Preparation and Ionic Conductivities of Tunnel-Type Oxides

\[ \text{Na}_{0.80}\text{M}_{0.40}\text{Ti}_{1.60}\text{O}_4 (\text{M} = \text{Co}^{II}, \text{Ni}^{II}) \]

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A number of quaternary oxides have been known to crystallize in one-dimensional structures such as hollandite, pridere and CaFe2O4.1 In these structures double blocks of octahedra are formed by edge-share and developed in lattice to form one-dimensional tunnels, where alkali or alkaline earth metals are placed. With existence of vacancies, alkali metal ions in such tunnel structures are susceptible of being highly mobile, leading to ionic conductivities.

\[ \text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4 (0.72 \leq x \leq 0.90), \] reported by Mumme and Reid,2 has a similar structure, with Z-shaped double blocks and double tunnels (Figure 1). Na+ ions are placed in distorted trigonal prisms which are face-shared one another along b-axis, so that they may move within the tunnels. Systematic syntheses of isostructural oxfluorides \[ \text{Na}_{0.5}\text{M}_{0.5}\text{Ti}_{1.5}\text{O}_{3.5}\text{F}_{0.5} \] (M=Mg, Ni, Co, Zn, Cu) were reported earlier,3 and their ionic conduction properties were also investigated.4 On the other hand, the electrical conduction studies on the original phase, \[ \text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4 \] (x=0.875) and its Na-extracted or Ti-substituted phases have been studied rather recently:5-7 It was evidenced that Na+ -ion is mobile within tunnels and a mixed conduction was found for Na-extracted phases due to the partial oxidation of Fe3+ to Fe4+. However, it appears necessary to prepare new materials susceptible to have pure ionic conduction, instead of mixed one, for understanding the ionic transport features in this structure more in detail. In the present paper, we report the preparation of one-dimensional compounds \[ \text{Na}_{0.80}\text{M}_{0.40}\text{Ti}_{1.60}\text{O}_4 \] (M =CoII, NiII) and their ionic conductivity properties.

Experimental Section

Polycrystalline samples of composition \[ \text{Na}_{0.80}\text{M}_{0.40}\text{Ti}_{1.60}\text{O}_4 \] (M=CoII, NiII) were prepared by direct solid state reactions using the appropriate amounts of Na2CO3, NiO (or CoO) and TiO2. An excess amount of sodium carbonate (10-12 mol%) was added to compensate for the loss due to the volatilization of sodium component. The mixture was ground using a mortar and calcined at 973 K for 12 hrs, then the powder was uniaxially pressed at 80 MPa into a pellet 13 mm in diameter. The pellet was heated at 1423 K for 36 hrs with two or three times of intermittent grindings. All the thermal treatments were made under Ar atmosphere to avoid an eventual oxidation of M2+ to M3+. The obtained products were leached into MeOH to remove the unreacted sodium components and dried under vacuum.

Identification of crystalline phases and determination of lattice parameters were carried out by X-ray powder diffraction (XRD) analysis using a Siemens D5005 diffractometer equipped with curved graphite monochromator with CuKα radiation and by a computer program based on a least-square-method. For electrical conductivity measurements, the pellets (d=7 mm, t=2 mm) were sintered at 1443 K for 12 hrs. Blocking electrodes were deposited on both sides of the pellets by silver paste. The conductivity was obtained every 30 K at the range of 530-873 K under argon flow by AC measurements with HP 4192A LF impedance analyzer at the frequency range of 5 Hz-13 MHz. Resistance values were derived by interpretation of the complex impedance diagrams.

Results and Discussion

XRD results. XRD patterns of both samples are shown in Figure 2. All the peaks were successfully indexed with the orthorhombic lattice parameters, confirming they are isostructural with \[ \text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4 \]. Co-phase was found to have a unit cell slightly larger than Ni-phase, mainly due to the large ionic radius of Co2+ (0.745; HS) with respect to Ni2+ (0.69).8 It is worth noting that Co-phase has also a larger cross section area \[ a^*c \] to \[ [010] \] direction.

\[ \text{Na}_{0.80}\text{Co}_{0.80}\text{Ti}_{1.60}\text{O}_4 \] In order to estimate the electronic contribution to the conductivity observed here, the measurements such as DC-polarization (at 1.0 V) and 4-probe DC conductivity were additionally performed, confirming that
the conduction in both samples is essentially of ionic one.

