

**The Synthesis and Characterisation of $\text{Ti}^{3+} s=1/2$
Mixed-Metal Fluorides**

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Abstract

Compounds containing d^1 transition metal ions, such as Ti^{3+} and Cu^{2+} where the electron spin $S = 1/2$, show interesting magnetic properties such as the potential to exhibit quantum spin behaviour. The greater redox stability of Cu^{2+} and other $S = 1/2$ systems has resulted less attention to the Ti^{3+} oxidation state [1-3]. The search to synthesise new Ti^{3+} magnetic materials is therefore a key area of interest for applications in quantum computing, energy, magnetism and superconductivity [4].

We have explored a variety of reducing agents with the goal of synthesising Ti^{3+} mixed-metal fluorides via the hydrothermal method. Ti^{3+} is typically a difficult oxidation state to reach through conventional solid-state techniques so developing new routes to reduce Ti^{4+} to Ti^{3+} is important [3]. The reducing agents explored were dimethylformamide (DMF) [5], polyvinylpyrrolidone (PVP) [6, 7] and triethylamine (TEA) [8], which previously have been successfully applied in reduced nanoparticle synthesis.

The compounds $Rb_2TiF_5 \cdot H_2O$ and $Cs_2TiF_5 \cdot H_2O$, as well as their deuterated counterparts, were successfully synthesised using hydrothermal methods with DMF as the sole reducing agent. PVP and TEA proved to be effective reducing agents in the synthesis of $Rb_2TiF_5 \cdot H_2O$ but not $Cs_2TiF_5 \cdot H_2O$. $Rb_2TiF_5 \cdot H_2O$ was successfully dehydrated and FTIR analysis combined with X-ray diffraction techniques showed a loss of water molecules with no changes to the rest of the structure. A synthetic route to form the analogous dehydrate $Cs_2TiF_5 \cdot H_2O$ was not successful. This work shows that a number of reducing agents can be used effectively to reduce Ti^{4+} to Ti^{3+} in solid-state hydrothermal synthesis.

$Rb_2TiF_5 \cdot H_2O$ ($Cmcm$; $a = 9.64164$, $b = 8.47313$ and $c = 7.86328$ Å) and $Cs_2TiF_5 \cdot H_2O$ ($Cmcm$; $a = 10.32487$, $b = 8.79496$ and $c = 8.01500$ Å) are alkali metal titanium fluorides with one dimensional (1D) chain structures made up of $Ti^{3+}F_6$ corner sharing octahedra. These octahedra experience Jahn-Teller distortion, consisting of varied F – Ti – F bond angles and Ti – F bond lengths, with the $Cs_2TiF_5 \cdot H_2O$ compound

exhibiting the most distortion [9]. The Ti – F bond lengths in $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ (*Cmcm*) were between 1.898 - 1.9601 Å (0.0621 Å range) and in $\text{Cs}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ (*Cmcm*) 1.89726 - 2.00023 Å (0.10297 Å range). Bond angles in $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ showed no distortion, whereas in $\text{Cs}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ some angles were distorted by up to 0.01578°. Structure determination was performed using single-crystal and powder X-ray diffraction techniques. The analogous deuterated compounds were analysed using neutron powder diffraction.

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Abbreviations and symbols

DMF	<i>N, N</i> -Dimethylformamide
TEA	Triethylamine
PVP	Polyvinylpyrrolidone
QSL	Quantum Spin Liquid
KLAF	Kagomé Lattice Antiferromagnet
XRD	X-Ray Diffraction
TGA	Thermogravimetric Analysis
XRF	X-Ray Fluorescence
FTIR	Fourier-Transform Infrared Spectroscopy

1

Introduction

1.1 Background

1.1.1 Early Reports of Ti^{3+} Compounds

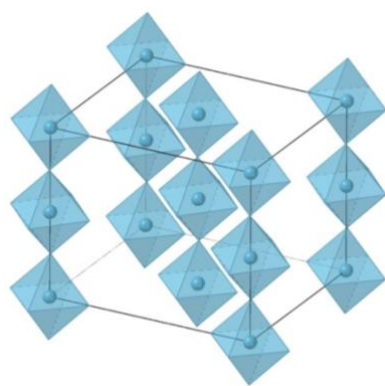
Over time advances in syntheses and scientific understanding have paved the way for new synthetic approaches to reach previously inaccessible oxidation states. These syntheses often require reducing agents and for the reaction to take place in an inert or controlled environment. The ability to synthesise and stabilise Ti^{3+} allowed the unique electronic configuration of these compounds to be analysed and explored, making this field a growing area of interest for chemists and physicists alike. Research so far has discovered a range of diverse applications for these compounds in energy, magnetism and superconductivity [1-4].

Although it is hard to pinpoint the first Ti^{3+} compound synthesised due to lack of historical records, it is evident that by the early 1900s scientists had discovered that sodium could reduce TiCl_4 (Ti^{4+}) [10], although whether this was to Ti or Ti^{2+} was debated later [11]. In the 1960s the sodium in this reaction was swapped for lithium, a more electronegative element. The resulting product was violet TiCl_3 (Ti^{3+}). Around the same time another group had discovered that hydrogen gas could be used to synthesise TiCl_3 and TiBr_3 from TiCl_4 and TiBr_4 respectively [12]. Early applications of TiCl_3 were in the field of catalysis which was led by Giulio Natta and Ziegler in the 1950s. They developed Ziegler-Natta catalysts which are used in the synthesis of α -olefins. Their advancements in catalysis and polymers awarded them jointly the Nobel Prize in Chemistry in 1963 [13].

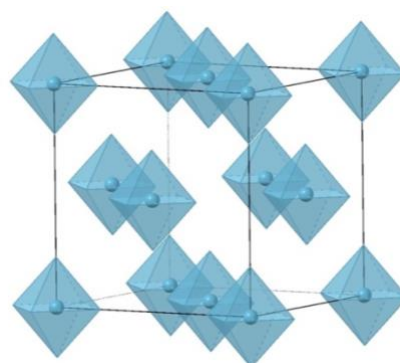
1.1.2 Alkali mixed-metal Ti^{3+} Fluoride Compounds

This literature review will cover all the known mixed-metal fluorides where $A = \text{Cs}^+ / \text{Rb}^+$, $B = \text{group 1 or 2 metal cations}$ and $M = \text{Ti}^{3+}$. The compounds that fit these criteria are beta-pyrochlores ABMF_6 ; double perovskites A_2BMF_6 ; low dimensional chain compounds $\text{A}_2\text{BM}_3\text{F}_{12}$ and $\text{A}_2\text{MF}_{5.n}\text{H}_2\text{O}$. All these compounds consist of Ti^{3+}F_6 corner-sharing octahedra which due to Jahn-Teller distortion consist of varied $\text{F} - \text{Ti} - \text{F}$ bond angles and $A - \text{F}$ bond lengths. These octahedra form chains of varying arrangements which are shown in the diagrams below.

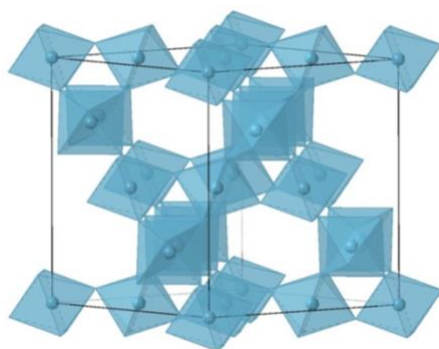
(Note: the octahedra shown in the ABMF_6 are not fully occupied by Ti^{3+} ; each site is half occupied by Ti^{3+} and the other half by B^{2+})



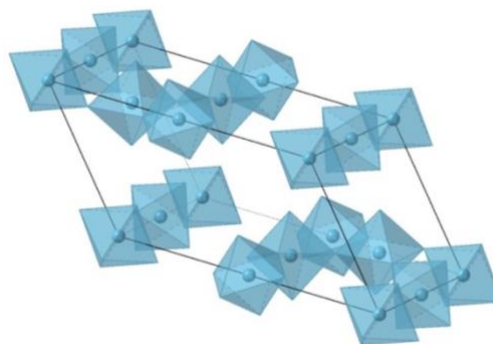
$\text{A}_2\text{MF}_{5.n}\text{H}_2\text{O}$



A_2BMF_6



ABMF_6



$\text{A}_2\text{BM}_3\text{F}_{12}$

Figure 1 Diagrams of structure types explored in this project

1.1.3 Magnetism

Magnetism is a force that occurs electrical charges (electrons) move. A magnetic field is generated around the atom/material. All magnetic materials have a magnetic dipole moment which is the vector sum of the motion of electrical charge and the spin angular momentum [14]. In other words, the movement of electrons around the nucleus and their intrinsic spin. This is mathematically represented as:

$$J = S + L$$

Where J is the total angular momentum, S is the spin angular momentum and L is the orbital angular momentum.

This magnetic dipole moment measures the material's tendency to align with a magnetic field.

Magnetic materials have very useful applications as permanent magnets, magnetic transformers for electricity, data storage and more. Not all forms of magnetism are the same however, and the differences offer exciting and novel applications. Although most of the compounds discussed in this section are anti-ferromagnetic other forms of magnetism exist including ferromagnetism, ferrimagnetism and paramagnetism [15].

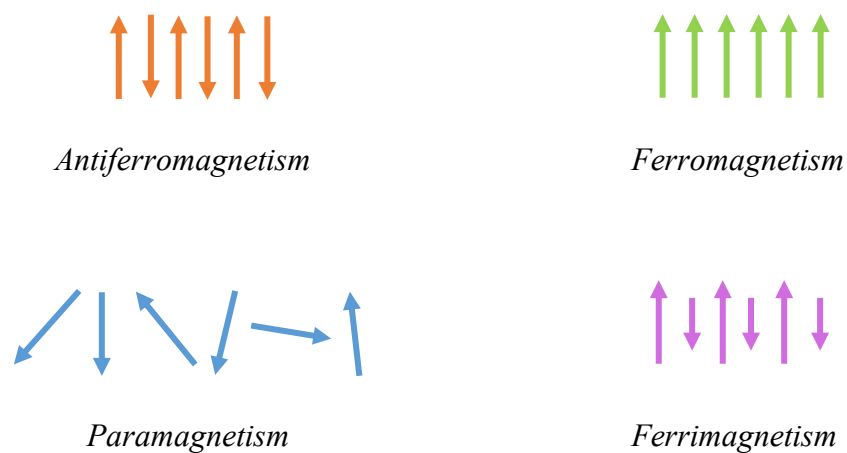


Figure 2 Diagrams of magnetic moments in different types of magnets

Anti-ferromagnetism

Magnetic moments align anti-parallel to each other and as all moments are of the same magnitude no overall magnetisation occurs.

Ferromagnetism

With a magnetic field applied the magnetic moments in ferromagnetic materials align parallel to each other. When this magnetic field is removed the alignment of magnetic moments remains parallel.

Ferrimagnetic

Like anti-ferromagnetism the magnetic moments are aligned anti-parallel to each other however the moments are not all the same magnitude, resulting in magnetisation.

Paramagnetism

Paramagnetic materials contain randomly orientated magnetic moments due to thermal motion which when a magnetic field is applied, will align parallel to each other. This magnetisation is parallel to the applied magnetic field, meaning any magnetisation disappears when this field is removed [16].

Curie's Law

Curie's law states that the magnetization in a paramagnetic material is directly proportional to the applied magnetic field and this magnetization is inversely proportional to temperature. Curie temperature refers to the temperature a ferromagnetic material becomes paramagnetic.

When taking into consideration magnetic interactions Curie-Weiss Law:

$$\chi = \frac{C}{T - \theta}$$

Where θ describes the average strength of interactions within a compound, C is a material-specific Curie constant, T is temperature

This can be rearranged to:

$$\frac{1}{\chi} = \frac{1}{C} (T - \theta)$$

Which allows linear plots of $1/\chi$ to be determined.

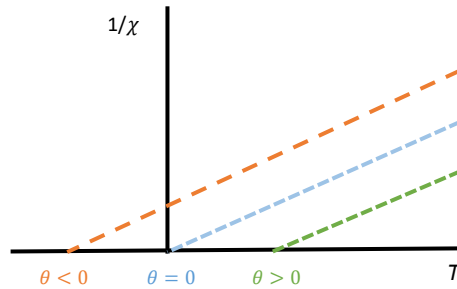


Figure 3 Plots of $1/\chi$ each illustrating different magnetic properties.

The interactions of neighbouring spins and their alignment results in a Weiss constant, θ , that is either less than 0, equal to 0 or greater than 0. When neighbouring spins are aligned antiparallel to each other the magnetic interactions are described as antiferromagnetic and have a negative θ . When neighbouring spins are aligned parallel to each other, the magnetic interactions are described as ferromagnetic and have a positive θ . If there are no magnetic interactions this material can be described as paramagnetic.

At high temperatures antiferromagnetic materials behave as paramagnets with a negative θ . Below the Néel temperature (T_N) their magnetic moments align antiparallel to each other and cancel out. This also causes their magnetic susceptibility to decrease. When not in an applied field Curie's law states that moments are oriented in a random direction and constantly fluctuating.

Superexchange

When neighbouring magnetic cations are close enough for electron orbitals to overlap, direct exchange of electrons can take place. If however there is a non-magnetic anion in between magnetic cations then direct exchange cannot take place. In this scenario if the magnetic cations are aligned antiferromagnetically then superexchange can occur. Superexchange uses the non-magnetic anion as an intermediary, allowing magnetic interactions to take place. This is commonly seen in transition metal oxides and fluorides [15, 17].

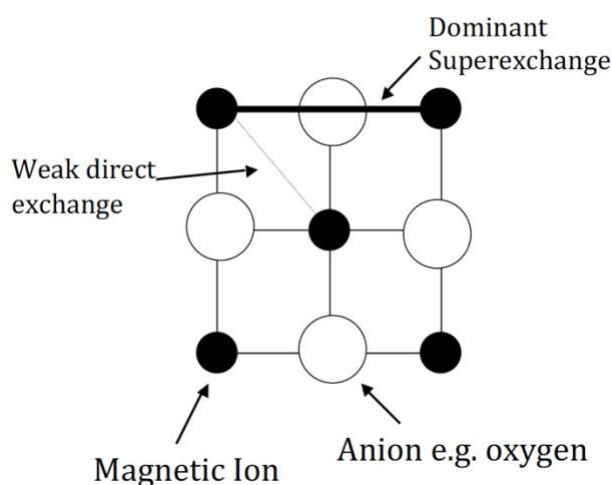


Figure 4 Diagram illustrating direct exchange and superexchange in a compound [18]

Magnetic moment dimensions

Magnetic moments can be multidimensional depending on the connectivity of octahedra in the crystal structure. Whether the level of anisotropy is high or low determines which dimension will allow for the most energetically favourable orientation. Magnetic cations with high anisotropy are limited to their magnetic moments pointing either up or down (1D), as this is most energetically favourable. This is referred to as an Ising-like model of magnetism. Magnetic cations with low anisotropy are referred to as Heisenberg-like (3D) as their magnetic moments can point in any direction with little difference in certain orientations being more energetically favourable. 2D magnetism refers to materials with magnetic interactions only within a plane. 2D antiferromagnets exhibit geometric frustration, preventing long range order from occurring. Geometric frustration is expanded on later in this

section. Magnetism does not have to have the same magnitude of strength in all directions [18].

