Inorg. Chem. **2006**, *45*, 3490–3492

Inorganic Chemistry
Communication

Synthesis and Structure of the Bilayer Hydrate $Na_{0.3}NiO_2 \cdot 1.3D_2O$

Sangmoon Park,[†,‡] Yongjae Lee,[‡] Margaret Elcombe,[§] and Thomas Vogt*[,†]

USC NanoCenter and Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, Department of Earth System Sciences, Yonsei University, Seoul 120749, South Korea, and Bragg Institute, Australian Nuclear Science & Technology Organization, Sydney, Australia

Received February 11, 2006

The metal oxide bilayer deuterate (hydrate) $Na_{0.3}NiO_2 \cdot 1.3D_2O$ ($Na_{0.3}NiO_2 \cdot 1.3H_2O$) were prepared from Na_xNiO_2 by extracting Na^+ cations and simultaneously intercalating fully and nondeuterated water. High-resolution neutron powder diffraction, thermogravimetric analysis, and inductively coupled plasma atomic emission spectroscopy were used to show that a $Na_{0.3}(D_2O)_{1.3}$ network separates layers of edge-sharing NiO_6 octahedra.

Structures with the general composition $A^+_x(H_2O)_y[MX_2]^{x-}$ provide the opportunity to tune the charge within the MX_2 layers by appropriate oxidation as well as to manipulate the distance between them by varying the degree of hydration. The discovery of superconductivity near 5 K in the systems $A^+_x(H_2O)_y[MX_2]^{x-}$ and $A^{2+}_{x/2}(H_2O)_y[MX_2]^{x-}$ for M = Nb and Ta, X = S, A^+ = Li, Na, K, Rb, and Cs, and A^{2+} = Ca, Sr, and Ba by Sernetz et al.[1] provided early evidence of the exciting physics present in the mono- and bilayer hydrates (MLH and BLH), where a single cation−water layer or a sequence of cation−water−cation layers separates the doped two-dimensional MS_2 layers by distances of approximately 7 and 10 Å, respectively. The recent discovery of superconductivity in the BLH $Na_{0.3}CoO_2 \cdot 1.3H_2O$ near 5 K and the subsequent exploration of this correlated electron system provided the impetus to systematically explore the chemistry and physics of other members of the $A_x(MO_2)(H_2O)_n$ family. Up to now, several compounds of the two-layer MLH systems have been prepared and, to varying degrees, characterized. These include $Na_{0.36}CoO_2 \cdot 0.7H_2O$,[2] $K_{0.3}CoO_2 \cdot 0.4H_2O$,[3] $Na_{0.3}RhO_2 \cdot 0.6H_2O$,[4] $Na_{0.22}RuO_2 \cdot 0.45H_2O$,[5] and the mineral birnessite $Na_{0.32}MnO_2 \cdot 0.67H_2O$.[6] A member of the three-layer MLH family $Na_{0.3}CoO_2 \cdot 0.6H_2O$ [7] has also been prepared. Several BLHs have also been made: the superconducting two- and three-layer BLH $Na_{0.3}CoO_2 \cdot 1.3H_2O$,[7] the mineral buserite $Na_{0.3}MnO_2 \cdot nH_2O$, and Mg-, Ca-, Ni-, and Co-exchanged birnessites.[8] We will show in this work that $Na_{0.3}NiO_2 \cdot 1.3H_2O$ is a two-layer BLH and isostructural to $Na_{0.3}CoO_2 \cdot 1.3H_2O$.