The Cole-Cole diagrams of Na\textsubscript{0.80}Co\textsubscript{0.40}Ti\textsubscript{1.60}O\textsubscript{4} sintered pellet, giving the imaginary part Z' of the complex impedance Z\* as a function of its real part were obtained at various temperatures. At 682 K, for example, it shows clearly one semicircle (Figure 3(a)), of which radius increases with temperature. Figure 3(b) shows a combined Z' and normalized M' (M'/M'\textsubscript{max}) plot as a function of frequency. M' has a similar frequency-dependence with the imaginary part of dielectric permeability e', and is known to emphasize the component with small capacitance, which corresponds to the bulk component.\textsuperscript{9} M' plot exhibits a single Debye-like peak with the same frequency maximum with Z' around 870 kHz. This means that the semicircle can be ascribed to pure bulk component and the arc observed at low frequency would result from the grain boundary and electrode polarization contributions. The bulk ohmic resistance was determined from the intercept Z\textsubscript{0} on the real axis of the zero phase angle extrapolation from the high-frequency side and the conductivity \(\sigma\) is obtained from Z\textsubscript{0} by means of the relation \(\sigma = 1/(Z_0)(e/S)\), where \((e/S)\) is the sample geometric factor. Frequency dependence of the normalized imaginary part of M'/M'\textsubscript{max} for Na\textsubscript{0.80}Co\textsubscript{0.40}Ti\textsubscript{1.60}O\textsubscript{4} at various temperatures is given in Figure 4(a). The modulus peak shifts towards higher frequencies as temperature increases, but the shape and full width at half height (FWHH) of M'/M'\textsubscript{max} (1.25 ± 0.02 decades) are not changed.

The M'/M'\textsubscript{max} curves are slightly non-symmetric, suggest-
ing a non-exponential behavior of conductivity relaxation that can be described by the Kohlrausch function, \( \phi(t) = \exp\left(-t/\tau_\alpha\right)^\beta \), where \( \tau_\alpha \) is the relaxation time and \( \beta \) the Kohlrausch parameter.\(^{10,11} \) \( \beta \) was determined as 0.90 ± 0.02 at each temperature, by dividing the FW HHH by the Debye breadth. The inverse temperature dependencies of \( \log(\sigma T) \) and \( \log f_{\text{max}} \) (\( f_{\text{max}} = 1/2\pi \tau_\alpha \)) are shown in Figure 4(b). Each linear fit of \( \sigma T = \sigma_0 \exp\left(-\Delta \sigma/kT\right) \) and of \( f_{\text{max}} = f_0 \exp\left(-\Delta \sigma/kT\right) \) shows an Arrhenius-type behavior with correlation coefficients \( r_\sigma = 0.999 \) and \( r_f = 0.989 \), respectively. The two plots exhibit the close activation energies \( \Delta \sigma \) and \( \Delta \sigma_\alpha \), suggesting that the Na\(^+\) ion transport is mainly due to a thermally activated hopping mechanism.\(^{11,12} \)

