Crystal Structure of Superconducting Sodium Cobalt Oxide

A sodium cobalt oxide with a bilayer-hydrate structure (BLH-Na$_2$CoO$_2$) was the first superconductor recently found in the cobalt oxide system [1]. It has a layered structure built up from CoO$_2$ layers with guest species in the galleries. Although the guest species had been believed to be Na$^+$ ions and H$_2$O molecules, the present structural analysis combined with our recent study based on chemical analysis and Raman spectroscopy has revealed that H$_3$O$^+$ ions are accommodated in the galleries as well [2].

The highly disordered arrangement of its guest species makes the structure analysis difficult. Diffraction data of higher quality will help us to clarify the complex structural aspects associated with guest species. In addition, we need to determine the crystal structure at low temperatures, where the superconducting transition takes place. The superconducting transition is, in general, not accompanied by a structural phase transition. However, in the present material, the crystal structure at low temperatures might be different from that at room temperature. Its guest species are mobile or diffusible; therefore, the structure may be modified by rearrangement of the guest species at low temperatures.

In fact, the first-order phase transition was observed in Na$_{0.75}$CoO$_2$. If such a phase transformation occurs at a temperature higher than $T_c$, the superconducting mechanism should be discussed on the basis of the low-temperature phase. From the above requirements, the crystal structure of superconducting BLH-Na$_2$CoO$_2$ was reinvestigated using synchrotron radiation in the temperature range down to 12.5 K.

Synchrotron XRD data were measured using a Debye-Scherrer-type camera installed at beamline BL02B2 [3]. The crystal structures were determined by Rietveld and maximum-entropy method (MEM) analyses using the computer programs RIETAN-2000 [4] and PRIMA [5], respectively.

Cooling BLH-Na$_2$CoO$_2$ down to 12.5 K did not bring about the appearance of any additional reflections in its diffraction patterns. All the reflections were indexable on the basis of hexagonal unit cells. Monotonous changes in lattice parameters given in Fig. 1 show the absence of phase transitions in this temperature range.

The structure parameters of BLH-Na$_2$CoO$_2$ were refined according to the previous structure model based on the space group P6$_3$/mmc (No. 194) [1] with some modifications. In the present structure model, the 2b (0, 0, 1/4) and 2d (2/3, 1/3, 1/4) sites are occupied not only by Na$^+$ ions but also by H$_2$O$^+$ ions, because the Raman spectrum evidenced the presence of H$_3$O$^+$ ions at these sites. In the final refinement, Na$^+$ and H$_2$O$^+$ ions at the 2b site were split into the 4e (0, 0, z) site with $z = 0.24$, because MEM analysis showed that the isosurfaces for number densities, $\rho$, of electrons around the 2b site were elongated along the c axis as shown in Fig. 2. Figure 3 shows the Rietveld refinement pattern, and Table 1 lists the refined structure parameters at room temperature.

**Table 1. Structure parameters for BLH-Na$_2$CoO$_2$ at room temperature**

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$g$</th>
<th>$U / \AA^2$</th>
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<tbody>
<tr>
<td>Co</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.0062(2)</td>
</tr>
<tr>
<td>O</td>
<td>4f</td>
<td>1/3</td>
<td>2/3</td>
<td>0.04578(12)</td>
<td>1</td>
<td>0.0091(5)</td>
</tr>
<tr>
<td>M1 (Na/H$_2$O)</td>
<td>4e</td>
<td>0</td>
<td>0</td>
<td>0.2413(12)</td>
<td>0.182(3)</td>
<td>0.047(4)</td>
</tr>
<tr>
<td>M2</td>
<td>2d</td>
<td>2/3</td>
<td>1/3</td>
<td>1/4</td>
<td>0.216*</td>
<td>0.030(4)</td>
</tr>
<tr>
<td>WO1(H$_2$O)</td>
<td>12k</td>
<td>0.137(2)</td>
<td>= 2x(WO1)</td>
<td>0.1700(5)</td>
<td>0.111(5)</td>
<td>0.026(5)</td>
</tr>
<tr>
<td>WO2</td>
<td>12k</td>
<td>0.875(6)</td>
<td>= x(WO2)/2</td>
<td>0.1757(6)</td>
<td>0.088*</td>
<td>0.023(8)</td>
</tr>
</tbody>
</table>

$a = 2.8237(10)$ Å and $c = 19.6576(8)$ Å; $R_{wp} = 5.10\%$ ($S = 2.67$), $R_F = 3.28\%$, $R_B = 1.75\%$, and $R_E = 1.70\%$. Virtual chemical species, WO and M, were used in the refinement. WO denotes an H$_2$O molecule whose atomic scattering factor was set to be equal to the sum of one O atom and three H atoms. M has mean scattering amplitude of Na$^+$ ions and H$_2$O$^+$ ions with the atomic scattering factor set equal to the sum of one O atom and three H atoms. The Na$^+$:H$_2$O$^+$ amount-of-substance ratio was fixed at 0.591:0.409, and the total contents of M and WO were fixed at 0.580 and 1.19, respectively, which were determined by the chemical analyses.
In BLH-Na$_x$CoO$_2$, the guest species in the galleries are highly disordered. MEM is quite effective for detailed structure analysis of such a compound, because disordered structures are much better expressed by electron densities in the unit cell used in MEM than by structure parameters in Rietveld analysis. Indeed, MEM-based whole-pattern fitting, in which structure factors were fixed at those evaluated from the electron density distribution calculated by MEM, decreased the $R$ factors from $R_{wp} = 5.10\%$, $R_B = 1.75\%$ and $R_F = 1.70\%$ in the Rietveld analysis to $R_{wp} = 4.99\%$, $R_B = 1.34\%$ and $R_F = 1.25\%$.

Final $R$ factors were low sufficiently, and most of the interatomic distances were consistent with those in other hydrates or Na$^+$-intercalation compounds, supporting this structure model.

The isotropic atomic displacement parameters, $U$, did not converge to reasonable values without any constraints, when the structure model did not include H$_3$O$^+$ ions. The introduction of H$_3$O$^+$ ions into the structure model made the values reasonable; they increased in the following order: $U$ parameters for the heavy Co ion, for oxygen bonded to Co, and for guest species (Na$^+$, H$_3$O$^+$, and H$_2$O) bound loosely, which strongly suggests that BLH-Na$_x$CoO$_2$ accommodates H$_3$O$^+$ ions as well as Na$^+$ ions and H$_2$O molecules in its galleries.

An interesting structural feature was an unusually short Co—O bond length (1.8622(12) Å). It was much shorter than the value of 1.91 Å estimated by bond valence calculation on the basis of the analyzed Co oxidation state of +3.42. In addition, the formation of the BLH-phase from the anhydrous one during the hydration process is accompanied by the reductive insertion of H$_3$O$^+$ ions [2], which donate electrons to the Co ions. The donation should increase the ionic radii of Co ions and thus the Co—O bond length; however it decreased from 1.8875(15) Å in the anhydrous phase [2]. In this structure, the electrons are encaged in unusually narrow spaces, which may enhance the correlation between electrons and induce the superconductivity.

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References