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A new series of sodium cobalt oxyhydrates

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We report a new series of sodium cobalt oxyhydrates that contains the same two dimensional building blocks as superconducting $Na_xCoO_2{\cdot}yH_2O$. The absence of superconductivity emphasises the importance of the CoO_2 stacking arrangement on the resultant electronic properties.

The discovery of superconductivity in the hydrated cobalt oxide, $Na_{0.3}CoO_2{\cdot}yH_2O$,[1] may well prove to be important in our understanding of high temperature superconductivity. The parent anhydrous layered cobaltates have themselves been the subject of much attention over recent years. The realisation of the electrolytic properties of Li_xCoO_2 by Goodenough,[2] has led to extensive commercial exploitation in Li-ion battery technology. The analogous sodium compounds are noted for their exceptionally high conductivity and thermoelectric properties,[3] where spin entropy has been suggested to play an essential role.[4] The superconducting transition temperature of this first superconducting cobaltate, $Na_{0.3}CoO_2{\cdot}yH_2O$, is significantly below that observed for the high T_c cuprates at ~5 K. Though they still remain rare, other layered systems, notably Sr_2RuO_4,[5] as well as other transition metal oxides from the first row, notably $LiTi_2O_4$,[6] have been reported to display superconductivity. Both of these systems show unusual characteristics; namely *p*-wave pairing[7] and high frequency Ti–O electron–phonon coupling,[8] respectively. However, when comparing detailed electronic properties, it is $Na_{0.3}CoO_2{\cdot}yH_2O$ that shares many of its characteristics with the cuprates, and is therefore thought to offer a new insight into high temperature superconductivity.[9–12] One of the key structural features of the cuprate superconductors is the stacking of CuO_2 planes. Here we have investigated the chemistry of β-$Na_{0.6}CoO_2$, which was originally reported in the *R*3*m* space group,[13] though other more recent work has suggested a monoclinic distortion.[14,15] The structure is commonly referred to as the Na_xTiS_2 structure, and possesses an ABCABC stacking sequence of edge-sharing CoO_2 planes along the *c*-axis, with Na^+ ions located in octahedral positions within the layers. Fig. 1 shows a comparison between the β-$Na_{0.6}CoO_2$ and γ-$Na_{0.74}CoO_2$ structures, the latter being the parent starting material of the superconductor, $Na_{0.3}CoO{\cdot}yH_2O$. The two structures are composed of the same edge-shared CoO_2 planes. However, the nearest neighbour planes are rotated by 180° within the *P*6$_3$/*mmc* space group of γ-$Na_{0.74}CoO_2$ giving two CoO_2 layers per unit cell, whereas the layers are identically orientated in the β-phase of $Na_{0.6}CoO_2$, but offset in the hexagonal arrangement with cobalt ions at (0, 0, 0), (2/3, 1/3, 1/3) and (1/3, 2/3, 2/3) giving three CoO_2 layers per unit cell. Investigation into the β-phase allows for the determination of the importance of CoO_2 stacking on the superconducting properties.

The synthesis of β-$Na_{0.6}CoO_2$ was performed through a solid state reaction of Na_2CO_3 and $CoCO_3$ at 610 °C under a flow of oxygen for 3 days, with intermittent regrinding. X-Ray diffraction and EDX analysis were used to characterise the products; the latter technique giving the composition, $Na_{0.61(1)}CoO_2$. The X-ray diffraction patterns, obtained using a Siemens D500 diffractometer (λ = 1.5418 Å), of β-$Na_{0.6}CoO_2$ and γ-$Na_{0.74}CoO_2$, which was prepared using a previously reported procedure,[1] are compared in Fig. 2. The main reflection at 16° is present in both materials, though indexed as the (002) and (003) for the γ- and β-phases, respectively. The two phases are best differentiated between by inspection of the scattering between 36 and 42°: the γ-phase shows a single reflection at ~40° whereas the β-phase has two distinct reflections, at ~37° and 38.5°. The presence of small amounts of γ-$Na_{0.74}CoO_2$ is observed in the diffraction patterns of β-$Na_{0.6}CoO_2$ when synthesised at temperatures above 610 °C or for longer heating periods, which restricts electronic properties measurements. However, small amounts of Na_2CO_3 and Co_3O_4 remain unreacted under these conditions. The lattice parameters for β-$Na_{0.6}CoO_2$ were $a = b = 2.8256(4)$ and $c = 16.466(2)$ Å.

