roughly as favourable as those observed at LT. Only one of these 14 favourable contact lengths is considerably shorter than the distance of 3.35 Å between layers in graphite.

Concluding remarks

Although the population factor p of 61.1 (8)% and the most probable orientation angle of C_{60} at RT are comparable to the corresponding quantities at LT, the RTS is probably not simply a somewhat more disordered version of the LTS. At the phase transition which is first order (Heiney *et al.* 1991), the molecular motion is profoundly modified. The molecules seem to move quite freely, but occasionally lock in a position of $\bar{3}m$ symmetry which is energetically favourable and very close to the major orientation of the LTS. A particularly favourable low-energy reorientation pathway which flips a molecule between different ⟨111⟩ directions passes through an orientation with cubic molecular site symmetry $m\bar{3}$. This transitional position is reached from the most favourable position by a rotation about the threefold axis of only 22°. The average number of favourable intermolecular contacts (75%) is unchanged after the flipping. The minor orientation observed in the LTS is not favoured in the RTS.

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Structure of $K_{1.0}Ti_8O_{16}$ and $K_{0.0}Ti_8O_{16}$

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Abstract

Potassium titanium bronze $K_{1.0}Ti_8O_{16}$ and its chemically oxidized '*exuviae*' oxide $K_{0.0}Ti_8O_{16}$ crystallize in a tetragonal system, $I4/m$, with the hollandite-type one-dimensional tunnel structure. For $K_{1.0}Ti_8O_{16}$, $M_r = 678.13$, $a = 10.1776\ (5)$, $c = 2.9614\ (2)$ Å, $V = 306.75\ (3)$ Å^3, $Z = 1$, $D_x = 3.67$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 5.55$ mm^{-1}, $F(000) = 323$, $T = 298$ K, $R = 0.048$ for 947 unique observations. For $K_{0.0}Ti_8O_{16}$, $M_r = 639.03$, $a = 10.164\ (2)$, $c = 2.9631\ (7)$ Å, $V = 306.1\ (1)$ Å^3, $Z = 1$, $D_x = 3.47$ Mg m^{-3}, $\mu = 5.21$ mm^{-1}, $F(000) = 304$, $R = 0.020$ for 1084 independent reflections. The structural modification caused by K deintercalation *via* oxidation of the host framework is followed using the present data as well as those from two previous studies of the bronze

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with different degrees of oxidation. One of the most distinct changes is the expansion of the tunnel diameter upon K removal.

Introduction

The mixed-valence compound $K_xTi^{III}_xTi^{IV}_{8-x}O_{16}$ (typically $1 \le x \le 1.5$) of hollandite-type structure has been reported to undergo oxidative K deintercalation by reaction with H_2O_2/HCl solution (Latroche, Brohan, Marchand & Tournoux, 1989) and also by treatment with HCl solution (Watanabe, Komatsu, Sasaki & Fujiki, 1991). The K removal from the one-dimensional tunnel proceeded to completion for polycrystalline samples but only partial reaction was observed for larger acicular single crystals (several hundreds micrometers in length). Recently we have found that the HNO_3/HCl system is powerful enough to achieve complete K extraction from single crystals (M. Watanabe, in preparation). This paper describes structural features for the resulting '*exuviae*' crystal ($x \simeq 0$) as well as its parent bronze ($x \simeq 1.0$). These data are compared with those from two other compounds with different values of x, in order to discuss how the structure is modified to accommodate the K deintercalation by chemical oxidation.

Experimental

Dark-blue acicular crystals of $K_{1.0}Ti_8O_{16}$ were grown by slow cooling of a $K_2B_4O_7$ flux melt with a 1:8 molar mixture of K_2O and TiO_2 under an H_2 flow (M. Watanabe, in preparation). The action of a hot HNO_3/HCl solution on the bronze single crystals resulted in oxidation of Ti^{3+} to Ti^{4+} accompanying nearly full deintercalation of the tunnel cations. This was easily detected by the loss of colour from black to transparent (M. Watanabe, in preparation). The chemical compositions determined by electron-probe microanalysis (EPMA) were $K_{1.04\pm0.03}Ti_8O_{16}$ and $K_{<0.02}Ti_8O_{16}$ for the starting and the oxidized crystals, respectively. Hereafter, these are referred to as $K_{1.0}Ti_8O_{16}$ and $K_{0.0}Ti_8O_{16}$, respectively, to distinguish their oxidation states clearly. The single crystals (dimensions: $0.05 \times 0.05 \times 0.25$ mm for $K_{1.0}Ti_8O_{16}$, $0.05 \times 0.05 \times 0.225$ mm for $K_{0.0}Ti_8O_{16}$) were mounted on glass fibers and data collection was undertaken with graphite-monochromated Mo $K\alpha$ radiation using Rigaku AFC-5 and Enraf–Nonius CAD-4 four-circle diffractometers, respectively. Unit-cell parameters were determined by least-squares refinements using 20–25 reflections in the 2θ range 47–66°. Intensity data were collected in ω–2θ scan mode up to $2\theta = 120°$ for the following ranges of indices: $0 \le h \le 22$, $0 \le k \le 22$, $0 \le l \le 7$, total 1240 for $K_{1.0}Ti_8O_{16}$, and $0 \le h \le 24$, $-24 \le k \le 24$, $0 \le l \le 7$, total 2634 for $K_{0.0}Ti_8O_{16}$. Three standard reflections were monitored at appropriate intervals, which showed the intensity variation -2.4 to 0.9%. The intensity data were corrected for Lorentz–polarization factors, intensity fluctuation and absorption (transmission factors of 0.655–0.777 for $K_{1.0}Ti_8O_{16}$ and 0.626–0.789 for $K_{0.0}Ti_8O_{16}$). The latter data set was reduced to 1230 independent reflections by averaging equivalent observations ($R_{\rm int} = 0.024$).

