**Figure 4.** The evolution of the carbonyl stretching mode as a function of (a) temperature; (b) salt concentration.

As the temperature increases, the partial bond rotation seems to occur around the ketone linkage of the aryl C-C($\neq$ O)O giving rise to the breakage of the intermolecular interactions between the mesogens. Also, a similar phen-omenon occurs in the case of the increase of the salt concentration. As the excess Li$^+$ ions are introduced for complete binding, the redundant Li$^+$ ions seem to play a role in breaking down the intermolecular interactions. Concomitantly, the free carbonyl groups are rearranged to release the steric strain about the aryl C-C(=O)O. Our experimental results, therefore, strongly indicate that the conformational changes in the mesogenic units occur not only due to the complexation of the dissociated salts, but also due to the intercalation of the nondissociated ones.

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# Preparation of Ag-Deficient Delafossite-Type Compounds $Ag_xCoO_{2-3}$ (x=0.95, 0.75)

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*Received April 10, 1997*

Delafossite type compounds[1] have a general formula $A^IB^{III}O_2$ (A=Cu, Ag, Pt, Pd; B=Al, Fe, Co, Ni, Rh, Ln...), and are characterized by their two-dimensional structure as represented in Figure 1. $B^{3+}$ cations are octahedrally coordinated by oxides to form $BO_6$ units, which are developed in **ab** plane by edge share, giving rise to [BO$_2$] plates in the plane. These plates are stacked along **c** axis and generate 2-fold linear sites between them where the monovalent cations, generally being of d$^{10}$ configurations, are situated. According to the stacking way of these [BO$_2$] plates in c direction, several structural polytypes are geometrically possible, among which 3R (S.G. R3m) and 2H (P6$_3$/mmc) structures are shown in Figure 1(b). The factors determining polytype structure have not been well understood, but the majority of delafossite phases have been reported to crystallize in 3R-type whereas only a few ones in 2H-type.[2,3]
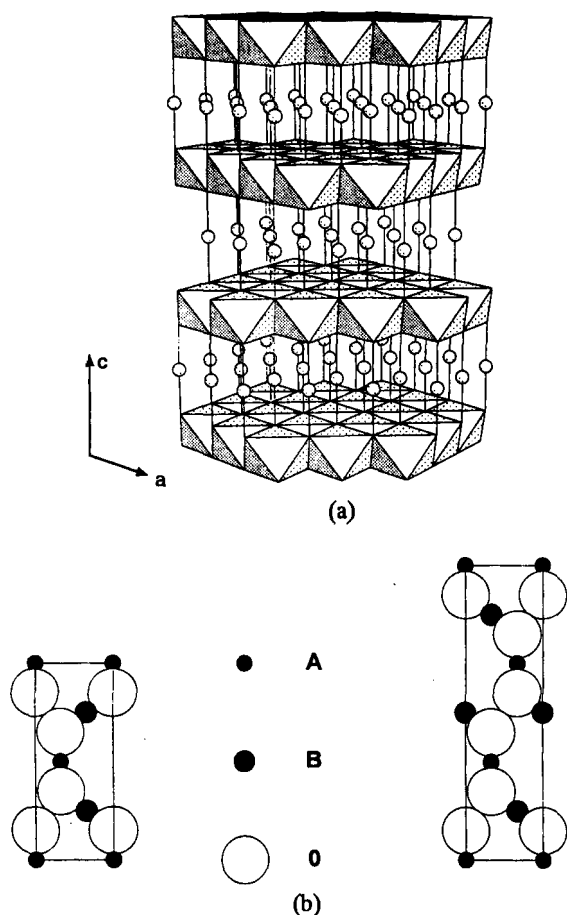
**Figure 1.** 3R-delafossite structure of $ABO_2$ oxides (a). Balls represent the $A^I$ ions. Projection on (110) plane (b) for polytype 2H (*left*) and for 3R (*right*).

