

## Low temperature synthesis of layered $\text{Na}_x\text{CoO}_2$ and $\text{K}_x\text{CoO}_2$ from NaOH/KOH fluxes and their ion exchange properties<sup>†</sup>

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**Abstract.** We report a low temperature synthesis of layered  $\text{Na}_{0.20}\text{CoO}_2$  and  $\text{K}_{0.44}\text{CoO}_2$  phases from NaOH and KOH fluxes at 400°C. These layered oxides are employed to prepare hexagonal  $\text{HCoO}_2$ ,  $\text{Li}_x\text{CoO}_2$  and Delafossite  $\text{AgCoO}_2$  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.  $\text{Na}_{0.20}\text{CoO}_2$  oxide exhibits insulating to metal like behaviour, whereas  $\text{AgCoO}_2$  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.  $\text{Na}_x\text{CoO}_2$  and  $\text{K}_x\text{CoO}_2$  layered oxides crystallizing in a variety of structure types and varied amount of Na or K ions are the precursors to  $\text{Li}_x\text{CoO}_2$ , which is a cathode material for Li ion batteries.  $\text{Na}_x\text{CoO}_2$  ( $x \leq 1$ ) was first prepared by Fouassier *et al.*<sup>1</sup> by heating stoichiometric amounts of  $\text{Co}_3\text{O}_4$  and  $\text{Na}_2\text{O}_2$ .  $\text{Na}_x\text{CoO}_2$  was also prepared by heating stoichiometric amounts of NaOH and Co metal. Alternatively, heating Co metal in  $\text{Na}_2\text{CO}_3$  at 850°C also gave  $\text{Na}_x\text{CoO}_2$  phases. Balsys and Davis<sup>2</sup> have refined the structure of  $\text{Na}_{0.7}\text{CoO}_2$  using neutron diffraction data. The structure of  $\text{Na}_x\text{CoO}_2$  consists of sheets of edge-sharing  $\text{CoO}_6$  octahedra between which sodium ions are intercalated within a trigonal prismatic or octahedral coordination. The structural change accompanied by ion-exchange is reported in  $\text{Na}_{0.7}\text{CoO}_2$  by Delmas *et al.*<sup>3</sup> In  $\text{Na}_{0.7}\text{CoO}_2$  the anion sequence is ABBA. When these material is ion-exchanged with LiCl, a metastable form of  $\text{LiCoO}_2$  with the layer sequence ABCBA is obtained. Recently, Takada *et al.*<sup>4</sup> reported superconductivity in  $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$  ( $x \approx 0.35$ ,  $y \approx 1.3$ ) with a  $T_c$  of about 5 K. There is a marked resemblance in superconducting properties between the  $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$  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  $\text{HTaWO}_6 \cdot \text{H}_2\text{O}$  phases has been reported by Groult *et al.*<sup>5</sup> The conversion of  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$  to  $\text{HNbO}_3$  and  $\text{HTaO}_3$  respectively, is done by the treatment with hot aqueous acid.<sup>6</sup> The exchange of

<sup>†</sup>Dedicated to Professor C N R Rao on his 70th birthday

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$\text{Li}^+$  by protons is accompanied by a topotactic transformation of the rhombohedral  $\text{LiNbO}_3$  structure to the cubic perovskite structure of  $\text{HNbO}_3$ . Bhat and Gopalakrishnan<sup>7</sup> have synthesized novel protonated layered oxides,  $\text{HMWO}_6 \cdot 1.5\text{H}_2\text{O}$  ( $\text{M} = \text{Nb}$  or  $\text{Ta}$ ) by topotactic exchange of lithium in trirutile  $\text{LiMWO}_6$  with protons by treatment with dilute  $\text{HNO}_3$ . Electrocatalytic activities of  $\text{HCoO}_2$  for the oxidation of hydrogen in solid oxide fuel cell has been studied,<sup>8</sup> and it was found to be an efficient anode material for the oxidation of hydrogen with the oxygen transported through the solid electrolyte.

$\text{K}_{0.5}\text{CoO}_2$  was prepared by heating stoichiometric amounts of  $\text{KOH}$  and  $\text{Co}_3\text{O}_4$  in  $\text{O}_2$  at  $450^\circ\text{C}$ .  $\text{KCo}_2\text{O}_4$ ,<sup>9</sup>  $\text{KCo}_{0.5}\text{O}_2$ ,  $\text{KCo}_{0.67}\text{O}_2$ , **a**- $\text{KCoO}_2$  and **b**- $\text{KCoO}_2$  phases<sup>10</sup> and also  $\text{RbCo}_2\text{O}_4$  and  $\text{CsCo}_2\text{O}_4$  have been identified.<sup>11</sup> The known  $\text{Na}_x\text{CoO}_2$  and  $\text{K}_x\text{CoO}_2$  phases and their structure are summarized in table 1.

