

단 신

$\text{Na}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ 의 이온교환반응에 의한 새로운 층상산화물 $\text{A}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ (A=Li, Cu and Ag)의 합성

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Synthesis of New Layered Oxides $\text{A}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ (A=Li, Cu and Ag) by Topotactic Cation-exchange from $\text{Na}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$

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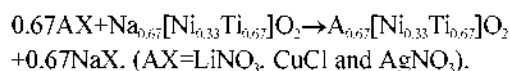
Layer-type oxides A_xMO_2 ($x < 1.0$) consist of two kinds of layers. MO_2 sheet developed in *ab* plane and hexagonal array of A^+ ions between MO_2 sheets. Those two layers are stacked alternately along crystallographic axis *c* and form various structural variants of A_xMO_2 depending on the stacking patterns, which determine the distinct sites for A^+ ion and the number of repeating units along *c*. When A is alkali metal, interaction between A^+ and O_2^- ions is dominantly ionic and so A^+ ions are placed at either of T_d , O_h , or sometimes P_r (trigonal prismatic) sites, giving rise to several variants like O2, O3, T1, P2, and so on¹⁻³. A_xMO_2 ($x < 1.0$) frequently exhibits both electronic and ionic conductions. Each occurs respectively within MO_2 sheet and hexagonal array of A^+ in inter-sheet space. In this case, the ionic mobility of A^+ ion is arisen from enhanced ionic character of A-O through competing bridge bond A-O-M.

When alkali ions are substituted with Ag^+ or Cu^+ ions having $(n-1)d^{10}ns^0$ configuration, the structure is usually converted into delafossite, being characterized by linear bond O-A-O between MO_2 sheets.⁴⁻⁶ This conversion can be attributed to the balance of

iono-covalency in bridge bond A-O-M. When Ag^+ or Cu^+ ions are placed at A site, the covalency of A-O is greatly increased due to the *sd* hybridization and thus the strong linear σ bond O-A-O is induced. The balance of iono-covalency in A-O-M is considered to play a key role for the layered oxide A_xMO_2 ($x < 1.0$). In this work, we report on the synthesis of new layered oxides $\text{A}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$, where A=Li, Na, Cu and Ag, and their crystallographic evolutions in relation with bond character.

EXPERIMENTAL SECTION

$\text{Na}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ was first prepared by solid state reaction by heating the mixture of stoichiometric amounts of starting materials, Na_2CO_3 , NiO , TiO_2 at 1000°C for 12 h under Ar-stream⁷. Samples of A=Li, Cu and Ag were prepared by cation-exchange reactions using $\text{Na}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ as a precursor and molten salt AX following the equation⁸.



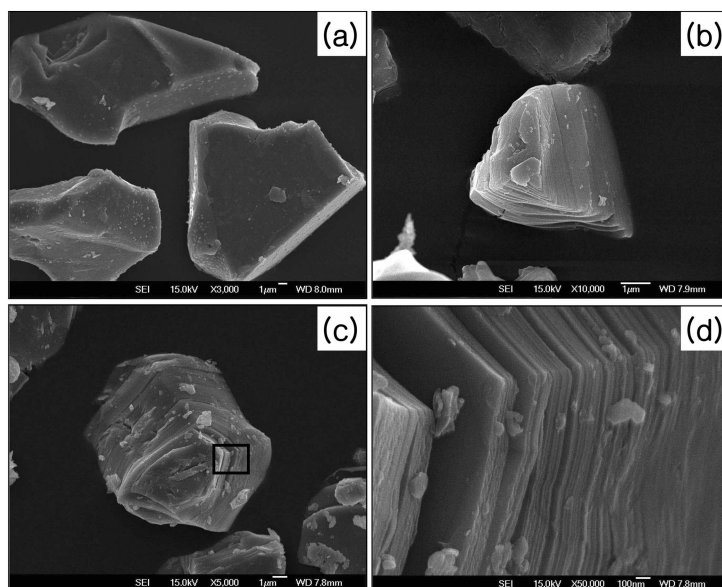


Fig. 1. FE-SEM micrographs of layered oxides $\text{Na}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ (a), $\text{Li}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ (b) and $\text{Ag}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ (c), (d).