**Na\(_{0.80}\)Ni\(_{0.40}\)Ti\(_{1.60}\)O\(_4\).** The Cole-Cole diagram of complex impedance and \( Z' \), \( M'/M''_{\text{max}} \) plot against \( \log(T) \) at 800 K are present in Figure 5(a). In contrast to Co-phase, The peak frequency \( f_{\text{max}} \) is apparently mismatched for \( Z' \) and \( M'/M''_{\text{max}} \). Consequently the semicircle of the Cole-Cole diagram should not be regarded as a pure bulk component, but grain boundary component being also included therein. The experimental semicircle is displaced below the real axis as \( \Delta E_f \) becomes smaller than the Debye-type relaxation. \( \Delta E_f \) seems to transport Na\(^+\) ions mainly by hopping mechanism,\(^{12} \) but Co-phase was found to have higher conductivities with smaller activation energies than Ni-phase. Because both compounds have the same framework and vacancy concentration, their ionic transport features would be compared mainly through two viewpoints, bond nature of Na-O and conductivity separately a model-circuit of three ZC elements in a serial array (RC)(RC)(RC), including CPE (constant phase element) was adopted, each corresponding to the ionic conductive paths in bulk, grain boundary and double layer of electrode/electrolyte.\(^{9,13} \) Here, \( \phi \) designates the elements therein run parallel. In each component the impedance \( Z_\text{p} \) is expressed as \( Z_\text{p}^* = R_j - i/(\omega c_j)^\phi \), where \( R_j \) and \( c_j \) represent resistance, capacitance and distribution factor of \( j\)-th component respectively. All the parameters have been determined for each temperature by fitting the experimental data using a fitting program LEVM 7.1., based on complex nonlinear least square method.\(^{14} \) Within the temperature range investigated, the bulk and grain boundary capacitances were determined as of 100-300 pF and 200-400 nF, and \( \Phi_{\text{bulk}} \) values ranges 0.83-0.86. Although the bulk capacitance is larger than the conventional value of ceramic materials (\( \sim 10^3 \) pF), its magnitude 10^{-3} times smaller than the grain-boundary capacitance supports this estimation.\(^{9} \) The FW HHH of \( M'/M''_{\text{max}} \) could not be determined because the plots were not well-defined at high-frequency region, but the estimation from the half width of low-frequency region implies that the FW HHH would be much larger than 1.14 decades, leading to a smaller \( \beta \) than with Co-phase, as reflected in \( \Phi \) values.

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\log(\sigma T) \text{ of bulk and grain boundary components and } \log f_{\text{max}} \text{ are plotted as a function of inverse temperature in Figure 6. All three plots exhibit good Arrhenius relations with } r = 0.98-0.99. \text{ Considering } f_{\text{max}}(M') \text{ is primarily related with the relaxation time } \tau_\alpha \text{ of the bulk component, the close values of } \Delta E_{\text{bulk}} \text{ and } \Delta E_{\alpha} \text{ strongly suggests that the bulk conduction also occurs mainly through a thermally activated hopping mechanism like in Co-phase.} \\
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**Na\(_{0.80}\)Co\(_{0.40}\)Ti\(_{1.60}\)O\(_4\) vs. Na\(_{0.80}\)Ni\(_{0.40}\)Ti\(_{1.60}\)O\(_4\).** Both compounds seems to transport Na\(^+\) ions mainly by hopping mechanism, but Co-phase was found to have higher conductivities with smaller activation energies than Ni-phase. Because both compounds have the same framework and vacancy concentration, their ionic transport features would be compared mainly through two viewpoints, bond nature of Na-O and Na\(^+\) ion transport is mainly due to a thermally activated hopping mechanism.
diffusion pathway of Na\(^+\) in material.

Firstly, the bond character of Na-O may be compared by competitive interaction of Na-O-M: the ionic-covalency of counter-bond M-O should influence directly to the nature of Na-O. The covalency of a bond M-O may be compared following Pauling’s formula 
\[ f_c(M-O) = -0.25 \times \exp\left(\chi_M - \chi_O\right)^2, \]
where \( \chi \) is the electronegativity.\(^{15,16}\) Since \( \chi \) value of Ni\(^{2+}\) is known as slightly larger (1.57) than Co\(^{2+}\) (HS; 1.54),\(^7\) Na-O in Ni-phase would be regarded as more ionic and therefore more favorable to the ionic conduction than Co-phase. However, the latter exhibits a larger unit-cell volume and cross section \( a^*c \) with respect to the former, being able to furnish more spacious diffusion pathway of Na\(^+\) ions along \( b \) axis. Considering the relatively small difference of cell dimension between two compounds, the higher ionic transport properties of Co-phase seems to suggest that the cell dimension might be more a important factor than the ionicity of Na-O for the ion conduction.

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References