

단 신

층상산화물 $\text{Na}_{0.67}\text{Co}_{0.33-y}\text{Mg}_y\text{Ti}_{0.67}\text{O}_2$ ($0 \leq y \leq 0.28$)의 이온전도성에
미치는 구조특성 연구

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Influences of Structural Feature on the Ionic Conduction in
Layered Oxides $\text{Na}_{0.67}[\text{Co}_{0.33-y}\text{Mg}_y\text{Ti}_{0.67}]\text{O}_2$ ($0 \leq y \leq 0.28$)

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INTRODUCTION

Layer type alkali transition metal oxides A_xMO_2 ($x=1.0$) have various structures characterized by the site available for the alkali metal A between MO_2 sheets,^{1,2} among which two structure types O3 and P2 are illustrated in Fig. 1. A_xMO_2 exhibits distinct features such as high structural tolerance toward x and mixed transport property consisting of electronic conduction within MO_2 sheets and ionic one by A ions at the inter-sheet space³⁻⁴. When electronic conduction is suppressed, A_xMO_2 exhibits purely ionic conduction as previously reported on $\text{Na}_x\text{M}_{x/2}\text{Ti}_{1-x/2}\text{O}_2$ ($\text{M}=\text{Ni}, \text{Co}; 0.60=x=1.0$), which were found to be fast-ionic conductors with conductivity of $\sim 10^{-2} \text{Scm}^{-1}$ at 770K.⁵⁻⁶

It has been believed that the threshold geometry of A ion is the crucial factor determining the ionic transport in A_xMO_2 . Actually, a large enhancement of conductivity of 10^2 - 10^3 times was observed, when the threshold shape changes from triangle (type O) to rectangle (type P) in potassium compounds.² However, the advantage of the rectangular threshold over the triangular one has not been properly

estimated, since the other factors such as the composition and the ionic-covalency of competitive bond A-O-M are inevitably involved at the structure change. So the proper estimation of the structural feature on conductivity depends on the existence of two allotropes of P and O, for a given composition.

Some oxides with large unit-cell volume such as RbScO_2 and CsLnO_2 ($\text{Ln}=\text{lanthanoids}$) exhibit a structure change from O3 into P2 as temperature increases.⁷⁻⁸ Such a change is deeply related to the increase of the configurational entropy at the structure change O3→P2, arising from doubled number of sites available for A ions in P2 (Fig. 1). Consequently, the free energy change at the transition O3→P2 possibly becomes negative at sufficiently high temperatures, where the lattice energy difference of the two structural variants can be compensated. Recent calculation of electrostatic lattice energy suggested that non-stoichiometric Na-phases may also exhibit the same kind of structural transition despite the smaller unit-cell volume.⁵ This idea has led us to investigate various systems, of which we report here on the structural evolution of $\text{Na}_{0.67}[\text{Co}_{0.33-y}\text{Mg}_y\text{Ti}_{0.67}]\text{O}_2$ ($0 \leq y \leq 0.28$) as a function of compo-

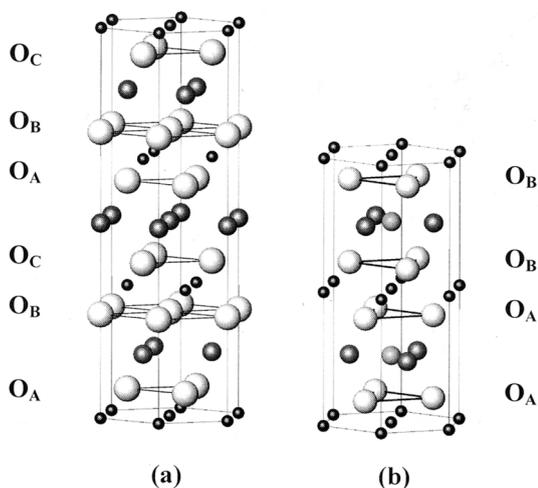
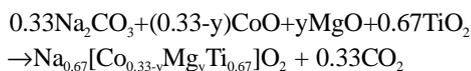


Fig. 1. O3 (a) and P2 (b) structures of layer-type AMO_2 . M (black ball) is present at octahedral sites of oxides (white ball) and A (gray ball) at octahedral O_h (a) and prismatic site P_r (b). While O3 has a single O_h site for M, two P_r sites at (0 0 1/4) (dark gray) and (1/3 2/3 1/4) (light gray) are available in P2.

sition and temperature, and on their ionic conduction properties.

