INTRODUCTION

Layer type oxides \( A^1M^{III}O_2 \) usually adopt delafossite structure when \( A = Cu, Ag \) or Pt, that can be characterized by linear coordination of \( A \) ions between \( MO_2 \) octahedral sheets.\(^\text{1-3} \) According to stacking ways of alternating \( MO_2 \) and \( A \) layers along \( c \) axis, delafossite has several polytypes including 3 R and 2 H.\(^\text{4-5} \) Ag-delafossite oxides have been usually prepared by cation exchange reaction between the alkali precursors \( AMO_2 \) (\( A = Li \) or Na) and CuCl or AgNO\(_3\),\(^\text{6-7} \) for which the strong covalency of linear O-Ag-O is regarded as a driving force that overcomes the unfavorable geometry for ionic interactions in lattice.

The bond nature of each A-O and M-O in bridge bond A-O-M as well as the two dimensional structure are considered to be key factors for the physical properties of delafossite. Each bond A-O can affect directly on the bond character of the counter bond M-O via common oxygen atom, for instance, the covalency in A-O can be considerably reduced by introducing strong covalent bond M-O. Such a viewpoint has been frequently adapted in various studies on the electronic properties of delafossite oxides, including the luminescence of linear clusters of O-Cu-O in CuLaO\(_2\),\(^\text{8} \) the electronic transport properties and magnetic properties AgMO\(_2\) (\( M = Ni, Fe, Co \)),\(^\text{9-11} \) where the Ag-O bond exhibit fairly strong covalent character. When the covalency in M-O is extremely reinforced as in our previous work on \( Na_xNi_{x/2}Ti_{1-x/2}O_2 \),\(^\text{12-13} \) the counter bond Na-O has been proved to have enhanced ionicity leading to a ionic conduction of Na\(^+\) within the interlayer space. Moreover, some selected compositions of \( x = 0.85 \) and 0.70 of \( Na_xNi_{x/2}Ti_{1-x/2}O_2 \) have been successfully applied to the preparation of the corresponding \( Ag_xNi_{x/2}Ti_{1-x/2}O_2 \) phases via cation-exchange route.\(^\text{14} \)

Recently a systematic preparation of \( Ag_xNi_{x/2}Ti_{1-x/2}O_2 \) over the entire compositional domain \( (0.60 \leq x \leq 1.0) \) has been successfully carried out in our lab. In this paper, the preparation of Ag-deficient layer-type oxides \( Ag_xNi_{x/2}Ti_{1-x/2}O_2 \) \( (0.60 \leq x \leq 1.0) \) synthesis and their structural and ionic conductivity properties have been investigated and discussed on the focus of evolution of bond character of Ag-O-(Ni,Ti) with the compositional variation.

EXPERIMENTS

Layered transition metal oxides \( Ag_xNi_{x/2}Ti_{1-x/2}O_2 \) \( (0.60 \leq x \leq 1.0) \) have been prepared by cation ex-
change reactions using corresponding alkaline phases NaxNi1-x/2Ti1-x/2O2 as precursors. Polycrystalline samples of NaxNi1-x/2Ti1-x/2O2 were synthesized by direct solid state reactions at 950 °C from the mixed powders of Na2CO3, NiO, and TiO2, where 5 ~ 10% excess of Na2CO3 for its volatile nature at high temperature. Mixtures of Na-precursor and silver nitrate were placed in evacuated and sealed pyrex tubes with oxidative flux potassium nitrate to prevent any eventual reduction of silver. The cation-exchange reactions were carried out by heating the tubes at 300 ~ 350 °C for 1 ~ 2 weeks. Obtained products were leached into methanol and/or acetonitrile to remove the remaining silver or potassium components and then 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. Measurements were made by a step-scanning mode in the 2θ range of 5 to 70° with a step width 0.02°. Silicon powder (99.999%) was used as an internal standard. In order to examine the Ag-content and thermal stability of the products, thermogravimetric analysis (TGA) was carried out using TA-SDT 2960 analyzer with a scan rate of 10 °C/min under Ar-flow up to 1000 °C.

For DC-polarization measurements, samples were made as disk-like pellets (d = 7 mm, t = ~2 mm) under a pressure of 75 MPa. Blocking electrodes were deposited on both sides of the pellets by DC gold sputter. Measurements were performed at 0.50 V, using a Keithly 2000 digital source meter at room temperature. Ionic conductivity was obtained at 300 K and 420 K under argon flow by AC-impedance measurement using HP 4192 A LF impedance analyzer at the frequency range of 5 Hz ~ 13 MHz.

