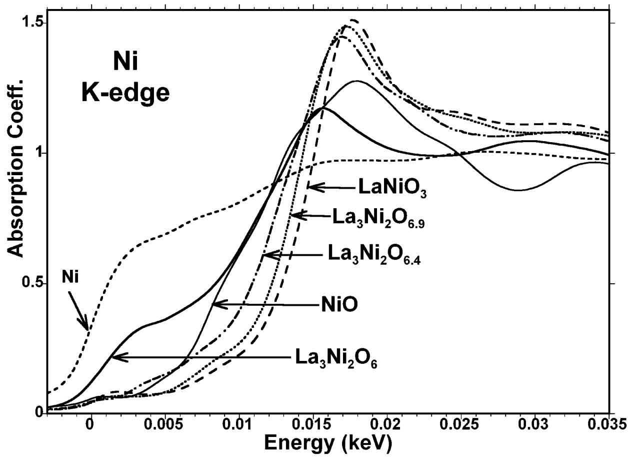

Figure 3. X-ray absorption spectra for $La_3Ni_2O_6$ and for standards.

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Supporting Information Available: Details of experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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