La₃Ni₂O₆: A New Double T-type Nickelate with Infinite Ni¹⁺/²⁺O₂ Layers

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Received May 1, 2006; E-mail: martha@rutchem.rutgers.edu

The Ni¹⁺/Ni²⁺ mixed-valent nickelates received much attention due to the same (3d⁹/3d⁸) electronic configuration of Ni¹⁺/Ni²⁺ as that of Cu²+/Cu⁺ in the high-temperature superconductors. The common structural feature of the superconducting cuprates is the presence of CuO₂ layers formed from corner-sharing square planar CuO₄, square pyramidal CuO₆, or octahedral CuO₆ units. In all these environments, Cu²⁺ (d⁹) is in a low-spin configuration, while a square-planar coordination of oxygen atoms is needed to force Ni²⁺ in the low-spin configuration. Therefore Ni¹⁺/Ni²⁺ compounds containing NiO₂ infinite layers are of special interest.

The only known examples of such nickelates are RNiO₂ and R₂Ni₃O₆ (R = La, Nd, and Pr).⁵⁻⁶ These phases, except NdNiO₂, were synthesized by hydrogen reduction of the parent perovskite LaNiO₂ or La₂NiO₄ phases at low temperature. Numerous attempts to prepare La₃Ni₂O₆ in a similar way were unsuccessful, leading to La₃Ni₂O₆₄ as the most reduced phase.⁷⁻⁸ Recently, metal hydrides were introduced as powerful low-temperature agents for topotactic oxygen deintercalation.⁹ In this communication, we report the low-temperature synthesis and structure of a new Ni¹⁺/Ni²⁺ nickelate, La₃Ni₂O₆, with infinite NiO₂ layers. Moreover, the phase crystallizes in a unique double T-type structure, which has not been observed earlier.

La₃Ni₂O₆ was prepared by the reaction of La₃Ni₂O₇ with calcium hydride (CaH₂) at 350 °C in a sealed Pyrex ampule for 4 days. At higher temperatures (above 375 °C), a complete decomposition to La₂O₃ 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 due to the same (3d⁹/3d⁸) electronic configuration of Ni¹⁺/Ni²⁺ as that of Cu²+/Cu⁺ in the high-temperature superconductors. Therefore Ni¹⁺/Ni²⁺ compounds containing NiO₂ infinite layers are of special interest.

Table 1. Crystallographic Data for La₃Ni₂O₆

| atom | Wyckoff position | x | y | z | 10⁶ 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    |

* Space group: I4/mmm (No. 139); a = 3.9686(1) Å, c = 19.3154(6) Å; χ² = 2.3%, wRp = 3.2%, Rp = 1.3%.

Figure 1. Rietveld refinement profiles for the PND data of La₃Ni₂O₆. 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 La₃Ni₂O₆₄ (space group I4/mmm) were used as the starting model of the Rietveld refinement. La₃Ni₂O₆₄ is the most reduced n = 2 RP lanthanum nickelate known, and the oxygen vacancies are located solely in the LaO₄ planes between two of the NiO₂ layers. This refinement converged with bad fit parameters χ² = 12.7. An attempt to introduce cation splitting due to oxygen vacancies did not result in significant improvement of the profile fitting: χ² = 10.6. A good fit of the pattern (χ² = 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 LnₓCu₄O₆ (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 NiO₂ layers and in the fluorite block were set to unity since no statistically significant deviations were found.

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by the refinement. The refined structural data for La3Ni2O6 and
goodness of fit parameters are listed in Table 1, and the experi-
mental, calculated, and difference profiles are shown in Figure 1.

The structure of La3Ni2O6 can be obtained by complete removal
of the oxygen atoms from the LaO layers in the perovskite blocks
of La3Ni2O7 and rearrangement of oxygen atoms in (LaO)2 blocks.
A similar type of transformation was observed by Lacorre during
the preparation of Ln2NiO3 (Ln = La, Nd, Pr).3 Such structural
transformation leads to exclusively square-planar nickel coordina-
tion and to the appearance of infinite NiO2 planes. Thus, the crystal
structure of La3Ni2O6 can be described as intergrowth of fluorite
and structural blocks: P, perovskite; RS, rock salt; IL, infinite layer; F,
fluorite.

Figure 2. Structure models of Ln3Ni2O7 and Ln3Ni2O6 with denoted layers
and structural blocks: P, perovskite; RS, rock salt; IL, infinite layer; F, fluorite.

particular, develops a dramatically down-shifted shoulder, in the
0–5 eV range, which is similar to the XAS shoulder, which
develops with increasing Cu2+ 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 4p3 states along
the missing O direction with d10 and d0L character (where the L
denotes an O ligand hole). By analogy, this Ni K-feature is
associated with 4p3, d10 and d0L states directed along the missing
O sites in this O-deficient compound. Thus the Ni K-XAS results
support both the expected Ni2+ admixture and the missing O
coordination as demanded by the structure determination.

Acknowledgment. This work was supported by the National
Science Foundation through DMR-0233697 at Rutgers and DMR-
0404781 at the University of Tennessee.

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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JA063031O

JA063031O

Figure 3. X-ray absorption spectra for La3Ni2O6 and for standards.