Despite various synthetic routes known for delafossite type compounds, Ag-phases have been prepared only through the low-temperature methods such as cation-exchange reaction from appropriate precursors or through the hydrothermal technique because of their poor thermal stability.[4,5] Considering that the latter has a limited applicability, it can be said that the successful synthesis of Ag-delafossite basically depends upon the existence of appropriate precursors. In fact, almost all of the known Ag-delafossites could be prepared using layer-type Li or Na metalates.[1,4] Although some of these precursors are well known to exhibit alkali metal-deficient states $A_xBO_2$ (A=Li or Na),[6-8] Ag-deficient delafossite phases have not been reported up to now to the authors' knowledge. This has led us to make an effort to prepare Ag-deficient delafossite compounds, and we report here the syntheisis of $Ag_xCoO_{2-\delta}$ (x= 0.95, 0.75) and their electrical conductivities.

## Experimental

Three samples, $AgCoO_2$ and two Ag-deficient phases, were prepared by cation-exchange reactions as follows: Precursors, $NaCoO_2$ and $Na_{0.7}CoO_{2-\delta}$ ($\delta \approx 0.03$)[8] were obtained by heating the mixtures of $Na_2O$ (> 97%) and $Co_3O_4$ (99.9%) under $O_2$ flow for 12-16 hrs at 600 °C and 700 °C,

respectively. 5-8% excess of $Na_2O$ was added for its volatility in both reactions. Cation-exchange reactions were carried out respectively by heating the mixtures of $AgNO_3$ (>99.5%), $KNO_3$ (reagent grade) and each of the Na-phases, in a vacuum-sealed pyrex tube at 300 °C for 10 days. About 50% excess of $AgNO_3$ was added to facilitate the reaction and $KNO_3$ was used to keep oxidizing ambient. The third sample was prepared from $Na_{0.7}CoO_{2-\delta}$ using relatively small excess (5%) of $AgNO_3$. Products were washed with methanol to get rid of remaining salts, and black powders were finally recovered after vacuum-drying.

The atomic ratio Ag/Co in two samples from $Na_{0.7}CoO_{2-\delta}$ was determined by ICP-AES method at the Korean Basic Science Institute (Seoul). Powder X-ray diffraction data were recorded on a rotating-anode installed M18XHF MAC-Science diffractometer using Cu K radiation ($\lambda$=1.5405 Å) monochromated by a curved graphite. For electrical resistivity measurements, disk-type ($\Phi$=7 mm; t≃1.2 mm) pellets were prepared with about 250 mg of each sample by pressing uniaxially under *ca.* 250 MPa. Conventional four-probe method was employed and the measurements were carried out at the temperature range of 30-300 K.

## Results and Discussion

From the elemental analysis data, the chemical formulae were determined to be $Ag_{0.95+0.02}CoO_{2-\delta}$ and $Ag_{0.75\pm0.01}CoO_{2-\delta}$, respectively for the two samples from 50% and 5% excessive usage of $AgNO_3$. Provided that $\delta$ is not significantly changed in both phases, the valence state of cobalt in $Ag_{0.95}CoO_{2-\delta}$ should be very close to 3+, while $Ag_{0.75}CoO_{2-\delta}$ should have a mixed-valence state.

