Synthesis of Anhydrous K_2TiOF_4 via a Mild Hydrothermal Method

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Abstract

The synthesis of anhydrous K_2TiOF_4 has been previously attempted by transforming precursor compounds, such as the peroxide ($\text{K}_2\text{Ti}(\text{O}_2)\text{F}_4$), hydrate ($\text{K}_2\text{TiOF}_4 \cdot \text{H}_2\text{O}$) and fluoride (K_2TiF_6). Due to the large structural differences between these precursors and the anhydrous oxyfluorides, however, these preparations have been unsuccessful. Therefore, a direct method of synthesis has been employed to grow single crystals of K_2TiOF_4 that were characterized by single crystal x-ray diffraction. K_2TiOF_4 was found to be isostructural with the previously known K_2VOF_4 .

1. Introduction

Compounds containing Ti^{4+} have been studied extensively for their photocatalytic activity,¹ as well as for their ability to support the reduction of CO_2 into fuels such as methane.² Given the success of TiO_2 , it is not surprising that more recent work has focused on developing even more efficient catalysts – either by doping TiO_2 with other transition metals or by synthesizing entirely new Ti^{4+} containing materials. One approach to improving TiO_2 via doping includes the introduction of fluoride ions into the structure as well as the preparation and investigation of new titanium-containing fluorides and oxyfluorides.^{3 4 5}

A good starting point for the preparation of new titanium containing fluorides and oxyfluorides is the substitution of titanium for vanadium in existing vanadium fluorides and oxyfluoride phases. The K/V/O/F phase space has been well explored, and within it there exists several potassium vanadium fluoride and oxyfluoride structures in which the vanadium can be substituted for by titanium. These substitutions have been quite successful, and these as well as other titanium fluorides and oxyfluorides are of interest for their photocatalytic activity. Among this group, K_2TiF_6 , K_3TiOF_5 , $\text{K}_2\text{Ti}(\text{O}_2)\text{F}_4$, $\text{K}_2\text{TiOF}_4 \cdot (\text{H}_2\text{O})$, and $\text{K}_7\text{Ti}_4\text{O}_4\text{F}_7$ have been structurally characterized. However, the synthesis and structural characterization of K_2TiOF_4 , first reported by Ginsberg and Holder and attempted by numerous groups since, has apparently not yet been achieved.^{3 6 5 7}

There are extensive reports in the literature describing work aimed at preparing K_2TiOF_4 . The reported structure characterizations indicate that two polymorphs, I and II,

exist. Synthetically, for example, Schmitz-Dumont and Deddmore^{8 9} showed that the thermal decomposition of K_2TiF_6 requires moisture to result in the target phase of K_2TiOF_4 plus HF, while according to Drossbach,¹⁰ the electrolytic reaction of K_2TiF_6 yields K_2TiOF_4 as an intermediate via the reaction of $\text{K}_2\text{TiF}_6 + \text{TiO}_2 + 2\text{KF}$. The group of Pausewang^{11 12} has pursued the preparation of K_2TiOF_4 via a number of synthetic approaches, including a solid state reaction between K_2TiF_6 , TiO_2 and KF , the thermal decomposition of $\text{K}_2\text{Ti}(\text{O}_2)\text{F}_4 \cdot \text{H}_2\text{O}$, and the pyrohydrolysis of K_2TiF_6 .

The dehydration of the peroxide containing $\text{K}_2\text{Ti}(\text{O}_2)\text{F}_4 \cdot \text{H}_2\text{O}$ was reported to proceed via a $\text{K}_2\text{Ti}(\text{O}_2)\text{F}_4$ intermediate to K_2TiOF_4 (I) where the decomposition of the peroxy group required temperatures of at least 230 °C.⁸ Unfortunately, due to the reported instability of K_2TiOF_4 (I), this has so far led to only mixed phase products containing K_2TiOF_4 (I), the cryolite composition $\text{K}_{2.67}\text{TiO}_{0.67}\text{F}_{5.33}$, and TiO_2 . K_2TiOF_4 (I) is reported to be tetragonal with $a = 7.697(1)$, and $c = 11.539(2)$ Å. High pressure thermal decompositions of $\text{K}_2\text{Ti}(\text{O}_2)\text{F}_4 \cdot \text{H}_2\text{O}$ were reported to proceed via the formation of $\text{K}_2\text{TiOF}_4 \cdot \text{H}_2\text{O}$ (130-230 °C) followed by a dehydration step ($T > 300^\circ\text{C}$), resulting in K_2TiOF_4 (II). The crystal structure of K_2TiOF_4 (II) was reported to adopt the K_2FeF_5 type orthorhombic structure with space group $Pn2_1a$, and lattice parameters: $a = 20.253(2)$, $b = 7.366(1)$ and $c = 12.951(1)$ Å.¹¹ Interestingly, while K_2TiOF_4 was originally reported as being a possible member of the potassium oxyfluorotitanate family, to date it has proven impossible to synthesize this composition via preparation from precursors, such as the hydrate and peroxide forms.^{11 12}

