High pressure synthesis, crystal growth and magnetic properties of TiOF

Citation for published version:

Digital Object Identifier (DOI):
10.1016/j.solidstatesciences.2018.03.018

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Peer reviewed version

Published In:
Solid state sciences

General rights
Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

Download date: 26. Mar. 2021
High Pressure Synthesis, Crystal Growth and Magnetic Properties of TiOF

J. Cumby, M. B. Burchell and J. P. Attfield

CSEC and School of Chemistry, University of Edinburgh, King’s Buildings, Mayfield Road, Edinburgh, EH9 3JZ, U.K.

Abstract

Polycrystalline samples of TiOF have been prepared at 1300 °C and 8 GPa, with small single crystals grown at the same conditions. The crystal structure remains tetragonal rutile-type down to at least 90 K (space group P4_2/mnm, a = 4.6533(2) Å and c = 3.0143(2) Å at 90 K) and the Ti(O,F)_6 octahedra are slightly compressed, consistent with Jahn-Teller distortion of 3d^1 Ti^{3+}. Diffuse scattering reveals disordered structural correlations that may arise from local cis-order of oxide anions driven by covalency. TiOF is paramagnetic down to 5 K and observation of a small paramagnetic moment and a substantial Pauli term indicates that the d-electrons are partially delocalised.

Introduction

Rutile-type oxides are important for their electronic and magnetic properties. High pressure is needed to access many rutile-types, such as the heavy transition metal dioxides investigated by Demazeau and colleagues.\(^1\),\(^2\),\(^3\) VO\(_2\) is a particularly interesting rutile-type material as it undergoes the much-studied Morin (metal-insulator) transition at 340 K, accompanied by a structural distortion due to dimerization of 3d\(^1\) V\(^{4+}\) cations, and changes in other properties such as the magnetic susceptibility and optical reflectivity.\(^4\),\(^5\) This gives rise to applications such as infrared imaging devices, smart windows and sensors.\(^6\),\(^7\)

The rutile-type oxyfluoride TiOF is of interest as a 3d\(^1\) Ti\(^{3+}\) analogue of VO\(_2\), but has not been extensively studied. The high pressure and temperature synthesis at 1200 °C and 6.5 GPa was reported by Chamberland et al.\(^8\) They reported TiOF to be a tetragonal rutile type phase with lattice parameters of a = 4.651 Å and c = 3.013 Å at room temperature. However a later study of the TiO\(_2\)-xF\(_x\) system reported that the upper limit of fluoride substitution is x = 0.7.\(^9\) We
have reinvestigated TiOF and we report here the synthesis and crystal growth at high pressures, and low temperature structural and magnetic measurements.

Experimental

TiOF was synthesised using a 1:1 stoichiometric mixture of Ti$_2$O$_3$ and TiF$_3$ sealed inside a Pt capsule in a BN container, and heated to 1200 or 1300 °C for 30 min at a pressure of 8 GPa, in a two-stage Walker-type module. Products were characterised using a Bruker D8 Advance diffractometer, with Cu Kα$_1$ radiation. Single crystal measurements were performed on an Oxford Diffraction SuperNova instrument using a Mo source, with temperature control provided by an Oxford Cryosystems 700 series cryostream.

Magnetic susceptibility data from a powder sample were collected using a Quantum Design MPMS XL magnetometer under zero field cooled (ZFC) and field cooled (FC) conditions between 5 and 300 K, using an applied field of 500 Oe. Data were corrected for diamagnetic contributions using tabulated constants.

Results and Discussion

Synthesis and Crystal Structure

High phase purity (>90%) TiOF samples were obtained when heating at 1300 °C and 8 GPa, with a lower purity of ~80% achieved at 1200 °C. The observed impurity was TiF$_3$. Attempts to prepare a well-sintered ceramic sample for electrical transport measurements were not successful, but small black, needle-like crystals of TiOF were grown from one run at 1300 °C and 8 GPa. Single crystals of the isostructural FeOF were previously grown under similar conditions (950 °C and 6 GPa) by Demazeau and coworkers. In both cases no flux was used, although traces of water or other volatiles may act as transport agents within the Pt capsule.

Rietveld analysis of powder X-ray diffraction data for several samples found all to contain tetragonal rutile-type TiOF with lattice parameters close to those reported in ref. 8 and considerably larger than those of TiO$_2$ ($a = 4.5922(1)$ Å and $c = 2.9590(1)$ Å$^{11}$. This confirms the original report by Chamberland et al that TiOF is an essentially stoichiometric material.
The fit shown in Fig. 1 is for a sample prepared at 1300 °C and 8 GPa, with refined lattice parameters $a = 4.6693(2)$ Å and $c = 3.0420(1)$ Å.