We were interested in synthesizing layered  $\text{Na}_x\text{CoO}_2$  and  $\text{K}_x\text{CoO}_2$  by soft chemistry route employing  $\text{NaOH}$  and  $\text{KOH}$  fluxes. In these layered oxides,  $\text{Co}$  is present in +3 and +4 states. Delmas *et al*<sup>12</sup> have reported that the non-stoichiometric alkali metal cobalt oxides are metallic, while stoichiometric  $\text{NaCoO}_2$  is a semiconducting.  $\text{KCo}_2\text{O}_4$ <sup>9</sup> and  $\text{NaCo}_2\text{O}_4$ <sup>13</sup> are metallic oxides.

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

**Table 1.** Compositions, crystal structure and lattice parameters of known  $\text{A}_x\text{CoO}_2$  and  $\text{A}\text{Co}_2\text{O}_4$  ( $\text{A} = \text{Na}, \text{K}, \text{Rb}$  and  $\text{Cs}$ ) phases.

Compositions	Structure	Lattice parameters ( $\text{\AA}$ )			Reference
		<i>a</i>	<i>b</i>	<i>c</i>	
$\text{Na}_{0.82}\text{CoO}_2$	Orthorhombic, $P3$	4.87	2.81	5.75	1
$\text{Na}_{0.90}\text{CoO}_2$	Orthorhombic, $P'3$	4.54	2.83	5.79	1
$\text{Na}_{0.95}\text{CoO}_2$	Orthorhombic, $O'3$	4.88	2.86	5.77	1
$\text{NaCoO}_2$	Orthorhombic, $O3$	4.99	2.88	6.17	1
$\text{Na}_{0.90}\text{CoO}_2$	Hexagonal	2.88	–	15.58	1
<b>a</b> '- $\text{Na}_{0.75}\text{CoO}_2$	Monoclinic	4.89	2.87	5.77	1
$\text{Na}_{0.55}\text{CoO}_2$	Orthorhombic	2.83	4.84	16.53	1
$\text{Na}_{0.72}\text{CoO}_2$	Hexagonal	2.83	–	10.88	1
$\text{NaCoO}_2$	Hexagonal, $O3$	2.88	–	15.58	1
$\text{Na}_{0.7}\text{CoO}_2$	Hexagonal, $P2$	2.83	–	10.82	2
$\text{Na}_{0.53}\text{CoO}_2$	Hexagonal, $P2$	2.84	–	10.81	1
$\text{Na}_{0.52}\text{CoO}_2$	Monoclinic, $P\bar{C}$	4.84	2.83	5.71	1
$\text{KCo}_2\text{O}_4$	Hexagonal	2.84	–	12.35	9
$\text{KCo}_{0.5}\text{O}_2$	Pseudo-hexagonal	2.83	–	18.46	10
$\text{KCo}_{0.67}\text{O}_2$	Hexagonal	2.83	–	12.26	10
<b>a</b> - $\text{KCoO}_2$	Tetragonal	5.37	–	7.87	10
<b>b</b> - $\text{KCoO}_2$	Tetragonal	5.71	–	7.29	10
$\text{K}_{0.5}\text{Co}_2\text{O}_4$	Hexagonal	2.84	–	12.26	10
$\text{RbCo}_2\text{O}_4$	Hexagonal	2.83	–	13.04	11
$\text{CsCo}_2\text{O}_4$	Hexagonal	2.84	–	13.98	11

## 2. Experimental

### 2.1 Synthesis of $\text{Na}_x\text{CoO}_2$ and $\text{K}_x\text{CoO}_2$

Layered  $\text{Na}_x\text{CoO}_2$  and  $\text{K}_x\text{CoO}_2$  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  $\text{Na}_x\text{CoO}_2$ , a typical run contains  $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  (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,  $\text{K}_x\text{CoO}_2$  phase is synthesized from KOH flux.

NaI was also used as a flux to prepare  $\text{Na}_x\text{CoO}_2$  phase.  $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  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  $\text{Na}^+$  ion was detected in the filtrate. The black solid was filtered and dried at 110°C.

**2.1a Preparation of  $\text{H}_x\text{CoO}_2$ :**  $\text{Na}_x\text{CoO}_2$  and  $\text{K}_x\text{CoO}_2$  phases are non-stoichiometric layered oxides. The ion exchange of sodium or potassium with proton was achieved by mixing 1 g of  $\text{Na}_x\text{CoO}_2$  or  $\text{K}_x\text{CoO}_2$  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  $\text{Ag}_x\text{CoO}_2$ :**  $\text{Na}_x\text{CoO}_2$  or  $\text{K}_x\text{CoO}_2$  precursor was mixed with two times excess of  $\text{AgNO}_3$ . The mixture was heated at 275°C, above the mp of  $\text{AgNO}_3$  (212°C) for 3 h. The melt was furnace cooled to room temperature, washed with distilled water until the filtrate was free from  $\text{Na}^+/\text{Ag}^+$  ions. Finally, the resulting black flaky crystals were isolated and dried at 110°C.