Often a different synthetic route can enable the synthesis of an elusive material,¹³
¹⁴ and in the case of K_2TiOF_4 the use of a hydrothermal route has now resulted in the

facile synthesis of K_2TiOF_4 in single crystal form. In this paper we report the mild hydrothermal synthesis of high quality single crystals of K_2TiOF_4 and the determination of its structure in space group *Pnma*. In addition, we discuss why the dehydration of the hydrated form is unlikely to result in the anhydrous K_2TiOF_4 due to the major structural rearrangement that would be required.

2. Experimental

2.1 Materials and Method

The following reagents were used as received: TiF_3 (Alfa Aesar), KF (Alfa Aesar, 99%), and HF (EMD, 48%). 1 mmol of TiF_3 and 5.00 g of KF were placed in a 23 mL PTFE lined stainless steel autoclave along with 2.5 mL of HF and 2.5 mL of H_2O . The autoclave was sealed and placed in a programmable oven and ramped to 200° C at a rate of 10.00°/min. It was held at 200°C for 24 hours. The oven was then cooled at a rate of 0.1°/minute until it reached a temperature of 40° C. The oven was then allowed to cool naturally to room temperature. After cooling, the autoclave was removed and the product obtained by vacuum filtration. Excess KF was removed by dissolution with water, and the product was washed thoroughly with water and acetone and then allowed to dry under vacuum at room temperature. The synthesis resulted in approximately 75% yield after washing, with an unknown side product being present as clear colorless crystals.

2.2 Structure Determination

X-ray intensity data was measured from a yellow polyhedral crystal of approximate dimensions 0.20 mm × 0.16 mm × 0.16 mm at 294(2) K on a Bruker SMART APEX CCD diffractometer utilizing $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The raw area detector data frames were reduced using SAINT+. ¹⁵ The multi-scan technique in

SADABS was used to correct for absorption effects.¹⁵ The unit cell parameters were determined by least-squares refinement of sets of strong reflections. Full matrix least-squares refinement against F^2 of the structural models and difference Fourier calculations were performed with SHELXTL.¹⁶

Crystallographic data from the structure refinements for K_2TiOF_4 can be found in Table 1. Atomic coordinates as well as selected interatomic distances are listed in Tables 2 and 3, respectively.

2.3 Scanning Electron Microscopy

Single crystals of K_2TiOF_4 were analyzed by SEM using an FEI Quanta SEM instrument in high vacuum mode. Energy dispersive spectroscopy (EDS) was used to verify the presence of K and Ti.

3. Results and Discussion

3.1 Structure Description of K_2TiOF_4 and Comparison to $K_2TiOF_4 \cdot H_2O$ ^{11, 12}

K_2TiOF_4 , as well as its hydrate, $K_2TiOF_4 \cdot H_2O$, are composed of one-dimensional chains of corner shared titanium octahedra. In the title compound, the infinite chains are composed of TiO_2F_4 octahedra that corner share exclusively through the F(1) position to yield staggered chains. Figure 1 shows the connectivity of the polyhedra that gives rise to the infinite chains. The oxide positions are *cis* equatorial with the F(1) position occupying the other equatorial sites. The F(3) and F(4) sites occupy the axial positions of the octahedra. The titanium octahedra are heavily distorted with the Ti^{4+} ion being offset significantly from the center. This is caused by the fact that *M*-O bonds are generally shorter than *M*-F bonds and explains why the Ti^{4+} ion appears to be pulled closer to the *cis* oxide ions. Figure 1 shows a close up of the local coordination environment of the

Ti^{4+} ions. The hydrate is similar in that it is also composed of TiO_2F_4 octahedra that corner share to form infinite one-dimensional chains. Unlike the title compound, however, the hydrate octahedra are connected only through the O(1) site and form linear chains. Figure 2 illustrates the linear chains of the hydrated compound. The O(1) oxide positions occupy the axial sites of the octahedra with the equatorial sites being occupied only by F(1) and F(2). In this case, the $M\text{-O}$ bond is actually longer than the $M\text{-F}$ bond due to the fact that the oxide ions linearly bridge two Ti^{4+} ions. The bond length is therefore increased to prevent the cations from being too close together. Figure 2 shows a single, fairly regular, TiO_2F_4 octahedron.