Initial atomic coordinates were derived from the data for isostructural $K_{1.35}Ti_8O_{16}$ (Vogt, Schweda, Wüstefeld, Strähle & Cheetham, 1989). The refinement for $K_{1.0}Ti_8O_{16}$ was based on the composition $K_{1.04}Ti^{III}_{1.04}Ti^{IV}_{6.96}O_{16}$ obtained from EPMA. Full-matrix least-squares refinements on F, which minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F_o)$, converged to the following reliability factors: $R = 0.048$, $wR = 0.041$ for 947 reflections with $F_o > 3\sigma$, $S = 0.100$, $(\Delta/\sigma)_{\max} = 0.0004$, $(\Delta\rho)_{\max} = +2.7$, $(\Delta\rho)_{\min} = -1.8$ e Å^{-3} for $K_{1.0}Ti_8O_{16}$; and $R = 0.020$, $wR = 0.026$ for 1084 reflections with $F_o > 3\sigma$, $S = 0.077$, $(\Delta/\sigma)_{\max} = 0.0008$, $(\Delta\rho)_{\max} = +0.9$, $(\Delta\rho)_{\min} = -0.7$ e Å^{-3} for $K_{0.0}Ti_8O_{16}$. The corrections for extinction were applied anisotropically to $K_{1.0}Ti_8O_{16}$ ($G_{11} = G_{22} = 6.22 \times 10^{-5}$, $G_{33} = 4.59 \times 10^{-6}$) and isotropically to $K_{0.0}Ti_8O_{16}$ ($G = 1.04 \times 10^{-8}$). Atomic scattering factors and anomalous-dispersion terms were from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were conducted on a FACOM M-360 computer employing programs such as *ACACA* (Wuensch & Prewitt, 1965), *RSSFR5* (Sakurai, 1967), *RADY* (Sasaki, 1982) and *BADTEA* (Finger & Prince, 1975).

Discussion

Final atomic coordinates are listed in Table 1.* Fig. 1 shows a perspective view of the hollandite-type structure along the c axis. The structure has square-sectioned one-dimensional tunnels encircled by 2×2 octahedra.

The Fourier map for $K_{1.0}Ti_8O_{16}$ revealed an electron density distributed anisotropically along the tunnel path. The density can be described by a single-sited [2(*b*)] K ion which has a large amplitude of vibration along the tunnel. This is different from the cases for the bronze $K_{1.35}Ti_8O_{16}$ (Vogt *et al.*, 1989) as well as the priderites, isomorphous to the bronze, such as $K_{1.5}Al_{1.5}Ti_{6.5}O_{16}$ *etc.* (Watanabe, Fujiki, Kanazawa & Tsukimura, 1987): the

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71163 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1010]

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	Position	Occupancy	x	y	z	B_{eq} (Å^2)
$K_{1.0}Ti_8O_{16}$						
K	2(*b*)	0.52	0	0	$\frac{1}{2}$	3.68 (14)
Ti($0.87Ti^{4+}$ + $0.13Ti^{3+}$)	8(*h*)	1.0	0.35019 (5)	0.16742 (5)	0	0.60 (1)
O(1)	8(*h*)	1.0	0.1566 (2)	0.2060 (2)	0	0.48 (6)
O(2)	8(*h*)	1.0	0.5399 (2)	0.1646 (2)	0	0.66 (6)
$K_{0.0}Ti_8O_{16}$						
K	2(*b*)	0.006 (3)	0	0	$\frac{1}{2}$	7.6 (91)
Ti(Ti^{4+})	8(*h*)	1.0	0.35380 (2)	0.17115 (2)	0	0.534 (4)
O(1)	8(*h*)	1.0	0.15669 (6)	0.20888 (6)	0	0.43 (1)
O(2)	8(*h*)	1.0	0.54109 (6)	0.16331 (7)	0	0.51 (2)