**2.1c Preparation of  $\text{Li}_x\text{CoO}_2$ :** Layered  $\text{Li}_x\text{CoO}_2$  phase was also synthesized by cation exchange reaction.  $\text{Na}_x\text{CoO}_2$  or  $\text{K}_x\text{CoO}_2$  precursor is mixed with twice the excess of  $\text{LiNO}_3$  and heated to 250°C for 3 h and cooled to room temperature. Excess  $\text{LiNO}_3$  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  $\text{K}\alpha$  (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  $\text{K}\alpha$  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 H<sub>2</sub>O. To this, 3 drops of xylenol 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.<sup>14</sup> 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 H<sub>2</sub>O 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, Na<sub>0.2</sub>CoO<sub>2</sub> is obtained from NaOH flux and H<sub>0.96</sub>Na<sub>0.04</sub>CoO<sub>2</sub>, Li<sub>0.29</sub>CoO<sub>2</sub> and AgCoO<sub>2</sub> from ion exchange of Na<sub>0.2</sub>CoO<sub>2</sub>. The composition of KOH flux grown oxide is K<sub>0.44</sub>CoO<sub>2</sub>. Composition of the ion exchanged phases from K<sub>0.44</sub>CoO<sub>2</sub> were H<sub>0.98</sub>K<sub>0.02</sub>CoO<sub>2</sub>, Li<sub>0.42</sub>CoO<sub>2</sub> and AgCoO<sub>2</sub>.

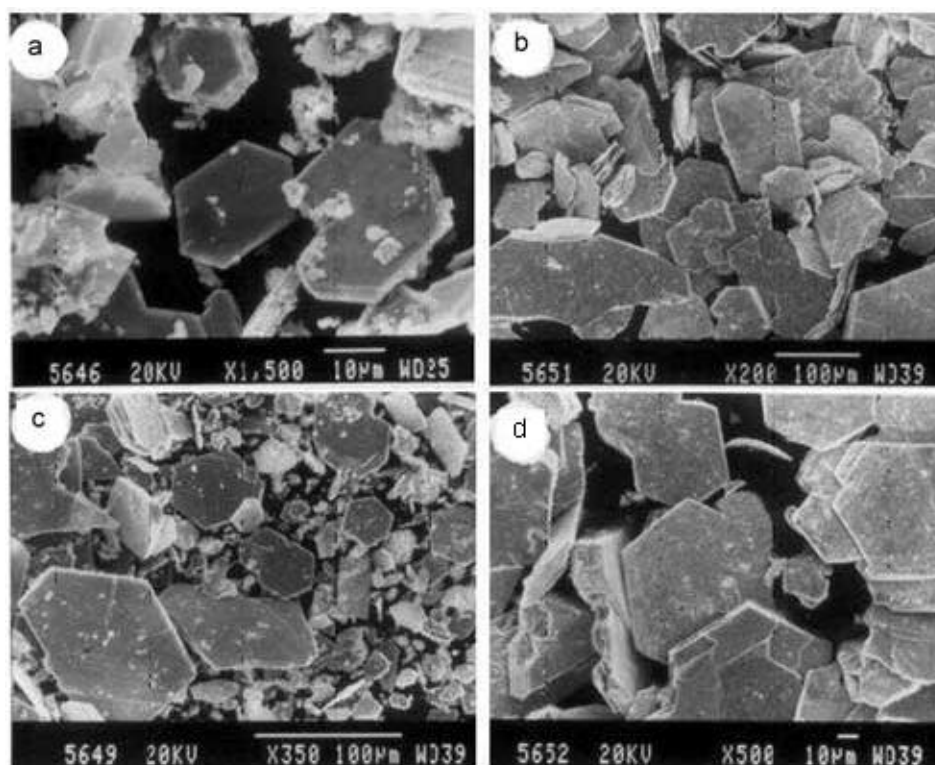
Scanning electron microscopy (SEM) study shows that the morphology of the parent Na<sub>0.2</sub>CoO<sub>2</sub> and K<sub>0.44</sub>CoO<sub>2</sub> compounds is hexagonal. Ion exchanged H<sub>0.98</sub>Na<sub>0.04</sub>CoO<sub>2</sub>, Li<sub>0.29</sub>CoO<sub>2</sub> and AgCoO<sub>2</sub> phases also showed hexagonal morphology. Typical SEM images of the parent Na<sub>0.2</sub>CoO<sub>2</sub> and those ion exchanged with H<sup>+</sup>, Li<sup>+</sup> and Ag<sup>+</sup> are given in figure 1a–d respectively. Na<sup>+</sup>, K<sup>+</sup>, Ag<sup>+</sup> and Co ion concentrations obtained from EDX analysis were close to the chemical analysis.

