Low temperature synthesis of layered Na$_x$CoO$_2$ and K$_x$CoO$_2$ from NaOH/KOH fluxes and their ion exchange properties

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Abstract. We report a low temperature synthesis of layered Na$_{0.7}$CoO$_2$ and K$_{0.44}$CoO$_2$ phases from NaOH and KOH fluxes at 400°C. These layered oxides are employed to prepare hexagonal HCoO$_2$, Li$_x$CoO$_2$ and Delafossite AgCoO$_2$ phases by ion exchange method. The resulting oxides were characterised by powder X-ray diffraction, X-ray photoelectron spectroscopy, SEM and EDX analysis. Final compositions of all these oxides are obtained from chemical analysis of elements present. Na$_{0.7}$CoO$_2$ oxide exhibits insulating to metal like behaviour, whereas AgCoO$_2$ is semiconducting.

Keywords. Layered oxides; ion exchange reaction; powder X-ray diffraction; NaOH and KOH fluxes.

1. Introduction

Layered oxides have interesting chemical and physical properties. They often allow the reversible insertion and extraction of cations or protons. They are used as electrodes in rechargeable batteries. Na$_x$CoO$_2$ and K$_x$CoO$_2$ layered oxides crystallizing in a variety of structure types and varied amount of Na or K ions are the precursors to Li$_x$CoO$_2$, which is a cathode material for Li ion batteries. Na$_x$CoO$_2$ ($x \leq 1$) was first prepared by Fouassier et al$^1$ by heating stoichiometric amounts of Co$_3$O$_4$ and Na$_2$O$_2$. Na$_x$CoO$_2$ was also prepared by heating stoichiometric amounts of NaOH and Co metal. Alternatively, heating Co metal in Na$_2$CO$_3$ at 850°C also gave Na$_x$CoO$_2$ phases. Balsys and Davis$^2$ have refined the structure of Na$_{0.7}$CoO$_2$ using neutron diffraction data. The structure of Na$_x$CoO$_2$ consists of sheets of edge-sharing CoO$_6$ octahedra between which sodium ions are intercalated within a trigonal prismatic or octahedral coordination. The structural change accompanied by ion-exchange is reported in Na$_{0.7}$CoO$_2$ by Delmas et al$^3$. In Na$_{0.7}$CoO$_2$ the anion sequence is ABBA. When this material is ion-exchanged with LiCl, a metastable form of LiCoO$_2$ with the layer sequence ABCBA is obtained. Recently, Takada et al$^4$ reported superconductivity in Na$_x$CoO$_2$,$y$H$_2$O ($x \approx 0.35, y = 1.3$) with a $T_c$ of about 5 K. There is a marked resemblance in superconducting properties between the Na$_x$CoO$_2$,$y$H$_2$O and high $T_c$ copper oxides, suggesting that the two systems have similar underlying physics. Inorganic solids exchanged with protons to give rise to new HTaWO$_6$,$y$H$_2$O phases has been reported by Groult et al$^5$. The conversion of LiNbO$_3$ and LiTaO$_3$ to HNbO$_3$ and HTaO$_3$ respectively, is done by the treatment with hot aqueous acid.$^6$ The exchange of

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$^4$Dedicated to Professor C N R Rao on his 70th birthday

*For correspondence
Li$^+$ by protons is accompanied by a topotactic transformation of the rhombohedral LiNbO$_3$ structure to the cubic perovskite structure of HNbO$_3$. Bhat and Gopalakrishnan$^7$ have synthesized novel protonated layered oxides, HMWO$_6$.1H$_2$O (M = Nb or Ta) by topotactic exchange of lithium in trirutile LiMWO$_6$ with protons with treatment with dilute HNO$_3$. Electrocatalytic activities of HCoO$_2$ for the oxidation of hydrogen with the oxygen transported through the solid electrolyte.

K$_{0.5}$CoO$_2$ was prepared by heating stoichiometric amounts of KOH and Co$_3$O$_4$ in O$_2$ at 450°C. KCoO$_2$.9 KCo$_{0.5}$O$_2$. KCo$_{0.67}$O$_2$. αKCoO$_2$ and βKCoO$_2$ phases$^9$ and also RbCoO$_3$ and CsCoO$_3$ have been identified.$^{10}$ The known NaCoO$_2$ and K$_2$CoO$_2$ phases and their structure are summarized in table 1.