Powder samples of Na_xNiO_2 ($x \leq 1$) were prepared by heating a 20 mol % excess of Na_2O_2 (Alfa, 97%) with amorphous NiO at 600 °C for 8 h in an O_2(g) atmosphere. NiO was made by heating $Ni(OH)_2$ (Alfa) or $Ni(NO_3)_2 \cdot 6H_2O$ (Alfa 99.9985%) at 300 °C for 1 day. Two types of samples were synthesized: the hydrated analogue $Na_xNiO_2 \cdot yH_2O$ used for characterization experiments and the deuterated (D_2O, Alfa, 99.8%) analogue $Na_xNiO_2 \cdot yD_2O$ used only for neutron powder diffraction. Both samples were oxidized and hydrated (or deuterated) by mixing an aqueous solution of $Na_2S_2O_8$ (pH ~ 10.5) in a molar ratio of 1.6:1 with Na_xNiO_2 and stirring it for 1 day in a Pyrex bottle. The Na ($x \sim 0.3$) and water contents ($y \sim 1.3$) in $Na_xNiO_2 \cdot yH_2O$ were determined by inductively coupled plasma atomic emission spectrometry and thermogravimetric analysis (TGA) upon heating at 0.25 °C/min in flowing Ar, respectively. Ni K-edge X-ray absorption spectroscopy experiments were performed on a Beamline X11A at the National Synchrotron Light Source and reveal an absorption edge shift toward higher energies in $Na_{0.3}NiO_2 \cdot 1.3H_2O$ compared to $Na_{0.7}NiO_2$. This indicates that because of the oxidation process Ni occurs in two possible electronic configurations: a combination of $3d^7$ ($S = {}^1/_2$) and $3d^6$ ($S = 0$) or $3d^7$ L states, with L representing a hole in the O p states. Neutron powder diffraction data of $Na_{0.3}NiO_2 \cdot 1.3D_2O$ with thermal neutrons of wavelength 1.885 Å were collected on the high-resolution neutron powder diffractometer at the Australian Nuclear Science and Tech-

---

* To whom correspondence should be addressed. E-mail: tvogt@gwm.sc.edu.

[†] University of South Carolina.

[‡] Yonsei University.

[§] Australian Nuclear Science & Technology Organization.

(1) Sernetz, F.; Lerf, A.; Schöllhorn, R. *Mater. Res. Bull.* **1974**, *9*, 1597−1602.

(2) Takada, K.; Sakurai, H.; Takayama-Muromachi, E.; Izumi, F.; Dilanian, R. A.; Sasaki, T. *J. Solid State Chem.* **2004**, *177*, 372−376.

(3) Park, S.; Lee, Y.; Si, W.; Vogt, T. *Solid State Commun.* **2005**, *134*, 607−611.

(4) Park, S.; Kang, K.; Si, W.; Yoon, W.-S.; Lee, Y.; Moodenbaugh, A. R.; Lewis, L. H.; Vogt, T. *Solid State Commun.* **2005**, *135*, 51−56.

(5) Shikano, M.; Delmas, C.; Darriet, J. *Inorg. Chem.* **2004**, *43*, 1214−1216.

(6) Jones, L. H. P.; Milne, A. A. *Mineral. Mag.* **1956**, *31*, 283−288.

(7) Foo, M. L.; Klimczuk, T.; Li, L.; Ong, N. P.; Cava, R. J. *Solid State Commun.* **2005**, *133*, 407−410.

(8) Le Goff, P.; Baffier, N.; Bach, S.; Pereira-Ramos, J. P. *Mater. Res. Bull.* **1996**, *31*, 63−75.

10.1021/ic060235x CCC: $33.50

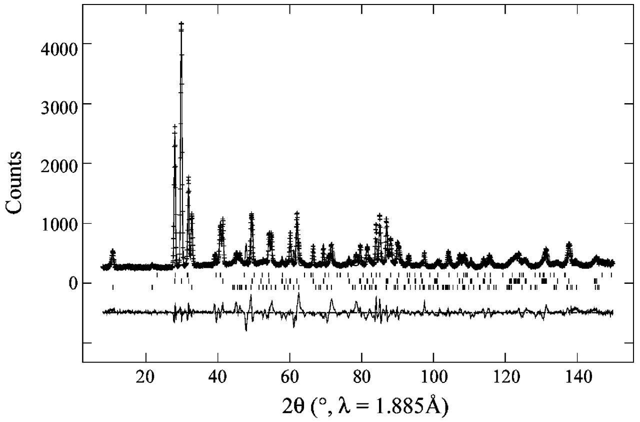

Figure 1. Rietveld refinement fit of the structural model of $Na_{0.3}NiO_2 \cdot 1.3D_2O$ to neutron powder diffraction data measured at 23 K. Points shown represent the observed intensities. The continuous lines through the sets of points are the calculated profiles from the refined model summarized in Tables 1 and 2. The sets of tick marks below the data indicate the positions of the allowed reflections (lower, $Na_{0.3}NiO_2 \cdot 1.3D_2O$; middle, ice XI; upper, Na_2SO_4). The lower curves represent the differences between observed and calculated profiles ($I_{obs} - I_{calc}$) plotted on the same scale as the observed data.

nology Organization's Research Reactor in Lucas Heights, Australia. All refinements were carried out using the Rietveld method and the GSAS package.