EXPERIMENTAL

Oxides $\text{Na}_{0.67}[\text{Co}_{0.33-y}\text{Mg}_y\text{Ti}_{0.67}]\text{O}_2$ ($0 \leq y \leq 0.28$) were prepared by thermal solid state reactions from the appropriate mixtures of Na_2CO_3 , CoO , MgO and TiO_2 according to the reaction:



An excess of sodium carbonate (10-15 mol%) was added to compensate for volatile sodium component. The starting materials were mixed and calcined at 1073 K for 12 hrs and finally at 1123 K under Ar atmosphere. Products were leached into MeOH to remove the sodium components. Completion of the synthesis was confirmed by X-ray powder diffraction (XRD) using a Siemens D5005 diffractometer. TA Instrument SDT 2960 was employed for an isothermal gravimetric analysis. In order for the ionic conductivity measurements, samples were sintered in disk-type pellet ($d=7$ mm, $t=2$ mm) at

1123K for 6hrs and Au blocking-electrodes were deposited on both sides of pellet by DC-sputtering. Impedance data were collected at every 30K at the range of 300-700 K under Ar-flow using YHP 4192A LF impedance analyzer at the range of 5 Hz-10 MHz.

RESULTS AND DISCUSSION

Powder XRD patterns of the $\text{Na}_{0.67}\text{Co}_{0.33-y}\text{Mg}_y\text{Ti}_{0.67}\text{O}_2$ ($0 \leq y \leq 0.28$) at 1123K are shown in Fig. 2 and their lattice parameters are listed in Table 1. No additional peak suggesting any ordered structure was observed. Interestingly, the lattice parameter a increases with Mg-content despite the small size of Mg^{2+} ($r=0.72\text{\AA}$) over Co^{2+} (HS; 0.745\AA)⁹. It strongly implies that the overall covalency in MO_2 sheet is diminished, because of the small electronegativity of Mg^{2+} (1.22) with respect to that of Co^{2+} (1.57).¹⁰⁻¹¹ As a result, the covalency of Na-O should be enhanced in the competitive bond Na-O-M. It is apparent that the evolution of bond character in Na-O-M also affect the value c/a , which actually

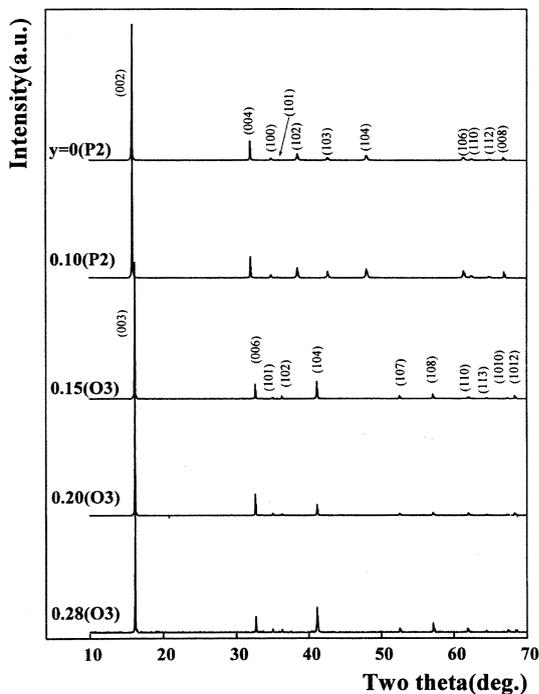


Fig. 2. XRD patterns of $\text{Na}_{0.67}\text{Co}_{0.33-y}\text{Mg}_y\text{Ti}_{0.67}\text{O}_2$ prepared at 1123 K.