We were interested in synthesizing layered NaCoO$_2$ and K$_2$CoO$_2$ by soft chemistry route employing NaOH and KOH fluxes. In these layered oxides, Co is present in +3 and +4 states. Delmas et al$^{12}$ have reported that the non-stoichiometric alkali metal cobalt oxides are metallic, while stoichiometric NaCoO$_2$ is a semiconducting. KCoO$_2$ with NaCoO$_2$ and NaCoO$_2$ are metallic oxides.

NaI and KI could also be employed to grow NaCoO$_2$ and K$_2$CoO$_2$ phases. Here we report low temperature synthesis of layered NaCoO$_2$ and K$_2$CoO$_2$ phases from NaOH and KOH fluxes. These layered oxides are employed to make H$_2$CoO$_2$, Li$_2$CoO$_2$ and also Ag$_2$CoO$_2$ by ion exchange method. We also report Na$_2$CoO$_2$ synthesised from molten NaI flux.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Structure</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Reference</th>
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<td>10</td>
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<tr>
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<td>–</td>
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Layered Na$_x$CoO$_2$ and K$_x$CoO$_2$ from NaOH/KOH fluxes

2. Experimental

2.1 Synthesis of Na$_x$CoO$_2$ and K$_x$CoO$_2$

Layered Na$_x$CoO$_2$ and K$_x$CoO$_2$ phases were synthesized from cobalt oxalate or nitrate salts mixed with NaOH or KOH (AR grade) in the weight ratio of 1:10 in a recrystallized alumina crucible. For the preparation of Na$_x$CoO$_2$, a typical run contains CoC$_2$O$_4$.2H$_2$O (3.6591 g) and NaOH (7.9798 g). The mixture was heated at 400°C for 12 h in a muffle furnace. Initially a clear blue solution was observed and gradually black flaky crystals precipitated. The furnace was put off after 12 h. Excess alkali was washed with distilled water and dried at 110°C. Similarly, K$_x$CoO$_2$ phase is synthesized from KOH flux.

NaI was also used as a flux to prepare Na$_x$CoO$_2$ phase. CoC$_2$O$_4$.2H$_2$O is mixed with 10 times excess of dry NaI in a recrystallized alumina crucible. The mixture was heated to 750°C for 24 h. The melt was furnace cooled and washed with hot distilled water until no Na$^+$ ion was detected in the filtrate. The black solid was filtered and dried at 110°C.

2.1a Preparation of H$_x$CoO$_2$: Na$_x$CoO$_2$ and K$_x$CoO$_2$ phases are non-stoichiometric layered oxides. The ion exchange of sodium or potassium with proton was achieved by mixing 1 g of Na$_x$CoO$_2$ or K$_x$CoO$_2$ samples in 50 ml of 1 M HCl. The solution was kept for 12 h and the acid was decanted. This ion exchange treatment was repeated thrice for the same sample, each time in fresh 1 M HCl solution. The exchanged sample was washed with distilled water and dried at 110°C.

2.1b Preparation of Ag$_x$CoO$_2$: Na$_x$CoO$_2$ or K$_x$CoO$_2$ precursor was mixed with two times excess of AgNO$_3$. The mixture was heated at 275°C, above the mp of AgNO$_3$ (212°C) for 3 h. The melt was furnace cooled to room temperature, washed with distilled water until the filtrate was free from Na$^+$/Ag$^+$ ions. Finally, the resulting black flaky crystals were isolated and dried at 110°C.

2.1c Preparation of Li$_x$CoO$_2$: Layered Li$_x$CoO$_2$ phase was also synthesized by cation exchange reaction. Na$_x$CoO$_2$ or K$_x$CoO$_2$ precursor is mixed with twice the excess of LiNO$_3$ and heated to 250°C for 3 h and cooled to room temperature. Excess LiNO$_3$ was washed with distilled water and dried at 110°C. Here also, black flaky crystals were isolated.

2.2 Characterisation

The flux-grown oxides were characterized by powder X-ray diffraction (XRD) using Siemens D5005 diffractometer with Cu Kα (1.5418 Å) radiation. The morphology and composition of these crystalline phases were obtained from scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis. Final composition of these phases was obtained by chemical analysis of the elements present. Oxygen content was determined by iodometric titration. Electrical resistivity measurements were done on the sintered pellets at 800°C using four-probe technique. X-ray photoelectron (XPS) study of selected phases were done using ESCA-3 Mark II spectrometer with Al Kα radiation. There was no charging of the samples. Binding energy of the core levels are calibrated with reference to C (1s) at 285 eV.
2.2a Cobalt estimation: About 50 mg of the compound was dissolved in 10 ml of 6 M HCl and evaporated to dryness. The salt was dissolved in 25 ml of distilled H2O. To this, 3 drops of xylene orange indicator was added followed by very dilute sulphuric acid until the colour just changes from red to yellow. Then powdered hexamine was added with constant stirring until the deep red colour is restored (pH = 6). The solution was warmed to 40°C and titrated with standard 0.025 M EDTA solution.14 Accuracy of the cobalt estimation is confirmed to be better than 0.5%.

