Synthesis and structure of Na\textsuperscript{+}-intercalated WO\textsubscript{3}(4,4′-bipyridyl)\textsubscript{0.5}

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We have prepared single crystals of WO\textsubscript{3}(4,4′-bipyridyl)\textsubscript{0.5} and doped these by Na-ion implantation. The structure of the resultant Na\textsubscript{x}WO\textsubscript{3}(4,4′-bipyridyl)\textsubscript{0.5} was determined by single-crystal x-ray diffraction to comprise atomic layers of corner-shared WO\textsubscript{3} octahedra linked by the 4-4′-bipyridine via the apical nitrogen. In the observed space group of \textit{Pbca}, the fully ordered bipyridyl molecules define cage-shaped structures, not the channels erroneously reported previously for the \textit{Cmca} polymorph. The Na ions are disordered bimodally about the cage centre, displaced in the \textit{c}-direction as to lie closer to the apical oxygens.

Organic-inorganic hybrid materials offer a rich variety of structures with low-dimensional electronic properties and the added benefit of synthesis at near-ambient conditions. One class of these materials is based on simple two-dimensional layers of tungsten (or molybdenum) oxide separated by organic molecules which either ionically or covalently bind the layers together\textsuperscript{1}. The structure of tungsten oxide systems is based on corner-and/or edge sharing WO\textsubscript{3} octahedra\textsuperscript{2}. The insertion of group I or II cations into (or deoxygenation of) WO\textsubscript{3} and WO\textsubscript{3}·H\textsubscript{2}O leads to an insulator-to-metal transition, produces the intense colour and metallic lustre of the tungsten bronzes, and induces bulk superconductivity in, for example, Na\textsubscript{x}WO\textsubscript{3} with \textit{T}\textsubscript{c}=3K for \textit{x}=0.2\textsuperscript{3}. Diffusion of Na into single crystals of WO\textsubscript{3} has even led to signatures of surface superconductivity around 91K\textsuperscript{4}. The varied structural phases, electronic, physical and optical properties of these systems have been the subject of much research over past few decades\textsuperscript{5-8}.

Recently, a related layered hybrid material WO\textsubscript{3}(4,4′-bipyridyl)\textsubscript{0.5} was reported\textsuperscript{9}. This consists of layers of single planes of corner-shared WO\textsubscript{3} octahedra with the axial organo-nitrogen (4,4′-bipyridyl) and oxo ligands of each WO\textsubscript{3} octahedron alternating in direction, thereby binding the layers together. The bipyridyls were reported to align along the [110] direction thus defining open structural channels in this direction\textsuperscript{10} and attracting our attention for ion implantation.

In a preliminary study Na\textsuperscript{+} was incorporated by aqueous electrochemistry\textsuperscript{10} causing an increase in conductivity and the appearance of W\textsuperscript{5+} species as evidenced by X-ray Photoelectron Spectroscopy. In this paper we report the structural characterization of Na\textsubscript{x}WO\textsubscript{3}(4,4′-bipyridyl)\textsubscript{0.5} where the Na ions are intercalated by ion implantation. We find that in the parent compound (\textit{x}=0) the bipyridyls define cages rather than the channels originally reported by Yan \textit{et al}\textsuperscript{11}. These studies confirm the bulk intercalation of Na\textsuperscript{+} and open up the investigation of the \textit{x}-dependent electronic phase behaviour of Na\textsubscript{x}WO\textsubscript{3}(4,4′-bipyridyl))\textsubscript{0.5} and related materials.

Bipyridyl tungstate was synthesized via hydrothermal reaction as described previously\textsuperscript{9,10}. After cooling for five hours to room temperature the hybrid material (in the form of fine yellow crystallites) was filtered and washed with ethanol and dried under vacuum. Crystals could even be prepared under ambient conditions but the crystallite size was smaller.