Powder X-ray diffractograms of three samples are shown in Figure 2. $AgCoO_2$ exhibits the characteristic peak pattern corresponding to the 3R type as already known,[1,4] however, both peak patterns of Ag-deficient phases could be indexed with the 2H-type structure. In case of $Ag_{0.75}CoO_{2-\delta}$, small amount of impurities was detected in diffractogram, suggesting a small portion of product was decomposed during the reaction (Figure 2(c)). These results seem to suggest strongly that the structure of Ag-delafossite should be inherently determined by the structural characteristics of the precursor: $NaCoO_2$ (used for $AgCoO_2$) has an isostructure with $\alpha$-$NaFeO_2$ structure (R3m), where oxide layers along c axis (hexagonal setting) are arrayed in ABCABC..., and $Na^+$ and $Co^{3+}$ ions are alternatively located at octahedral sites along c axis. In order to get the delafossite structure, the substitution of $Ag^+$ for $Na^+$ ions is accompanied by a series of structural changes. Since the reaction is performed at relatively low temperature which cannot provide a sufficient activation energy for overall atomic rearrangement, the linear sites for $Ag^+$ ions should be induced only by the cooperative movements of $[BO_2]$ plates. They would move along [001] direction to increase the inter-distance between themselves and addtionally a cooperative displacement in ab plane should take place to furnish 2-fold linear sites. For example, a $[BO_2]^-$ plate being fixed, the upper and lower adjacent plates should move respectively a distance of $a/\sqrt{3}$ back and forth or vice versa in one of the three directions as demonstrated in Figure 3. All of the cooperative rearagements of $[BO_2]^-$ plates to create the linear coordination
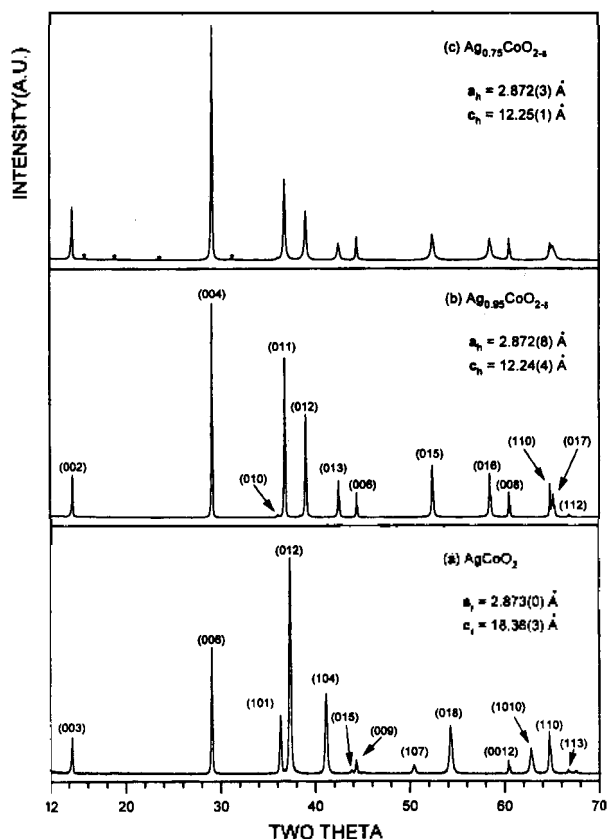
**Figure 2.** Powder X-ray diffractograms of $AgCoO_2$ (a), $Ag_{0.95}CoO_{2-\delta}$ (b) and $Ag_{0.75}CoO_{2-\delta}$ (c). Impurity peaks were marked with asterisks.



**Figure 3.** Projection of oxide layers stacked in the order of AB-CABCA... on (001) plane showing the relative positions A, B and C and the three directions of displacement leading linear coordination sites (a). Transformation from $\alpha$-$NaFeO_2$ structure to 3R-delafossite one in the course of cation-exchange reaction (b). Circles represent $Na^+$(open) and $Ag^+$ ions(solid).

sites starting from $\alpha$-$NaFeO_2$ structure result only in the stacking pattern of ABBCCAAB..., which corresponds to the 3R-type delafossite structure. On the other hand, $Na_{0.7}$ $CoO_{2-\delta}$ (used for $Ag_xCoO_{2-\delta}$) is known to have the P2 structure[8], where the oxide layers are stacked in the order of AB-BAABB... so that $Co^{3+}$ ions at octahedral and $Na^+$ ions at prismatic sites are alternately located along $c$ axis. Consequently, the [$BO_2$] plates do not move in **ab** plane during the reaction but a simple movement along **c** axis is sufficient for the generation of the linear coordination sites for $Ag^+$'s. In this case, the stacking order of oxide layers remains unchanged, inducing the 2H-type delafossite structure. Therefore, It can be said that a delafossite phase synthesized by cation-exchange method have a structure pre-determined by the structural type of a used precursor.