The X-ray powder diffraction pattern showed that the monoclinic symmetry ($C2/m$) is preserved during the transformation from Na_xNiO_2 to $Na_{0.3}NiO_2 \cdot 1.3H_2O$. The structural response to the oxidation and hydration of Na_xNiO_2 occurs in a manner similar to what is observed in $Na_{0.7}CoO_2$: a large expansion of the *c* axis occurs as a result of water intercalation accompanied by a slight contraction of the *a* and *b* axes due to shortening of the Ni−O bond distances in the NiO_6 octahedra, resulting from partial oxidation of formally Ni^{3+} to Ni^{4+}. The neutron powder diffraction pattern measured at 23 K reveals a mixture of three crystalline phases, with the majority phase identified as sodium nickel oxydeuterate. Also present were two impurity phases: ice XI (∼5%) and Na_2SO_4 (∼5%). The water impurity phase is due to dehydration occurring during the filling of the V container done under standard humidity conditions in a glovebag, and the Na_2SO_4 impurity is a reaction product of the deintercalation that was not completely removed from the product. The structural refinement of $Na_{0.3}NiO_2 \cdot 1.3D_2O$ proceeded using the space group $C2/m$ in an expanded layer model with Ni and O atoms located at the positions (0, 0, 0) and (0.7, 0, 0.1), respectively. Difference Fourier maps were generated that allowed the location of the intercalated water molecules. O atoms at (0.32, 0, 0.63) and D atoms at (0.07, 0.24, 0.32) were constrained during the refinement to conform to the ideal molecular geometry of water. Successive difference Fourier sections were calculated to locate the residual scattering density within the D_2O layers at (0.11, 0, 0.52). Subsequently, this site was modeled by placing a Na atom with a fixed site occupancy according to the chemical analysis results. In the final refinement, the occupancies for the O and D atoms of water were constrained to be 1:2, and additional constraints were used for the isotropic displacement parameters of all atoms. The final profile fit is depicted in Figure 1. The refined structural model is summarized in Table 1, and selected interatomic distances are listed in Table 2. TGA measurements carried out showed that the completely dehydrated phase was obtained after a weight loss of about 19% relative to $Na_{0.3}NiO_2 \cdot 1.3H_2O$, with a rapid weight drop observed below 150 °C. An intermediate phase at a weight loss of about 11% corresponding to 0.7 mol % water per formula unit was observed. This phase is a MLH phase similar to the one observed in sodium cobalt oxyhydrate $Na_{0.36}CoO_2 \cdot 0.7H_2O$[2] and will be discussed in a forthcoming paper.[9] The structure of $Na_{0.3}NiO_2 \cdot 1.3D_2O$ at 23 K consists of layers of NiO_2 octahedra separated by layers of D_2O molecules coordinating to Na cations (Figure 2). It is confirmed that the NiO_2 octahedra are in a triangular arrangement typical of BLHs. The refined water content, 1.35(2) D_2O per formula unit, is very close to the independently determined value obtained by TGA. This agreement gives us confidence that the presence of water as an impurity occurred only in the neutron measurement and certainly to a lesser degree because of the smaller sample size in the TGA measurement. The D_2O layers sandwich the central Na layer, consistent with the BLH model, as observed in the sodium

Table 1. Atomic Coordinates of $Na_{0.3}NiO_2 \cdot 1.3D_2O^a$

atom	*x*	*y*	*z*	occupancy	U_{iso} (Å^2)
Ni	0	0	0	1	0.049(3)
O	0.719(1)	0	0.0926(6)	1	0.049(3)
Na	0.11(4)	0	0.52(2)	0.15	0.049(3)
OW	0.323(5)	0	0.630(3)	0.67(1)	0.049(3)
D	0.069(3)	0.239(1)	0.326(2)	0.67(1)	0.049(3)

[a] Space group $C2/m$; $a = 4.890(2)$ Å, $b = 2.9361(9)$ Å, $c = 10.542(2)$ Å, $\beta = 107.81(2)°$, $V = 144.09(6)$ Å^3. $_wR_p = 11.8\%$, $R_p = 9.01\%$. OW denotes the water O atom. Restraints were used to tie isotropic displacement parameters for all atoms. Bond distance/angle constraints were used for D_2O molecules.