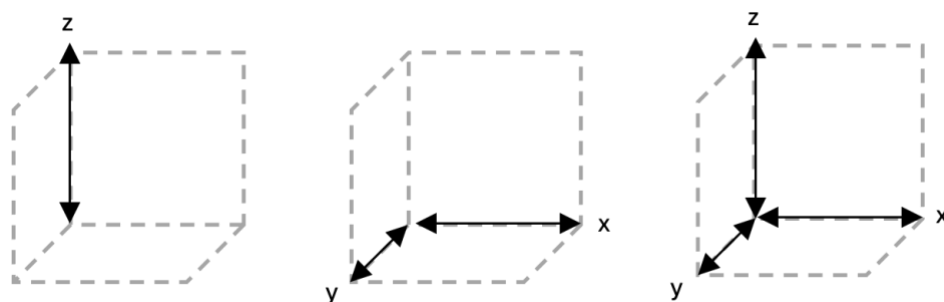


Figure 5 Diagrams from left to right: Ising-like model (1D); XY (2D); Heisenberg (3D)

1.1.4 Geometric Frustration

The compounds listed in 1.1.2 experience some degree of frustration, disorder or distortion. Distortion (e.g. Jahn-Teller distortion) refers to the length of bonds becoming shorter/longer and angles smaller/larger due to spin configuration. Disorder refers to the entropy of a compound, a highly disordered compound has high entropy and contains an arrangement of atoms lacking a fixed pattern. Frustration, or geometric frustration, arises when the lattice structure is unable to satisfy all interactions, leading to the whole system becoming frustrated. Geometric frustration is a key feature in magnetic materials, where it describes the arrangement of spins. A simple example of geometric frustration is a triangle arrangement in magnetic materials. Each triangle has antiferromagnetically interacting Ising spins on each of its vertices. Two of its spins point in opposite directions; up or down; leaving the third spin unable to satisfy the other 2 competing spins. This causes the system to become frustrated as no spin configuration possesses stability. The kagomé lattice, one of the most geometrically frustrated lattices, is a 2D arrangement of these triangles connected to form a repeating star motif. The kagomé lattice can satisfy the competing interactions by orientating the spins of each triangle component to all point in or out. The orientation of the spins follows an alternating pattern where the spins on neighbouring triangles are pointing in the opposite orientation [1, 3]. Other frustrated systems include the honeycomb

lattice, hexagonal ice and the pyrochlore lattice which is discussed later on in this section [19, 20].

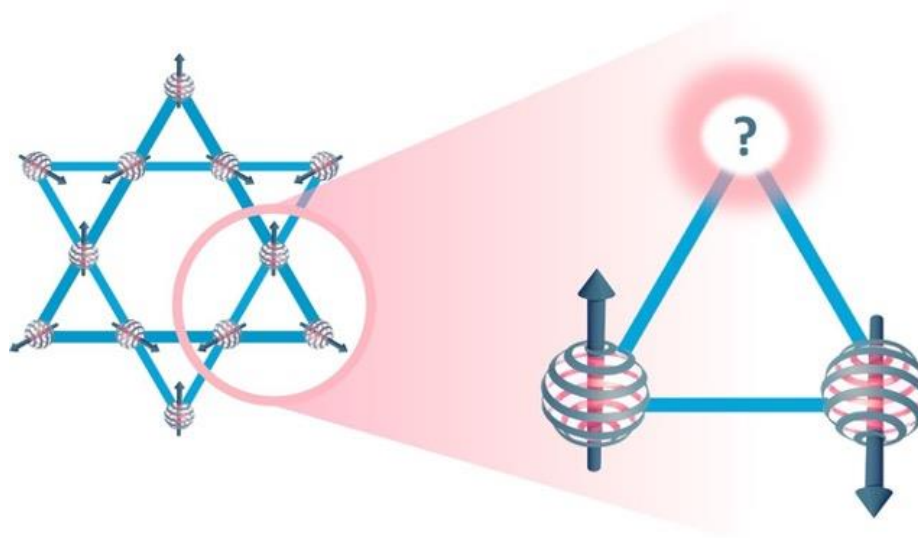


Figure 6 Diagram highlighting the spins in a kagomé lattice [1]

1.1.5 Quantum Spin Liquids (QSLs)

A quantum spin liquid (QSL) refers to the ground state of a $s = \frac{1}{2}$ kagomé lattice antiferromagnetic (KLAF) material. When magnetic materials reach low enough temperatures they experience magnetic ordering - where the electrons become stabilized and fixed in position as if in the solid phase. In a QSL however the magnetic frustration it experiences theoretically prevents magnetic ordering down to 0 K. Even at this extreme temperature its electrons remain constantly fluctuating as if in the liquid phase. The electronic and magnetic properties of a QSL are so unique that it is classed as a new phase [1, 3, 4, 19]. These compounds have potential applications in quantum computing and data storage, and so since they were theorized in 1973, scientists have been racing to synthesise one. Recently in 2021, QSL behaviour was analysed using a quantum simulator, but a physical QSL compound is yet to be synthesised [21].

Previous research has focused on synthesising Cu^{2+} KLAFs that have a d^9 electron configuration. The oxidation states of Ti^{3+} and V^{4+} are other candidates, however they have been less explored as they have less redox stability compared to Cu^{2+} [1-3]. This

section will explore the promising results and advances made by scientists in synthesising Ti^{3+} KLAfS.

1.1.6 $\text{A}_2\text{BM}_3\text{F}_{12}$

Goto and co-workers synthesised a new class of compound which are KLAfS, advancing the search for synthesising a geometrically perfect $s = \frac{1}{2}$ KLAf. In 2016 they synthesised the first $\text{A}_2\text{BM}_3\text{F}_{12}$ low dimensional chain compounds $\text{Rb}_2\text{NaTi}_3\text{F}_{12}$, $\text{Cs}_2\text{NaTi}_3\text{F}_{12}$ and $\text{Cs}_2\text{KTi}_3\text{F}_{12}$. The crystal structure of these compounds can be described as an ordered beta-pyrochlore structure type of RbNiCrF_6 with the same alternating kagomé and triangular layer stacking. The main difference being these chain compounds have an ordered structure where Ti occupies sites on the kagomé lattice and B occupying sites on the triangular lattice. These compounds are kagome lattice antiferromagnets (KLAfS), each with a slightly distorted kagomé lattice. The distortion decreases as the size of the alkali metal on the B site increases, making the kagome lattice in $\text{Cs}_2\text{KTi}_3\text{F}_{12}$ the least distorted and closer to a 2D magnetic system. $\text{Rb}_2\text{NaTi}_3\text{F}_{12}$ and $\text{Cs}_2\text{NaTi}_3\text{F}_{12}$ have greater distortion and are therefore closer to 1D magnetic systems. This lattice distortion has a large impact on the magnetic states present in KLAfS. The TiF_6 octahedra are arranged in distorted chains, each chain contains exclusively one Ti^{3+} site.

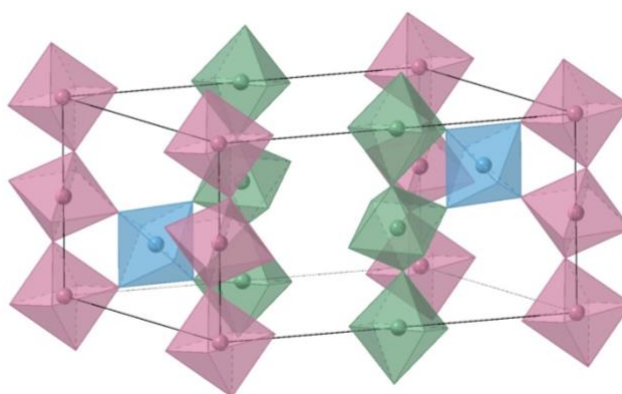


Figure 7 Diagram showing the arrangement of TiF_6 octahedra in $\text{A}_2\text{BM}_3\text{F}_{12}$ compounds. The different Ti^{3+} sites are highlighted for distinction (Pink = $\text{Ti}1$; Green = $\text{Ti}2$; Blue = $\text{Ti}3$)

This new series of kagome fluorides paved the way to synthesise other Ti^{3+} low dimensional compounds and offered an alternative way to synthesise potential QSLs [22]. In 2018 members of Goto's group were able to synthesise $\text{Cs}_2\text{LiTi}_3\text{F}_{12}$ which has the largest kagome lattice distortion of the 4 compounds mentioned so far. Their work extensively compared the magnetic properties of these 4 compounds and highlighted areas for future work [23].

In 2020 La Pierre and co-workers synthesised another KLAF, $(\text{CH}_3\text{NH}_3)_2\text{NaTi}_3\text{F}_{12}$ (**1-Ti**), which exhibits unusual magnetic phase behaviours. Its kagome lattice is perfect, showing no distortion however the methylammonium cations between its layers are disordered [3]. In efforts to synthesise a KLAF with no disorder in its structure the same group later synthesised $(\text{CH}_3\text{NH}_3)_2\text{KTi}_3\text{F}_{12}$, (**2-Ti**) via hydrothermal methods. This structure was successful in possessing no disorder, however its kagome lattice was slightly distorted, a problem plaguing the majority of $s=1/2$ KLAFs. The same distorted lattice with no disorder can be seen in the gapless spin liquid $(\text{NH}_4)_2(\text{C}_7\text{H}_{14}\text{N})(\text{V}_7\text{O}_6\text{F}_{18})$. Both compounds are close to the ideal structure needed to be considered quantum spin liquid candidates. Despite not being a total success, La Pierre's findings contributed a new potential quantum spin candidate to this search [19]. The only reported KLAF with no disorder or distortion in its structure is $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$, made by Nocera and co-workers in 2005. Although this KLAF exhibits no disorder, the resulting product replaced a small percentage of its Zn^{2+} ions with Cu^{2+} which will ultimately affect the compound's magnetic properties [24]. Thus, the goal to synthesise a structurally perfect $s=1/2$ KLAF with no disorder is yet to be achieved.

These compounds are relatively new so optimized synthetic routes have not been established yet. Flux and hydrothermal methods have been the main approaches used so far, with Goto's group favouring flux methods and La Pierre's group hydrothermal.

As discussed in this section, these compounds often exhibit distortion or disorder. Another drawback is the Dzyaloshinsky-Moriya (DM) interaction. DM interactions occur due to a lack of an inversion centre between two magnetic sites. This is a symmetry feature seen in the kagome lattice magnetic system and therefore only affects this compound in the scope of this review. DM interactions can cause magnetic

ordering in compounds such as Fe and Cr based jarosites where it was previously thought exchange interactions were responsible. Out of all the difficulties facing this type of compound, DM interactions are the most difficult to eliminate, particularly for Cu^{2+} KLAfS. Goto's group suggested that DM interactions in these Ti^{3+} compounds are weaker than compared to their Cu^{2+} counterparts, further highlighting the advantages of utilising Ti^{3+} in magnetic systems [22].

As the review [1] points out, there is still much to understand about the magnetic ground states of these compounds, with future research likely to focus on analysing the magnetic properties and phase changes of these compounds at low temperatures.

1.1.7 1D Chains $\text{A}_2\text{TiF}_5 \cdot n\text{H}_2\text{O}$

In efforts to explore transition metal fluorides further, with a particular focus on the d^1 electron configuration of Ti^{3+} , Kang Min Ok and co-workers synthesised a new series of alkali metal titanium fluoride 1D chain compounds in 2011. They synthesised $\text{Cs}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$, $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ and $\beta\text{-K}_2\text{TiF}_5$, all of which have the formula $\text{A}_2\text{TiF}_5 \cdot n\text{H}_2\text{O}$. These compounds are all made up of Ti^{3+} F_6 corner sharing octahedra which due to Jahn-Teller distortion consist of varied $\text{F} - \text{Ti} - \text{F}$ bond angles and $\text{A} - \text{F}$ bond lengths [9].

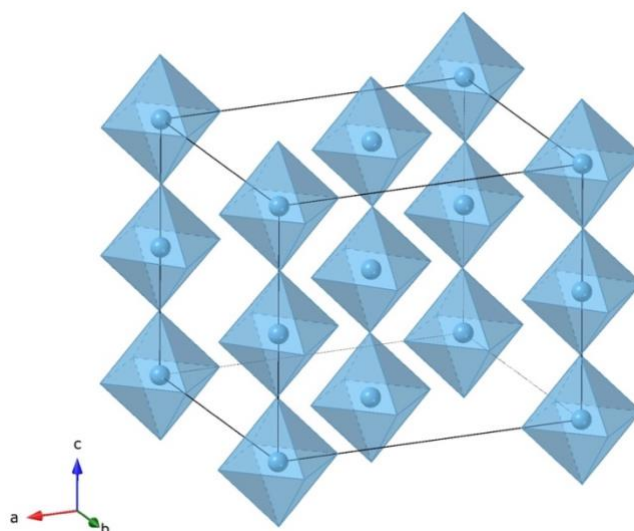


Figure 8 TiF_6 octahedra chains in the structure of $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ (A site cations are omitted for clarity) [9]

These compounds follow the same formula as the perovskite-type crystals $\text{Rb}_2\text{MnF}_5 \cdot \text{H}_2\text{O}$ and $\text{K}_2\text{FeF}_5 \cdot \text{H}_2\text{O}$ described by Galicka and co-workers in 2004. These compounds belong to the orthorhombic and monoclinic space groups respectively. The $\text{Rb}_2\text{MnF}_5 \cdot \text{H}_2\text{O}$ structure is made up of Mn^{3+}F_6 connecting octahedra, identical to the Ti^{3+}F_6 octahedra making up the $\text{A}_2\text{TiF}_5 \cdot n\text{H}_2\text{O}$ structures synthesised by Kang Min Ok. $\text{K}_2\text{FeF}_5 \cdot \text{H}_2\text{O}$ however consists of $\text{FeF}_5 \cdot \text{H}_2\text{O}$ octahedra which puts the water molecules in a different position. This arrangement gives way to hydrogen bonding between these zig-zag chains instead of the trans-links seen in the other structures [25].

Kang Min Ok and co-workers were also able to dehydrate $\text{Cs}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$, $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ to obtain Cs_2TiF_5 and Rb_2TiF_5 however these compounds have not been fully characterised, only powder X-ray diffraction has been performed on them. These compounds are the only $s = \frac{1}{2}$ compounds in this series so their magnetic properties, which have yet to be studied, are of significant interest. All diffraction measurements were taken at room temperature so it would be interesting to look at low temperatures and, as this compound has not been reported before, investigate potential phase transitions [9]. Further analysis of this series of compounds became the focus point for this research project. A deeper understanding of these compounds could lead to a further understanding of their unique magnetic properties and uncover any potential applications.

1.1.8 Perovskites and Double Perovskites A_2BMF_6

Perovskites have the formula ABX_3 which is described as cubic although orthorhombic, tetragonal and trigonal perovskites also exist. The phase of a perovskite is temperature dependent, with the cubic phase favoured at high temperatures. The double perovskite which is the focus here has a unit cell double that of the original perovskite, making its formula $\text{A}_2\text{B}_2\text{X}_6$. A better representation of this formula is A_2BMF_6 (where A, B, M = cations, X = anion) as this shows the ordering of the B and M cations on the B site which can be different charges or elements [20, 26].

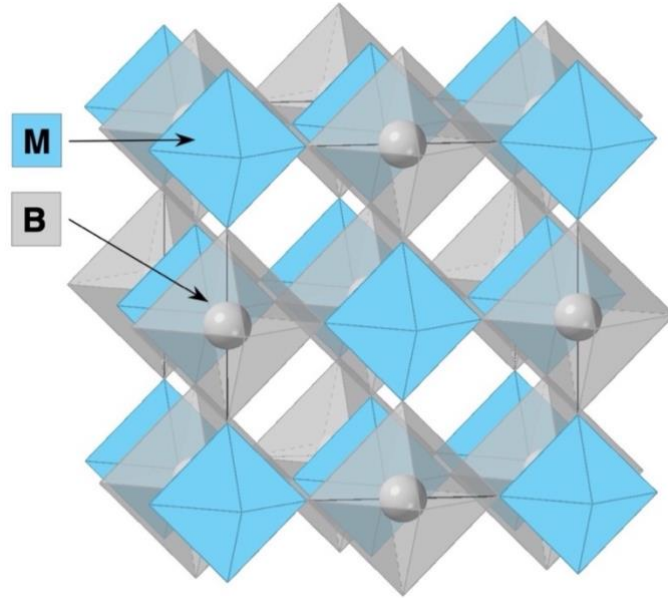


Figure 9 Diagram of M and B sites in double perovskites

The TiF_6 chains in the $\text{A}_2\text{MF}_5 \cdot n\text{H}_2\text{O}$ compounds follows a consistent ‘A’ arrangement throughout the structure. (This ‘A’ arrangement refers to the layout of TiF_6 chains seen in Figure 10, it does not refer to A site cations). However, in perovskites the TiF_6 chains deviate from this and follow an alternating ABAB pattern.