refinements on these materials have demonstrated two kinds of K ions; one is located at the 2(*b*) position $(0,0,\frac{1}{2})$ and the other at the 4(*e*) position $(0,0,\frac{1}{2}+\delta)$. The K contents found in these compounds, appreciably larger than unity per formula weight, inevitably give rise to a direct K—K contact. These K pairs should bring about the displacement from the 2(*b*) to the 4(*e*) position to relax Coulombic repulsion between paired K ions. However, few K ions, whose K contents are around or below unity per formula weight, need to have the unfavorable K—K pairs. The K ions could stay at the most stable sites [or position 2(*b*)], if sandwiched by vacancies on both sides. In practice, the introduction of the off-centered K ion for $K_{1.0}Ti_8O_{16}$ did not improve the reliability factors.

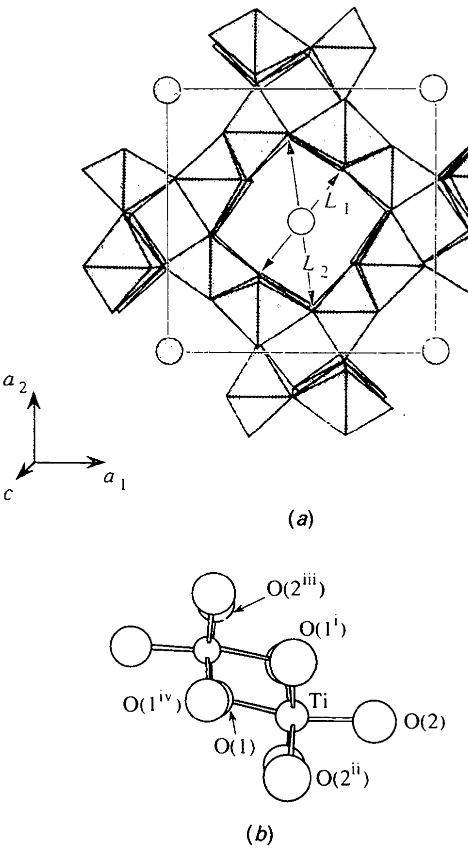

Fig. 1. (*a*) Perspective view of the structure along the *c* axis. Open and shaded circles represent the 2(*b*) position ($z = \frac{1}{2}$ and 0, respectively) for K ions. (*b*) Double chain of edge-sharing octahedra. Symmetry codes: (i) $-x+\frac{1}{2}, -y+\frac{1}{2}, \frac{1}{2}$; (ii) $-y+\frac{1}{2}, x-\frac{1}{2}, \frac{1}{2}$; (iii) $y, 1-x, 0$; (iv) $x, y, 1.0$.

For $K_{0.0}Ti_8O_{16}$, a faint peak was detected along the tunnel in a difference Fourier map synthesized based on a structural model in which K ions are neglected. The peak was assigned to residual K ions and then its anisotropic temperature factors and occupancy were refined, which led to the composition $K_{0.012}Ti_8O_{16}$. The obtained stoichiometry agrees well with the EPMA data, which confirms a substantially void tunnel, that is, $K_{0.0}Ti_8O_{16}$ is TiO_2 with the hollandite-type structure. The production of the '*exuviae*' oxide means that the integrity of the one-dimensional tunnel is surprisingly high; two or more defects in the one-dimensional path would rule out complete K removal. Note that the crystal examined contains 2.5×10^9 [$=(0.05\text{ mm}/10\text{ Å})^2$] tunnels along which 7.5×10^5 ($=0.225\text{ mm}/3\text{ Å}$) unit cells arrange linearly.

Besides the present structural data sets with different oxidation states ($x = 0.01, 1.04$), two comparable data sets have been published so far: $x = 0.48$ (Latroche *et al.*, 1989) and $x = 1.35$ (Vogt *et al.*, 1989). Interatomic distances for this series exhibit a

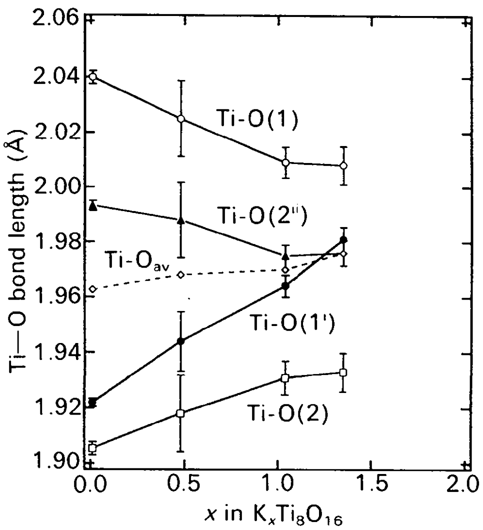

Fig. 2. Titanium–oxygen interatomic distances as a function of the composition x in $K_xTi_8O_{16}$. Symbols of atoms and symmetry codes correspond to those in Fig. 1. The error bars representing $\pm 3\sigma$ are given except for Ti—O_{av}. Values for $x = 0.48$ and 1.35 are calculated based on the data of Latroche *et al.* (1989) and Vogt *et al.* (1989), respectively.

well defined dependence on the composition x (Figs. 2 and 3). The decrease in x from 1.35 to 0.01 means two changes in chemical nature: (i) the oxidation of Ti^{3+} to the relatively smaller Ti^{4+}; (ii) the substantial removal of K ions from the tunnel.