Sodium ions, 23Na\textsuperscript{+}, were implanted into both faces of selected single crystals at 30 KeV using an lab-built low-energy ion implanter\textsuperscript{11}. Crystal sizes were typically \textit{(10-50)×(10-50)×(0.1-0.3)} \textmu m\textsuperscript{3}. Samples were implanted with 23Na\textsuperscript{+} at estimated levels of 2% and 4% of the total number of atoms in the host material based on Monto Carlo calculations\textsuperscript{12} using the TRIM-DYNAMIC package. The calculation also indicated that most of the 23Na\textsuperscript{+} ions resided in the top 120 nm of each surface and hence have penetrated the entire sample, though a bimodal concentration profile is likely. The pale yellow crystals darken to a green hue on ion implantation.

Single crystal X-ray diffraction (XRD) patterns were recorded with a Rigaku-Spider X-ray diffractometer with wrap-around image-plate detector and three-axis kappa goniostat. A number of single crystals were selected for size and quality, mounted on quartz fibres, characterised by single-crystal XRD, then implanted while still mounted on the fibres and re-characterised by single-crystal XRD. Diffraction data for both un-implanted and implanted samples were collected at room temperature and low temperature. A problem with the cryocooling device prevented collection of the 4 % Na\textsuperscript{+}-implanted sample at low temperature; in any event, earlier data collections had established the negligible changes in crystal properties on cooling. Thus for simplicity, detailed structural comparisons are made among the low-temperature structures (100 K) for unimplanted and 2 % implanted samples (same crystal) and the room-temperature (20 ±0.2 °C) structure for the 4 % implanted sample (different crystal). Key crystal and refinement parameters are summarised in Table 1.

Unimplanted and Na\textsuperscript{+}-implanted crystals at 293 and 100 K are closely isomorphous. The asymmetric unit comprises a W atom, two equatorial oxygen atoms, an axial oxygen atom and...
Residual electron density was concentrated near W atoms disordered either side of the line joining pairs of W atoms. The equatorial oxygen atoms are, however, stochastically leading to undulating WO₄ octahedra alternate in direction in both a and b directions, compared with 0.0124(2) Å in the unimplanted crystal, as well as a small general increase in mosaicity for the implanted samples: 2% Na⁺-implanted samples, electron density, absent in the unimplanted structure, lying on the W=O line approximately 3.0 Å from the axial oxygen atom and disordered about a centre of inversion, was evident. This was assigned to the implanted Na⁺ ion. The resulting structural unit is shown in Fig. 1. The consequences of ion implantation are mainly apparent in small changes in the slippage of one WO₄ layer relative to the next and in the displacement of the W atom from the plane of the pyridyl ring. The slippage of WO₄ layers, which also leads to a small and alternating tilt, layer-by-layer, of the bipyridyl group linking pairs of W atoms in the c direction, is greater parallel to the b axis (0.382 Å) than parallel to the a axis (0.162 Å). The slippage is perceptibly smaller for the Na⁺-implanted samples: 2% Na⁺-implanted crystal compared with the unimplanted crystal, as well as a small general increase in atomic displacement parameters (U_eq(W) = 0.0146(3) Å, compared with 0.0124(2) Å).

The axial W=O(N) and W-N(bipyridyl) bonds of WO₄N octahedra alternate in direction in both a and b directions, leading to a undulating WO₄ plane in the ab plane. The bipyridyl group and the axial oxygen atom are well ordered. The equatorial oxygen atoms are, however, stochastically disordered either side of the line joining pairs of W atoms. Residual electron density was concentrated near W atoms indicating possible unresolved disorder, concomitant with the disorder of equatorial O atoms, or a missed superstructure. Close inspection of data frames, with calculated reflections displayed, revealed no missing weak reflections. As the residual electron density peaks were placed a distance from the W atom similar to the resolution of the data (0.81 Å), no attempt was made to model this disorder.