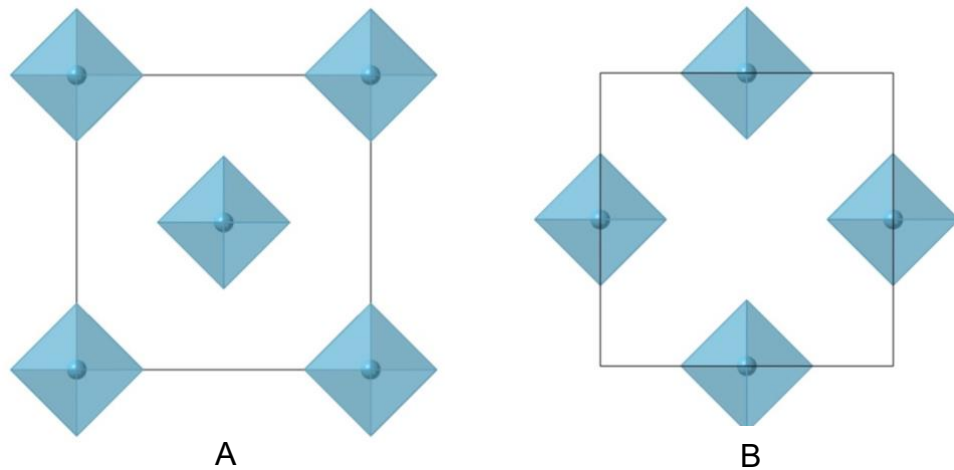


Figure 10 Diagram showing the different arrangement of M sites in the structure

Perovskites experience lattice instability, spin frustration and Jahn-Teller distortion to varying degrees. These factors compete to lift the degeneracy of the d states and relieve the frustration within the compound [20].

Perovskites and their derivatives are famous for their applications in solar cells, light-emitting diodes (LEDs) and thin-film transistors due to their optical bandgap. The double perovskites discussed in this section offer promising candidates for lead-free halide perovskites. Scientists have been trying to find good alternatives to lead perovskites in solar cells for several years. Lead-containing solar cells pose serious environmental and health hazards as lead is toxic and, when a solar cell becomes wet in the rain or breaks, the lead dissolves in water [27] and can end up in the soil and the food chain [28].

In 1958 Bright and Wurm synthesised K_2NaTiF_6 , a new titanium-containing fluoride with a double perovskite structure [29]. The same compound was made again in 1971 by Peter Nassiff and co-workers who discovered the correlation between the size of the cation and the distortion of the TiF_6 octahedra. They concluded that generally larger cations result in greater distortion in the TiF_6 octahedra [30]. This is the opposite affect seen in the 1D chain compounds where cations with a larger coordination environment (Rb^+ and Cs^+) exhibit less distortion than compared to smaller cations (K^+) [9].

The following structures to be synthesised in this group were Cs_2KTiF_6 , Rb_2KTiF_6 and $\text{Cs}_2\text{NaTiF}_6$ and $\text{Rb}_2\text{NaTiF}_6$ in 1974 by Alter and Hoppe. Unlike the other compounds $\text{Cs}_2\text{NaTiF}_6$ formed an elpasolite structure [31]. Single-crystals studies were performed on this compound in 1989 by Hoppe and Becker, but they were still unable to determine why this compound does not readily adopt a cubic perovskite structure despite its similarities in chemical composition to the double perovskites [32].

In 2013 Goto's group performed a study on the perovskites mentioned so far and synthesised a new double perovskite, $\text{Cs}_2\text{RbTiF}_6$. Their work investigated the phase transitions and magnetism of these compounds at variable temperatures. They also confirmed Hoppe's findings that $\text{Cs}_2\text{NaTiF}_6$ does not adopt a double perovskite structure, and instead forms a rhombohedral one, but they did not investigate this further. Goto's work looking into these perovskites revealed much about their phase transitions. Perovskites exhibit several phase transitions at low temperatures [20].

Goto and co-workers posted the comment ‘*Rich Phase Diagram from the Simplest d^1 System*’ on their 2013 paper a couple months after it was published [20]. This comment surmises that when cooled to low enough temperatures (specific to each double perovskite) a phase transition from cubic to one of 2 tetragonal phases occurs. The difference in these 2 tetragonal phases is whether lattice parameter a or c is greater. A large tolerance factor favours a lattice distortion where $a > c$ and a small tolerance factor favours $a < c$. An additional orthorhombic phase can be seen in K_2NaTiF_6 close to the boundaries of these tetragonal phase transitions. It has been reported that a $\sqrt{5}/2 \times \sqrt{5}/2$ superlattice accompanies the tetragonal distortion which favours $a < c$ but its reasoning is yet to be established. They highlight the interest to further study these compounds and their different phases to understand the physics of their orbitals.

1.1.9 Pyrochlores ABMF_6

The term pyrochlore refers to a crystalline compound with the formulae $\text{A}_2\text{B}_2\text{X}_6\text{Y}$ (A, B = metal cations; X, Y = anions). This class of pyrochlores are referred to as alpha-pyrochlores [33], which are isostructural to the mineral pyrochlores $(\text{Na,Ca})(\text{Nb,Ta})_2\text{O}_6(\text{OH,F})$ [34] that can be found in alkaline rocks and greisen [35]. The structure of an alpha-pyrochlore can be described as a distorted fluorite [34]. This compound adopts a cubic structure and belongs to the $\text{Fd-}3\text{m}$ space group. It is worth noting that other structure types have been observed. The A, B, X and Y atoms are located on the 16d, 16c, 48f and 8b sites respectively. The pyrochlore group is structurally diverse and not limited to this alpha-pyrochlore type. Another structure type, and the one of most interest here, is the beta-pyrochlore. The main difference in its structure is that the A metal cations occupy the 8b site, leaving the 16d site vacant. This vacancy ($\square$) is illustrated in the formula $\square_2\text{B}_2\text{X}_6\text{A}$, making the general formula of the beta-pyrochlore AB_2X_6 . ABMF_6 will be used throughout this section as it offers a better representation of its charge-ordered structure where the B and M cations can be of different charges and elements. The beta-pyrochlore structure is complex so it is best described as a three-dimensional network of corner-sharing TiF_6 octahedra that form a cage-like structure with vacant cavities [36]. Charge-ordering and geometric frustration are both responsible for the strong magnetic frustration beta-pyrochlores experience [37].

The frustrated and complex structure of pyrochlores gives rise to many functional properties such as multiferroic behaviour [37], luminescence, low thermal conductivity, superconductivity, high ionic conductivity at high temperatures and high chemical stability [33]. Pyrochlores have proven to be superconductive, offering alternatives to the standard copper oxide superconductors. This cage-structure gives beta-pyrochlores their thermoelectric and superconductivity properties. The superconductivity in β -pyrochlores is of particular interest as it arises from the rattling effect of A site cations within the 16d vacant cavities in the cage framework. This property offers alternatives to the standard copper oxide materials found in superconductors [38]. Other applications of pyrochlores include solid oxide fuel cells, nuclear waste immobilisation and thermal barrier coatings [33].

To the best of our knowledge CsCuTiF_6 synthesised in 1974 by Jesse and Hoppe is the only reported Ti^{3+} β -pyrochlore with *any* alkali metal on the A site, not just limited to Cs or Rb [39]. β -pyrochlores can be difficult to synthesise due to their complex crystal structure which can exhibit structural disorder. A slight imbalance of reagents or traces of impurities can lead to failure, causing the reaction to favour the formation of less desired products or phases. Specific reaction conditions and stoichiometric control are therefore required for successful synthesis. The synthesis of β -pyrochlores and Ti^{3+} compounds respectively are challenging, so the task of synthesising a combination of both compounds presents an exceptionally difficult task. The difficulty of this task is highlighted by the scarcity of reported compounds of this type.

1.1.10 Fluoride Compounds

Oxide compounds have dominated this field for decades. The graphs below show the number of published reports referring to pyrochlore oxides compared to pyrochlore fluorides reported through the years. Pyrochlore fluorides reported 11 reports in 2022 compared to a staggering 138 pyrochlore oxides in the same year.

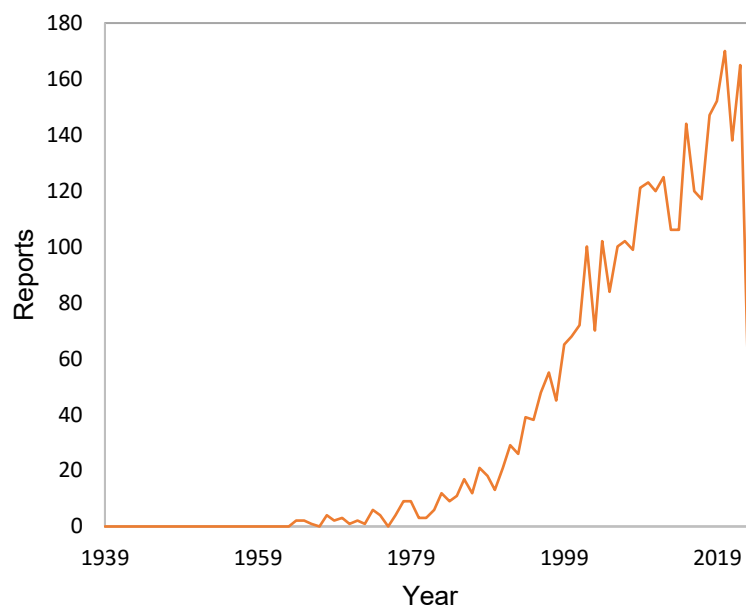


Figure 11 Reports referring to pyrochlore oxides by year (Data obtained from Scorpio)

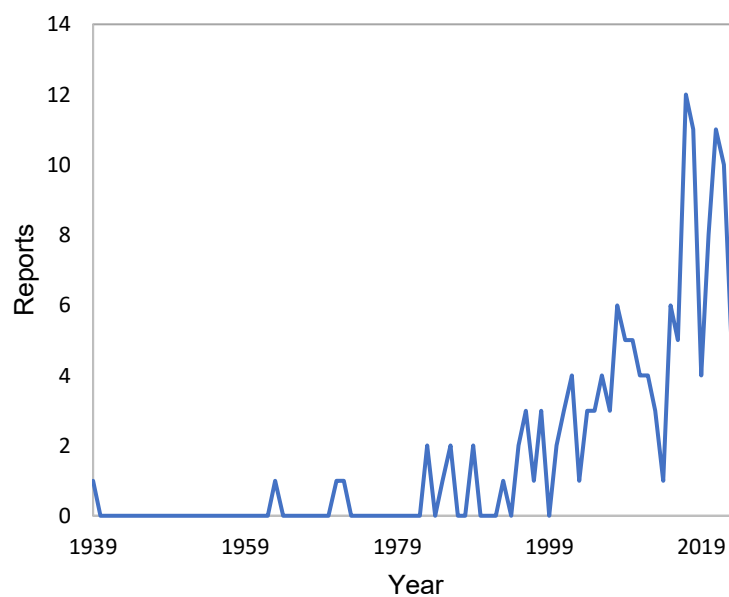


Figure 12 Reports referring to pyrochlore fluorides by year (Data obtained from Scorpio)

It would be a mistake to assume that this disproportion is down to fluoride compounds being less of an interest. The reason behind this imbalance is in fact due to fluorine's

thermal and chemical instability. Fluorine is the most electronegative element with the electron configuration $1s^2 2s^2 2p^5$. Its electron configuration is very close to an ideal configuration making it highly reactive. Oxides are more thermodynamically stable and naturally abundant on Earth with many rocks containing oxides that can be utilized in synthesis. Though some fluoride compounds can be found naturally (e.g. CaF_2 and Na_3AlF_6), elemental fluorine is too reactive to exist in nature. More advanced methods had to be invented to synthesise fluorine containing compounds, thus slowing down and demotivating research progress. Another major disadvantage of fluorine is its toxicity, both fluorine itself and fluorine containing compounds such as HF are extremely hazardous, requiring specialised equipment and safety measures. The process to understanding and synthesising fluorine compounds resulted in many dangerous accidents and even deaths. Producing fluorine compounds is therefore more dangerous, expensive and time-consuming compared to the synthesis of oxide compounds, making them less accessible and therefore less studied.

Despite its dangers and difficulties fluorine is gaining more interest due to its unique properties being the most electronegative element. This unique feature gives fluorine a lower melting point compared to oxygen, high ionic conductivity, low thermal conductivity, a lower refractive index due to weak polarizability and large energy gaps making them ideal for insulating compounds. The uniqueness of its electronegativity means properties of compounds often can't be predicted – offering exciting but potentially hazardous properties [40, 41].

Applications of fluorine so far include rocket fuels, uranium production, agrochemicals, fluorescence, optics, refrigerants, the production of polymers, plastics and Teflon as well as in public water purification [41]. As will be seen throughout this section fluorides have the potential to be viable alternatives to oxide compounds, with the potential of offering more attractive properties.

2

Experimental

2.1 Solid-state Synthesis

Background

There is a plethora of methods to synthesise crystalline solid-state materials from high pressure methods like the hydrothermal method, high temperature methods like the solid-state and flux methods to in solution or gas phase methods such as vapour deposition [42]. The method used determines the type of product synthesised, its purity, phase and morphology. Only the methods mentioned in this project and related syntheses are described in this section, plus one other which is included for comparison. The other methods are beyond the scope of this work.

Solid-state (or Ceramic Method)

This reaction takes place in the solid phase where the reagents are either ground into a fine powder or pressed into a pellet before placed inside a furnace. They are then heated to extremely high temperatures ($> 1000^{\circ}\text{C}$) for several hours to days. The furnace is then cooled slowly to ensure good crystallinity in the resulting crystals. The simplicity of this method results in a loss of control over crystal growth. Compared to other syntheses this method uses very high amounts of energy and is very slow [42, 43].

Hydrothermal

Hydrothermal synthesis is the most common method for synthesising inorganic nanomaterials. It utilizes less energy than the solid-state method by using lower temperatures ($100 - 250^{\circ}\text{C}$) and the solvent (water) acts as a pressure transmitting medium, producing autogenous pressures up to 15 bar relatively easily. In hydrothermal synthesis reagents are added to a Teflon container with water as the

solvent. The Teflon container is sealed inside an autoclave which is then put into a furnace oven. Alternatively, the reagents can be placed directly into a sealed glass tube. Hydrothermal methods allow for good control over crystal properties and as both high temperatures and pressures are used, it is effective in dissolving hard to dissolve materials [42, 44].

Similar methods called ionothermal and solvothermal synthesis work in the same way except ionic liquids or nonaqueous solvents are used instead of water respectively. Solvothermal synthesis uses organic solvents such as alcohols and ionothermal synthesis utilizes ionic liquids instead of water. This is effective for materials not stable or soluble in water. Using nonaqueous solvents changes the polarity and boiling point of the reaction solution, allow for a wider range of materials to be produced. The possibilities of what in solution syntheses can produce are limited by the solubility of reagents, as the reaction takes place in solution insoluble reagents will not react. One of the main advantages of hydrothermal synthesis is that in one reaction a variety of different crystals are synthesised [44].