The lattice constants a and c in all three samples were determined to be practically the same. The c values of 3R ($c_r$) and 2H structure ($c_h$) are correlated by $2c_r=3c_h$. These results appear to be rational for $Ag_{0.95}CoO_{2-\delta}$, in which the oxidation states of cations are practically unchanged from $AgCoO_2$. However, the situation is not so simple for $Ag_{0.75}CoO_{2-\delta}$ which is believed to have some mixed-valence state. Considering that the $Co^{4+}$ is smaller even in high-spin state (r=0.53 Å) than $Co^{3+}$ (0.545 Å; LS),[9] the observed ah in $Ag_{0.75}CoO_{2-\delta}$ phase implies that the concentration of $Co^{4+}$ ion is very small and hence the valency of cobalt is actually 3+, like in the other two samples. It may be consequently assumed that the silver ion should be oxidized to a higher
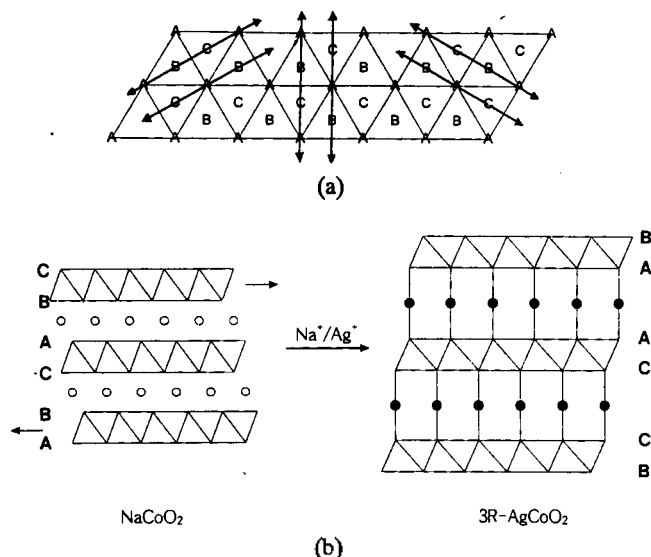
valent state. In previous works done with $AgNiO_2$,[10,11] an equilibrium between two cations, $Ag^+ + Ni^{3+} \rightleftharpoons ^? Ag^{2+} + Ni^{2+}$ was proposed. Even though it may be strongly shifted to the left-hand side, the silver ions are considered to be slightly oxidized to create holes in Ag (4d) subband, leading to a metallic transport property. Because $Co^{4+}$ is generally believed to be a stronger oxidant than $Ni^{3+}$, a charge transfer between $Co^{4+}$ and $Ag^+$ through oxygen bridge Co-O-Ag seems to be highly probable. But in order to clarify this charge transfer process, the valence states of silver and cobalt in $Ag_{0.75}CoO_{2-\delta}$ should be investigated in more detail.

Resistivity measurements (Figure 4) reveal that all the samples are semiconductors. The similar thermal behaviors of $AgCoO_2$ and $Ag_{0.95}CoO_{2-\delta}$ support that the oxidation state of
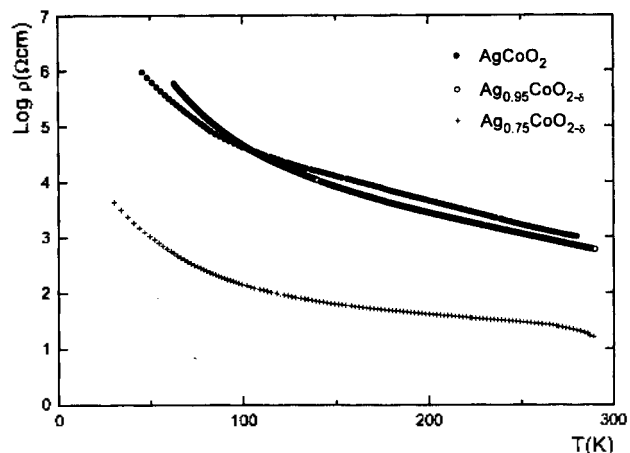