In the hydrated compound, the linear chains of octahedra create channels in which the waters of hydration reside. This is illustrated in Figure 3, which shows four chains surrounding the channel. The waters of hydration within these channels can form hydrogen bonds with the fluoride ions of the titanium octahedra and act to connect the infinite chains to each other, which strengthens the lattice. In the title compound, K_2TiOF_4 , the staggered nature of the chains accompanied by a canting of the chains relative to the hydrated compound fills the space occupied by the channels in the hydrated compound. This leaves no room for waters of hydration. Figure 4 illustrates the absence of channels in the title compound.

In both compounds, the structure is held together by the potassium ion. In the hydrated compound, the ten-coordinate potassium polyhedra fill all space. The three-dimensional potassium lattice is formed by face- and edge-sharing KO_4F_6 polyhedra that connect along all three axes, as illustrated in Figure 5, which shows a slab of potassium polyhedra. In K_2TiOF_4 , there are two unique potassium sites that are located between the

one-dimensional chains that hold the structure together. The K(1) site forms infinite staggered one-dimensional chains of ten-coordinate potassium polyhedra. The polyhedra consist of four oxide ions arranged in a *cis* fashion to form a square face. The remaining vertices of the polyhedron are fluoride ions. The polyhedra are connected via edge sharing exclusively through the oxide positions to form the staggered chains. Each polyhedron corner shares through each of the fluoride positions, connecting to six additional polyhedra; this connects the staggered chains to each other. Figure 6 shows the one-dimensional potassium chains as well as their connectivity to one another. The K(2) position forms staggered one-dimensional chains of face shared polyhedra. These chains are corner-shared to form layers. The ten coordinate polyhedra have four oxide ions arranged in pairs *trans* to one another. Fluoride ions make up the remaining vertices. Face sharing occurs exclusively through the triangular face formed by the two O(1) sites and the F(4) site. Corner sharing within layers occurs exclusively through the F(3) position. The layers are interconnected via corner-sharing through the F(2) position. Figure 7 shows two views highlighting the chains of face-shared polyhedra and the layers. Figure 8 highlights the differences between the title compound and the hydrate by giving an overall structural representation.

3.2 Bond Valence Sum Analysis

Bond Valence Sum (BVS) calculations were performed for the title compound. BVS calculations were performed for the K(1)⁺, and K(2)⁺ sites, yielding 1.04, and 1.25, respectively. The Ti site yielded a value of 4.03, while the fluorine and oxygen positions gave values of O/F : 1.76; F(2) : 0.85; F(3) : 1.01; and F(4) : 1.01. These values fall

within expected values for their respective oxidation states and support the assignments of the fluorine and oxygen atom locations.^{17 18 19 20}

3.3 Synthetic Considerations

K_2TiOF_4 has been a sought after compound for many years, and several methods for its synthesis have been tested. Specifically, past groups have tried to synthesize the title compound by thermal decomposition of the peroxide precursor $\text{K}_2\text{Ti}(\text{O}_2)\text{F}_4$ and by dehydration of the hydrated precursor $\text{K}_2\text{TiOF}_4 \cdot \text{H}_2\text{O}$. The previous section compared the crystal structures of the title compound and the hydrate. By comparing the two different structures, some conclusions can be drawn as to why previous synthetic attempts have been unsuccessful.

In order to successfully transform the structure from that of the hydrate to that of the title compound, several large changes have to occur. First, the dehydration would have to occur. This would involve removing the waters of hydration from inside the channels formed by the linear one-dimensional chains of the hydrate. This is problematic because the waters play a role in the integrity of the structure due to the hydrogen bonding between the waters and the fluoride ions in the octahedra. Without hydrogen bonding to stabilize the structure, it would collapse.

Secondly, the connectivity of the titanium octahedra and the one-dimensional chains would have to change during the structural transformation. Both compounds are composed of TiO_2F_4 octahedra, but in the hydrate the oxide ions are located axially and *trans* to one another while in the title compound they are located equatorially and *cis* to one another. In the hydrate the octahedra are connected exclusively through the oxide site, while the octahedra are only connected via fluoride in the title compound.

Additionally, the chains would have to go from linear to a staggered configuration as well as rotate to fill the space left by the hydration waters.

Finally, the potassium polyhedra must transform from a cubic configuration filling all space to a much more complicated structure of interconnected one-dimensional chains and layers of face-, edge-, and corner-sharing polyhedra. Such drastic changes would be surprising under the mild dehydration conditions and render such a crystal-to-crystal transition unlikely. It is for this reason that a direct synthesis of the title compound, such as the one discussed herein, is a more favorable approach for this system than a synthesis utilizing precursors such as the peroxide or hydrated compounds.