Powder X-ray diffraction patterns of the parent Na<sub>0.2</sub>CoO<sub>2</sub> and ion-exchanged phases are shown in figure 2a–d respectively. Similarly, XRD patterns of the K<sub>0.44</sub>CoO<sub>2</sub> and

**Table 2.** Chemical analysis data, synthetic condition and lattice parameters of Na<sub>x</sub>CoO<sub>2</sub> and K<sub>x</sub>CoO<sub>2</sub> obtained from NaOH/NaI and KOH melts and H<sup>+</sup>, Li<sup>+</sup> and Ag<sup>+</sup> ion exchanged compounds.

Composition*	Synthetic condition	Structure	Lattice parameters (Å)	
			<i>a</i>	<i>c</i>
Na <sub>0.20</sub> CoO <sub>2</sub> (A)	400°C/12 h; NaOH	Hexagonal	2.873 (4)	20.646 (3)
H <sub>0.96</sub> Na <sub>0.04</sub> CoO <sub>2</sub>	A → RT/12 h; 1 M HCl	Hexagonal	2.860 (7)	13.158 (8)
Li <sub>0.29</sub> CoO <sub>2</sub>	A → 275°C/3 h; LiNO <sub>3</sub>	Hexagonal	2.835 (4)	14.038 (4)
AgCoO <sub>2</sub>	A → 250°C/3 h; AgNO <sub>3</sub>	Hexagonal	2.859 (5)	36.644 (3)
Na <sub>0.27</sub> CoO <sub>2</sub>	750°C/24 h; NaI	Orthorhombic	<i>a</i> = 2.83 (4) <i>b</i> = 4.84 (5)	16.52 (3)
K <sub>0.44</sub> CoO <sub>2</sub> (B)	400°C/12 h; KOH	Hexagonal	2.854 (4)	18.652 (3)
H <sub>0.98</sub> K <sub>0.02</sub> CoO <sub>2</sub>	B → RT/12 h; 1 M HCl	Hexagonal	2.676 (8)	13.167 (4)
Li <sub>0.42</sub> CoO <sub>2</sub>	B → 275°C/3 h; LiNO <sub>3</sub>	Hexagonal	2.816 (4)	14.037 (5)
AgCoO <sub>2</sub>	B → 250°C/3 h; AgNO <sub>3</sub>	Hexagonal	2.861 (3)	36.648 (4)

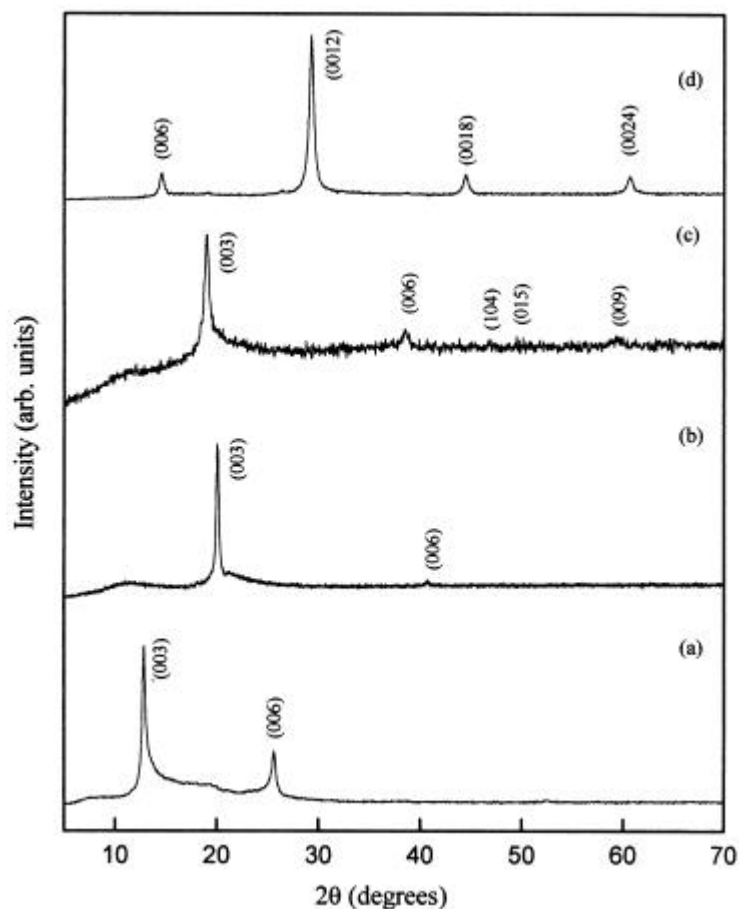
\*Analysis accurate within ± 0.005



**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 (001) 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  $\text{Na}_{0.2}\text{CoO}_2$  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°/min), clearly shows large number of diffracted lines indexed in hexagonal structure with lattice parameters  $a = 2.862(1) \text{ \AA}$ ,  $c = 36.684(4) \text{ \AA}$ . These parameters agree well with the reported  $\text{AgCoO}_2$  phase<sup>15</sup> (JCPDS 25-0761).