Flux growth

In the flux method the reagents and solvent (flux) are heated to a temperature above the flux's melting point and maintained until a homogenous solution forms. Crystals are obtained by cooling the furnace to a desired temperature at a controlled rate and then removing any excess solidified flux. Common fluxes are either metallic or metal oxides. This method is ideal for synthesising bulk single crystals of phosphates, arsenates and ceramics which are too difficult to obtain via the solid-state method. The challenge with this method is removing the excess flux without damaging the crystal product [42].

2.2 Reducing Agents

To synthesise Ti^{3+} compounds a reducing agent is needed to reduce Ti^{4+} to Ti^{3+} , a typically difficult oxidation state to reach through conventional solid-state techniques due to its redox instability. Common methods involve the use of highly hazardous reagents such as HF [25] or HPF_6 via hydrothermal synthesis [3] or flux methods that require an inert atmosphere and the use of alkali chlorides [22]. We wanted to

synthesise via hydrothermal synthesis and utilize milder reagents that have less hazards.

2.2.1 Synthesis using DMF

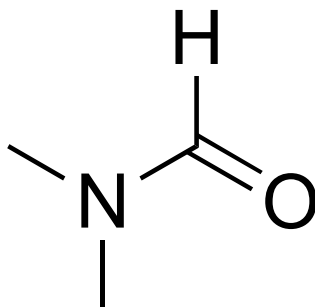


Figure 13 Structure of DMF obtained via ChemDraw

N,N-Dimethylformamide (DMF) is a commonly used organic polar solvent used for both industrial and commercial applications as an industrial solvent and to manufacture synthetic fibres, plastics and other chemicals. It is colourless or pale yellow and has a strong odour. Despite being an organic solvent DMF is not exclusively used in organic synthesis. Due to its chemical versatility it is a multipurpose reagent which can be applied in the fields of organometallic chemistry, catalysis and nanoparticle synthesis. In 1999 the Pastoriza-Santos group reported the first use of DMF to synthesise nanoparticles [5] and ever since DMF has become a commonly used solvent and reducing agent in nano particle synthesis. Its wide solubility range for both organic and inorganic compounds combined with its temperature dependent reducing capabilities make it the ideal reaction medium for nanoparticle synthesis involving a reduction of metal salts. DMF has proven successful in reducing Au, Ag and Cu in the process of nanoparticle formation. DMF is only a mild reducing agent so high temperatures or the use of a catalyst such as PVP is required, but despite this DMF has been proven to reduce room temperature Ag ions [5]. This led to the utilization of DMF to reduce other metals in inorganic compounds. The applications of DMF in inorganic synthesis have only just begun being explored.

In 2011 DMF was used in hydrothermal synthesis to synthesise a new series of alkali metal titanium fluoride compounds $A_2TiF_5 \cdot nH_2O$ [9]. Although not a reducing agent itself DMF can break down into reducing agents under suitable conditions [5]. The possible reduction reaction for this synthesis:



Up to 100° C DMF remains stable and at high temperatures above 350°C carbamic acid produced from DMF decomposes into CO_2 and Me_2NH [45]:



Further investigation in-situ is required to determine what reducing agents are being produced in this method.

2.2.2 Synthesis using polyvinylpyrrolidone (PVP)

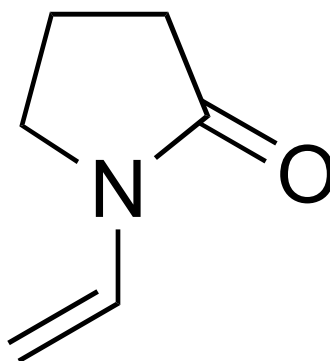


Figure 14 Structure of PVP obtained via ChemDraw

PVP is a white powder and can act as a weak reducing agent. The success of DMF to act as an effective reducing agent in the synthesis of $Rb_2TiF_5 \cdot H_2O$ inspired the use of other reducing agents that are commonly used to synthesise nanoparticles. The main roles of PVP in nanoparticle synthesis are as a surface stabiliser, growth modifier, nanoparticle dispersant, and the property of interest here, reducing agent. [6] It has

been proven to reduce Ag(I) under certain conditions in solution and to be an effective reducing agent when used with DMF in synthesis [7].

2.2.3 Synthesis using triethylamine

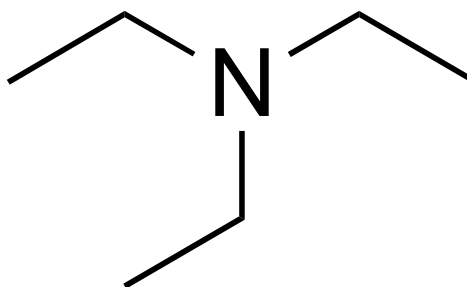


Figure 15 Structure of TEA obtained via ChemDraw

Triethylamine (TEA) is a colourless, volatile liquid with a fishy odour. Its main applications are in organic synthesis, serving as a base in the synthesis of esters and amides. Its uses in nanoparticle synthesis are of interest as TEA can act as both a protecting agent and reducing agent.

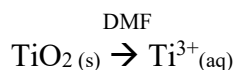
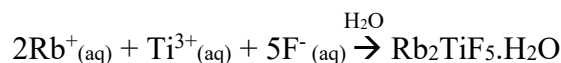
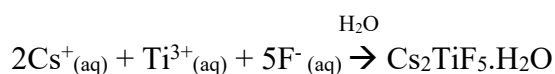
In the synthesis of Au and Ag nanoparticles amines have been used as both reducing agents and as stabilizers once nanoparticles have formed. A variety of amines have been experimented with in the synthesis of Au nanoparticle synthesis, being used for their reducing and stabilizing capabilities. Amines are found abundantly in nature, making them particularly attracting for chemical applications. It remains unclear whether the structural or chemical properties of amines are responsible for their reducing and stabilizing capabilities. Triethylamine in particular has proven to reduce Au(III) to Au in the formation of gold nanoparticles [8].

2.3 Materials Synthesis

All compounds were purchased from Sigma Aldrich.

Rb₂TiF₅.H₂O and Cs₂TiF₅.H₂O

Crystals of Rb₂TiF₅.H₂O were synthesised hydrothermally by adding RbF (1.567 g, 15 mmol) and TiO₂ (0.1203 g, 1.5 mmol) to a Teflon container. DMF (1.5 ml, 0.019 mol dm⁻³) and H₂O (4 ml) were pipetted into the container and the solution stirred to distribute any stubborn powder clumps. The Teflon container was sealed inside an autoclave and placed inside an oven set at 230 °C for 72 – 144 hours. Once cooled the products were filtered using distilled water and acetone and then left to dry in a drying cabinet set at < 50 °C. Cs₂TiF₅.H₂O was synthesised the same way using CsF (1.393 g, 7.5 mmol) and TiO₂ (0.0599 g, 0.75 mmol).



In later synthesis the DMF was substituted for other reducing agents: triethylamine (1.5 ml, 0.0107 mol dm⁻³), PVP (0.2006 g, 1.8 mmol) on its own and PVP (0.2006 g, 1.8 mmol) combined with DMF (1.5 ml, 0.019 mol dm⁻³).

Rb₂TiF₅.D₂O and Cs₂TiF₅.D₂O

The deuterated versions of these compounds were synthesised using the same method except that D₂O was used instead of H₂O. All reagent quantities were kept the same. To avoid the D₂O becoming contaminated by water in the air the D₂O was added in a moisture box purged with nitrogen gas.

Dehydration of Rb₂TiF₅.H₂O

Samples of Rb₂TiF₅.H₂O (~ 0.1 g) were added to a ceramic weighing boat and placed inside a vacuum oven to dehydrate. The temperature of the oven and the length of time the samples spent inside the oven varied from 6 – 120 hours and 130°C – 190°C.

3

Instrumentation

3.1 X-ray Generation

X-rays are a form of transverse electromagnetic radiation with a very short wavelength. X-rays have a wavelength of order 10^{-10} m [46] making them shorter than ultraviolet light but longer than gamma rays. X-rays in laboratories are generated in either a sealed-tube or via a rotating anode where a metal is hit with a beam of high-energy electrons. The differences between the two are intensity and the type of radiation produced [47]. The former method of X-ray generation involves a filament of metal being heated inside an X-ray tube to produce electrons. A voltage is applied to accelerate these electrons across the potential towards the target metal (typically Cu or Mo). As the electrons hit the metal they decelerate, generating a continuous spectrum of X-rays called Bremsstrahlung [46] (also known as white radiation) [47].

The shortest wavelength $\lambda(\text{min})$ obtained can be calculated using the following equations:

$$E = e V$$

Where $E(\text{max})$ is the maximum energy lost, e is the electron charge, V is the accelerating voltage.

This can be simplified to:

$$\begin{aligned} e V &= h c / \lambda \\ \lambda &= 12.398 \text{ \AA} / V \end{aligned}$$

where h is Planck's constant and c is the speed of light.

Increasing the accelerating voltage of the X-ray generator results in a shorter $\lambda(\text{min})$ [47].

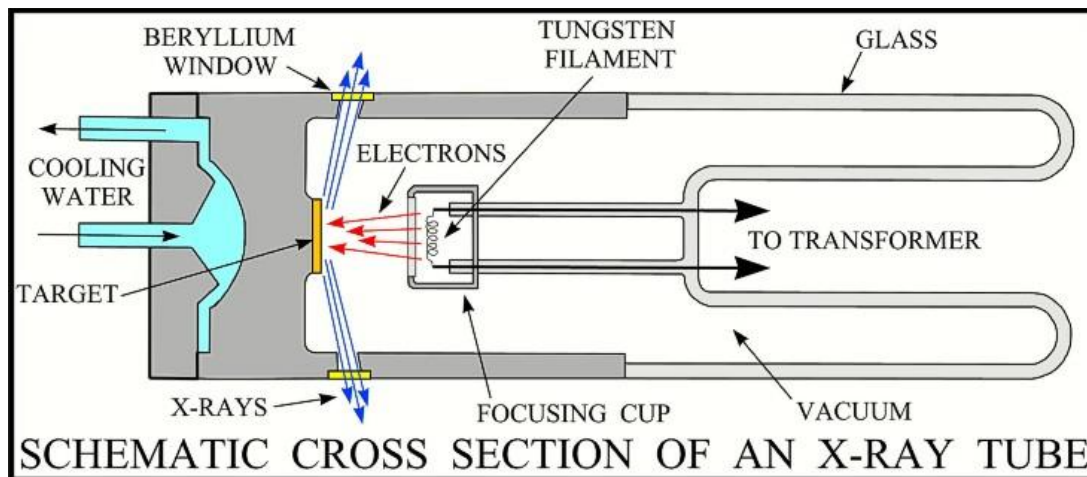


Figure 16 Cross section of an X-Ray tube [48]

When these X-rays are directed at a sample they collide with the electrons inside the inner shell of the sample atoms and force them to be ejected. Outer shell electrons in the sample fill the vacant spaces left by the ejected electrons and in the process emit the difference in energy between the inner and outer shell as a characteristic X-ray. This produces a spectrum consisting of discrete peaks which is superimposed on top of the white radiation spectrum. The energy of these characteristic X-rays are different for each element so they can be used to determine the elemental composition of a sample. Characteristic radiation is labelled according to the transition of an electron from an outer shell to a vacancy in the inner shell, with for example the letter K, L or M to indicate the energy shell of the vacancy being filled and either α or β [46]. If the transition of an electron filling a vacancy is to an adjacent orbital then the radiation is labelled α and if the transition between orbitals is further then the radiation is labelled β which has a slightly higher energy. The most common radiation are $K\alpha$ and $K\beta$ as they have the highest energy [47].

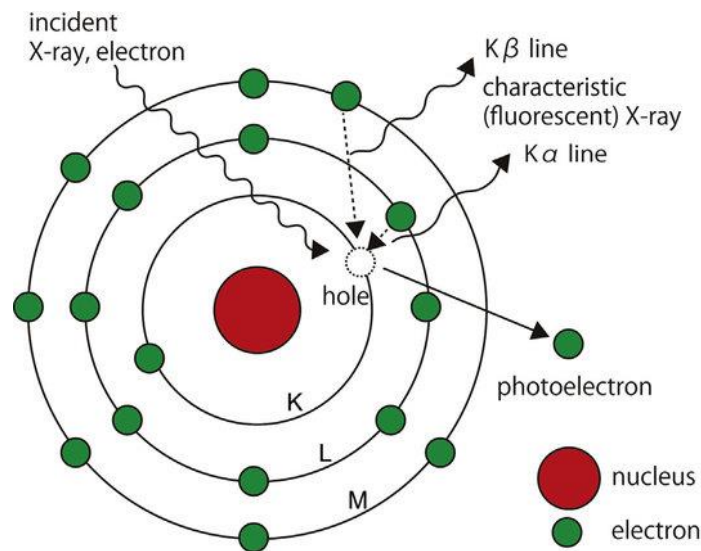


Figure 17 The generation of a characteristic X-ray [49]

3.2 The Theory of X-Ray Diffraction

X-ray diffraction is a non-destructive technique based on the constructive interference of monochromatic X-rays and a crystalline sample. When the incident X-ray radiation hits the sample the X-rays scatter and are scattered off the atoms in the sample. As seen in Figure 18, there are rows spaced out at regular intervals which are defined as atomic planes with distance, d between planes [50].

Bragg's Law is used to explain the relationship between X-rays hitting and diffracting off a crystal. If radiation (of a similar wavelength to the d spacing between atoms in the crystal) is scattered by the atomic planes of a crystal at the same angle of incidence, and if the d spacing multiplied by $2\sin\theta$ is equal to an integer, n , that is a multiple of the wavelength then Bragg's Law is satisfied.

Bragg's Law:

$$n\lambda = 2d \sin \theta$$

Where λ is the wavelength of the X-ray, n is an integer, d is the spacing between crystal planes and θ is the angle between the incident X-ray and the scatter plane.

Constructive interference occurs when the scattering of multiple points within a crystal satisfies Bragg's Law and the path length between X-rays being diffracted from one layer to an adjacent layer is an integer multiple of the wavelength, λ . Constructive interference results in a diffraction pattern [51].

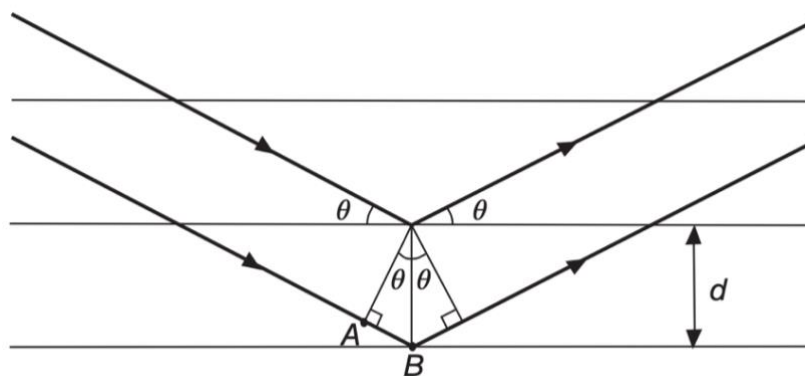


Figure 18 Diagram depicting the diffraction of incident X-ray radiation according to Bragg's Law. The rows of lines represent the atomic planes, separated by distance, d [51].

In X-ray diffractometers (both powder and single-crystal) a detector measures the angle of diffracted X-rays producing a diffraction pattern. Using Bragg's Law the peaks in a diffraction pattern can be used to determine the distance between lattice planes within the sample. When X-rays interact with the sample, they are specifically interacting with the electron clouds surrounding the atoms in the sample. Each crystalline compound has a unique diffraction pattern. Atoms with a larger atomic number (Z) will diffract more intensely. This makes hydrogen atoms very difficult to be detected via X-ray diffraction, often the hydrogen atom positions in the sample are predicted based on what atom/s they are bonded to and therefore different techniques such as neutron diffraction are used to obtain more accurate data on the hydrogen atoms [51].