RESULTS AND DISCUSSION

All the ion-exchange reactions produced single phase layer-type oxides. Selected XRD pattern of the AgxNi1-x/2Ti1-x/2O2 (0.60 ≤ x ≤ 1.0) were plotted in Figure 1 and the evolution of lattice parameter a and c of AgxNi1-x/2Ti1-x/2O2 was shown in Figure 2 in comparison with the corresponding precursor Na-phases. AgxNi1-x/2Ti1-x/2O2 were found to exhibit two consecutive structural variants with x, a delafossite structure (3 R; R3 m) for 0.80 ≤ x ≤ 1.0 followed by a six-layered structure (6 L) for 0.60 ≤ x ≤ 0.80. For the latter, a systematic absence of (hkl) diffraction peaks with -h + k + l ≠ 3n was found, suggesting that it has also a rhombohedral symmetry. The boundary composition x = 0.80 was prepared several times but its structure could not be fixed since both structures were detected depending on the samples and sometimes a mixture of both structures was obtained. As x decreases, the peak intensities except for (00l) series rapidly became weak, which should be originated from the decrease of occupancy of silver ions that are randomly distributed within ab plane and thus leading to an increase of noncrystallinity within ab plane. Considering that the cation-exchange reaction takes place via topotactic route at moderate reaction temperature, only cooperative displacements of MO2 sheets of Na-precursors within ab plane are possible to furnish the Ag-sites in the
The evolution of lattice parameters $a$ and $c$ of $\text{Ag}_x\text{Ni}_{1-x/2}\text{Ti}_{1-x/2}\text{O}_2$ ($0.60 \leq x \leq 1.0$) (square) and the corresponding Na-precursors (circle) are plotted together. Parameter $c$ was presented per layer.

Fig. 2. The evolution of lattice parameters $a$ and $c$ of $\text{Ag}_x\text{Ni}_{1-x/2}\text{Ti}_{1-x/2}\text{O}_2$ ($0.60 \leq x \leq 1.0$) (square) and the corresponding Na-precursors (circle) are plotted together. Parameter $c$ was presented per layer.

lattice. Consequently it has been found that 6 L does provide rock-salt oxide layers in which Ag$^+$ ions are present in contrast to the usual linear coordination sites parallel to the axis $c$ as in delafossite structure.\(^{14}\)

The evolution of $a$ of Ag-phases with $x$ can be primarily attributed to the difference of ionic radii between Ni$^{2+}$ (0.69 Å) and Ti$^{4+}$ (0.605 Å).\(^{15}\) Ag-phases exhibited neatly larger $a$ than corresponding Na-phases, for which two major reasons can be considered. When Na$^+$ ions are substituted with Ag$^+$ ions, the covalent bond character of M-O in bridging bond A-O-M should be decreased due to the increased covalency of competing bond Ag-O, resulting in the increase of bond distance of M-O. Secondly the direct repulsion of Ag$^+$-Ag$^+$ in the delafossite structure should also render $a$ increased in Ag-phases. For the delafossite domain, $c$ slightly increases as $x$ decreases. It seems to reflect that the electrostatic repulsion between negatively charged MO$_2$ sheets increases according to the decreased population of Ag$^+$ ions in interlayer space.\(^{6}\) Additionally the covalency of Ag-O is supposed to become weak and so the bond distance tends to increase as $x$ decreases, since covalency of competing bond (Ni$_{1/2}$Ti$_{1/2}$)-O is reinforced. The drastic decrease of $c$ at the structural transition 3 R $\rightarrow$ 6 L strongly supports that at least all the Ag$^+$ ions could not be in those linear sites of delafossite any more. It strongly suggests that the ionicity of Ag-O is greatly increased so that all the Ag$^+$ ions could not be located at the linear coordination but rather in rock salt-like environment, much more favorable for electrostatic interaction of Ag$^+$ with oxide ions.

