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Anomalous Change of y' and z in $Na_x(H_3O)_zCoO_2 \cdot y'H_2O$ at $x \approx 0.33$

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Abstract

We prepared some Na_r(H₃O)_zCoO₂·y H₂O with BLH single phase and examined the Na⁺ content (x), H₃O⁺ content (z) and H₂O content (y⁻). Na_r(H₃O)_zCoO₂·y H₂O with BLH single phase and $0.28 \le x \le 0.36$ were prepared by changing the amount of Br₂ used. The drastical changes in the *c*-axis length and *z*, Co valence, y⁻ around x=0.33 were observed, strongly suggesting that there exists a phase transition here.

Introduction

After the Na_xCoO₂·yH₂O was found to be superconductive with a T_c around 5 K¹, much attention has been paid to this compound because it is a superconductor that is prepared in solution, where H₂O is intercalated between the CoO₂ layers after deintercalation of excess sodium. This compound, including 3*d* transition metal Co, can provide new insights into metal oxide superconductors such as copper oxides.

The compound has two-dimensional CoO₂ layers separated by a Na⁻ ion and a H₂O molecule, which are analogous to that of copper oxide superconductors. Schaak et al.²⁾ reported that there is an optimum sodium composition for the occurrence of superconductivity, namely x=0.30. This variation of T_c with the degree of electronic doping of the CoO₂ planes is analogous with the behavior observed in the copper oxides.

It was reported that there is a magnetically ordered phase sandwiched by two superconducting phases ^{3),4),} and that Na⁻ content plays an important role in the occurrence of superconductivity. Takada et al.

⁵⁾ discovered that partial dehydration brings about shrinkage of the interlayer distance to yield a monolayer hydrate, in which the superconductivity vanishes.

Many works ^{2,6-9)} show the possible ordered phases of Na_{0.3}CoO₂·*y*H₂O with water content*y* =0, 0.3, 0.6, 0.9, 1.3, or 1.8, corresponding to the coordination number n = 0, 1, 2, 3, 4, or 6 with the sodium ion. In this case, the phases are transformed by only the change of water content*y*, from 0 to 1.8 while keeping the Na⁻ content *x* at 0.3. Since the existence of oxonium ions in the material is reported ¹⁰, it is crucial to estimate theH₂O content considering an oxonium ion. In this case, the chemical formula of this compound is expressed as Na_x (H₃O)_z CoO₂ · *y* H₂O, where y = z + y.

Sakurai et al.¹¹⁾ had measured the contents of Na (x), H₃O (z), and H₂O (y) independently and found that the content of z is decreased, with the increasing of x from 0.331 to 0.351. The purpose of this study is to clarify the interactions between Co valence, y', z, x and T_c for 0.28<x<0.36.

Experimental

The parent oxide $Na_{0.7}CoO_2$ was prepared from powders of Na_2CO_3 and Co_3O_4 by the conventional solid-state reaction method. Mixtures of the powders were calcined at 60 0°C for six hours, sintered at 800°C under oxygen gas flow for eight hours to prepare $Na_{0.7}CoO_2$, and ground in an agate mortar.

The obtained Na_{0.7}CoO₂ was oxidized by an acetonitrile solution of Br₂ for five days. The amount of acetonitrile was fixed at 100 ml, and that of Br₂ was varied from 2.5 ml down to 0.1 ml. After rinsing the compound by the acetonitrile for stopping deintercalation of sodium, 2.5gNa₄CoO₂ was immersed in 100 ml water for a day to intercalate H₂O molecules between the CoO₂layers and to form



Fig.1 XRD patterns of $Na_s(H_3O)_sCoO_2 \cdot y H_2O$ with various amounts of Br_2 . Peaks of BLH phase are indexed. Solid circles represent peaks of the impurity phase, anhydrate Na_sCoO_2 .

 $Na_x CoO_2 \cdot vH_2O_1$ After the intercalation, the compound was dried in an ambient atmosphere. To prevent deintercalation ofH2O, the prepared specimens were stored in a closed vessel at 70% relative humidity⁷⁾. The X-ray powder patterns were taken with CuK α radiation and the reflections were indexed according to the assignment of Cmaidalka et al.¹²⁾. The content of Na⁺, x in the Na_xCoO₂·y H₂O was measured by inductively coupled plasma atomic-emission spectroscopy (ICP-AES). The H₂O content was studied by the thermogravimetric (TG) method. The specimen was weighed as a function of increasing temperature from 20°C to 400°C at a heating rate of 8.0°C/min under nitrogen gas By measuring the difference of the flow. weights at 20 °C and 400 °C, the amount of water, y was determined.