3.4 Energy Dispersive Spectroscopy (EDS)

EDS was used to confirm the presence of potassium, titanium, oxygen, and fluorine. EDS suggested that potassium and titanium are present in roughly a 2:1 potassium to titanium ratio. EDS does not give reliable quantitative data for oxygen and fluorine.

4. Conclusion

K_2TiOF_4 is a compound that has been long sought after due to its potential photocatalytic activity, but previous attempts at its synthesis have proven to be problematic. Attempts to synthesize K_2TiOF_4 from the peroxide and hydrate precursors have been unsuccessful, and led to the reporting of incorrect structural data. This work has determined that K_2TiOF_4 synthesized via a mild hydrothermal route crystallizes in the orthorhombic space group *Pnma*, which is in the same space group that the known vanadium analog, K_2VOF_4 , crystallizes in. This work has determined that synthesis of the

title compound from precursors is unlikely due to the structural differences, and thus a direct synthetic method such as the one reported here should be utilized.

5. Acknowledgements

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References

- (1) Y. Shiraishi; T. Hirai, J. Jpn. Petrol. Inst. 55 (2012), 287-298.
- (2) S. Yamagata; M. Nishijo; N. Murao; S. Ohta; I. Mizoguchi, Zeolites 15 (1995), 490-493.
- (3) A. Hattori, J. Sol-Gel Sci. Technol. 22 (2001), 47.
- (4) J. Kou; J. Gao; Z. Li; H. Yu; Y. Zhou; Z. Zou, Catal. Lett. 145 (2015), 640.
- (5) J. Sheng; K. Tang; W. Cheng; J. Wang; Y. Nie; Q. Yang, J. Hazard. Mater. 171 (2009), 279-287.
- (6) D. W. Aldous; P. Lightfoot, Solid State Sciences 11 (2009), 315-319.
- (7) V. H. Ginsberg; G. Holder, Z. anorg. allg. Chemie 196 (1931), 188.
- (8) O. Schmitz-Dumont; P. Poggenhoff, Z. Anorg. Allg. Chem. 268 (1952), 57.
- (9) D. Z. Deddmore; J. G. Machin; Q. W. Allen, J. Amer. Ceram. Soc. 45 (1962), 120.
- (10) P. Drossbach; E. Rossberger, Z. Elektrochem. Ber. Bunsenges. Phys. Chem. 60 (1956), 470.
- (11) M. Schabert; G. Pausewang, Z. Anorg. Allg. Chem. 559 (1988), 143.
- (12) R. Schmidt; G. Pausewang, Z. Anorg. Allg. Chem. 523 (1985), 213.
- (13) J. Yeon; A. S. Sefat; T. T. Tran; P. S. Halasyamani; H.-C. zur Loye, Inorg. Chem. 52 (2013), 6179-6186.
- (14) D. E. Bugaris; H.-C. zur Loye, Angew. Chem. Int. Ed. Engl. 51 (2012), 3780-3811.
- (15) SMART Version 5.625, SAINT+ Version 6.45 and SADABS Version 2.05, Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, (2001)
- (16) SHELXTL Version 6.14, Bruker analytical X-ray Systems, Inc., Madison, WI, (2000)
- (17) S. Adams, Acta. Cryst. B57 (2001), 287-287.
- (18) R. Allmann, Monatshefte Chem. 106 (1975), 779.
- (19) N. E. Brese; M. O'Keefe, Acta. Cryst. B47 (1991), 192-197.
- (20) I. D. Brown; D. Altermatt, Acta. Cryst. B41 (1985), 244-247.

Figures and Tables

Table 1. Crystal Data and Structure Refinement for K₂TiOF₄

Empirical Formula	K ₂ TiOF ₄
Color	Yellow
Crystal Size	0.20 mm × 0.16 mm × 0.16 mm
Formula Weight	218.10 g/mol F.U.
Temperature	294(2) K
Wavelength	0.71073 Å
Crystal System	Orthorhombic
Space Group	<i>Pnma</i>
Unit Cell Parameters	a = 7.3891(2) Å b = 5.6458(2) Å c = 11.4220(4) Å $\alpha = 90^\circ$
Volume	476.50(3) Å ³
Z	4
Density (calculated)	3.040 Mg/m ³
Absorption Coefficient	3.524 mm ⁻¹
Reflections Collected	6633
Independent Reflections	791
Absorption Correction	Semi-empirical from equivalents
Data / Restraints / Parameters	791 / 0 / 46
Goodness-of-Fit on F ²	1.196
Final R Indices	R ₁ = 0.0303 wR ₂ = 0.0787
Largest Diff. Peak and Hole	0.460 and -1.333 e.Å ³