Two mathematical constructs scientists use to help understand and visualise the crystal lattice in terms of structure and orientation are the *reciprocal lattice* and the *Ewald sphere*. The *reciprocal lattice* is a function of the crystal's unit cell and orientation, it is a hypothetical set of lattice points with each lattice point representing a reflection generated by a specific family of planes in the crystal. Lattice points in the reciprocal

space are perpendicular to planes of atoms in the real space. These lattice points can be indexed using the Miller indices (hkl) where h , k and l each represent a plane orthogonal to the reciprocal lattice vector [52, 53].

Symmetry elements of a crystal can be determined by inspecting any systematic absences of reflections in the reciprocal space. An absence of a reflection is caused by *destructive interference*. This occurs when waves which don't satisfy Bragg's Law are not aligned in-phase with each other as their path lengths do not meet the conditions for constructive interference. This causes the waves to cancel each other out causing an 'extinction'. Computer software will methodically go through extinction conditions starting with unit cell centering, glide planes and lastly screw axes to assign the most likely space group/s for a crystal sample.

The Ewald sphere is a function of the incident X-ray radiation's wavelength. It provides a three dimensional representation of the crystal lattice in the reciprocal space (see Figure 30). A reflection is observed for each reciprocal lattice point that intersects the Ewald sphere and its angle of diffraction. To obtain reflections for the entire crystal the crystal needs to be rotated in multiple directions. This rotation process is to help align the many reciprocal lattice points with the surface of the Ewald sphere [52].

X-rays have a form factor, also called *atomic form factor*, which lowers the amplitude of scattered X-rays at higher angles. This form factor decreases with increasing Bragg angle as during diffraction destructive interference occurs at higher 2θ angles.

When 2θ equals 0 no phase shift appears in the X-ray pattern, however as the angle increases a phase shift begins to appear due to the position and wave vectors of the X-rays as shown by:

$$\Delta\phi = (\mathbf{k}_i - \mathbf{k}_s) \cdot \mathbf{r}.$$

Where $\mathbf{r}$ is the position of the scattered X-ray, $\mathbf{k}_i$ is the wave vector for the incident X-ray and $\mathbf{k}_s$ is the wave vector for the scattered X-ray.

This equation can be used to calculate the *atomic form factor* through the proportional relationship between the position of the scattered X-ray, r , and the electron density $p(r)$ at that position:

$$\int d^3r p(r) \exp[i(k_i - k_s) \cdot r]$$

Neutrons do not have a form factor as they are scattered by the nuclei of atoms which are extremely small in comparison to the distance between atoms so no destructive interference occurs. Neutron diffraction is therefore independent to the angle 2θ [54, 55].

3.3 Powder X-Ray Diffraction

Crystalline samples produce distinct, sharp peaks whereas amorphous materials like glass will show large broad peaks as they lack crystallinity and long-range order. This technique can determine phase and purity of a sample and it can be used with samples containing multiple products. Some issues that can occur from powder X-ray diffraction are preferred orientation, absorption or sample decomposition. The set up for powder diffraction is easier compared to single-crystal as alignment of the sample is not a key factor and any crystalline product can be ground down and measured.

Sample preparation for X-Ray experiments

To prepare samples for powder XRD the crystals were first ground down into a powder. A thin layer of petroleum jelly was smeared onto a plate and the powder was sprinkled on top of plate. Any excess powder was tapped off to avoid loose granules dislodging from the plate and damaging the diffractometer.

PANalytical X'Pert³ powder X-ray diffractometer

The X'Pert XRD operates using Cu dual wavelength ($K\alpha_1 = 1.54059 \text{ \AA}$ and $K\alpha_2 = 1.54443 \text{ \AA}$, $K\beta$ is removed by Ni filter). Samples were measured at room temperature using a continuous scan from 5-80 in the 2θ degree, with a step size of 0.017° , at a rate of 2.05 seconds per step and at a speed of 0.0085 degrees per step, leading to a total time of 2 hours 31 minutes per sample.

Rigaku MiniFlex 600 X-ray diffractometer

The MiniFlex XRD operates using Cu dual wavelength ($K\alpha_1 = 1.54059 \text{ \AA}$ and $K\alpha_2 = 1.54443 \text{ \AA}$, $K\beta$ is removed by Ni filter). Samples were measured at room temperature like the X'Pert XRD. The MiniFlex however has a much lower resolution than the X'Pert XRD. The MiniFlex XRD was used for short scans (20 – 180 mins) to identify if the sample was crystalline and if its diffraction pattern showed similarities to its reference pattern. Each sample was measured from 5-80 in the 2θ degree with varying step sizes and time per step, depending on the length of time desired for each sample. These quick scans helped to save time when analysing many samples; samples that looked promising enough for further analysis were then taken for XRD on the X'Pert X-ray diffractometer..

PANalytical Empyrean 2 powder X-ray diffractometer

The Empyrean XRD unlike the other two x-ray diffractometers uses only one wavelength of copper ($K\alpha_1 = 1.54059 \text{ \AA}$), via a Ge (111) monochromator. Using this one wavelength results in higher quality data. Sample scans were performed at room temperature in scanning line detector mode from 5-80 in the 2θ degree. Scans were performed for 4-6 hours per sample.

3.4 Neutron Diffraction

Background on neutron diffraction

Neutron diffraction is similar to X-ray diffraction so it can be used to compliment X-ray data. Neutrons are generated via nuclear fission: a reaction where neutrons collide with the nucleus of another atom, splitting it into two or more smaller nuclei and releasing extremely large amounts of energy in the process. The immense levels of power needed for nuclear fission requires a whole nuclear power plant. As a result access to neutrons produced from this source are not easily accessible, compared to the easy accessibility of a multitude of different X-ray diffractometers in laboratories. The neutrons generated must be slowed down before being guided to scientific instruments. Neutrons, unlike X-rays have a neutral charge. Because of this they only interact weakly with matter so they can penetrate deep into the nuclei of atoms without destroying matter. This allows for the distinguishing of isotopes in a sample and atoms

with a small atomic number (Z) to be picked up on. This is a major advantage of neutron diffraction as unlike X-ray diffraction it allows for hydrogen and deuterium atoms – which are present in all the samples mentioned in this project - to be detected with accuracy. The neutron's spin interacts with magnetic moments, so neutron diffraction can be used to help determine the magnetic structure of a material [56, 57].

D2B High-Resolution Two-Axis Diffractometer

This diffractometer is located at the ILL in Grenoble, France. It operates using a beam of neutrons at a wavelength of 1.594 Å. Measurements were taken at variable temperatures from 1.6K – 300K. For each measurement two data sets were obtained, a high-resolution file and a high-intensity file.

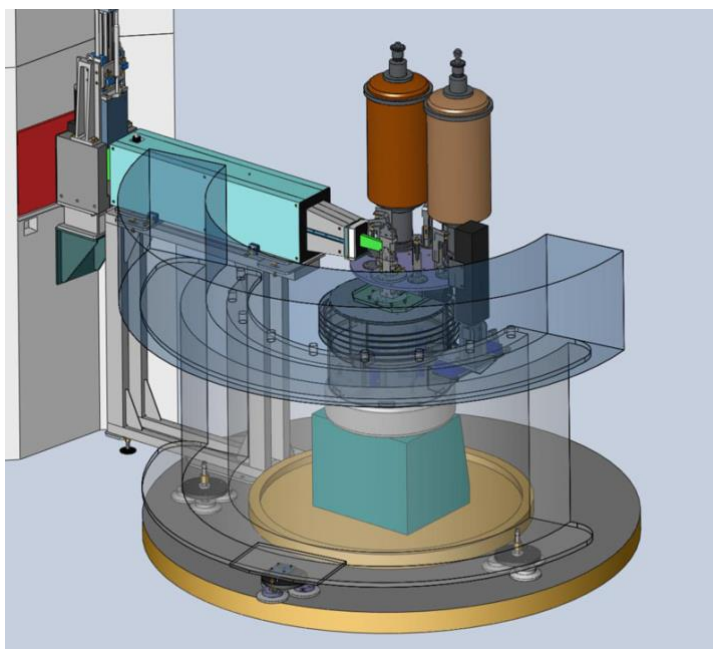


Figure 19 Instrument layout of the D2B diffractometer [58]

3.5 Structural Model Refinement

The refinement of both the powder X-ray diffraction data and neutron diffraction data were performed using the FullProf suite of programs [59]. The shape and intensity of a peak in a diffraction pattern provide all the key structural information about the compound. Sharp, distinct peaks show the compound is crystalline. Characteristic peaks are typically present at lower angles and appear more intense. Peaks at very high angles are less intense and less distinct due to form factors. The angle at which a peak

is present corresponds to Miller plane indices (h , k , l). This information is used to determine the unit cell of the sample.

Rietveld refinement utilizes the least squares method which calculates the difference between observed and calculated data points and works to minimise these differences. A χ^2 value is calculated which indicates how closely aligned the sample data is to the reference data. A low chi squared value indicates a closer match. The main issues which could potentially cause a higher χ^2 value than expected are the presence of impurities or other compounds. Multiple compounds present in a sample is common for samples made via hydrothermal synthesis where smaller molecules such as metal oxides have been made as some metal ions have not been fully reduced to the desired oxidation state. Another issue is preferred orientation which occurs when crystals in the sample are not randomly arranged and are instead pointing along the same axis, this can greatly affect peak intensities and can result in peaks appearing as 'missing'.

HighScore [60] is another piece of software that can be used to identify the likely compounds present in the sample and oxidation states of any heavy metals quickly. This proved useful in determining likely impurities.

3.6 Single-crystal X-ray Diffraction

3.6.1 Sample Preparation

This technique requires crystals of a certain size and shape, thus limiting what products can be analysed. Main errors occur from twinned crystals and crystals of poor quality. The set up for this technique is more difficult as crystal samples must be set up in a certain alignment and crystal selection under the microscope involves delicate movements to select the desired crystal from the sample and attach it onto the loop without breaking the crystal or the loop.

Selection

A couple drops of fomblin oil were smeared onto a glass panel and a clump of a sample placed on top. The panel was placed under a microscope shining polarised light to check for crystalline products.

Mounting

Individual crystals that extinguished were selected and attached to the head of a loop with the fomblin oil acting as a glue which freezes in place during the experiment. The loop was mounted in the diffractometer and the camera used to check the size, quality and placement of the crystal. A crystal that is too big is an issue as the X-rays hitting the crystal can become scattered by multiple points within the crystal. This is called secondary diffraction [61], and results in extra reflections being present as well as unreliable beam intensities. If a crystal is too small the experiment will take too long, so crystal size was kept to approximately between 0.1 and 0.5 mm.

Alignment

The alignment is adjusted along x,y and z axes through rotating the goniometer head through 360° and manually turning the pegs on the goniometer head. Alignment can be checked using the video camera. Crystal must be centred in all directions to ensure the x-rays hit the sample, any x-rays that miss the sample will result in an incomplete data set. The use of a lower temperatures slows down vibrations in the crystal, allowing for more accurate atomic positions to be obtained. Temperatures below 150K were not tried as lower temperatures will cause too much freezing on the crystal surface to occur which will damage the data as an ice diffraction pattern will also be collected.

Rigaku Oxford Diffraction single crystal X-ray diffractometer

Two of these diffractometers; one in house and one at the University of Silesia, Katowice, Poland were used to measure crystals less than 0.5 mm. The diffractometer operates using Mo x-rays ($K\alpha_1 = 0.71 \text{ \AA}$ and $K\alpha_2 = 0.63 \text{ \AA}$). Mo x-rays are harder (higher energy and greater penetrating than Cu x-rays). The cryostat was set to 150K for all measurements. Using the software CrysAlis [62] a pre-experiment scan was performed on all crystal samples to give a good indication on what specific settings would give the best data result in the experiment scan. For most crystal samples data from the whole sphere of the sample was obtained in case of any asymmetric structures.

3.6.2 Data Processing

The data can then be processed using the same software as was used to collect the data. In CrysAlis the unit cell is determined via automatic data processing or for more challenging data sets, 'Data reduction with options' can be used which allows for some manual input options. The latter option allows selected lattice extinctions to be filtered out. A table showing suggested space groups for the lattice is given. The best fitting space groups can be individually reduced to see which space group results in the best fitting data.

The finalised reduced data set can then be output into VESTA a 3D visualization programme [63], or Olex2 [64] a crystallographic structure solution and refinement software. These create a 3D representation of the unit cell, displaying atom positions, bond distances, bond angles and in VESTA isosurfaces and electron density maps can be displayed as well. ShelXT the most popular structure refinement software for small compounds [65], can be used in conjunction to this software.

3.7 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed using a NETZSCH STA 409 PC/PG thermogravimetric analyser. The crystal samples were weighed and placed into aluminium crucibles. A hole was pierced in the centre of the aluminium crucible lids, which were then pressed and sealed to the crucible. The samples were heated at a rate of $10^{\circ}\text{C min}^{-1}$ up to 300°C under flow of nitrogen. As the sample is heated its mass is recorded. Results show the amount of mass lost over the experiment and at what temperature range this occurs. A change in mass can indicate the sample has dehydrated, decomposed or a chemical reaction such as reduction has taken place [66].

3.8 X-Ray Fluorescence (XRF)

A PANalytical Epsilon 3 X-ray fluorescence spectrometer was used to determine the elemental composition of the samples. It is important to note that fluorine is too light so only the composition of alkali metals and transition metals could be determined. This spectrometer works by directing X-rays at the sample. Electrons in the lower energy levels absorb the energy from these X-rays and as a result are ejected. Electrons from higher energy levels replace the ejected electrons, emitting fluorescent X-rays

which hit the detector. A computer processes the raw data to output a table of elements and their corresponding percentage weight in the sample [67, 68].

3.9 Fourier-Transform Infrared Spectroscopy (FTIR)

Infrared spectra of the samples were obtained using an IRAffinity-1S Fourier Transform Infrared Spectrophotometer in the 400-4000 cm^{-1} range. This absorption spectroscopy technique works by shining a beam of light at the sample and measuring what wavelengths in the infrared radiation region are absorbed by the sample. The data are processed via a computer using the Fourier transform mathematical operation. Peaks in the spectra can be used to identify chemical bonds in the sample and therefore aid in structure characterisation [69, 70].

4

Synthesis using DMF

As discussed in the synthesis chapter DMF (see Figure 13) is a versatile solvent which upon heating decomposes into reducing agents. This in-situ reaction has been used to successfully reduce many metals, mainly in the nanoparticle field, and its applications in inorganic synthesis are just beginning to be explored. DMF can be used as a less hazardous reagent to produce Ti^{3+} crystals via hydrothermal synthesis.

4.1 $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$

4.1.1 The Structure of $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$

This structure as described in the background section is orthorhombic and belongs to the *Cmcm* space group. It has infinite parallel chains of disordered TiF_6 corner-sharing octahedra along the *c* axis (see Figure 8). These TiF_6 octahedra experience Jahn-Teller distortion, resulting in 4 normal Ti-F equatorial bonds and 2 elongated Ti-F bonds in the axial position.

As shown in the figures below $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ exhibits large reflections at 13.9° , 28.0° , 29.3° and 36.3° as well as low angle reflections at 17.9° and 18.3° . These characteristic peaks will act as reliable indicators of successful synthesis before proceeding with further analysis.