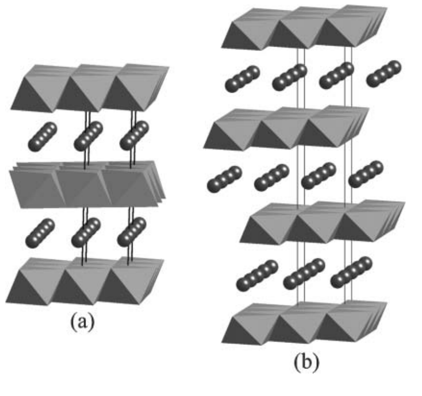

Fig. 1 Structure of (a) γ-$Na_{0.74}CoO_2$ and (b) β-$Na_{0.6}CoO_2$. The former contains alternating orientations of CoO_2 planes producing two per unit cell, whereas the unit cell of the latter is defined by three CoO_2 identically orientated planes in an ABCABC hexagonal stacking arrangement.

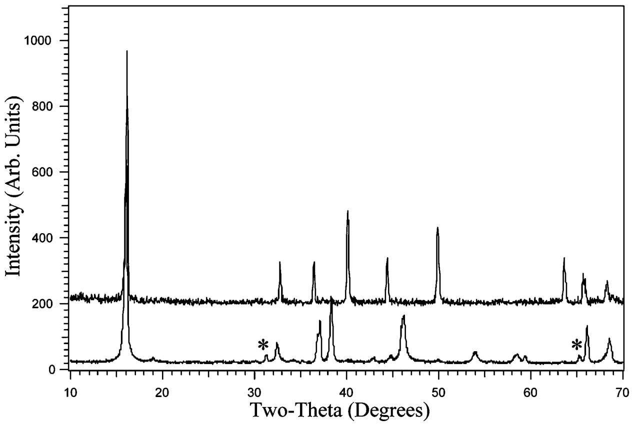

Fig. 2 X-Ray diffraction pattern of γ-$Na_{0.74}CoO_2$ (top) and β-$Na_{0.6}CoO_2$ (bottom). The * indicates Na_2CO_3 and Co_3O_4 impurities.

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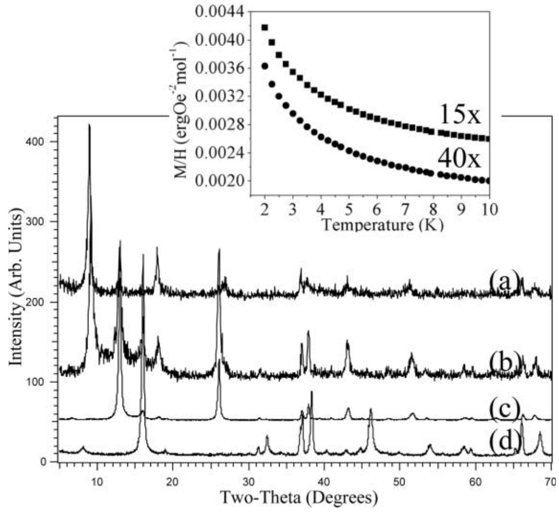

Fig. 3 X-Ray diffraction patterns of (a) fully hydrated phase with (003) at ~9°, (b) mixed fully and semi-hydrated phase, (c) semi-hydrated phase with (003) at ~13° and (d) unhydrated phase with (003) at ~16°. Inset shows zero field cooled magnetic susceptibility at 10 Oe of the fully hydrated phase after 15× and 40× excess Br_2 treatment.