Table 1. Lattice constants and β values of $\text{Na}_{0.67}\text{Co}_{0.33-y}\text{Mg}_y\text{Ti}_{0.67}\text{O}_2$

| $\text{Na}_{0.67}\text{Co}_{0.33-y}\text{Mg}_y\text{Ti}_{0.67}\text{O}_2$ | $a(\text{\AA})$ | $c(\text{\AA})^*$ | c/a | $\beta = x f_i(\text{Na-O}) f_i(\text{M-O})$ |
|---|-----------------|-------------------|-------|--|
| $y=0.00(\text{P2})$ | 2.965(3) | 16.75(2) | 5.649 | 0.324 |
| 0.10(P2) | 2.975(1) | 16.74(3) | 5.627 | 0.337 |
| 0.15(P2) | 2.974(6) | 16.77(1) | 5.639 | 0.323 [†] |
| 0.15(O3) | 2.993(2) | 16.45(3) | 5.496 | 0.343 |
| 0.20(O3) | 2.994(3) | 16.44(1) | 5.491 | 0.350 |
| 0.28(O3) | 2.996(1) | 16.42(2) | 5.481 | 0.358 |

*For P2 phases, each c was multiplied by 1.5 for comparison.

[†]Estimated as $\text{Na}_{0.67-8}\text{Co}_{0.18}\text{Mg}_{0.15}\text{Ti}_{0.67}\text{O}_{2.82}$ ($\delta \approx 0.04$).

decreases with Mg-content indicating the lattice expansion is rather two-dimensional. The structure change from P2 to O3 was observed near $y=0.15$. The drastic change of a implies that the bond character in Na-O-M is greatly influenced by structure change (or vice versa): Comparing with O3, P2 induces highly enhanced covalency in M-O and thus gives rise to stronger interaction within MO_2 sheet than across the sheets. It means that the bond Na-O is essentially ionic in P2, whereas it takes some covalency in O3.

Delmas classified successfully the structure of A_xMO_2 using the parameter $\beta = x f_i(\text{A-O}) f_i(\text{M-O})$, where x stands for the A-content and $f_i(\text{Z-O})$ for the bond ionicity defined as $f_i(\text{Z-O}) = 1 - \exp\{-0.25(\chi_Z - \chi_O)^2\}$ ($Z = \text{A}, \text{M}$; $\chi = \text{Pauling's electronegativity}$).¹² In his work, the structure of $\text{Na}_x(\text{M}_i^{3+}/\text{M}_i^{4+})\text{O}_2$ was determined as P for $\beta > 0.30$, or O for $\beta < 0.30$, respectively. A similar result was obtained in $\text{Na}_x\text{M}^{2+}_{x/2}\text{Ti}^{4+}_{1-x/2}\text{O}_2$ ($\text{M} = \text{Co}, \text{Ni}$), but with a different critical value $\beta = 0.34-0.35$.⁵⁻⁶

With $\text{Na}_{0.67}\text{Co}_{0.33-y}\text{Mg}_y\text{Ti}_{0.67}\text{O}_2$, β was calculated within 0.32-0.36 (Table 1) and the transition occurs around $\beta = 0.34$. It supports the previous argument that type P can be maintained up to higher β when the M-site ions are coupled as $\text{M}_i^{2+}/\text{M}_i^{4+}$ instead of $\text{M}_i^{3+}/\text{M}_i^{4+}$, because the former induces greater electrostatic interaction than the latter.⁵

In order to induce the structure change with temperature, O3 phases ($y=0.15$) were heated at elevated temperatures. Compositions $y=0.20$ and 0.28 showed no transition below 1273K but melted incongruently at higher temperatures. However, $y=0.15$ has shown a complete structure change into P2 after