2.2b Sodium and potassium estimation: Sodium and potassium contents were estimated by flame photometry. About 50 mg of the compound was dissolved in 10 ml of 6 M HCl, evaporated to dryness, and redissolved in H2O to 100 ml. Standard solutions were prepared from analytical grade NaCl and KCl salts dried at 200°C. Accuracy of estimation is better than 0.5%.

3. Results and discussion

The flux grown crystalline phases obtained from NaOH and subsequent ion exchanged oxides were analysed and their compositions are summarized in table 2. Accordingly, Na0.2CoO2 is obtained from NaOH flux and H0.98Na0.02CoO2, Li0.29CoO2 and AgCoO2 from ion exchange of Na0.2CoO2. The composition of KOH flux grown oxide is K0.44CoO2. Composition of the ion exchanged phases from K0.44CoO2 were H0.98K0.02CoO2, Li0.42CoO2 and AgCoO2.

Scanning electron microscopy (SEM) study shows that the morphology of the parent Na0.2CoO2 and K0.44CoO2 compounds is hexagonal. Ion exchanged H0.98Na0.02CoO2, Li0.29CoO2 and AgCoO2 phases also showed hexagonal morphology. Typical SEM images of the parent Na0.2CoO2 and those ion exchanged with H+, Li+ and Ag+ are given in figure 1a–d respectively. Na+, K+, Ag+ and Co ion concentrations obtained from EDX analysis were close to the chemical analysis.

Powder X-ray diffraction patterns of the parent Na0.2CoO2 and ion-exchanged phases are shown in figure 2a–d respectively. Similarly, XRD patterns of the K0.44CoO2 and

<p>| Table 2. Chemical analysis data, synthetic condition and lattice parameters of Na0.2CoO2 and K0.44CoO2 obtained from NaOH/NaI and KOH melts and H+, Li+ and Ag+ ion exchanged compounds. |</p>
<table>
<thead>
<tr>
<th>Composition*</th>
<th>Synthetic condition</th>
<th>Structure</th>
<th>Lattice parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na0.2CoO2 (A)</td>
<td>400°C/12 h; NaOH</td>
<td>Hexagonal</td>
<td>a = 2.873 (4) c = 20-646 (3)</td>
</tr>
<tr>
<td>H0.98Na0.02CoO2</td>
<td>A → RT/12 h; 1 M HCl</td>
<td>Hexagonal</td>
<td>a = 2.860 (7) c = 13-158 (8)</td>
</tr>
<tr>
<td>Li0.29CoO2</td>
<td>A → 275°C/3 h; LiNO3</td>
<td>Hexagonal</td>
<td>a = 2.835 (4) c = 14-038 (4)</td>
</tr>
<tr>
<td>AgCoO2</td>
<td>A → 250°C/3 h; AgNO3</td>
<td>Hexagonal</td>
<td>a = 2.859 (5) c = 36-644 (3)</td>
</tr>
<tr>
<td>Na0.2CoO2</td>
<td>750°C/24 h; NaI</td>
<td>Orthorhombic</td>
<td>a = 2.83 (4) b = 4-84 (5)</td>
</tr>
<tr>
<td>K0.44CoO2 (B)</td>
<td>400°C/12 h; KOH</td>
<td>Hexagonal</td>
<td>a = 2.854 (4) c = 18-652 (3)</td>
</tr>
<tr>
<td>H0.98K0.02CoO2</td>
<td>B → RT/12 h; 1 M HCl</td>
<td>Hexagonal</td>
<td>a = 2.676 (8) c = 13-167 (4)</td>
</tr>
<tr>
<td>Li0.42CoO2</td>
<td>B → 275°C/3 h; LiNO3</td>
<td>Hexagonal</td>
<td>a = 2.816 (4) c = 14-037 (5)</td>
</tr>
<tr>
<td>AgCoO2</td>
<td>B → 250°C/3 h; AgNO3</td>
<td>Hexagonal</td>
<td>a = 2.861 (3) c = 36-648 (4)</td>
</tr>
</tbody>
</table>