In both the 2% and 4% Na⁺-implanted samples, electron density, absent in the unimplanted structure, lying on the W=O line approximately 3.0 Å from the axial oxygen atom and disordered about a centre of inversion, was evident. This was assigned to the implanted Na⁺ ion. The resulting structural unit is shown in Fig. 1. The consequences of ion implantation are mainly apparent in small changes in the slippage of one WO₄ layer relative to the next and in the displacement of the W atom from the plane of the pyridyl ring. The slippage of WO₄ layers, which also leads to a small and alternating tilt, layer-by-layer, of the bipyridyl group linking pairs of W atoms in the c direction, is greater parallel to the b axis (0.382 Å) than parallel to the a axis (0.162 Å). The effect of this slippage is to leave the W atoms slightly displaced from the plane of the pyridyl ring: for unimplanted, the displacement is 0.128 Å, for 2% 0.358 Å and 0.082 Å. The effect of this slippage is perceptibly smaller for the Na⁺-implanted samples: 2% Na⁺-implanted crystal compared with the unimplanted crystal, as well as a small general increase in atomic displacement parameters (U_eq(W) = 0.0146(3) Å, compared with 0.0124(2) Å).

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The disposition of the Na\(^+\) ions in the staggered cages formed by the bipyridyls is shown in Fig. 1(b). The orientational ordering of the bipyridyls with planes aligned alternately in the [110] then [1\(\bar{1}\)0] directions presumably arises from minimisation of proton repulsion between adjacent bipyridyls and from optimal space filling. The synthetic method used was that of Yan et al.\(^9\), who reported the characterisation of their material in space group \(Cmca\). We observe the same unit cell as Yan et al.\(^9\), but observe instead systematic absences uniquely consistent with space group \(Pbca\), an intriguing example of polymorphism that underscores the need for careful crystallographic analysis. Contrary to statements in their paper and to the published figure that there are channels parallel to the [110], we were disconcerted to discover, using the downloaded cif file (XEDGOC), that the bipyridyl rings, which lie parallel to (110), are in fact disordered by the crystallographic mirror plane perpendicular to the [100], and so as to fill space efficiently are likely to form cages similar to those that we observed. Similarly, in the description and diagram displaying the bipyrazine material, which notes channels parallel to [010], Yan et al.\(^9\) fail to realise the disorder (and absence of channels) that is the ineluctable consequence of the tetragonal space group \(I4/mmm\), which equivalences the [100] and [010] directions. Interestingly, the bipyridyl material of Yan et al.\(^7\) shows crystallographic equivalence in W-O-W bond lengths in the [010] direction and a marked asymmetry in the [100] direction, a pattern very similar to that which we observed for the unimplanted crystal. Curiously, whereas equatorial oxygen atoms are disordered and bipyridyl rings are ordered in space group \(Pbca\), the converse is true in space group \(Cmca\).

We have intercalated Na\(^+\) ions into small single crystals of \(\text{WO}_3(4,4'\text{-bipyridyl})_{0.5}\) using a low-energy ion implanter and have determined the structure before and after implantation using single-crystal x-ray diffraction. The associated colour change reflects changes in the band structure, carrier doping and the appearance of \(W^{5+}\) species\(^39\). The structure consists of planes of corner-shared \(\text{WO}_3\) octahedra bound together by bipyridyl columns linking oxotungstate layers. The bipyridyls in the unimplanted \(\text{WO}_3(4,4'\text{-bipyridyl})_{0.5}\) are ordered along the [110] and [1\(\bar{1}\)0] directions so as to define cages rather than the [110] channels erroneously reported previously\(^2\). The intercalated Na\(^+\) ions reside within these cages, distributed bimodally about the cage centre so as to lie closer to one or the other of the axial oxygens in the \(\text{WO}_3\) octaheda. The generic \(M_2\text{WO}_3(4,4'\text{-bipyridyl})_{0.5}\) system (\(M=\text{Na}^+, \text{K}^+, \text{Ca}^{++}, \text{etc.}\)) and related materials represent a potentially phase-rich model system for exploring doping-dependent electronic properties and possible correlated states.

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