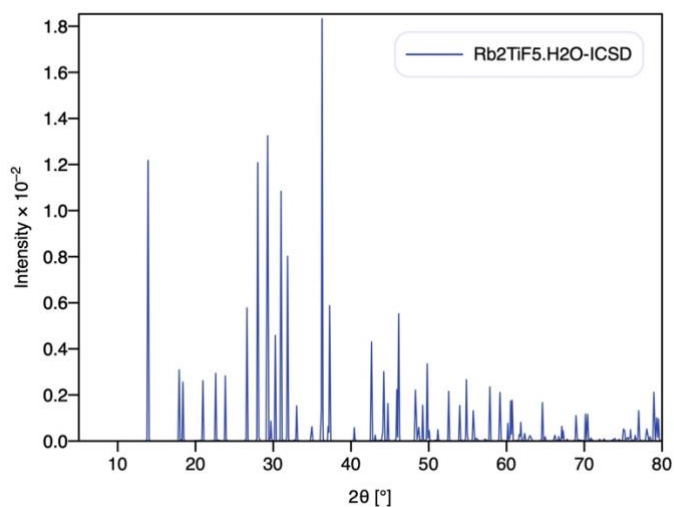


Figure 20 X-ray diffraction pattern of $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ [9]

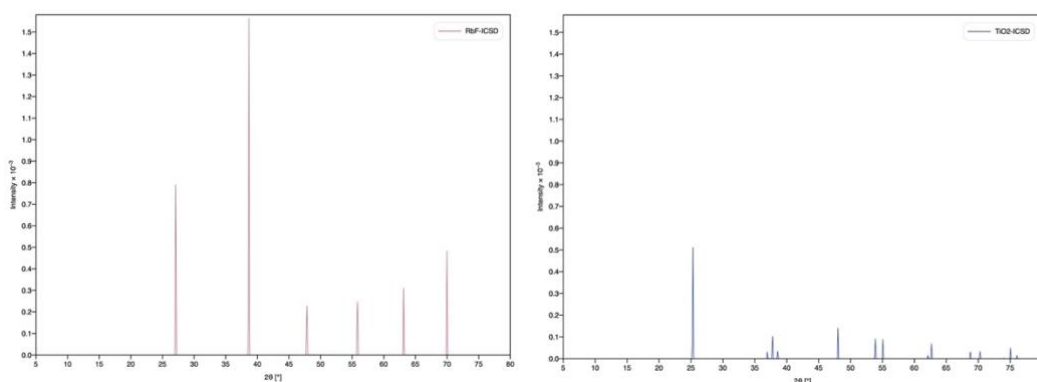


Figure 21 X-ray diffraction patterns of reagents RbF (left) [71] and TiO_2 (right) [72]

4.1.2 Synthesis Results and X-ray Characterisation

The synthesis method for this compound was replicated from the method used by Vinna Jo et al [9] for $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$. This synthesis involved rubidium fluoride and titanium dioxide reacting hydrothermally in a solution of DMF (dimethylformamide) and water. Light purple single crystals were reported to be synthesised. Within this chapter synthesis attempts are labelled as RbDMF_1, RbDMF_2 and RbDMF_3 as outlined in Table 1.

Synthesis	Reaction conditions	Reagents	Product
RbDMF_1	230°C, 72 hours in oven	RbF (1.567 g, 15 mmol); TiO ₂ (0.1203 g, 1.5 mmol); DMF (0.9 ml, 0.011 mol dm⁻³) ; H ₂ O (4 ml)	Grey/white/light purple granules
RbDMF_2	230°C, 72 hours in oven	RbF (1.567 g, 15 mmol); TiO ₂ (0.1203 g, 1.5 mmol); DMF (2 ml, 0.025 mol dm⁻³) ; H ₂ O (4 ml)	No crystalline product
RbDMF_3	230°C, 72 hours in oven	RbF (1.567 g, 15 mmol); TiO ₂ (0.1203 g, 1.5 mmol); DMF (1.5 ml, 0.019 mol dm⁻³) ; H ₂ O (4 ml)	Light purple, needle-shaped crystals

Table 1 Synthesis attempts and conditions for Rb₂TiF₅.H₂O

RbDMF_1 (see Table 1) followed the procedure reported in Vinna Jo et al exactly, using the same quantities of reagents and reaction conditions. This synthesis produced granules of a mixture of grey, white and light purple colours (see Figure 22) in contrast to the light violet crystals synthesised by Jo et al. Figure 25 shows the powder x-ray diffraction of this sample. The major product in this sample was identified as the double perovskite Rb₃TiOF₅, isostructural to Rb₂KTiOF₅. Even though the purple areas in this sample are responsible for some peaks which align with Rb₂TiF₅.H₂O, these peaks are not associated with the target phase. The titanium ions in this compound, Rb₃TiOF₅, have an oxidation state of 4+, indicating that the reducing power of the reaction solution was not strong enough and therefore attempts at a higher concentration of DMF was used to encourage the reduction of the titanium ions. As discussed previously in synthesis section DMF can reduce Ti⁴⁺ ions to Ti³⁺ under certain conditions. Jo et al offered this possible reduction process for Ti⁴⁺ to Ti³⁺:



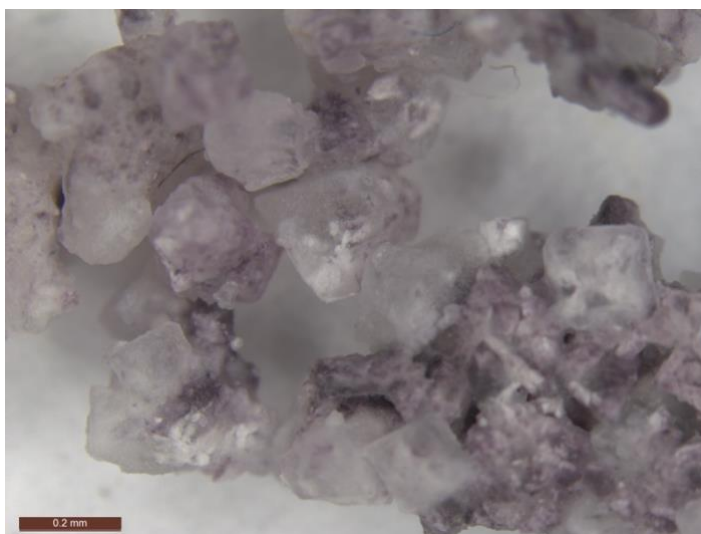


Figure 22 Microscope photo of RbDMF_1 crystals

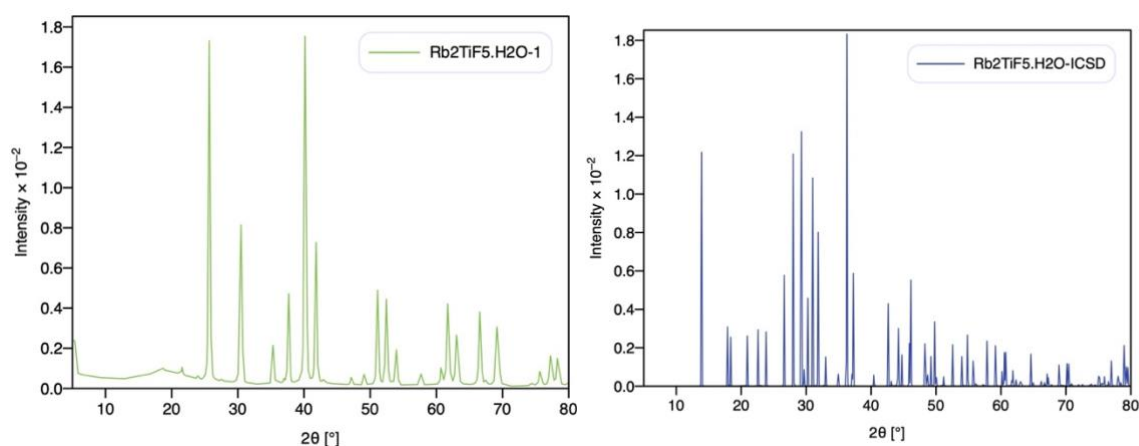


Figure 23 Powder X-ray diffraction patterns of the crystals from RbDMF_1 (left) and reference spectrum (right)

In RbDMF_2 the amount of DMF was doubled to 2.0 ml whilst keeping everything else the same which meant an increase in concentration from $0.011 \text{ mol dm}^{-3}$ to $0.025 \text{ mol dm}^{-3}$ in terms of the reducing agent. RbDMF_2 however failed to produce any crystalline product so no x-ray data was obtained. The reducing power may have been too strong which caused any crystalline products to dissolve, proving that the concentration of DMF is critical.

RbDMF_3 was attempted using 1.5 ml of DMF ($0.019 \text{ mol dm}^{-3}$), a middle point between the concentration used in RbDMF_1 and RbDMF_2. The reaction successfully produced the expected light purple single crystals as well as long clear shards (see Figure 24). The light purple colour is commonly reported with the presence of Ti^{3+} ions [9], signifying the targeted reduction had occurred.

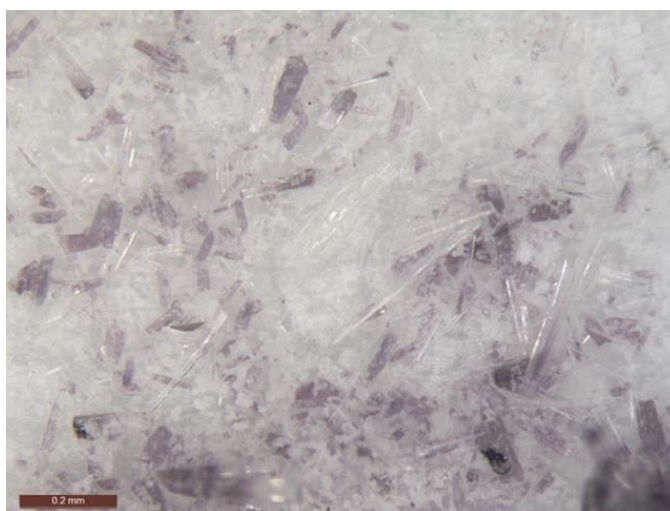


Figure 24 Microscope photo of RbDMF_3 crystals

The powder x-ray diffraction of this product is shown in Figure 24. Powder x-ray diffraction and single-crystal diffraction verified that these light purple crystals match the structure of the $\text{Rb}_2\text{TiF}_5\cdot\text{H}_2\text{O}$ structure from [9].

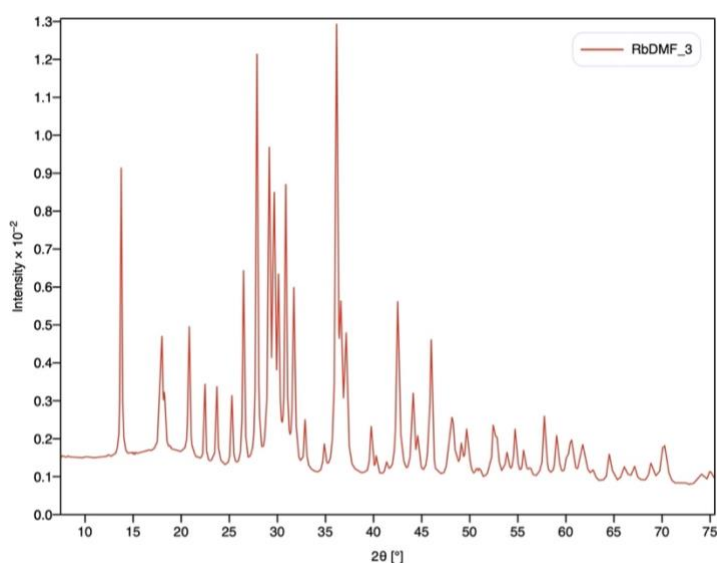


Figure 25 Powder X-ray diffraction pattern of RbDMF_3 crystals

The RbDMF_3 X-ray powder diffraction pattern displays all the characteristic peaks expected in $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$. Additional peaks are present at 25.3° , 39.8° , 41.4° which are believed to belong to impurities. The peak at 29.7° in the sample is significantly more intense than seen in the reference pattern. The impurity's peaks overlap with characteristic peaks making it difficult to distinguish. For instance, in the $17.5^\circ - 18.5^\circ$ region there are 3 overlapping peaks in the sample whereas in the reference pattern there are two single peaks. This is seen again in the $36 - 37.5^\circ$ region.

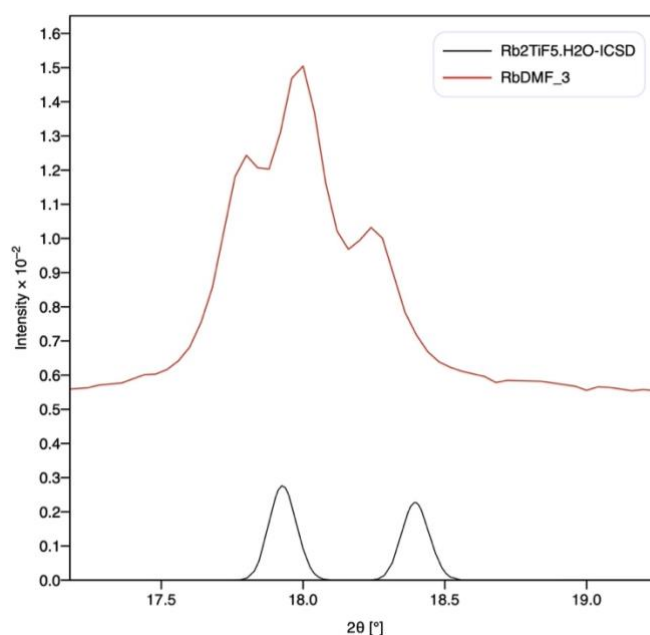


Figure 26 Close-up look at the X-ray diffraction pattern of RbDMF_3 crystals in the $36 - 37.5^\circ$ region

A sample from RbDMF_3 was taken for analysis on the Empyrean x-ray diffractometer to obtain a higher resolution pattern in hopes the impurity peaks would become more distinguishable. The Empyrean has a higher resolution as it uses only one wavelength whereas the X'Pert uses dual-wavelength. The Empyrean X-ray pattern showed small improvements in resolution compared to the X'Pert X-ray pattern. As can be seen in Figure 27, the peaks between $17.5^\circ - 18.5^\circ$ are more defined in the diffraction pattern taken on the Empyrean than the X'Pert, but the peaks are still not clearly distinguishable.

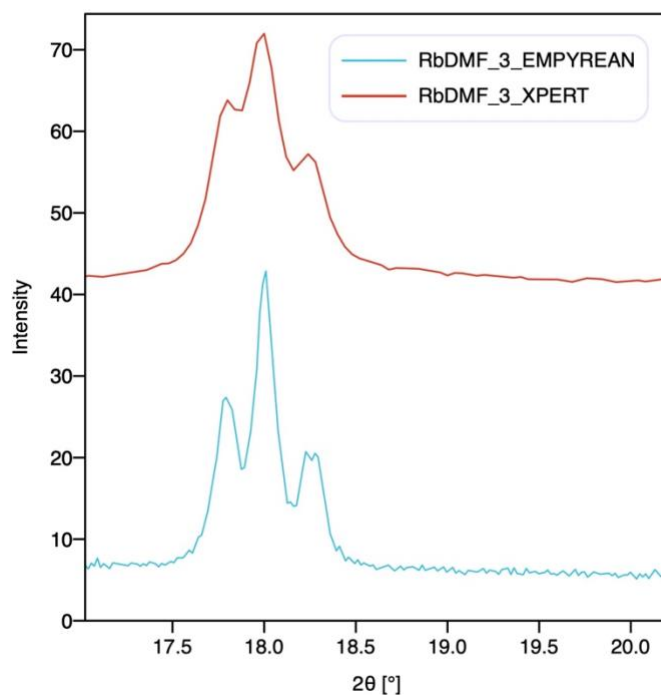


Figure 27 Close up look at the 17.5° - 18.5° range in the RbDMF_3 diffraction patterns taken from the X'Pert x-ray diffractometer (red) and the Empyrean x-ray diffractometer (blue)

To identify the impurities all related Rb, Ti and F binary and ternary compounds as well as oxides were checked using ICSD. But none of these compounds matched the peaks from the impurity. These impurity peaks which appear in the low angle region must be a complex structure, and as it has a clear / white colour the impurity may be an organometallic compound formed from the DMF.