*Analysis accurate within ± 0.005
Layered \( \text{Na}_x\text{CoO}_2 \) and \( \text{K}_x\text{CoO}_2 \) from NaOH/KOH fluxes

Figure 1. Scanning electron micrographs of (a) \( \text{Na}_{0.20}\text{CoO}_2 \), (b) \( \text{H}_{0.96}\text{Na}_{0.04}\text{CoO}_2 \), (c) \( \text{Li}_{0.29}\text{CoO}_2 \) and (d) \( \text{AgCoO}_2 \).

those ion exchanged with \( \text{H}^+ \), \( \text{Li}^+ \) and \( \text{Ag}^+ \) are given in figure 3a–d respectively. All these patterns can be indexed in the hexagonal structure and the lattice parameters are summarized in table 2. Since the flux-grown compounds are large flaky crystals, even on fine grinding, powder X-ray patterns show large peaks due to the \( c \)-axis oriented (00l) reflections. However, expansion of small peaks at higher angles (2\( \theta \) from 40 to 90°, not shown in the figures 2 and 3) gave peaks such as (104) and (015) reflections. Lattice parameters of \( \text{Na}_{0.27}\text{CoO}_2 \) is given in table 2. However, indexed powder X-ray pattern of \( \text{AgCoO}_2 \) phase given in figure 4 (data were collected at a scan rate of 1\( ^\circ \)/min), clearly shows large number of diffracted lines indexed in hexagonal structure with lattice parameters \( a = 2.862(1) \) Å, \( c = 36.684(4) \) Å. These parameters agree well with the reported \( \text{AgCoO}_2 \) phase\(^{15} \) (JCPDS 25-0761).

The compound synthesized from NaI flux has the composition \( \text{Na}_{0.27}\text{CoO}_2 \). In this preparation, there is no flaky type oriented crystals, unlike in the compound prepared from NaOH melt. The diffraction lines are indexed in the orthorhombic structure with lattice parameters \( a = 2.83(4) \), \( b = 4.84(5) \) and \( c = 16.52(3) \) and the corresponding XRD pattern is given in figure 5. There are no diffraction lines assignable to impurity phases. Lattice parameters of \( \text{Na}_{0.27}\text{CoO}_2 \) compound obtained from NaI flux is close to \( \text{Na}_{0.55}\text{CoO}_2 \) orthorhombic phase.\(^1 \)
The proton-exchanged compound from Na$_{0.2}$CoO$_2$ has the compositions H$_{0.96}$Na$_{0.04}$CoO$_2$ and H$_{0.96}$K$_{0.02}$CoO$_2$ from K$_{0.44}$CoO$_2$ indicating that Co is in +3 state. Therefore, during the protonation, Na$_{0.2}$CoO$_2$ gets reduced to H$_{0.96}$Na$_{0.04}$CoO$_2$. The lattice parameters of H$_{0.96}$Na$_{0.04}$CoO$_2$ (\(a = 2.851\) Å, \(c = 13.150\) Å) agree well with those reported by Delaplane et al.\textsuperscript{16} It should be possible to remove Na$^+$ or K$^+$ completely by prolonged treatment of the compound in dilute HCl.

However, there is only a small amount of cobalt gets reduced from Co\(^{4+}\) to Co\(^{3+}\) state in the case of Li ion exchange reaction from Na$_{0.2}$CoO$_2$ to Li$_{0.26}$CoO$_2$. Li ion exchange reaction from K$_{0.44}$CoO$_2$ yielded Li$_{0.42}$CoO$_2$ indicating nearly quantitative ion exchange reaction.

It is important to note that stoichiometric Delafossite-type AgCoO$_2$ phase has been obtained from Na$_{0.2}$CoO$_2$ or K$_{0.44}$CoO$_2$ with molten AgNO$_3$. In this method of ion exchange reaction, all the cobalt in +4 state gets reduced to +3 state. In fact, this ion exchange method turns out to be a simple method to prepare AgCoO$_2$. 

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**Figure 2.** Powder XRD patterns for (a) Na$_{0.2}$CoO$_2$; (b) H$_{0.96}$Na$_{0.04}$CoO$_2$; (c) Li$_{0.26}$CoO$_2$; and (d) AgCoO$_2$. 

