CRYSTAL STRUCTURE OF SUPERCONDUCTING SODIUM COBALT OXIDE

A sodium cobalt oxide with a bilayer-hydrate structure (BLH-Na_xCoO_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_2O molecules, the present structural analysis combined with our recent study based on chemical analysis and Raman spectroscopy has revealed that H_3O^+ 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_xCoO_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_xCoO_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_xCoO_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_3O^+ ions, because the Raman spectrum evidenced the presence of H_3O^+ ions at these sites. In the final refinement, Na^+ and H_3O^+ ions at the 2b site were split into the 4e (0, 0, z) site with $z \approx 0.24$, because MEM analysis showed that the isosurfaces for number densities, ρ, 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.
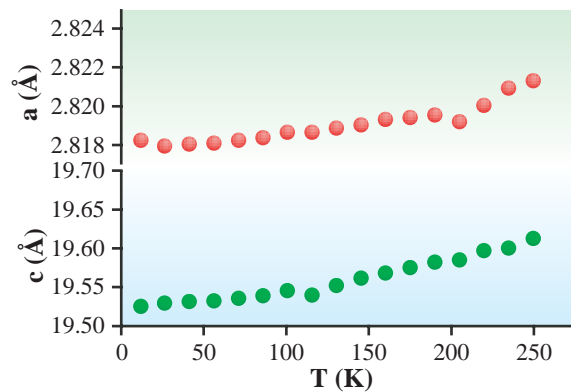

Fig. 1. Lattice parameters at various temperatures.

Table1. Structure parameters for BLH-Na_xCoO_2 at room temperature

Atom	Site	x	y	z	g	U / Å^2
Co	2a	0	0	0	1	0.0062(2)
O	4f	1/3	2/3	0.04578(12)	1	0.0091(5)
M1 (Na/H$_3$O)	4e	0	0	0.2413(12)	0.182(3)	0.047(4)
M2	2d	2/3	1/3	1/4	0.216*	0.030(4)
WO1(H$_2$O)	12k	0.137(2)	= 2x(WO1)	0.1700(5)	0.111(5)	0.026(5)
WO2	12k	0.875(6)	= x(WO2)/2	0.1757(6)	0.088*	0.023(8)

a = 2.82374(10) Å and c = 19.6576(8) Å; R_{wp} = 5.10% (S = 2.67), R_p = 3.28%, R_B = 1.75%, and R_F = 1.70%. Virtual chemical species, WO and M, were used in the refinement. WO denotes an H_2O molecule whose atomic scattering factor was set to be equal to the sum of one O atom and two H atoms. M has mean scattering amplitude of Na^+ ions and H_3O^+ ions with the atomic scattering factor set equal to the sum of one O atom and three H atoms. The $Na^+:H_3O^+$ 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.
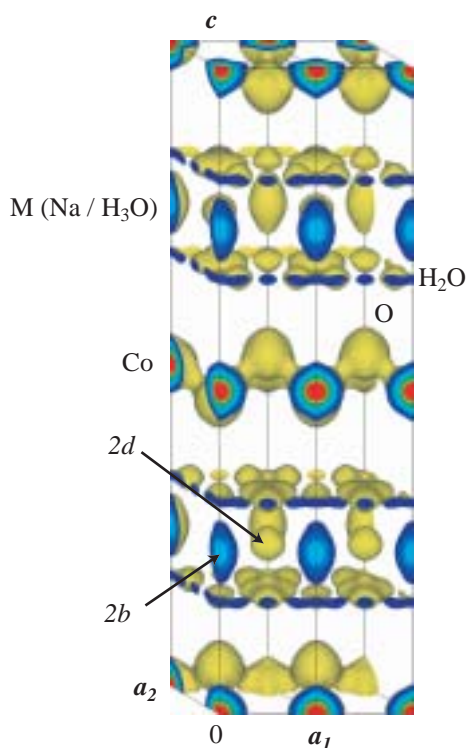
An interesting structural feature was an unusually short Co−O bond length (1.8622(12) Å). It was much shorter than the value of 1.91 Å estimated by bond valence calculation on the basis of the analyzed Co oxidation state of +3.42. In addition, the formation of the BLH-phase from the anhydrous one during 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.
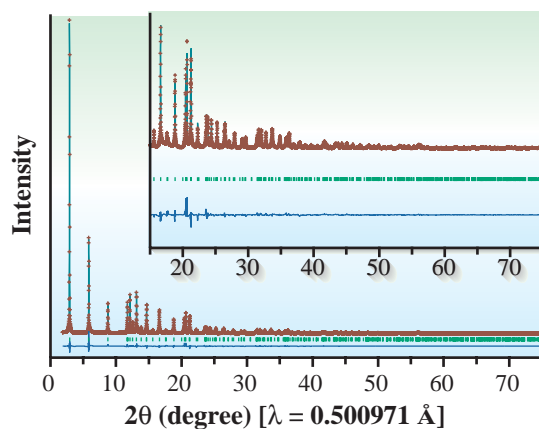

Fig. 3. Rietveld refinement pattern of BLH-Na$_x$CoO$_2$ at room temperature.

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Fig. 2. Isosurfaces for number densities of electrons. Equidensity level: 1.0 Å^{-3}.