It was reported that the water in theNa_zCo O₂ · yH₂ O consists of H₂ O and H₃ O⁺. Therefore, this compound is represented byNa_x(H₃O)zCoO₂·y H₂O. The amounts of z and y were estimated separately as follows. The oxidation state of Cobalt in the specimen was determined by the iodometric titration ^{13),14)}. The oxonium ion content was estimated by equation z = 4 - (Co valence) - x. Therefore, the amount of H₂O, y is calculated by y' = y - z.

Results and Discussion

In Fig.1, XRD patterns of $Na_xCoO_2 \cdot yH_2O$ are shown for several values of the Br₂ volume in the 100 ml acetonitrile. The data show that the patterns of the samples deintercalated in the acetonitrile solution with Br₂ of 0.7 to 2.5 ml can be indexed as a single phase of Na_xCo $O_2 \cdot yH_2O$. When the Br₂ amount is smaller than 0.5 ml, not only Bilayer Hydrate (BLH) phase but also anhydrous (AH) phase, Na_xCoO₂, represented by the dark circles was formed, indicating that the samples are composed of the BLH and AH phases. The appearance of the AH phase with smaller amount of Br_2 has also been reported by Takada et al.⁵⁾.

The x, y', Co valence, z, and a-and c-axis length T_c of Na_x(H₃O)_zCoO₂·y'H₂O are shown in table.1. Firstly, the relation between Na⁺ content (x) and a-axis length and also, Na⁺ content and c-axis length are shown in Fig.2(a)



Fig.2. Na⁺ content (x) vs. a-axis length (a) and caxis length (b) in BLH single-phase Na₂CoO₂·yH₂O



Fig.3. Na⁺ content (x) in Na_x(H₃O)CoO₂·y H₂O vs. H₃O⁺ content (z) in Na_x(H₃O)₂CoO₂·y H₂O.

and Fig.2(b) respectively. Compared with caxis length, the change of a-axis length with different Na⁺ content is not so obvious. It may be due to the fact that $Na_{x}(H_{3}O)_{z}CoO_{2}\cdot y$ H_2O is a layered oxide, and the *a*-axis length of this compound is related to the direction of layer bonded. It is considered thatCoO2 layer has strongest bonding in that compound, and Co-O bonding length is influenced for a-axis length of $Na_x(H_3O)_zCoO_2 \cdot y H_2O$. Besides, we examine the changes in Co valence. As shown in Table 1, the change of Co valence is varying from 3.47 to 3.51, which is less than 0.04. We estimate the change of a-axis length by considering the change in Co valence affected by the change in ionic radii between Co^{3+} and Co^{4+} . The change in *a*-axis length estimated from ionic radii of Co3+(0.545Å) and ionic radii of Co4+ (0.530Å) is estimated to be 0.008Å. There is ± 0.005 Å of error by XRD measurement, and in this work, it is difficult to reveal such a small change in a-axis length.

On the other hand, the change is revealed inc-axis length versus, Na^+ content. Especially, thec-axis length drastically decreased from 19.62Å to 19.58~19.61Å at Na^+ content around



Fig.4. Na⁺ content (x) vs. H₂O content (y') (a) and y/x (b) in Na_x(H₃O)_zCoO₂·y·H₂O.

0.33. It is to be noted that in $x \ge 0.33$ region, the error of *c*-axis length in Na_x(H₃O)_zCoO₂·y' H₂O becomes large (Fig.2). Considering the stability of each phase affect the error of crystal parameters such as *c*-axis length, it may be suggest the existence of phasex ≥ 0.33 for Na_x(H₃O)_zCoO₂·y'H₂O.

The c-axis length of layered compound generically changed by, (1) coulomb force between layers, and (2) the size of the ionic radius that enters between interlayer. As for (1), the change in Co valence, Na⁻, and H₃O⁻ content were considered. However, because of the change in Co valence is very small as discussed in Fig.2 (a), therefore it is difficult to consider that the change in Co valence changed c-axis length. On the other hand, Na⁻ and H₃O⁻ content changes as they compensate each other. Since H₂O shieldes the coulomb force of Na⁻¹⁵, the Coulomb force is shielded as increasing of Na⁻ content, which will increase the c-axis length. Therefore, it is difficult to consider that Coulomb's force between layers originates the increase in the Secondly, We consider the *c*-axis length. change in ionic radii. In this system, it is reported that H₃O⁻ decreases with increase in Na⁻. Therefore we examined whether a similar result could be seen in this study or not. In Fig.3, the variation of H_3O^- content with Na⁻ content was shown. It clearly showed that H_3O^- content decreased with increasing of Na⁻ content. As shown in Table 1, the Co valence of Na_x (H₃ O)_z CoO₂ · y H₂ O was in range of 3.47~3.51. Hence, from the charge neutrality condition, H₃ O⁻ content will decrease with increasing of Na⁻ content. We assume that the Co valence is not changed, since the plot of Fig.3 is nearly a straight line. By using the least-squared method, the line was simulated as the following two equations,

> $z = 0.53 - x (x \le 0.33)$ (1) $z = 0.50 - x (x \ge 0.33)$ (2).