The compound synthesized from  $\text{NaI}$  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  $\text{NaOH}$  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  $\text{NaI}$  flux is close to  $\text{Na}_{0.55}\text{CoO}_2$  orthorhombic phase.<sup>1</sup>

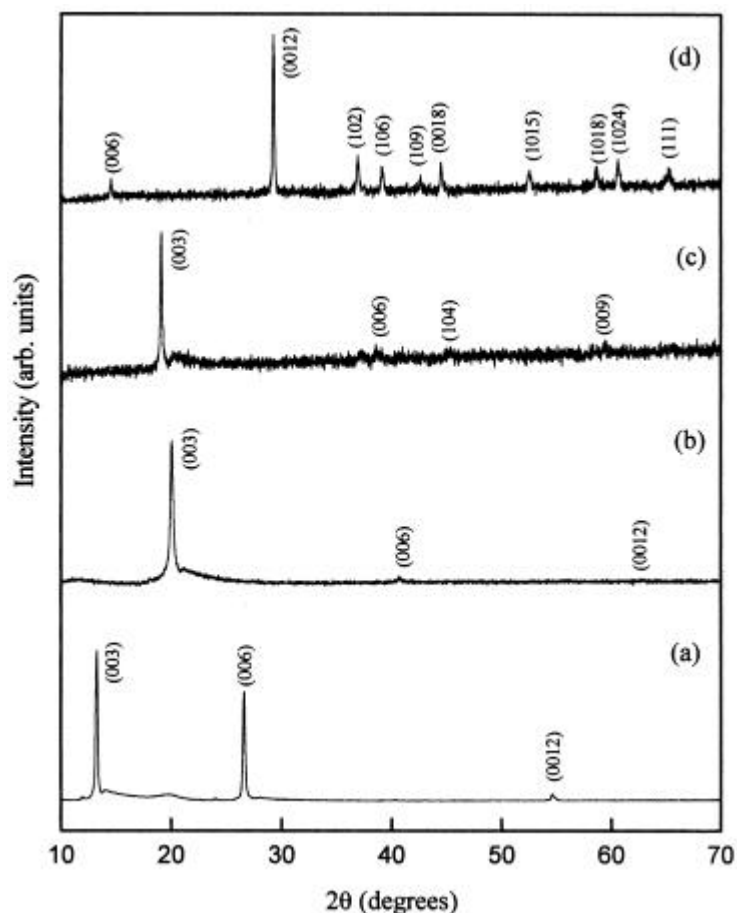


**Figure 2.** Powder XRD patterns for (a)  $\text{Na}_{0.20}\text{CoO}_2$ , (b)  $\text{H}_{0.96}\text{Na}_{0.04}\text{CoO}_2$ , (c)  $\text{Li}_{0.25}\text{CoO}_2$  and (d)  $\text{AgCoO}_2$ .

The proton-exchanged compound from  $\text{Na}_{0.2}\text{CoO}_2$  has the compositions  $\text{H}_{0.96}\text{Na}_{0.04}\text{CoO}_2$  and  $\text{H}_{0.98}\text{K}_{0.02}\text{CoO}_2$  from  $\text{K}_{0.44}\text{CoO}_2$  indicating that Co is in +3 state. Therefore, during the protonation,  $\text{Na}_{0.2}\text{CoO}_2$  gets reduced to  $\text{H}_{0.96}\text{Na}_{0.04}\text{CoO}_2$ . The lattice parameters of  $\text{H}_{0.96}\text{Na}_{0.04}\text{CoO}_2$  ( $a = 2.851 \text{ \AA}$ ,  $c = 13.150 \text{ \AA}$ ) agree well with those reported by Delaplane *et al.*<sup>16</sup> It should be possible to remove  $\text{Na}^+$  or  $\text{K}^+$  completely by prolonged treatment of the compound in dilute HCl.

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

It is important to note that stoichiometric Delafossite-type  $\text{AgCoO}_2$  phase has been obtained from  $\text{Na}_{0.2}\text{CoO}_2$  or  $\text{K}_{0.44}\text{CoO}_2$  with molten  $\text{AgNO}_3$ . 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  $\text{AgCoO}_2$ .