X-ray diffraction data from a small single crystal (approximately $0.06 \times 0.08 \times 0.15$ mm) were collected at 90 and 200 K and results are shown in Table 1. The crystal was found to possess two independent domains and exhibited the tetragonal $P4_2/mnm$ rutile structure at both temperatures. No evidence for superstructure arising from long range O/F order was observed. Little structural change is evident between 90 and 200 K other than due to thermal expansion. The Ti(O,F)$_6$ octahedra are slightly distorted and their small tetragonal compression is consistent with Jahn-Teller distortion arising from the degenerate ground state of $3d^1$ Ti$^{3+}$. A crystal structure model showing the anisotropic thermal ellipsoids is displayed in Fig. 2.

Diffuse scattering within the $(hk0)$ plane is also observed in the single crystal diffraction patterns, with prominent rods of diffuse intensity aligned along $(110)^*$ directions for $(hk0)$ reflections where $h = \pm k$ (Fig. 3). Diffuse scattering has previously been observed in rutile type FeOF from electron diffraction, and is related to ordering of F and O anions within $(110)$ planes causing correlated displacements of Fe parallel to the $[1\overline{1}0]$ direction. The diffuse scattering for TiOF does not obey the same rules; here, the diffuse scattering occurs parallel to the scattering direction, suggesting that Ti displacements have a component perpendicular to the $(110)$ atomic plane, and the same argument applies to the $(1\overline{1}0)$ planes.

Local structural correlations in TiOF could arise from Ti-Ti dimerization analogous to that in VO$_2$, however, this would be expected to give rise to doubling of the $c$-axis or at least planes of diffuse scattering perpendicular to $c$ which is not observed. The local correlations may instead arise from the tendency of more covalent anions (here oxide) to adopt $cis$-positions within the coordination octahedron around a d$^0$ or d$^1$ transition metal cation. This is observed in isolated [MoO$_3$F$_3$]$^3$ complexes which have the $fac$-configuration where the three fluorides or oxides are all mutually $cis$, e.g. in Na$_3$MoO$_3$F$_3$. The effect is extensively documented in AMO$_2$N and AMON$_2$ type oxynitrides where $cis$- MN or MO chains spontaneously order into planes, e.g. SrTaO$_2$N and LaTaON$_2$. Strong Ti-O covalency in TiOF would lead to $fac$-TiO$_3$F$_3$ octahedra at all Ti sites, and a resulting correlated disorder of intersecting $cis$- TiO (and TiF) chains analogous to those proposed in the perovskite EuWO$_{1.5}$N$_{1.5}$. X-ray contrast between O and F atoms is very poor, but the corresponding displacements of the Ti...
atoms towards the O₃-octahedral faces, which are analogous to the Ti-displacements in the low temperature phase of BaTiO₃, may be responsible for the diffuse X-ray scatter. Further analysis of the diffuse features, and other experiments such as electron diffraction, will be required to ascertain the nature of the local structural correlations.

**Magnetic Behaviour**

Magnetic susceptibility data from polycrystalline TiOF are shown in Fig. 4. The sample shows paramagnetic behaviour between 5 and 300 K with no long range spin ordering or dimerization transition apparent. A small anomaly observed at 43 K could indicate a subtle electronic transition but is more likely to arise from an impurity; TiF₃ is reported to order magnetically at 48 K.

The inverse susceptibility in Fig. 3b shows a non-linear temperature dependence indicating that the paramagnetic behaviour is not simple Curie-Weiss. However, a good fit is obtained with the sum of Curie-Weiss and constant susceptibility terms; \( \chi^{-1} = [C/(T - \theta) + \chi_0]^{-1} \). The fitted parameters are Curie constant \( C = 0.1119 \text{ emu K mol}^{-1} \), Weiss temperature \( \theta = -19.3 \text{ K} \) and constant \( \chi_0 = 7.2 \times 10^{-4} \text{ emu mol}^{-1} \). The Curie constant gives an effective paramagnetic moment of \( \mu_{\text{eff}} = 0.95 \mu_B \) per Ti, which is substantially lower than the expected value of 1.73 \( \mu_B \) for a localised \( d^1 \) configuration. The large \( \chi_0 \) term indicates a significant Pauli paramagnetism, which in combination with the reduced moment, shows that d-electrons are partially delocalised. TiOF may be close to metallic behaviour, but with disorder leading to localisation of many spins, which interact antiferromagnetically as indicated by the negative Weiss temperature. Neutron scattering will be valuable to explore possible magnetic correlations at low temperatures.