Each mixture of molten salt and Na-precursor (3 g; 30 mmol) was put into silica tube, sealed under vacuum, and subsequently heated for 10 days at 420°C for Li- and Cu-substitution, or at 250°C for Ag-substitution. As for Cu-derivative, an additional composition of $\text{Cu}_{0.75}[\text{Ni}_{0.36}\text{Ti}_{0.625}]\text{O}_2$ was prepared to compare the structures. In case of Cu, an excess CuCl of 5 mol% (2.07g; 21mmol) was used due to the difficulty to remove the remaining CuCl after reaction. When A=Li or Ag, about 50 mol% of excessive nitrates (30-40 mmol) were used to facilitate the reaction. KNO_3 was also added for $\text{Ag}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ to keep the oxidative ambient and thus prevented the reduction of Ag^+ into Ag^0 . Products were recovered by washing out the remaining nitrates or chlorides with ethanol and dried under vacuum. The remaining trace of CuCl after reaction was removed with 0.5M aqueous ammonia solution. For $\text{Li}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$, a solution reaction was also performed. $\text{Na}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ was introduced into the LiNO_3 -saturated n-hexanol and subsequently refluxed for 10h at 160°C with vigorous stirring, resulting in low-temperature phase of $\text{Li}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$.

Particle morphology of samples was monitored by FE SEM using JSM6700 FE-SEM II, JEOL. 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 $\text{CuK}\alpha$ radiation ($\lambda=0.1506$ nm). For electrical conductivity measurements, samples were prepared as pellets ($d=7$ mm, $t=2$ mm) by pressing at 20 MPa. Blocking Au-electrodes were deposited by DC-sputtering. The AC-conductivity was measured using IIP 4192A LF impedance analyzer at the range of 5 Hz-13 MHz under Ar atmosphere.

RESULTS AND DISCUSSION

FE SEM photographs of $\text{A}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ (A=Na, Li, and Ag) are presented in Fig. 1. They show topotactic features of the cation-exchange reactions. $\text{Na}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ obtained from direct thermal reaction exhibited disk-shaped large particles of 20-30 μm , reflecting the hexagonal crystallographic feature. After the cation-exchange reactions, the product particles exhibited nano-scale

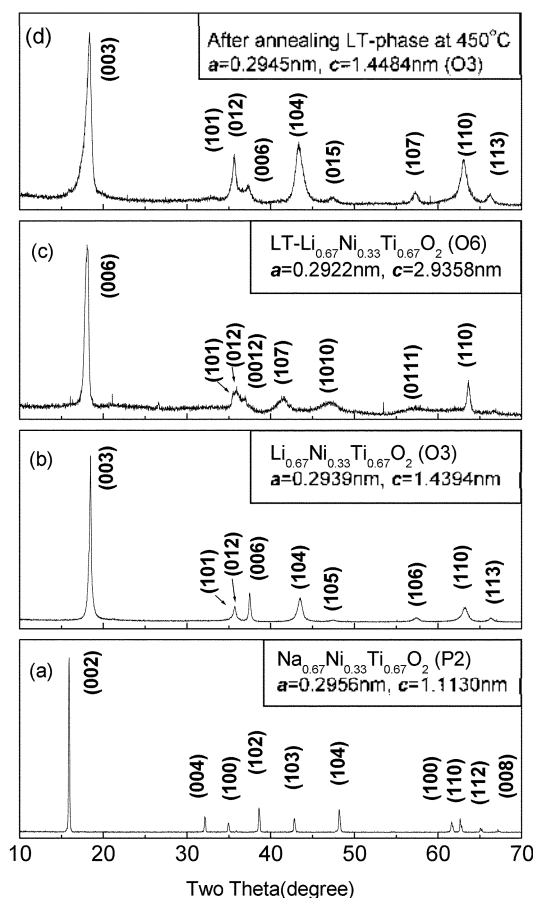


Fig. 2. XRD patterns of $\text{Na}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ (a) and $\text{Li}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ obtained from the molten-salt method at 420 (b), $\text{Li}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ from the reflux in n-hexanol solution (c) and after annealing at 160 °C.

platelet texture and this indicates the reactions were topotactic.