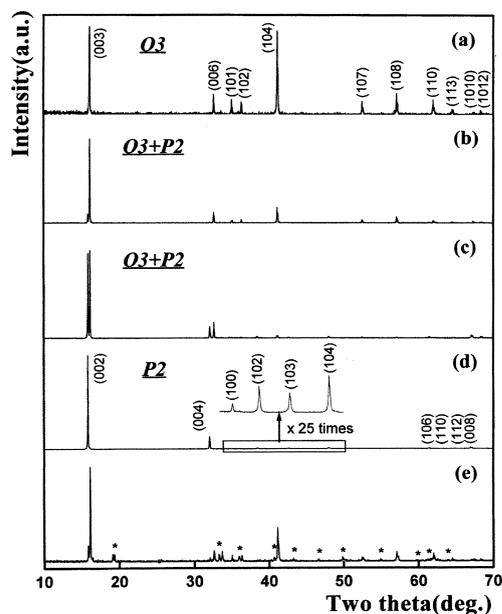
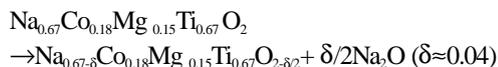


Fig. 3. Evolution of XRD pattern of $\text{Na}_{0.67}\text{Co}_{0.18}\text{Mg}_{0.15}\text{Ti}_{0.67}\text{O}_2$ with temperature up to 1123 K (a), 1173 K (b), 1223 K (c), and 1243 K (d). The P2 phase obtained at 1243 K does not neatly get back into O3, but becomes a mixture of P2, O3 and decomposed component (*) for prolonged re-heating at 1123 K (e).

heating at 1243K for 5 days as shown in Fig. 3: At 1123 K, $y=0.15$ exhibits the initial O3 phase (a), but an additional P2 phase appears at elevated temperature (b) and grows with temperature. It stayed in mixed phase until the temperature reaches to 1243K, where P2 was finally obtained as a single phase (d). Below 1243K, only mixtures of two phases were obtained, even after a prolonged heat treatment (max. 2 weeks). This structure change was irreversible, as revealed in XRD result after re-heating at 1123K (Fig. 3(e)).

An isothermal gravimetric analysis performed for about 110 hrs at 1243 K under Ar atmosphere revealed that the sample gradually lost weight of *c.a.* 1.2 wt% during the structure change. Since the obtained P2 phase did not contain any detectable impurities, the weight loss may be attributed to the volatilization of Na-component as Na_2O :



Due to the stacking feature of MO_2 sheets along axis *c*, the transformation $\text{O3} \leftrightarrow \text{P2}$ cannot be achieved by simple cooperative movements of MO_2 sheets like sliding or rotation,¹³ but occurs through an overall rearrangement at high temperature. The modified composition $\text{Na}_{0.63}\text{Co}_{0.18}\text{Mg}_{0.15}\text{Ti}_{0.67}\text{O}_{1.98}$ corresponds to $\beta=0.32$, well within the domain of P. Therefore the structure change $\text{O3} \rightarrow \text{P2}$ observed in this work includes a small change of composition inducing higher β , in addition to the configurational entropy effect as mentioned above. Nevertheless, as-prepared two variants of $y=0.15$

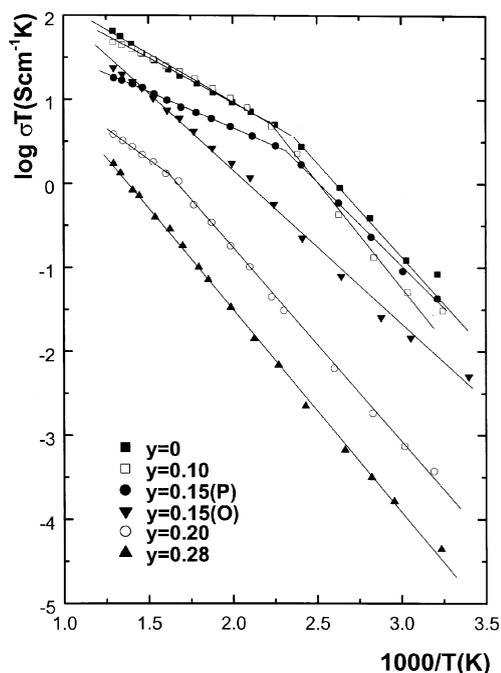


Fig. 4. Plot of $\log(\sigma T)$ vs. $1000/T$ of $\text{Na}_{0.67}\text{Co}_{0.33-y}\text{Mg}_y\text{Ti}_{0.67}\text{O}_2$ at the range of $300 \text{ K} \leq T \leq 770 \text{ K}$.