**Conclusions**

The above results confirm the original report that TiOF is an essentially stoichiometric rutile-type phase that can be prepared under high pressure and temperature conditions, with crystals grown at 1300 °C and 8 GPa. The crystal structure remains tetragonal rutile-type down to at least 90 K, and the Ti(O,F)₆ octahedra are slightly compressed, consistent with
Jahn-Teller distortion of $3d^1 \, Ti^{3+}$. Diffuse scattering reveals planes of structural correlation that may arise from local \textit{cis}-order of oxide anions driven by covalency. TiOF is paramagnetic down to 5 K and observation of a small paramagnetic moment and a substantial Pauli term indicates that the d-electrons are partially delocalised.

\textbf{Acknowledgements}

We thank Dr. Gary Nicol for assistance with single crystal data collection and ERC for financial support.

\begin{thebibliography}{9}
\bibitem{4} F.J. Morin, Phys. Rev. Lett. 1959, 3 (1959) 34.
\bibitem{5} Z. Hiroi, Prog. Solid State Chem. 43 (2015) 47.
\end{thebibliography}
Table 1: Structural results for TiOF from X-ray single crystal diffraction analysis at 90 and 200 K.\textsuperscript{a} $U$ values are $\times 100$ Å$^2$, bond distances in Å, and bond angles in degrees.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>90 K</th>
<th>200 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>4.6533(2)</td>
<td>4.6569(2)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>3.0143(2)</td>
<td>3.0191(2)</td>
</tr>
<tr>
<td>Ti $U_{is}$</td>
<td>1.27(4)</td>
<td>1.39(4)</td>
</tr>
<tr>
<td>$U_{11}$</td>
<td>1.29(4)</td>
<td>1.41(4)</td>
</tr>
<tr>
<td>$U_{33}$</td>
<td>1.24(6)</td>
<td>1.35(5)</td>
</tr>
<tr>
<td>$U_{12}$</td>
<td>0.34(2)</td>
<td>0.35(2)</td>
</tr>
<tr>
<td>O/F $x$</td>
<td>0.301(9)</td>
<td>0.301(10)</td>
</tr>
<tr>
<td>O/F $U_{is}$</td>
<td>0.72(5)</td>
<td>0.86(4)</td>
</tr>
<tr>
<td>O/F $U_{11}$</td>
<td>0.65(6)</td>
<td>0.80(5)</td>
</tr>
<tr>
<td>O/F $U_{33}$</td>
<td>0.87(8)</td>
<td>0.96(8)</td>
</tr>
<tr>
<td>O/F $U_{12}$</td>
<td>-0.06(5)</td>
<td>-0.11(5)</td>
</tr>
<tr>
<td>$R1$</td>
<td>0.0226</td>
<td>0.0194</td>
</tr>
<tr>
<td>$wR2$</td>
<td>0.0563</td>
<td>0.0493</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>1.160</td>
<td>1.245</td>
</tr>
<tr>
<td>Parameters varied</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>Ti-O/F (x 2)</td>
<td>1.981(2)</td>
<td>1.984(2)</td>
</tr>
<tr>
<td>Ti-O/F (x 4)</td>
<td>1.996(1)</td>
<td>1.998(1)</td>
</tr>
<tr>
<td>O/F-Ti-O/F</td>
<td>82.06(8)</td>
<td>81.84(7)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Space group P4$_2/\text{mmm}$; Ti (0,0,0), O/F (x,x,0)
Fig. 1: Rietveld fit to room temperature powder X-ray diffraction data for a sample of TiOF prepared at 1300 °C and 8 GPa; TiOF - cyan reflection bars, TiF₃ (9 wt % impurity) - green bars, BN (from sample container during high pressure reaction) – magenta bars.

Fig. 2: Ball-and-stick model of the refined TiOF structure showing the thermal vibration ellipsoids. Ti/O – blue/red.
Fig. 3: Precession images of the \((hk0)\), \((0kl)\) and \((h0l)\) planes reconstructed from single crystal data at 90 K. Diffuse scattering along \{110\}* directions for \((hh0)\) and \((hh0)\) reflections is evident.
Fig. 4: Magnetic susceptibility data from a powder TiOF sample. (a) Field-cooled and zero-field cooled susceptibilities under a 500 Oe applied field. The inset shows a small anomaly at 43 K. (b) Inverse ZFC magnetic susceptibility showing a fit of the sum of Curie-Weiss and constant susceptibility terms to data above 50 K.