4.1.3 Rietveld Refinements

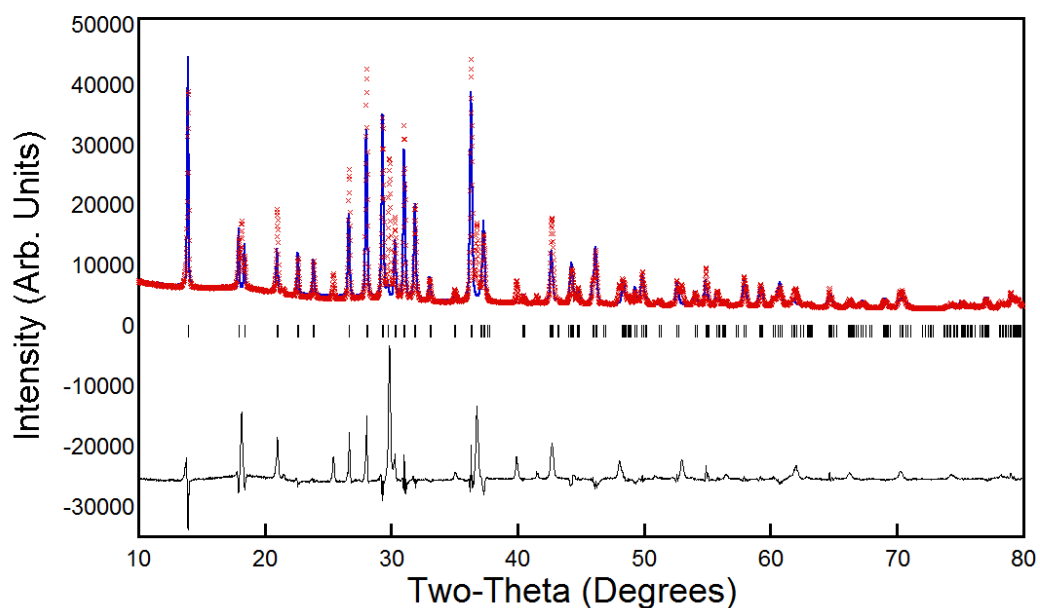


Figure 28 X'Pert powder diffraction data from RbDMF_3 sample. Observed (red), calculated (blue) and the difference (black).

Rietveld refinement of the powder x-ray data taken from the RbDMF_3 crystals confirms the presence of $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ crystals. The χ^2 value is very high, indicating the sample data has different peak intensities, peak shapes and impurities compared with the reference pattern. This is unsurprising as there are evident impurities in the sample. Despite this large χ^2 value and being unable to identify the impurities for certain, the data confirms the desired product was made.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy
Rb(1)	0.28406 (2)	0.21805(5)	0.25(0)	1
Ti(1)	0(0)	0(0)	0(0)	1
F(1)	0.20544(2)	0(0)	0(0)	1
F(2)	0(0)	-0.23547(2)	-0.00953(3)	1
F(3)	0(0)	-0.02465(3)	0.25(0)	1
O(1)	0(0)	-0.46581(4)	-0.25(0)	1

Table 2 RbDMF_3 refined atomic coordinates taken from Rietveld refinement data of the X'Pert x-ray powder diffraction at 298K in the Cmc₂m space group with cell parameters: $a = 9.64164(4)$, $b = 8.47313(4)$ and $c = 7.86328(3)$ Å. χ^2 value of 154.3929

The best way to characterise the crystals is through single-crystal X-ray diffraction as the desired crystals can be picked out of the sample and analysed, impurity data is therefore not present in the results.

4.1.4 Single-crystal X-ray Diffraction

To confirm the product's space group, look for any signs of phase transitions and to obtain data of a higher resolution, a crystal was selected from the sample for single-crystal analysis. The measurements were performed using the in-house diffractometer at the University of Kent and the Cryostat set to 150K.

Unit cell determination

The data were both obtained and refined using the software *CrysAlis*. On first inspection of the data the distribution histograms show reflections along the a^* and b^* axis which were unaccounted for in the original proposed unit cell. This is assumed to be from displaced peaks called modulation. Modulation is common in perovskites and magnetic materials. The unit cell was therefore doubled in attempts to account for these displaced peaks as shown in the figure below. Doubling the unit cell was not able to include all the displacement peaks but did improve the fit of the unit cell. The original unit cell and the double unit cell were solved individually.

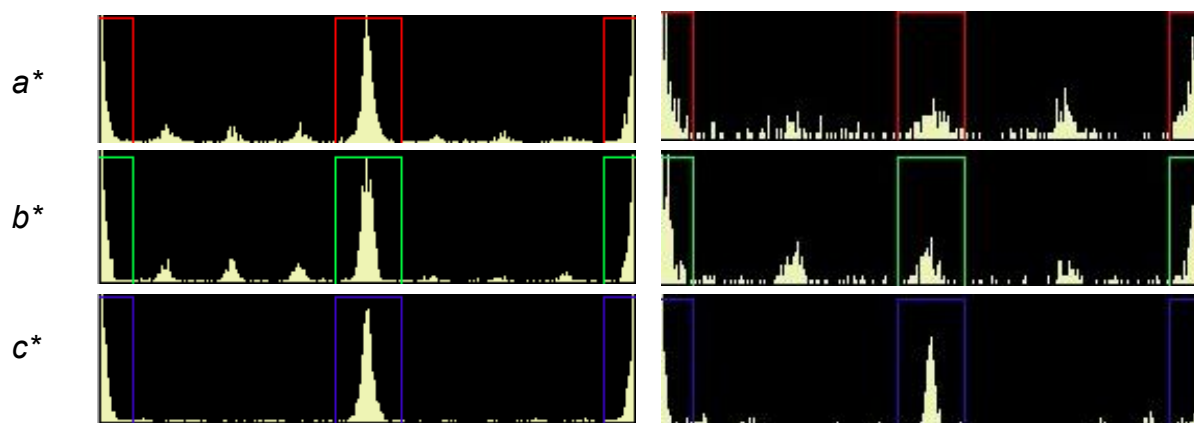


Figure 29 Distribution histogram of reflections along the a^* , b^* and c^* axis in the original unit cell (left) and the doubled unit cell (right) taken from CrysAlis

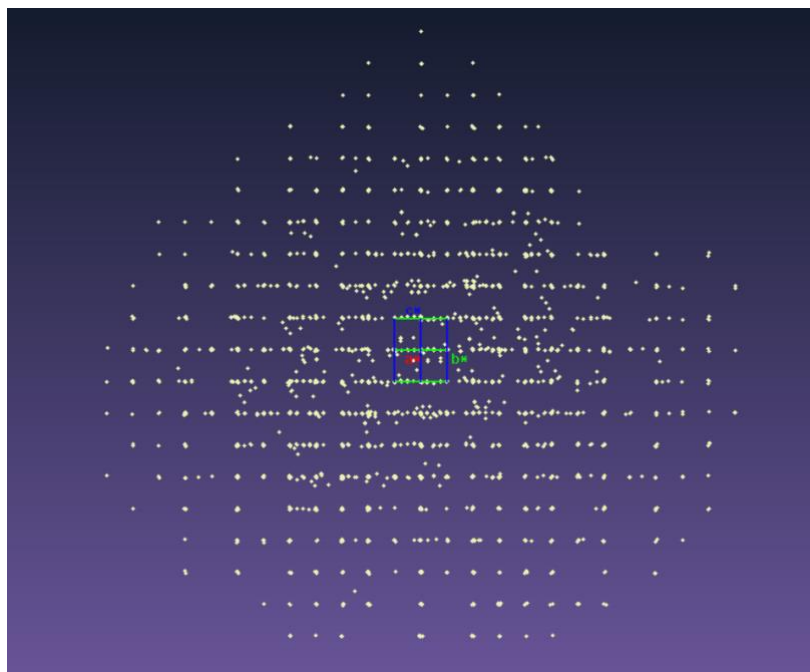


Figure 30 Ewald sphere of the original unit cell

Space group	No.	C/A	En.	O.A.	Pie.	Pyr.	CCDC	R(int)
Cmc2(1) (ba-c)	36	A	N	?	Y	Y	395	0.055
Cmcm (ba-c)	63	C	N	N	N	N	289	0.059
Ama2 (cab)	40	A	N	?	Y	Y	52	0.056

Table 3 Suggested space groups and their criteria for the original unit cell obtained from CrysAlis during data reduction

Original unit cell data reduction

The next step in data reduction involved the symmetry of the crystal. Cmcm and Cmc2(1) were given as space group suggestions for both the original unit cell and double unit cell of this compound. The key difference between these space groups is symmetry, Cmcm is centrosymmetric and Cmc2(1) is non-centrosymmetric. The best way to determine for certain the symmetry and therefore the space group for this crystal would be to perform pyroelectric or piezoelectric experiments, as seen in the table below Cmcm is not piezoelectric or pyroelectric but Cmc2(1) is. Literature determines the space group for this compound to be Cmcm and, as equipment to measure for piezoelectricity and pyroelectricity is not easily accessible, the space group selected for the reduction of both unit cells was Cmcm.

The structure determination and data finalisation for this space group was carried out using SHELXS alongside VESTA. This provided the atom positions (see supplementary material), unit cell parameters and electron density maps of the structures.

Sample name		RbDMF_3	RbDMF_3
Determined	chemical	Rb ₂ TiF ₅ .H ₂ O	Rb ₂ TiF ₅ .H ₂ O
formula			
Crystal system		Orthorhombic	Orthorhombic
Space group		Cmcm double	Cmcm original
a (Å)		19.0376(1)	9.5161(6)
b (Å)		16.8410(1)	8.4187(5)
c (Å)		7.8335(6)	7.83171(5)
a		90	90
b		90	90
y		90	90
Z		16	4
V (Å ³)		2511.5(3)	627.42(7)
Temperature (K)		150	150
R(int)		0.072	0.059
Crystal colour		Clear	Clear
Crystal shape		Needle	Needle

Table 4 RbDMF_3 single-crystal crystallographic data from original and double unit cell

RbDMF_3 double unit cell			
Ti(1) - F(1)	1.96255(2)	Ti(3) - F(7)	1.94722(1)
Ti(1) - F(2)	1.87585(1)	Ti(3) - F(8)	1.86986(1)
Ti(1) - F(3)	1.88451(1)	Ti(3) - F(9)	1.96183(2)
Ti(2) - F(4)	1.89528(1)		
Ti(2) - F(5)	1.92002(1)		
Ti(2) - F(6)	1.95951(2)		

Table 5 RbDMF_3 double unit cell selected bond distances (Å)

RbDMF_3 double unit cell

F(1) - Ti(1) - F(1)	180(0)
F(1) - Ti(1) - F(2)	90(0)
F(1) - Ti(1) - F(3)	87.5562(6), 92.4438(6)
F(8) - Ti(3) - F(7) x2	90(0)
F(8) - Ti(3) - F(9)	89.9999(0)
F(8) - Ti(3) - F(8)	180(0)
F(6) - Ti(2) - F(5)	91.4016(0), 88.5984(0)
F(6) - Ti(2) - F(4)	90.2075(0), 89.7925(4)
F(6) - Ti(2) - F(6)	180(0)

Table 6 RbDMF_3 double unit cell selected bond angles (°)

RbDMF_3 normal unit cell

Ti(1) - F(1)	1.898(3)
Ti(1) - F(2)	1.9601(3)
Ti(1) - F(3)	1.9(3)

Table 7 RbDMF_3 normal unit cell selected bond distances (Å)

RbDMF_3 normal unit cell

F(1) - Ti(1) - F(1)	180(0)
F(1) - Ti(1) - F(2)	90(0)
F(1) - Ti(1) - F(3)	90(0)

Table 8 RbDMF_3 normal unit cell selected bond angles (°)

Bond distances and bond angles obtained from the original unit cell and the doubled unit cell reduction gave a similar range of values which align with those stated in literature, the variations aligning with data from the reference paper [9], highlighting the Jahn-Teller distortion that the TiF_6 octahedra experience.

As seen in Table 5 there are 3 different types of titanium sites in the doubled unit cell. The twisted TiF_6 octahedra causes the titanium sites to not all be the same. In the original unit cell there is only 1 type of titanium site.

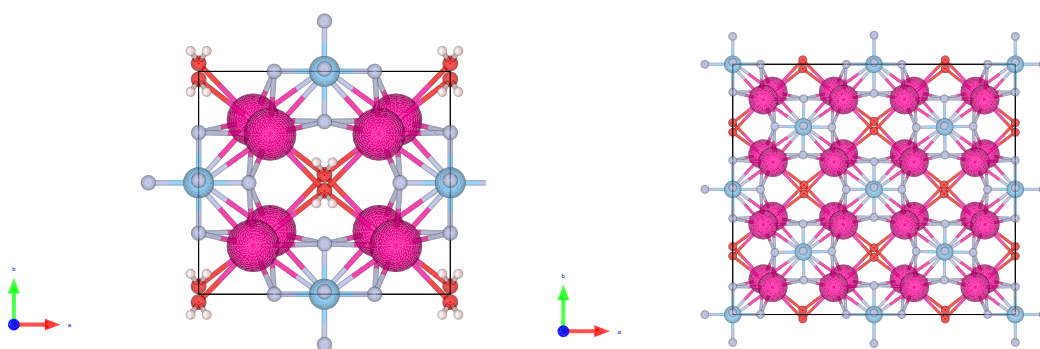


*Figure 31 Electron density map of $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ shown along the c axis derived from the original unit cell (left) and double unit cell (right)
Rb (pink spheres), Ti (light blue spheres), F (grey spheres), oxygen (red spheres) and hydrogen (white spheres).*

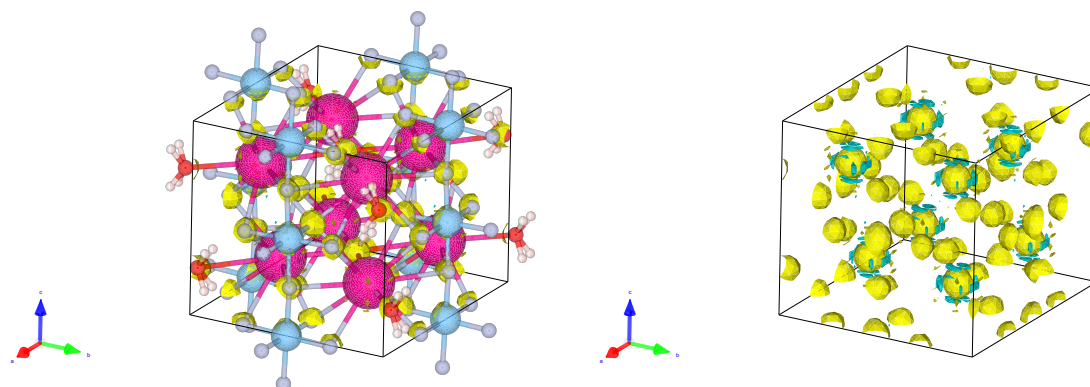


Figure 32 Electron density map of the original unit cell structure with overlaid isosurface level of $0.8 \text{ fm}\text{\AA}^{-3}$ (left) and without electron density map (right). Positive electron density is shown in yellow and negative in blue.

Negativity on the isosurface level diagram (blue) is due to modulation or possible covalency between Rb and water molecules, the software assumes 100% ionic and therefore does not account for any degree of covalency between atoms.