**Figure 3.** Powder XRD patterns for (a)  $\text{K}_{0.44}\text{CoO}_2$ , (b)  $\text{H}_{0.98}\text{K}_{0.02}\text{CoO}_2$ , (c)  $\text{Li}_{0.42}\text{CoO}_2$  and (d)  $\text{AgCoO}_2$ .

### 3.1 XPS studies

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

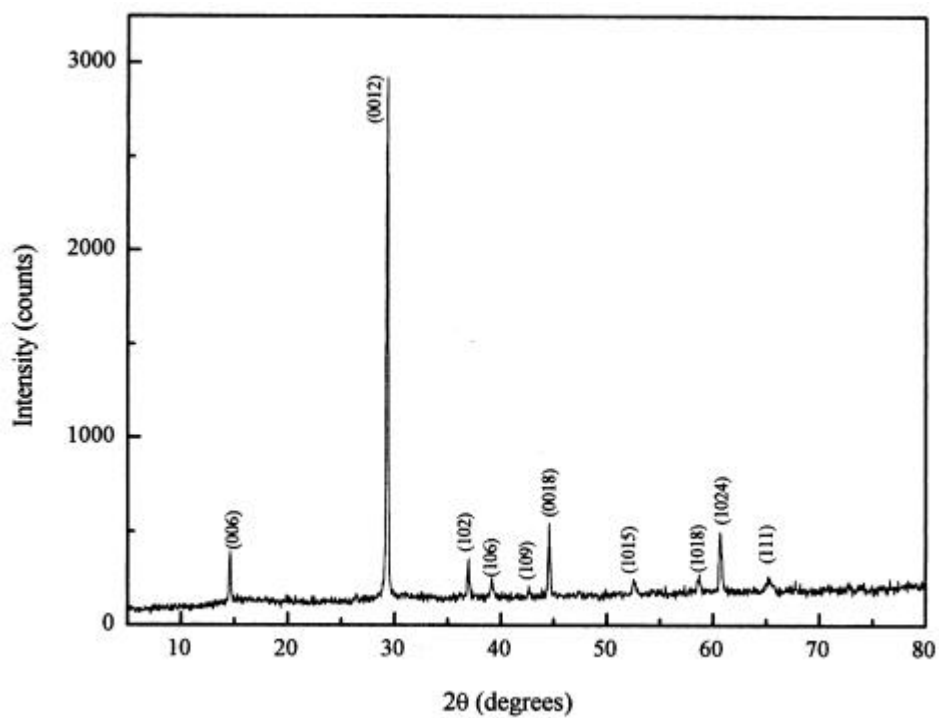


Figure 4. Powder XRD pattern for  $\text{AgCoO}_2$  ion exchanged from  $\text{K}_{0.44}\text{CoO}_2$ .