By separating the simulated equation into two parts at $x \approx 0.33$, standard deviations were drastically decreased, indicating that there is a jump among two equations at $x \approx 0.33$. This jump conforms to the relationship between *c*-axis length and *x*. Co valence calculated by (1) is $V_{\rm Co}$ =4.00-0.53=3.47, and Co valence calculated by (2) is $V_{\rm Co}$ =4.00-0.50=3.50. Therefore, it has been understood that there is a discrete change of Co valence at $x \approx 0.33$. The discrete changes of *c*-axis length, H₃O⁻, and Co valence suggests a phase transitions.

Lastly, we consider the H₂O content. The relations between Na⁻ content and H₂O content (a), and H₂O content per one Na⁻ ion (y'/x) are

Table.1 The x, Co valence, z, y, a- and c-axis length of $Na_x(H_3O)_zCoO_2 \cdot yH_2O$.

Amount of Br ₂	x	Co valence	Z	<i>y</i> ′	а	с
2.5	0.33	3.47	0.20	1.19	2.822	19.583
2.3	0.36	3.51	0.13	1.28	2.825	19.581
2.1	0.31	3.47	0.22	1.13	2.823	19.618
1.9	0.32	3.48	0.20	1.06	2.826	19.621
1.7	0.28	3.47	0.25	1.09	2.828	19.624
1.5	0.33	3.50	0.17	1.27	2.825	19.597
1.3	0.33	3.51	0.16	1.31	2.825	19.606
1.1	0.30	3.49	0.22	1.17	2.825	19.621
0.9	0.36	3.51	0.13	1.33	2.825	19.593
0.7	0.36	3.49	0.15	1.29	2.829	19.605

shown in Fig.4. When x<0.33, H₂O content is in the range of 1.05~1.17. On the other hand, when x>0.33, y' is drastically increased to 1.30. And then, H₂O content remains constant. The change in H₂O content also suggests a phase transition at around $x\approx0.33$. Besides H₂O per one Na⁻ is constant around 3.5~4.0. This result is similar to the previous report.⁶

It is suggested that there are two phases in this system. We represent $BLH-Na_xCoO_2(I)$ as first phase and $BLH-Na_xCoO_2(II)$ as second phase, then the physical property of each phases are described in Table 2.

Although differences of *c*-axis length, composition and Co valence among these two phases could be identified, it is too difficult to determine which one is the origin. However other measurements for more detail structure determination and physical properties are needed.

Conclusion

We prepared Na_x(H₃O)_zCoO₂ y H₂O with $0.28 \le x \le 0.36$, $1.05 \le y \le 1.34$ and $0.13 \le z \le 0.25$, which were prepared by varying the Br₂ content from 2.5ml to 0.7ml. The *a*-axis length is almost constant in all samples. On the other hand, the *c*-axis length changes with the change of Na⁻ content, Co valence and H₃O⁻ content. Relationship between Na⁻ and *c* -axis length drastically changes at $x \approx 0.33$. However, it is difficult to consider the change

in the Coulomb force determined by Co valence changes the *c*-axis length. Because the change of Co valence is too small to change thec-axis length. In addition, it is considered thatNa⁻ content and H₃O⁻ content changes as they compensate each other. H₂O shields Coulomb force of Na, and the c-axis length increases linearly because Coulomb force is shielded by the increase of Nacontent but actually, that is inversely. Therefore it is difficult to consider that Coulomb's Force between layers originates the increase in thec-axis length. From the relation between x and z, the z decreases as the xincreases and discrete change at $x \approx 0.33$ is observed. It is approximated by two equations z=0.53-x ($x \le 0.33$) and z=0.50-x ($x \ge 0.33$) up to and down to 0.33. Co valence V_{Co} calculated by that equations are 3.47 and 3.50, respectively. This drastic change also occurs in z and c-axis length. In addition, there is a discrete change of H₂O at x=0.33. For $x \ge 0.33$ y is $1.05 \sim 1.17$, and for $x \ge 0.33$ y is 1.30. These results suggest the existence of phase transition around $x \approx 0.33$.

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Table.2 c-axis length, z, y and Co Valence of BLH-Na_xCoO₂(I) and BLH-Na_xCoO₂(II).

	С	Ζ	<i>y</i> ′	Co Valence
BLH-Na _x CoO ₂ (I)	19.62	0.25-0.20	1.3	3.47
BLH-Na _x CoO ₂ (II)	19.58-19.61	0.17-0.14	1.01.20	3.50

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