**Figure 4.** Thermal variation of the electrical resistivity of Ag-delafossites.

the latter is practically of 3+ and hence the charge carriers are dominantly created by interband thermal activation like in the former. This result also indicates that the structural difference of 2H and 3R does not apparently have any significant influence on the electronic transport properties. The enhanced conduction observed in $Ag_{0.75}CoO_{2-\delta}$ can be attributed to the presence of charge carriers induced by the mixed-valence state. But they are obviously localized, probably due to the partial absence of $Ag^+$ ions and the increase of non-crystallinity in Ag sublattice, that should cause the localization of the charge carriers. The transport process in this phase should occur through the mobility activation of carriers.

In conclusion, Ag-delafossites prepared by cation-exchange reation at low temperature are considered to have the structures pre-determined by the structural type of precursor. Ag-deficient delafossite-type oxides $Ag_xCoO_{2-\delta}$ (x= 0.95, 0.75) obtained from nonstoichiometric $Na_{0.7}CoO_{2-\delta}$ crystallize in 2H-type structure, and exhibit semiconductivity even in the presence of mixed-valency.

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# Synthesis of Enkephalin Degrading Peptidase Inhibitors

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Since their isolation from pig brain,[1] enkephalins (Tyr-Gly-Gly-Phe-Leu and Tyr-Gly-Gly-Phe-Met) have come under intensive study because they may afford an alternative potential method of pain relief. In addition to their opiate-like properties they are known to have roles as neurotransmitters or neuromodulators in the central nerve system.[2] One of the major difficulties associated with use of these compounds as analgesic is their short half life.[3] Both Leu- and Met-enkephalin are rapidly inactivated by enzymes in serum and in brain. Three mechanisms for inactivation of enkephalins in brain have been observed: (a) cleavage at the Tyr-Gly bond by enkephalin aminopeptidase; (b) cleavage at the Gly-Phe bond by enkephalinase; (c) cleavage at the Phe-Met or Phe-Leu bond by carboxypeptidase. Most efforts directed at obtaining longer acting enkephalins have centered on the synthesis of enkephalin analogous resistant to enzymatic degradation. For example, a simple substitution of with D- has been resulted in a compound which is active via intracerebral or vascular administration.[3] Recently, by synthetic combinational library containing tens of millions of D-amino acid hexapeptides,

the peptide, Ac-D-Arg-D-Phe-D-Trp-D-Ile-D-Asn-D-Lys-$NH_2$ which bears no resemblance to any known opioid peptide was reported to show strong analgesic effect.[4] Another approach to increase the effective action of enkephalins would be to limit their rate of degradation by blocking enzymatic pathways associated with catabolism. A variety of aminopeptidase or enkephalinase inhibitors with Zn-chelating function consisting of a thiol, carboxyl, phosphoryl, or hydroxamate group have been studied. Recently, Nishimura and Hazato isolated endogenous inhibitor of enkephalin degrading enzymes from bovine spinal cord. This new substance, designated spinorphin, is composed of a heptapeptide (Leu-Val-Val-Tyr-Pro-Trp-Thr).[5] In order to obtain longer acting enkephalins, it seems to be necessary to block the activities of enkephalin aminopeptidase and enkephalinase simultaneously. Therefore, simultaneous administration of thiophan, an inhibitor of enkephalinase and bestatin, an inhibitor of membrane-bound aminopeptidase, induced stronger analgegesic effects than thiophan alone.[6] In a continuing search for inhibitors, we have synthesized a new type of inhibitor, that can inhibit enkephalin am-