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3.1 XPS studies

X-ray photoelectron spectra of Co(2p), K(2p) and O(1s) core levels from spectra of K$_{0.44}$CoO$_2$, H$_{0.98}$K$_{0.02}$CoO$_2$ and AgCoO$_2$ samples were recorded. XPS of Co(2p) region from K$_{0.44}$CoO$_2$, H$_{0.98}$K$_{0.02}$CoO$_2$ and AgCoO$_2$ are shown in figure 6a–c respectively. Co(2p$_{3/2}$, 1/2) from K$_{0.44}$CoO$_2$ shows peaks due to Co$^{3+}$ and Co$^{4+}$ states with binding energies of Co(2p$_{3/2}$) at 779.5, 780.5 eV respectively (see figure 6a). The satellite intensity at 6.0 eV below Co(2p$_{3/2}$) and Co(2p$_{1/2}$) peaks are absent and the presence of weak satellite at ~9.0 eV below the main peak clearly shows that Co$^{3+}$ and Co$^{4+}$ ions are in low spin state. Contrary to this, Co(2p$_{3/2}$, 1/2) peaks from H$_{0.98}$K$_{0.02}$CoO$_2$ are sharp and the binding energies of Co(2p$_{3/2}$) at 780.3 eV agree well with Co in +3 state. Further, small satellite at ~9.0 eV below the main peaks clearly demonstrated that the Co ions are in +3 state with low spin.
Figure 4. Powder XRD pattern for AgCoO$_2$ ion exchanged from K$_{0.44}$CoO$_2$.

Figure 5. Powder X-ray diffraction pattern for Na$_{0.27}$CoO$_2$ obtained from NaI melt.
Figure 6. X-ray photoelectron spectra of (a) Co(2p) in $K_{0.4}CoO_2$, (b) Co(2p) in $H_{0.98}K_{0.02}CoO_2$, (c) Co(2p) in AgCoO$_2$. 
The Co(2p) spectra in $H_{0.98}K_{0.02}CoO_2$ and AgCoO$_2$ resemble that of Co in $Bi_2Sr_2CoO_9$\cite{17} where Co is in +3 state with low spin. Thus, XPS study confirms that Co, which is in mixed valent +3 and +4 states in $K_{0.44}CoO_2$ is transformed to $Co^{3+}$ in $H_{0.98}K_{0.02}CoO_2$. AgCoO$_2$ also shows Co in +3 state similar to $H_{0.98}K_{0.02}CoO_2$ (see figure 6c). Ag$^+(3d_{5/2})$ peak is observed at 368.0 eV as expected. O(1s) peaks are observed at ~530.0 eV. XPS study thus provides the electronic state of Co in $K_{0.44}CoO_2$, $H_{0.98}K_{0.02}CoO_2$ and AgCoO$_2$ phases.

3.2 Electrical properties

Electrical resistivity measurements were done on the sintered pellets by four-probe method. Figure 7 shows the resistivity vs. temperature plots of (a) $Na_{0.3}CoO_2$ and (b) AgCoO$_2$ respectively. Unlike $Na_{0.3}CoO_2$ which is metallic,\cite{13} $Na_{0.2}CoO_2$ sample shows semiconductor to metal like transition at ~100 K and AgCoO$_2$ compound exhibit semiconducting behaviour. However, highly semiconducting behaviour of AgCoO$_2$ is clear from the plot. $K_{0.44}CoO_2$ showed metallic behaviour from 300 to 20 K similar to $K_{0.3}CoO_2$. 

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure7.png}
\caption{Resistivity vs temperature plots for (a) $Na_{0.3}CoO_2$ and (b) AgCoO$_2$.}
\end{figure}
4. Conclusions

Layered Na\(_x\)CoO\(_2\) and K\(_x\)CoO\(_2\) phases obtained from molten NaOH and KOH fluxes show the following.

(a) Na\(_{0.8}\)CoO\(_2\) is obtained where 80% of Co is in +4 state; structure of this phase could not be determined.

(b) K\(_{0.44}\)CoO\(_2\) is obtained from KOH flux where lattice parameters are close to K\(_{0.5}\)CoO\(_2\) pseudohexagonal phase. However, its structure needs to be determined.

(c) Both Na\(_{0.20}\)CoO\(_2\) and K\(_{0.44}\)CoO\(_2\) give HCoO\(_2\) and Delafossite-type AgCoO\(_2\) phases. Their structure and properties are the same as those reported in the literature. The study shows that large single crystals of these phases can be easily made by this method.

(d) Li ion exchange takes place almost to the same extent of Na or K in the parent A\(_x\)CoO\(_2\) (A = Na, K) phases.

(e) Na\(_{0.27}\)CoO\(_2\) crystallizing in orthorhombic structure is obtained from NaI flux.

Acknowledgements

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References