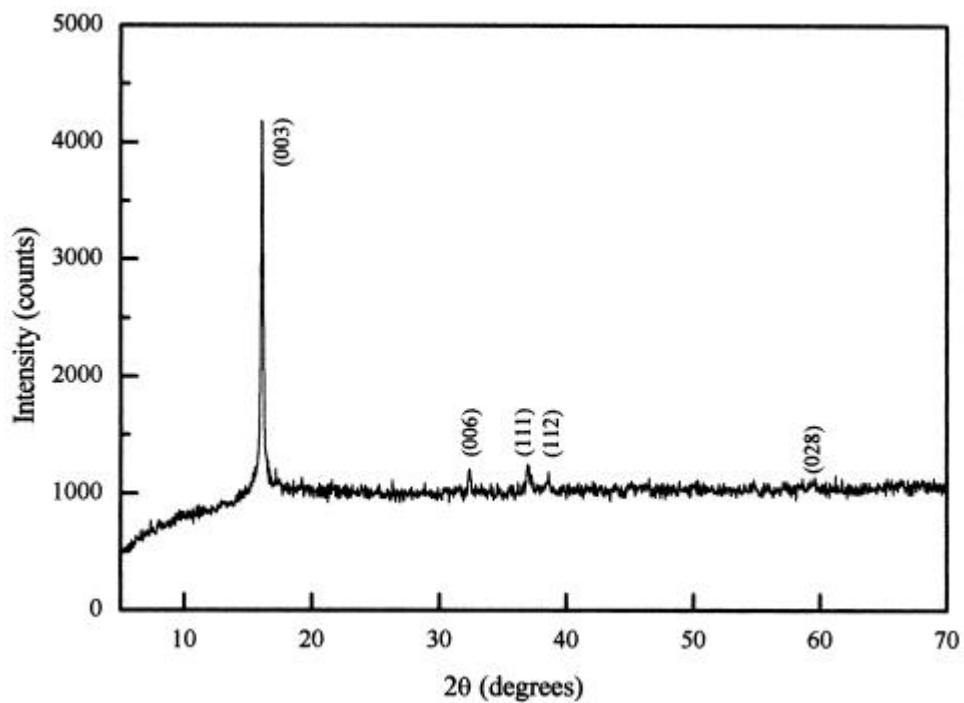
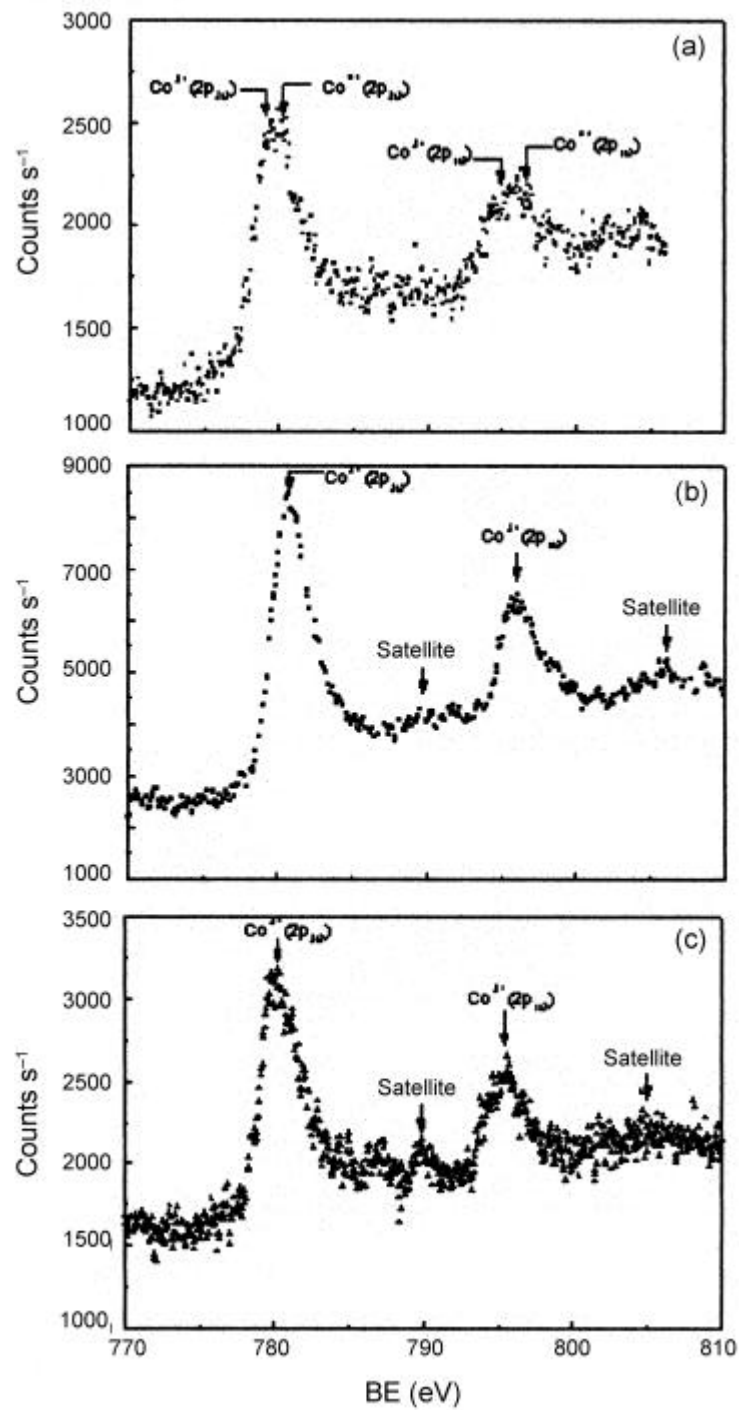
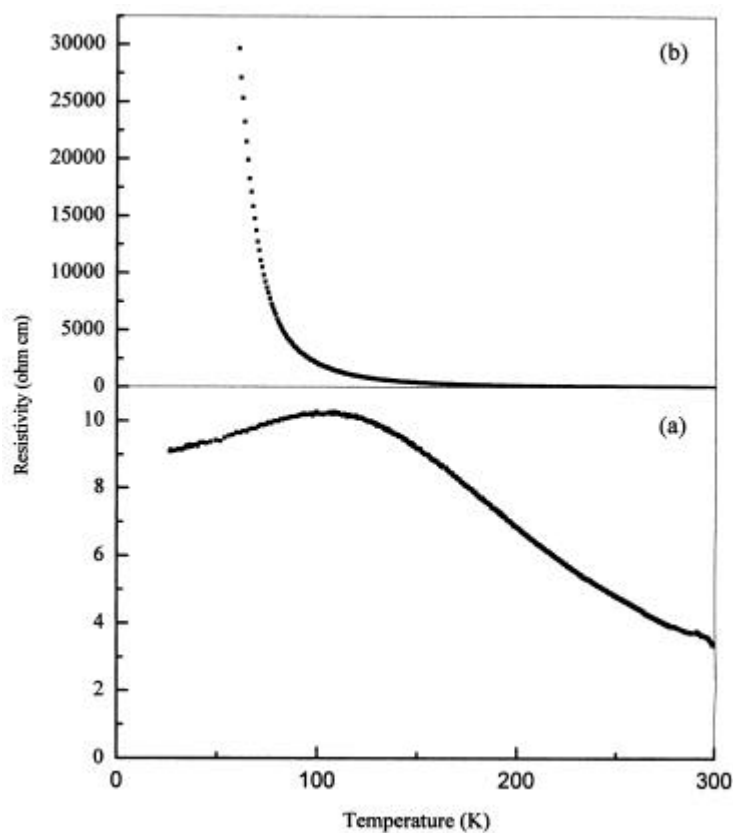