The reactivity of bromine with β-$Na_{0.6}CoO_2$ was explored, as has previously been done with the γ-phase.[1,9,16] This was performed by stirring a known concentration of bromine in acetonitrile with β-$Na_{0.6}CoO_2$, followed by washing with distilled water and filtering. The degree of removal of the Na with bromine was dependant on the bromine concentrations, which is well characterised for the γ-phase.[9] The samples are highly sensitive to moisture once some of the Na ions have been removed, both from the atmosphere and at the washing stages in the bromine reaction. There are two distinct hydrated phases formed, as shown by the X-ray diffraction patterns in Fig. 3. The first, characterised by the (003) reflection at 9° in the X-ray diffraction pattern, has lattice parameters of $a = b = 2.773(2)$ Å and $c = 29.91(3)$ Å. As with the γ-phase, these dimensions are consistent with incorporation of water molecules in layers above and below the Na layers, see Fig. 4(c) and represents an expansion of 13.44 Å, which is equivalent to 2.24 Å per H_2O layer. In the γ-phase, the expansion to include four new H_2O layers is 8.96 Å giving the identical value of 2.24 Å per layer.[1] This is significantly less than the effective diameter of a rotationally diffuse water molecule and indicates a degree of orientational order.[17] It is this structure in the γ-phase which is superconducting, with T_c relatively insensitive to actual water content.[18] Fig. 3(a) is the X-ray diffraction pattern obtained immediately after the reaction with bromine. This structure is metastable with loss of water occurring when the sample is left in the open or more rapidly when placed into a drying oven. For example, Fig. 3(b) is a mixture of the fully hydrated and a semi-hydrated phase obtained after being left in air for 12 h.

Fig. 3(c) is the X-ray diffraction pattern of the sample after 24 h in air when the structure has transformed to a semi-hydrated phase. This phase, characterised by the (003) reflection at 13°, has lattice parameters of $a = b = 2.8268(3)$ and $c = 20.579(2)$ Å. The observed lattice expansion of ~4.1 Å in the semi-hydrated β-phase corresponds to an expansion of 1.37 Å per layer, which is insufficient to support water molecules in unique layers coordinated above and below the Na ions. This level of expansion is also known in the γ-$Na_{0.6}CoO_2$ phases and corresponds to incorporation of water molecules within the same layers as the Na ions, as represented by Fig. 4(b). The semi-hydrated phase can be reverted to the fully hydrated one on exposure to a humid atmosphere for several hours. The unhydrated $Na_{0.6}CoO_2$ phase is also shown as a comparison in Fig. 3(d) and Fig. 4(a). It is interesting to note that an isostructural series of hydrated phases is also known for $NaRuO_2$.[19]

Bromine concentrations used were 1×, 5×, 10×, 15× and 40× excess, which chemical analysis showed to form a series of compounds ranging from $Na_{0.42(1)}CoO_2$ to $Na_{0.19(1)}CoO_2$ and encompassing the optimal cobalt oxidation state of 3.7+ for superconductivity in the γ-phase. However, in contrast to the γ-phase, magnetic susceptibility measurements (Fig. 3 inset) using a Quantum Design MPMS SQUID magnetometer showed no evidence of bulk superconductivity in any of the hydrated β-phases, but a large temperature independent contribution implying bulk metallic properties in the majority phase. A small paramagnetic term is assigned to the cobalt oxide impurity phase. This demonstrates that the different symmetry and stacking of CoO_2 planes could be critical to superconductivity. This has important implications on the mechanism for superconductivity as it demonstrates that the presence of edge-shared CoO_2 planes is not the only requirement for superconductivity. The ordering of the Na ions and water molecules may well differ in the β-phase as compared to the γ-phase and their interaction with the CoO_2 planes be influential in determining the electronic structure.

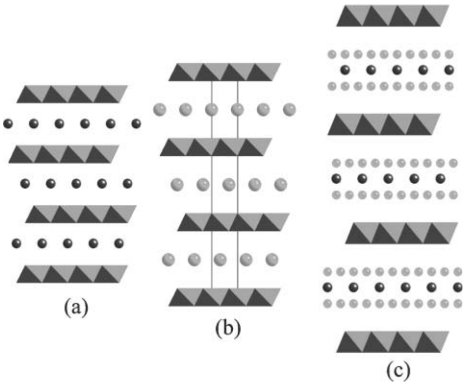

Fig. 4 Representation of the structure of Na_xCoO_2 in its (a) unhydrated (spheres are Na), (b) semi-hydrated (spheres are Na and H_2O) and (c) fully hydrated (dark spheres are Na, light spheres are H_2O) forms.

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