Table 2. Selected Bond Distances and Angles of $Na_{0.3}NiO_2 \cdot 1.3D_2O$

bond	distance or angle	bond	distance or angle
Ni−O	1.916(5) × 2	OW−OW	2.852(1)
	1.900(4) × 4		2.936(1)
Na−OW	2.20(20)		2.99(4)
	2.53(18) × 2	OW−D^a	0.967(5)
	2.25(18) × 2	D−OW−D^a	104.7(7)
OW−O	2.996(32)		

[a] Bond distance/angle constraints were used for D_2O molecules.

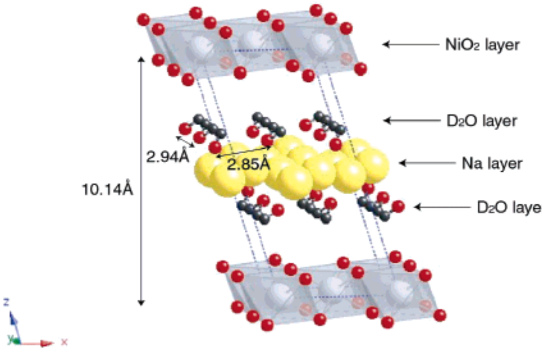

Figure 2. Polyhedral representation of the structure of $Na_{0.3}NiO_2 \cdot 1.3D_2O$ viewed along the *a* and *b* axes. The dotted lines in the figures define unit cells.

---

(9) Park, S.; Vogt, T. Unpublished.

cobalt hydrate with a similar water content. The interlayer spacing of $Na_{0.3}NiO_2\cdot1.3D_2O$ is expanded to ca. 10.14 Å compared to ca. 9.81 Å observed in $Na_{0.3}CoO_2\cdot1.3H_2O$. Ni^{3+} (t^6_{2g} e^1_g) is a Jahn–Teller active ion, and the electronic e_g levels will split. The elongated NiO_6 octahedra at 23 K with two axial Ni–O distances of 1.916(5) Å and four equatorial ones at 1.900(4) Å are both significantly shorter than those observed in $RNiO_3$ materials (R = La, Pr, Nd, and Sm) where the Ni–O distances are all larger than 1.93 Å.[10] In $NaNiO_2$, the elongated NiO_6 octahedra are comprised of two Ni–O distances at 2.17 Å and four at 1.95 Å.[11] Short distances similar to those found in $Na_{0.3}NiO_2\cdot1.3D_2O$ have only been observed in $BaNiO_3$ (Ni–O at 1.89 Å), where Ni has a formal valence state of 4+.[12] It is interesting to note that the shortest O–O distance [2.85(1) Å] in each D_2O layer is along the diagonal of the *xy* plane, whereas along the *y* axis, the O–O separation is 2.94(1) Å (Table 2). Another similar O–O separation [3.00(3) Å] is found between the D_2O and NiO_2 layers, indicating weak H bonding between them. On average, each D_2O molecule is H-bonded to four neighboring D_2O molecules within its layer and an O atom in the adjacent NiO_2 layer. Furthermore, the D_2O molecule is coordinated to a Na cation in the central layer.

The magnetic properties of the new metal oxide BLH $Na_{0.3}NiO_2\cdot1.3H_2O$ were investigated. Dc and ac magnetic susceptibility measurements revealed this compound to be a spin glass at low temperatures. These results will be discussed in a forthcoming publication in more detail.

Acknowledgment. T.V. thanks the Bragg Institute at the Australian Nuclear Science & Technology Organization for its repeated hospitality during extended periods of visitation.

IC060235X

---

(10) Garcia-Munoz, J. L.; Rodriguez-Carvajal, J.; Lacoore, P.; Torrance, J. B. *Phys. Rev. B* **1992**, *46*, 4414–4425.

(11) Dyer, L. D.; Borie, B. S., Jr.; Smith, G. P. *J. Am. Chem. Soc.* **1954**, *76*, 1499–1503.

(12) Krischner, H.; Torkar, K.; Kolbsen, B. O. *J.* Solid State *Ch*em. **1971**, *3*, 349–357.