In Fig. 2, XRD patterns of $\text{Li}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ are represented. While the precursor $\text{Na}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ exhibited a primitive hexagonal lattice (type P2)⁷, $\text{Li}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ obtained at 420 showed a structural conversion into type O3 with the periodicity of 3-layer unit along axis *c* and Li^+ ions at octahedral sites. When the cation-exchange was done in n-hexanol solution at 160, slightly different XRD pattern of $\text{Li}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ was obtained as shown in Fig. 2(c). It exhibited two supplementary peaks which could be indexed as (101) and (107) on the basis of structural type O6, though the broad peak pattern

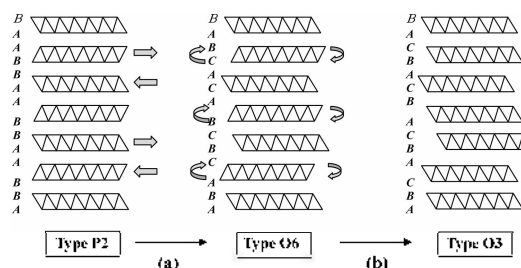


Fig. 3. Schematic diagram of structural evolution from type P2 to O3. At low temperature, the structure changes by the cooperative movement of MO_2 sheets (a), but when temperature is elevated, some bond rupture may be involved in the structural conversion (b).

prevented accurate structural analysis. Since any atomic rearrangement involving the bond rupture of M-O cannot be expected at the temperature as low as 160 °C^{6,8}, the structural conversion in this condition should occur only by the cooperative movements of MO_2 sheets as illustrated in Fig. 3. The low-temperature O6-phase of $\text{Li}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ was a meta-stable phase, for it converted into type O3 after annealing for 12h at 450, where some transient bond rupture of M-O seems possible and thus gives rise to the conversion into type O3.

Fig. 4 shows the XRD patterns of Cu^+ - and Ag^+ -phases. $\text{Cu}_{0.75}[\text{Ni}_{0.375}\text{Ti}_{0.625}]\text{O}_2$ was found to have a well-crystallized 3R-delafoosite structure. Since its precursor $\text{Na}_{0.75}[\text{Ni}_{0.375}\text{Ti}_{0.625}]\text{O}_2$ has the structural type O3⁷, the structural conversion from O3 to 3R can be interpreted by a simple topotatic process accompanied with cooperative movement of MO_2 sheets to furnish linear site for Cu^+ ion⁶. For $x=0.67$, the XRD pattern could be indexed with more complicate 6H-delafoosite structure⁹ with small amount of decomposed impurity NiTiO_3 ¹⁰. The appearance of 6H-delafoosite $\text{Cu}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ can be rationalized by the elevated reaction temperature where the atomic rearrangement is possible, though the reason why the product did not crystallize in 2H-delafoosite which is closely related with P2 is not yet understood. Anyway, the fact that both compositions exhibit delafoosite structure signifies that the covalency in Cu-O is sufficiently strong for maintaining the linear symmetry O-Cu-O.