Figure 5. Powder X-ray diffraction pattern for  $\text{Na}_{0.27}\text{CoO}_2$  obtained from NaI melt.





**Figure 6.** X-ray photoelectron spectra of (a)  $\text{Co}(2p)$  in  $\text{K}_{0.44}\text{CoO}_2$ , (b)  $\text{Co}(2p)$  in  $\text{H}_{0.98}\text{K}_{0.02}\text{CoO}_2$ , (c)  $\text{Co}(2p)$  in  $\text{AgCoO}_2$ .



**Figure 7.** Resistivity vs temperature plots for (a)  $\text{Na}_{0.20}\text{CoO}_2$  and (b)  $\text{AgCoO}_2$ .

The  $\text{Co}(2p)$  spectra in  $\text{H}_{0.98}\text{K}_{0.02}\text{CoO}_2$  and  $\text{AgCoO}_2$  resemble that of Co in  $\text{Bi}_2\text{Sr}_3\text{Co}_2\text{O}_9$ <sup>17</sup> 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  $\text{K}_{0.44}\text{CoO}_2$  is transformed to  $\text{Co}^{3+}$  in  $\text{H}_{0.98}\text{K}_{0.02}\text{CoO}_2$ .  $\text{AgCoO}_2$  also shows Co in +3 state similar to  $\text{H}_{0.98}\text{K}_{0.02}\text{CoO}_2$  (see figure 6c).  $\text{Ag}^+(3d_{5/2})$  peak is observed at 368.0 eV as expected.  $\text{O}(1s)$  peaks are observed at ~530.0 eV. XPS study thus provides the electronic state of Co in  $\text{K}_{0.44}\text{CoO}_2$ ,  $\text{H}_{0.98}\text{K}_{0.02}\text{CoO}_2$  and  $\text{AgCoO}_2$  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)  $\text{Na}_{0.2}\text{CoO}_2$  and (b)  $\text{AgCoO}_2$  respectively. Unlike  $\text{Na}_{0.5}\text{CoO}_2$  which is metallic,<sup>13</sup>  $\text{Na}_{0.2}\text{CoO}_2$  sample shows semiconductor to metal like transition at ~100 K and  $\text{AgCoO}_2$  compound exhibit semiconducting behaviour. However, highly semiconducting behaviour of  $\text{AgCoO}_2$  is clear from the plot.  $\text{K}_{0.44}\text{CoO}_2$  showed metallic behaviour from 300 to 20 K similar to  $\text{K}_{0.5}\text{CoO}_2$ .

#### 4. Conclusions

Layered  $\text{Na}_x\text{CoO}_2$  and  $\text{K}_x\text{CoO}_2$  phases obtained from molten NaOH and KOH fluxes show the following.

- (a)  $\text{Na}_{0.2}\text{CoO}_2$  is obtained where 80% of Co is in +4 state; structure of this phase could not be determined.
- (b)  $\text{K}_{0.44}\text{CoO}_2$  is obtained from KOH flux where lattice parameters are close to  $\text{K}_{0.5}\text{CoO}_2$  pseudohexagonal phase. However, its structure needs to be determined.
- (c) Both  $\text{Na}_{0.20}\text{CoO}_2$  and  $\text{K}_{0.44}\text{CoO}_2$  give  $\text{HCoO}_2$  and Delafossite-type  $\text{AgCoO}_2$  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  $\text{A}_x\text{CoO}_2$  ( $\text{A} = \text{Na}, \text{K}$ ) phases.
- (e)  $\text{Na}_{0.27}\text{CoO}_2$  crystallizing in orthorhombic structure is obtained from NaI flux.

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