Item (i) gives rise to a smooth decrease in mean Ti—O and O—O bond lengths in Figs. 2 and 3. Structure refinements on a series of priderites have revealed that the average octahedral metal–oxygen bond length is linearly dependent on the composition-weighted mean of the octahedral cationic radius (Watanabe, 1989). The shrinking of octahedron dimension observed in the present study fits quite well with the dependence quoted.

The marked contraction of edge-sharing O—O bonds [O(1)—O(2^{iii}) and O(1)—O(1^{i})] may be accounted for by item (i). This effectively screens the Ti—Ti repulsion that grows with the increase in the amount of Ti^{4+}.

Upon K extraction, Ti—O(1) and Ti—O(2^{ii}) bonds elongated considerably while contrasting shrinkage occurred in Ti—O(1^{i}) and Ti—O(2). This remarkable displacement of the Ti atom in its octahedral cavity may be ascribed to item (ii) rather than (i). The Ti atom tends to recede from the K ions, due to the repulsion between them, when they are situated in the tunnel. Note that the closest K is at $(0,0,\frac{1}{2})$ (3.7 Å apart) and second nearest one at $(\frac{1}{2},\frac{1}{2},0)$ (4.2 Å apart).

Table 2. *Tunnel diameters in the course of the oxidative* K *deintercalation*

The lengths L_1 and L_2 are the diagonals in Fig. 1(*a*). The values for $x = 0.48$ and 1.35 are calculated in the same way as for Fig. 2.

x in $K_xTi_8O_{16}$	0.01	0.48	1.04	1.35
L_1 (Å)	5.308 (2)	5.298 (4)	5.268 (4)	5.244 (4)
L_2 (Å)	6.895 (2)	6.886 (4)	6.874 (4)	6.849 (4)

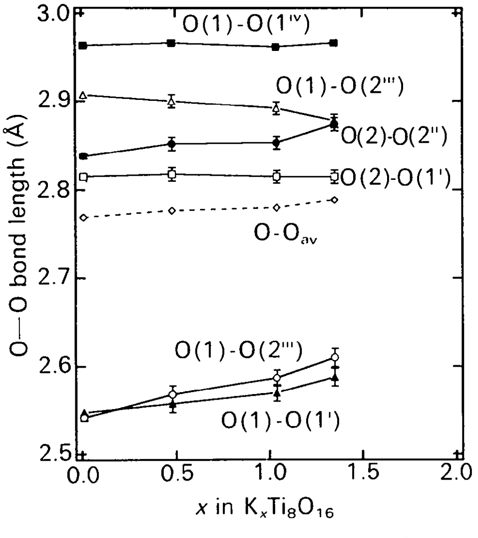

Fig. 3. Oxygen–oxygen interatomic distances as a function of the composition x. Symbols and symmetry codes correspond to those in Fig. 1. The error bars and values for $x = 0.48$ and 1.35 are similar to those in Fig. 2.

One of the most interesting features is a pronounced expansion of a lateral tunnel dimension on removal of the K ion, as exemplified by the diagonals, L_1 and L_2 in Table 2. It has been demonstrated from the refinements of the above-cited priderites, $K_{1.5}Al_{1.5}Ti_{6.5}O_{16}$, $K_{1.5}Ga_{1.5}Ti_{6.5}O_{16}$, $K_{1.5}Zn_{0.75}Ti_{7.25}O_{16}$ and $K_{1.5}Mg_{0.75}Ti_{7.25}O_{16}$, that the tunnel diameter depends on the octahedral cationic size (Watanabe, 1989): the L_1 diagonal expands by 0.8% through four kinds of composition which have a 4% gain in average radius of the octahedral cation. On the other hand, 1.0% elongation in L_1 was observed in the course of oxidation of the bronze from $x = 1.35$ to $x = 0.01$ where the octahedral cationic size is diminished by 1.8%. Note that the magnitude of the expansion is large and opposite to the dependence expected from the change in octahedral cationic radii. These facts suggest that item (ii) is responsible for the phenomenon. The effect of a loss of Coulombic attraction between K and O atoms of the framework is large enough to compensate for the contribution from octahedral cationic radii.

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