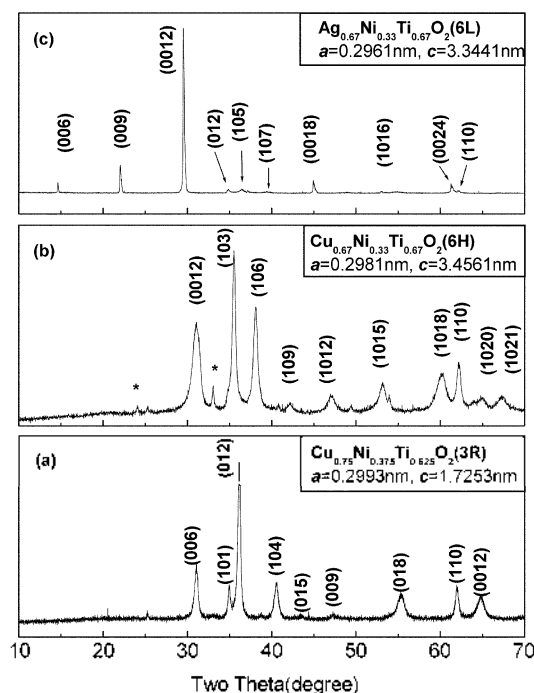


Fig. 4. XRD patterns of $\text{Cu}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ (a) and $\text{Cu}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ (b) obtained at 420, and $\text{Ag}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ at 250 °C. Peaks labeled with asterisk (*) correspond to NiTiO_3 ¹⁰, due to the partial decomposition.

On the other hand, the XRD pattern of $\text{Ag}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ could be indexed in six-layered lattice but not interpreted by any delafossite structure. Systematic absence condition $-h+k+l=3n$ was obeyed in this composition, indicating a rhombohedral symmetry. Since the structural conversion of $\text{Ag}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ could be carried out only by cooperative movement of MO_2 sheets due to low reaction temperature, its rhombohedral symmetry suggests that some of Ag^+ ions should be placed between the close-packed oxygen layers. It means that Ag-O bond should largely lose covalent character, and becomes no more sufficient to keep the linear symmetry of O-Ag-O bond. In such circumstances, the balance of covalency in competitive bond A-O- $(\text{Ni}^{2+}_{0.33}\text{Ti}^{4+}_{0.67})$ should be sensitively shifted to O- $(\text{Ni}^{2+}_{0.33}\text{Ti}^{4+}_{0.67})$ from A-O for A=Ag, whereas Cu-O bond is considered still highly covalent enough to hold the linear coordination.

In Table 1, the ac-conductivity values at 25 °C

Table 1. AC-conductivity of some layered oxides $\text{A}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ (A=Na, Li, Cu, Ag)

Composition	Type	$\sigma_{25^\circ\text{C}}(\text{Scm}^{-1})$	$\sigma_{300^\circ\text{C}}(\text{Scm}^{-1})$
$\text{Na}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$	P2	1.7×10^{-4}	2.98×10^{-3}
$\text{Li}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$	O3	$< 10^{-8}$	1.19×10^{-6}
$\text{Cu}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$	6H	$< 10^{-8}$	1.2×10^{-7}
$\text{Ag}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$	6L	3.67×10^{-4}	4.58×10^{-3}

and 150 °C are listed for $\text{A}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ (A=Na, Li, Ag, and Cu). $\text{Na}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ exhibited a good ionic conduction as reported earlier^{11,12}. For $\text{Li}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$, the ionic conductivity was nearly zero, indicating that the reduced unit-cell volume and thus increased covalency of Li-O as well as the trigonal diffusion window of LiO_6 octahedron should establish an energy barrier too high for Li ions to cross over. In case of $\text{Cu}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$, Though the inter-sheet space for Cu^+ ions is largely increased, the ionic conduction of Cu^+ ion is greatly restricted by the strong covalency of the linear bond O-Cu-O. It is worthy noting that no delafossite oxide with linear bond O-A-O has been reported to exhibit significant ionic conduction. In this sense, the enhanced ionic conductivity found in $\text{Ag}_{0.67}[\text{Ni}_{0.33}\text{Ti}_{0.67}]\text{O}_2$ strongly supports the presence of Ag^+ ions within the rock-salt layer, AgO_3 , where Ag-O is highly ionic. Such Ag^+ ions are therefore expected to diffuse within the rock-salt layer, leading to the enhanced ionic conduction. A systematic study on $\text{Ag}(\text{Ni,Ti})\text{O}_2$ focused on the correlation of crystallographic features and the conduction mechanism is now under progress in our lab.

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