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$)

	x	y	z	U(eq)*
Ti(1)	0.1989(1)	0.2500	0.5693(1)	0.014(1)
K(1)	0.6904(1)	0.2500	0.5927(1)	0.024(1)
K(2)	-0.0220(1)	0.2500	0.2827(1)	0.021(1)
O(1)	0.3221(2)	0.0223(2)	0.6115(1)	0.028(1)
F(1)	0.3221(2)	0.0223(2)	0.6115(1)	0.028(1)
F(2)	0	0	0.5000	0.022(1)
F(3)	0.0358(2)	0.2500	0.6952(1)	0.025(1)
F(4)	0.2741(2)	0.2500	0.4081(1)	0.022(1)

*U(eq) is defined as one third of the trace orthogonalized U^{ij} tensor.

Table 3. Selected interatomic distances for K_2TiOF_4 ($\text{\AA}$)

Ti(1)-O(1)	1.6472(13)
Ti(1)-F(1)	1.6472(13)
Ti(1)-F(2)	2.1860(3)
Ti(1)-F(3)	1.8768(16)
Ti(1)-F(4)	1.9231(15)
K(1)-O(1)	2.7947(14)
K(1)-O(1)	3.0174(15)
K(1)-F(1)	2.7947(14)
K(1)-F(2)	2.8892(5)
K(1)-F(3)	2.6783(17)
K(1)-F(3)	2.8078(18)
K(1)-F(4)	2.83509(18)
K(2)-O(1)	2.8935(13)
K(2)-O(1)	2.9565(14)
K(2)-F(1)	2.8935(13)
K(2)-F(1)	2.9565(14)
K(2)-F(2)	2.8596(5)
K(2)-F(3)	2.83597(19)
K(2)-F(4)	2.6146(16)
K(2)-F(4)	2.6494(15)

Table of Contents

Synthesis of anhydrous K_2TiOF_4 has been previously attempted by transforming precursor compounds such as the peroxide ($\text{K}_2\text{Ti}(\text{O}_2)\text{F}_4$), hydrate ($\text{K}_2\text{TiOF}_4 \cdot \text{H}_2\text{O}$) and fluoride (K_2TiF_6). Due to the large structural differences between these precursors and the anhydrous oxyfluorides, these preparations have been unsuccessful. Therefore, a direct method of synthesis has been employed to grow single crystals of K_2TiOF_4 that were characterized by single crystal X-ray diffraction.

Figure 1: *Left:* Staggered one-dimensional chain consisting of TiO_2F_4 octahedra. The octahedra corner-share exclusively through the F(1) site. *Right:* The local coordination environment of the Ti^{4+} ion. The octahedron is distorted with the Ti^{4+} ion being shifted toward the oxide containing edge.

Figure 2: *Left:* A nearly perfectly linear chain of the hydrated compound. The chains are formed by corner-sharing octahedra. The sharing is exclusively through oxide ions. *Right:* The local environment of the titanium ion in the hydrated compound. The octahedron is regular, and the oxide ions are positioned *trans* to one another.

Figure 3: A channel created by four infinite chains in the hydrated compound. The channel is occupied by waters of hydration (shown as purple spheres). The waters can hydrogen bond to the fluoride ions in the chains, reinforcing the crystal structure.

Figure 4: The arrangement of the one-dimensional chains of the title compound in space. The staggered nature and rotation of the chains relative to each other fill the space occupied by the waters in the hydrated compound.

Figure 5: The arrangement of the potassium polyhedra in the hydrate fills all space. The polyhedra consist of potassium ions coordinating four oxide and six fluoride ions.

Figure 6: *Top:* The staggered one-dimensional chains formed by 10-coordinate potassium(1) polyhedra in the title compound. The four oxide ions in the polyhedra are arranged *cis* to one another. *Bottom:* The connectivity of the chains in space. Each chain corner shares with others to form a three-dimensional network.

Figure 7: *Left:* The layered structure of the K(2) site in the title compound. The layers are connected via corner sharing, and are offset from one another. Unlike in the K(1) position, the oxide ions are arranged in pairs that are *trans* to one another. *Right:* a 90° rotation of the left view. This shows how the layers are built up of face sharing polyhedra.

Figure 8: A structural comparison of the overall title and hydrated structures.
Top: K_2TiOF_4 *Bottom:* $K_2TiOF_4 \cdot H_2O$