Table 2. Ionic conductivity properties of $\text{Na}_{0.67}\text{Co}_{0.33-y}\text{Mg}_y\text{Ti}_{0.67}\text{O}_2$

| y | $\sigma_{300 \text{ K}}(\text{Scm}^{-1})$ | $\sigma_{770 \text{ K}}(\text{Scm}^{-1})$ | $E_a(\text{eV})$ |
|----------|---|---|------------------|
| 0.00(P2) | 2.69×10^{-4} | 8.43×10^{-2} | 0.23(T>425 K) |
| | | | 0.38(T<425 K) |
| 0.10(P2) | 9.95×10^{-5} | 6.19×10^{-2} | 0.21(T>450 K) |
| | | | 0.50(T<450 K) |
| 0.15(P2) | 5.37×10^{-5} | 2.33×10^{-2} | 0.17(T>430 K) |
| | | | 0.40(T<430 K) |
| 0.15(O3) | 1.71×10^{-5} | 3.06×10^{-2} | 0.36 |
| 0.20(O3) | 1.19×10^{-6} | 4.98×10^{-3} | 0.45 |
| 0.28(O3) | 1.41×10^{-7} | 2.23×10^{-3} | 0.48 |

are still useful to examine the influence of structure on ionic conductivity, in that the small decrease of Na-content $\delta \approx 0.04$ in type P does not affect significantly on the conductivity.⁶

AC-conductivity results are plotted as $\log(\sigma T)$ vs. T^{-1} in Fig. 4 and the conductivity at 300 and 770K and activation energy are summarized in Table 2. Activation energies were calculated from Arrhenius equation $\sigma = (\sigma_0/T) \cdot \exp(-E_a/k_B T)$, where σ_0 , E_a , k_B represent pre-exponential factor, activation energy and Boltzmann constant, respectively. Substitution of Co^{2+} by Mg^{2+} apparently made the material less conductive despite the enlarged threshold window. It can be primarily attributed to the increased covalency of Na-O, which sets up increased activation energy Na ion to move into other site.

The structural effect on conductivity was estimated from the difference between two variants of $y=0.15$. The ratio $\sigma(\text{P2})/\sigma(\text{O3})$ is determined smaller than 10 and even becomes less than 1 at high temperatures (>670 K), being much smaller than 10^2 - 10^3 as previously reported.² On the contrary, the variation of bond character of Na-O-M has shown to be capable of changing conductivity more than 10^2 times. This result indicates that the bond character can play even more an important role than structural feature for the ionic conductivity of A_xMO_2 .

The activation energy change observed with P2 phases around 430-450K was considered associated with the thermal relaxation of local distortion in lattice and discussed in detail in the previous work⁶: The large differences in dimension of Co^{2+} , Mg^{2+} , Ti^{4+} should randomly introduce the local distortions into matrix, leading to a wide distribution

of the size and shape of the trigonal prisms for Na^+ ions. When the temperature increases, Na^+ ions at highly distorted sites are considered to gain some degree of mobility by thermal relaxation of the distortion, giving rise to a gradual increase of their contribution to conduction process. In other words, the effective carrier concentration increases through thermal activation at relatively low temperatures. At more elevated temperatures where such a thermal relaxation of matrix distortion is saturated, the effective carrier concentration cannot be activated any more, leading to the decrease of activation energy as observed above 450 K.

In summary, $\text{Na}_{0.67}\text{Co}_{1-y}\text{Mg}_y\text{Ti}_{0.67}\text{O}_2$ ($0 \leq y \leq 0.28$) changes its structure P2 to O3 around $y=0.15$ at 1123 K, and an irreversible structure change from O3 to P2 was observed for $y=0.15$ by increasing the temperature up to 1243 K with a small weight-loss of the volatilization of Na_2O . The ionic conductivity results indicate that the bond character of Na-O-M can change conductivity more greatly (c.a. 10^2 times) than the structure does (<10). The activation energy change of type P2 around 430-450K was considered as related with the thermal relaxation of local distortions by the different size of M-site ions $\text{Co}^{+2}/\text{Mg}^{+2}/\text{Ti}^{+4}$.

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