**La$_3$Ni$_2$O$_6$: A New Double T'-type Nickelate with Infinite Ni$^{1+/2+}$/O$_2$ Layers**

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The Ni$^{1+/2+}$ mixed-valent nickelates received much attention due to the same (3$d^9$/3$d^8$) electronic configuration of Ni$^{1+/2+}$ 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$^{2+}$ (d$^9$) 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. Therefore Ni$^{1+/2+}$/Ni$^{2+}$ compounds containing NiO$_2$ infinite layers are of special interest.

The only known examples of such nickelates are RNiO$_2$ and R$_3$Ni$_2$O$_5$ (R = La, Nd, and Pr). These phases, except NdNiO$_2$, were synthesized by hydrogen reduction of the parent perovskite LaNiO$_3$ or $n = 3$ Ruddlesden–Popper (RP) La$_{3}$Ni$_{2}$O$_{10}$ phases at low temperature. Numerous attempts to prepare La$_3$Ni$_2$O$_6$ in a similar way were unsuccessful, leading to La$_3$Ni$_2$O$_{6.4}$ as the most reduced phase. Recently, metal hydrides were introduced as powerful low-temperature agents for topoactic oxygen deintercalation. In this communication, we report the low-temperature synthesis and structure of a new Ni$^{1+/2+}$/Ni$^{2+}$ nickelate, La$_3$Ni$_2$O$_6$, with infinite NiO$_2$ layers. Moreover, the phase crystallizes in a unique double T'-type structure, which has not been observed earlier.

La$_3$Ni$_2$O$_6$ was prepared by the reaction of La$_3$Ni$_2$O$_7$ 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$_2$O$_3$ 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$_4$Cl in degassed methanol under argon. After being filtered, the black La$_3$Ni$_2$O$_6$ was dried under vacuum. The X-ray diffraction pattern of the reduced nickelate can be indexed in the tetragonal system with lattice constants of $a = 3.9686$ Å and $c = 19.3154(6)$ Å; $\chi^2 = 2.3\%$, $wR_p = 3.2\%$, $R_p = 1.3\%$.

The crystal structure of La$_3$Ni$_2$O$_6$ 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 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

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* Table 1. Crystallographic Data for La$_3$Ni$_2$O$_6$.

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<th>atom</th>
<th>Wyckoff position</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$10^4 \frac{U}{\AA^2}$</th>
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<td>0.50(3)</td>
<td>1</td>
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<tr>
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<td>0</td>
<td>0.3170(1)</td>
<td>0.72(2)</td>
<td>1</td>
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<tr>
<td>Ni</td>
<td>4e</td>
<td>0</td>
<td>0.0826(1)</td>
<td>0.69(1)</td>
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<tr>
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<td>0.0838(1)</td>
<td>0.97(2)</td>
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</tbody>
</table>

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* Figure 1. Rietveld refinement profiles for the PND data of La$_3$Ni$_2$O$_6$: observed intensities (crosses), calculated pattern (solid line), difference curve (bottom solid line), and Bragg positions (tick marks).

the sample container were observed in the PND pattern. The atomic coordinates of La$_3$Ni$_2$O$_{6.4}$ (space group $I4/mmm$) were used as the starting model of the Rietveld refinement. La$_3$Ni$_2$O$_{6.4}$ 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 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 La$_3$Cu$_2$O$_7$ (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.
by the refinement. The refined structural data for \( \text{La}_3\text{Ni}_2\text{O}_6 \) 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 \( \text{La}_3\text{Ni}_2\text{O}_6 \) can be obtained by complete removal of the oxygen atoms from the \( \text{La}_2\text{O}_2 \) layers in the perovskite blocks of \( \text{La}_2\text{Ni}_2\text{O}_5 \) and rearrangement of oxygen atoms in \( \text{La}_2\text{O}_3 \) blocks. A similar type of transformation was observed by Lacorre during the preparation of \( \text{Ln}_4\text{Ni}_3\text{O}_8 \) (\( \text{Ln} = \text{La}, \text{Nd}, \text{Pr} \)). Such structural transformation leads to exclusively square-planar nickel coordination and to the appearance of infinite \( \text{NiO}_2 \) planes. Thus, the crystal structure of \( \text{La}_3\text{Ni}_2\text{O}_6 \) can be described as intergrowth of fluorite \( (\text{La}/\text{O}_2/\text{La}) \) blocks and double infinite layer \( (\text{La}/\text{NiO}_2/\text{La}/\text{NiO}_2/\text{La}) \) blocks. Figure 2 shows the structural relationship between the \( \text{La}_3\text{Ni}_2\text{O}_6 \) and \( \text{La}_3\text{Ni}_2\text{O}_7 \) RP phase.

Interestingly, all the known Ni\(^{1+}/\text{Ni}^{2+} \) compounds with infinite \( \text{NiO}_2 \) layers, namely, \( \text{RNiO}_2 \), \( \text{LaNi}_2\text{O}_6 \), and \( \text{R}_2\text{Ni}_3\text{O}_6 \) (\( \text{R} = \text{La}, \text{Nd}, \text{Pr} \)), can be considered as a T\(^{-}\)-type homologous series \( \text{Ln}_{n+1}\text{Ni}_n\text{O}_{2n+2} \). All these phases were prepared by “soft chemistry” methods, which emphasize the importance of synthesis in the design of inorganic materials. \( \text{La}_3\text{Ni}_2\text{O}_6 \) is the 2 member of this series with a crystal structure, which was not reported before.

Apparently, the Jahn–Teller distortion of the Ni\(^{1+}\) (d\(^5\)) coordination environment, preference for the Ni\(^{2+}\) (d\(^6\)) 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 \( \text{La}_3\text{Ni}_2\text{O}_6 \) in air at room temperatures results in the \( \text{La}_3\text{Ni}_2\text{O}_{7-\delta} \) 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 \( \text{La}_3\text{Ni}_2\text{O}_{7-\delta} \) materials, clearly confirming the decreasing Ni valence. The \( \text{La}_3\text{Ni}_2\text{O}_6 \) 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. In the cuprates with structures where there has been apical O removal, such a strong low-energy feature is associated with 4p\(_{x}\) states along the missing O direction with d\(^{10}\) and d\(^{10}\)L character (where the L denotes an O ligand hole). By analogy, this Ni K-feature is associated with 4p\(_{x}\) d\(^{10}\) and d\(^{10}\)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.

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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.

References