Thermogravimetry analysis (TGA) results of $\text{Ag}_x\text{Ni}_{1-x/2}\text{Ti}_{1-x/2}\text{O}_2$ ($x = 0.60, 0.67, 0.70, 0.75, 0.85$) in Figure 3. Thermal decomposition was detected around 973 K for all samples and the XRD results on the decomposed product indicated that the reaction could be described as following.

$$\text{Ag}_x\text{Ni}_{1-x/2}\text{Ti}_{1-x/2}\text{O}_2 \rightarrow x\text{Ag} + x/2 \text{NiTiO}_3 + (1-x)\text{TiO}_2 + x/4\text{O}_2$$

The observed weight losses of $\text{Ag}_x\text{Ni}_{1-x/2}\text{Ti}_{1-x/2}\text{O}_2$ were found in good accordance with the calculated ones based on the chemical equation above within ±5%.

DC-polarization results of $\text{Ag}_x\text{Ni}_{1-x/2}\text{Ti}_{1-x/2}\text{O}_2$ ($0.60 \leq$
새로운 이온전도성 층상 산화물 Ag$_{x}$Ni$_{x}/2$Ti$_{1-x}/2$O$_2$ ($0.60 \leq x \leq 1.0$)의 합성

Table 1. Ionic conductivity of Ag$_{x}$Ni$_{x}/2$Ti$_{1-x}/2$O$_2$ at 300 K and 423 K

<table>
<thead>
<tr>
<th>$x$</th>
<th>type</th>
<th>$\sigma_{300,K}$ (Scm$^{-1}$)</th>
<th>$\sigma_{423,K}$ (Scm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.60</td>
<td>6 L</td>
<td>$7.52 \times 10^{-5}$</td>
<td>$1.75 \times 10^{-5}$</td>
</tr>
<tr>
<td>0.67</td>
<td>6 L</td>
<td>$3.66 \times 10^{-4}$</td>
<td>$4.58 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.75</td>
<td>6 L</td>
<td>$7.18 \times 10^{-5}$</td>
<td>$1.60 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.85</td>
<td>3 R</td>
<td>$6.28 \times 10^{-7}$</td>
<td>$7.27 \times 10^{-5}$</td>
</tr>
<tr>
<td>1.0</td>
<td>3 R</td>
<td>$1.30 \times 10^{-8}$</td>
<td>$9.11 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

$x \leq 1.0$) at 0.50V are represented in Figure 4. For the conventional delafossite phases $x = 1.0$ and 0.85, no polarization was practically observed, while 6 L phases exhibited significant polarization. It means that Ag$^+$ ions in linear O-Ag-O group stay immobile even with significant vacancy concentration due to strong covalency of Ag-O. Cole-Cole diagrams of Ag$_{x}$Ni$_{x}/2$Ti$_{1-x}/2$O$_2$ ($x = 0.60, 0.85$) at 300 K are plotted in Figure 5. The plot for $x = 0.60$ shows a semicircle in the high frequency region and a spur in the low frequency region. The capacitance extracted from the maximum of semicircle was determined to be $\sim 60$ pF, which confirmed this semicircle to be of bulk component. The low frequency domain is regarded from grain boundary and double layer component. In this case, the bulk resistivity was determined from the intercept on the real axis of the zero phase angle extrapolation from the high frequency side. The ionic conductivity results at 300 K and 423 K are listed in Table 1. The obtained results show a clear difference of conduction properties between the two structural variants. The type 6 L shows the conductivity $10^2-10^3$ times greater than the conventional delafossite type. It means that the covalent bonding of oxide in bridge bond Ag-O-M are greatly shifted to M-O and thus the interaction with Ag$^+$ should be essentially ionic. The rock salt-like oxide array around Ag$^+$ should also facilitate the diffusion path, being compared with the linear sites of delafossite.

We have successfully prepared a new series of layer-type oxides Ag$_{x}$Ni$_{x}/2$Ti$_{1-x}/2$O$_2$ over a wide range of $0.60 \leq x \leq 1.0$. Consecutive structural domains of type 3 R delafossite ($0.85 \leq x \leq 1.0$) and a new layered structure 6 L characterized by rock salt-like oxide array around Ag$^+$ ion ($0.60 \leq x \leq 0.80$) have been found as $x$ decreases. The evolution of bond nature in bridge bond Ag-O-M has been regarded as the major motive of this structural transition. Such a modulation of ionic-covalency in Ag-O has been found effective enough to make the Ag$^+$ ions mobile, giving rise to the ionic conductivity as high as $3.66 \times 10^{-4}$ Scm$^{-1}$ for $x = 0.67$ at 300 K.

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REFERENCES