4.1.5 X-Ray Fluorescence

Fluorine, hydrogen and oxygen are not included in these values as they are too light to be picked up.

Atom	Weight %	Experimental	Theoretical
		Atomic %	Atomic %
Rb	78.373	66.96	66.67%
Ti	21.627	33.04	33.33%

Table 9 RbDMF_3 X-ray fluorescence data

The experimental data aligns very closely to the theoretical values, confirming the expected 2:1 ratio of Rb to Ti in the compound $\text{Rb}_2\text{TiF}_5\cdot\text{H}_2\text{O}$.

4.1.6 Thermogravimetric Analysis (TGA)

A mass loss of 6.96 % was observed between 75 and 200°C when RbDMF was heated to 300°C. This value is 1.87 % greater than the literature value. Literature claims this mass loss is due to the water molecules evaporating although no formal analysis was used to back this up.

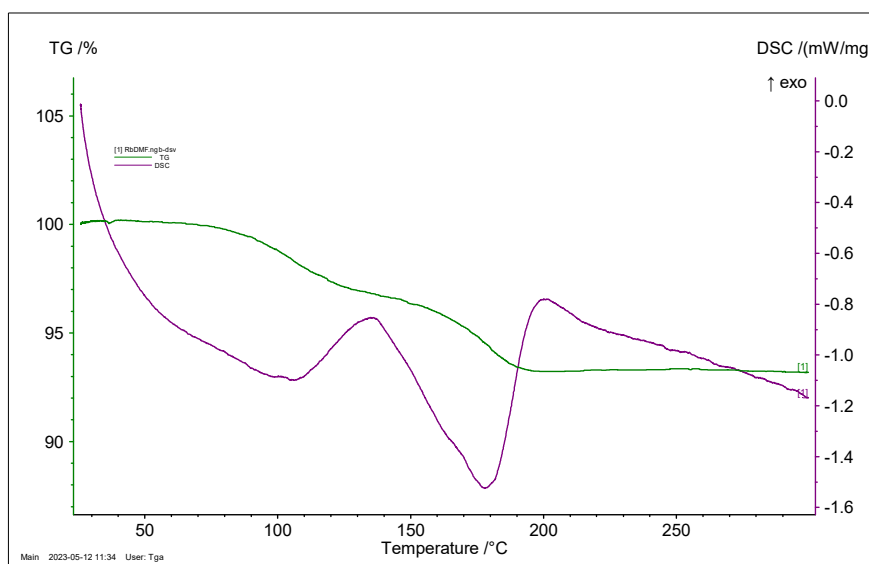


Figure 33 TGA plot showing sample mass % decreasing with increasing temperature

4.2 Rb₂TiF₅.D₂O

4.2.1 Synthesis

The atom positions of the hydrogen and oxygen atoms in Rb₂TiF₅.H₂O and Cs₂TiF₅.H₂O obtained via powder XRD and single-crystal XRD are not accurate as hydrogen is not picked up by x-rays. To solve this these compounds were deuterated which required a slightly altered method as described in the synthesis chapter. Synthesis with D₂O proved more difficult than H₂O, sometimes not producing crystals for no clear reason. Before these deuterated compounds were taken for neutron experiments at the ILL in Grenoble, France, the identity of each sample of Rb₂TiF₅.D₂O was analysed to ensure uniformity. Many samples of RbD₂O (abbreviation of Rb₂TiF₅.D₂O) were synthesised and then combined as a large quantity of sample (approximately > 2.5 g) is needed to achieve the best results.

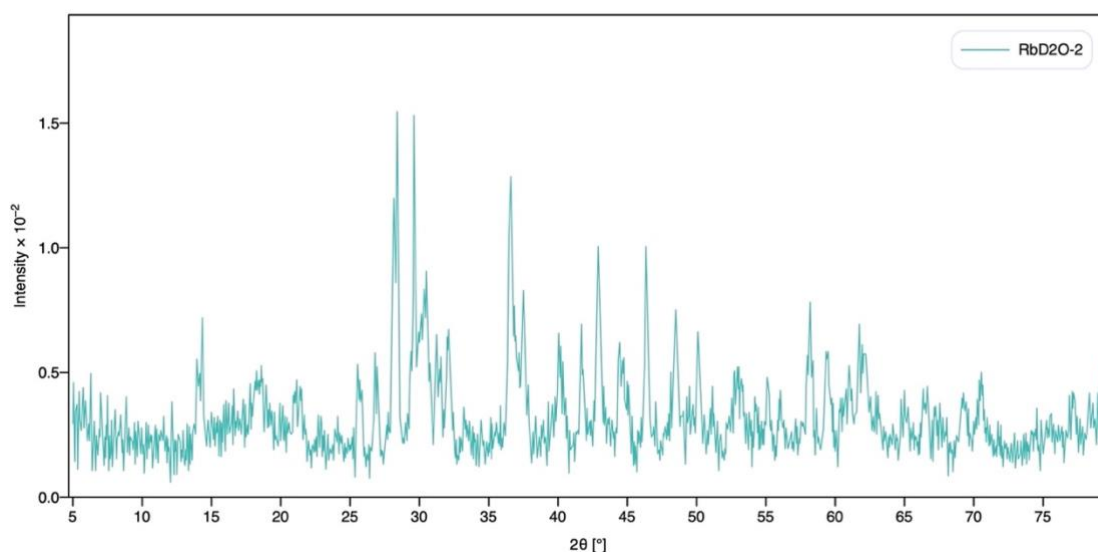


Figure 34 Powder x-ray diffraction pattern of a sample of RbD₂O crystals

The powder X-ray diffraction pattern for this sample of RbD₂O shows a very noisy background. Rietveld analysis was performed on this pattern and then cross-referenced with both the RbDMF_3 sample and the ICSD reference pattern, verifying the RbD₂O sample as the correct product.

4.2.2 Neutron Diffraction

Powder diffraction measurements were performed on the D2B beamline (high-resolution two-axis diffractometer). Measurements were taken at variable temperatures from 1.6K – 300K. Both a high-resolution file and a high intensity file were obtained at each measured temperature. The high-resolution data selected for further analysis contain extra peaks that are missing in the high intensity data sets.

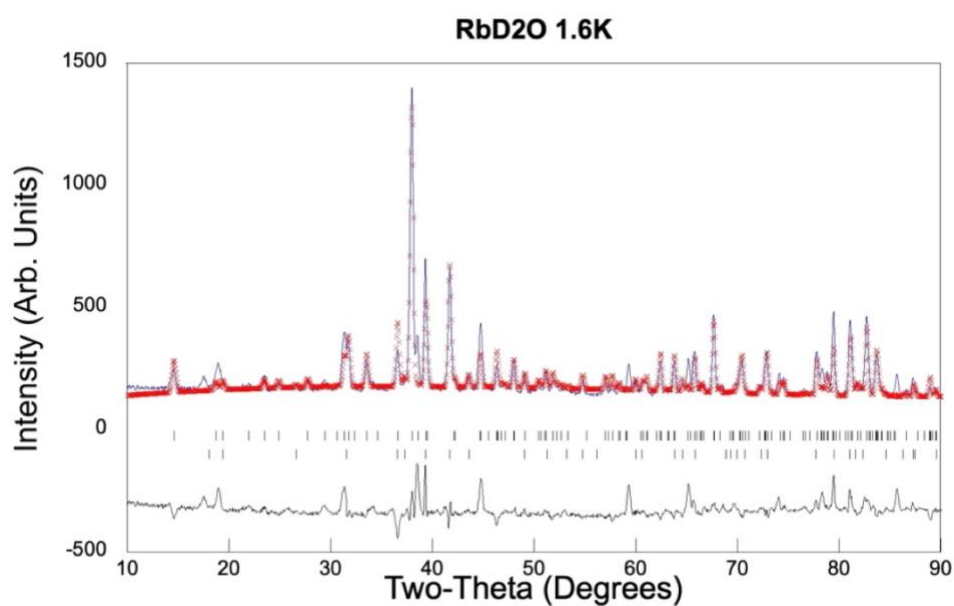


Figure 35 Neutron diffraction data from $\text{Rb}_2\text{TiF}_5 \cdot \text{D}_2\text{O}$ sample at 1.6K. Observed (red), calculated (blue) and the difference (black).

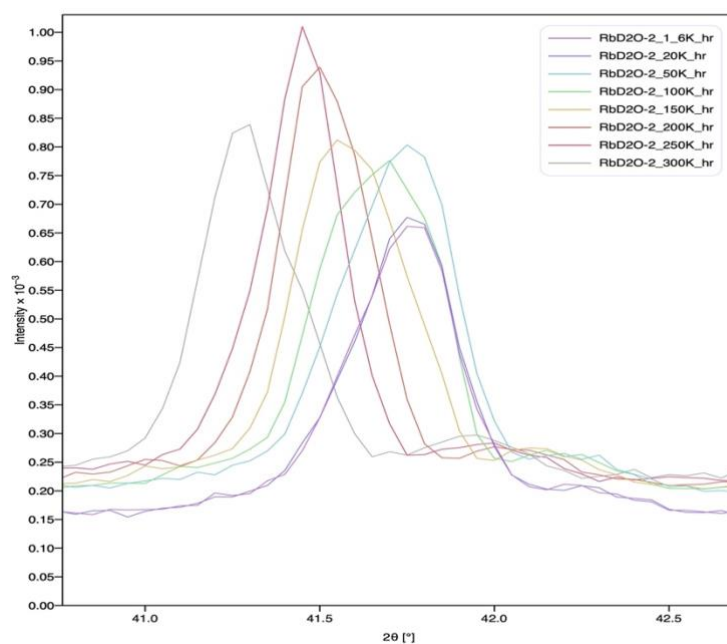


Figure 36 Close-up look at the shift in peak position as temperature increases

Peaks shift to lower angles as the temperature increases because the heat causes the sample to expand which is expected. This increases the value of the lattice parameters. The data were analysed using WinPLOTR from the FullProf suite and Rietveld refinements performed using edpcr.

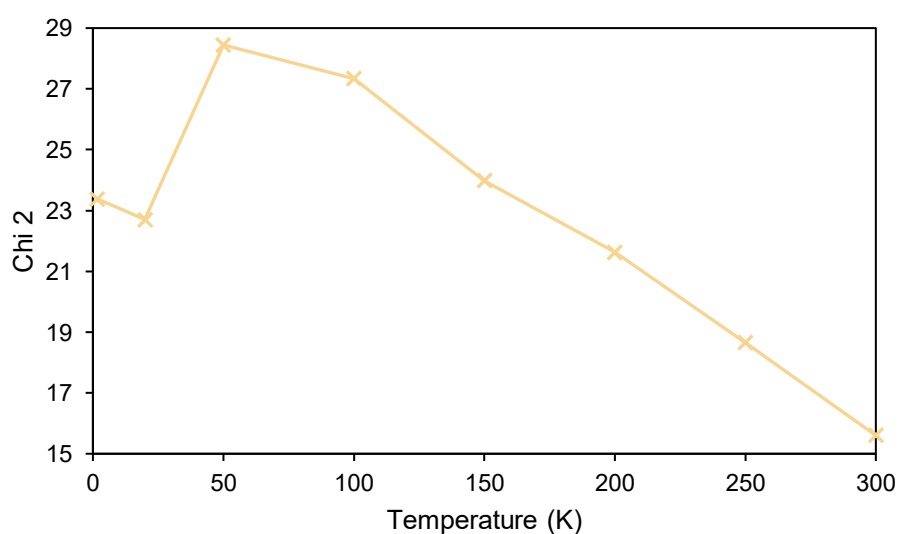


Figure 37 The χ^2 values obtained from Rietveld refinement of measurements taken at different temperatures

From 50K onwards the χ^2 value decreases with increasing temperature. One reason could be that the reference data is measured at room temperature so lower temperatures cause atom positions to change, thus causing the χ^2 values to stray further away.

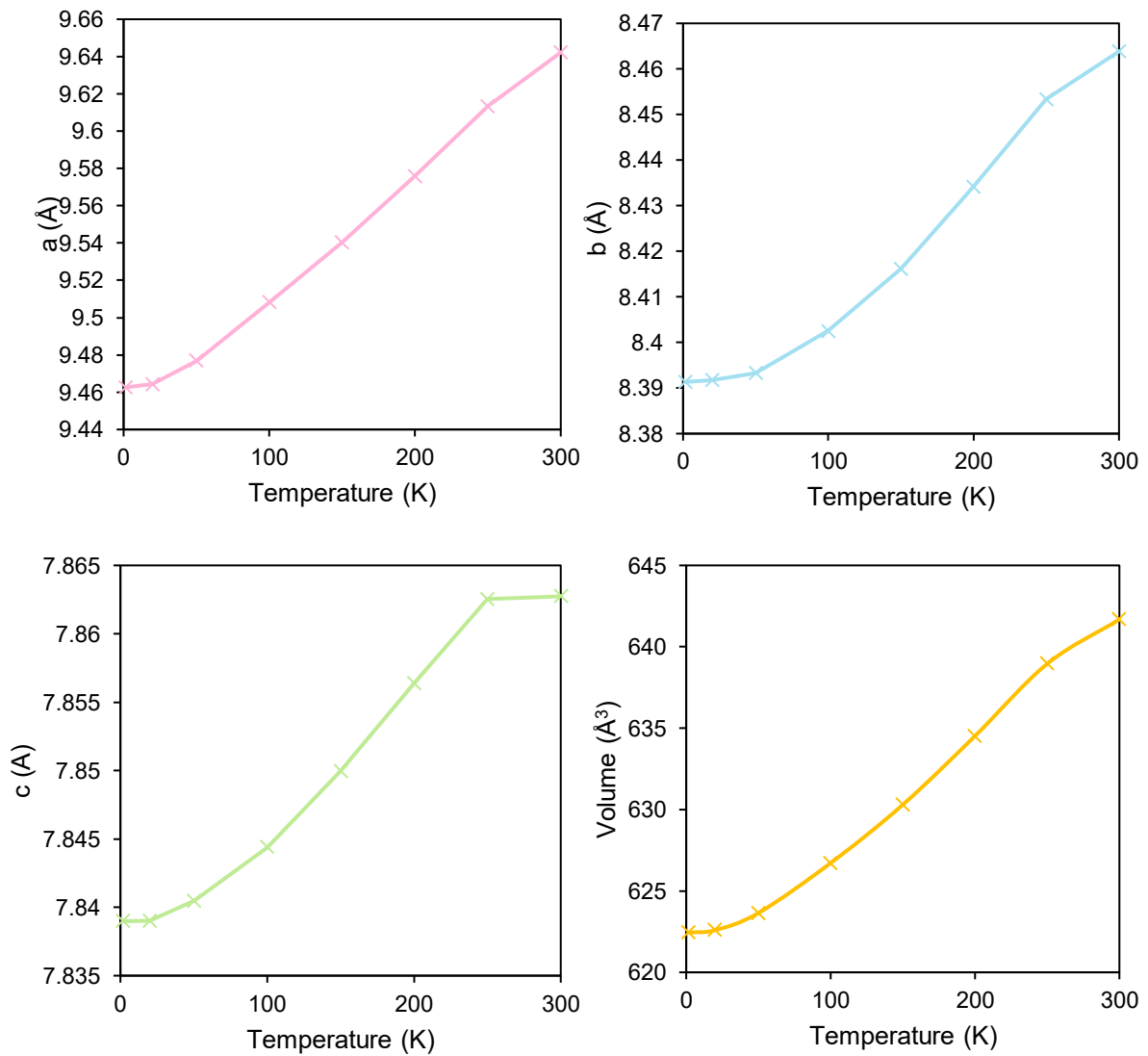


Figure 38 (a) The change of lattice parameter a with temperature. (b) The change of lattice parameter b with temperature. (c) The change of lattice parameter c with temperature (v) The change of volume with temperature

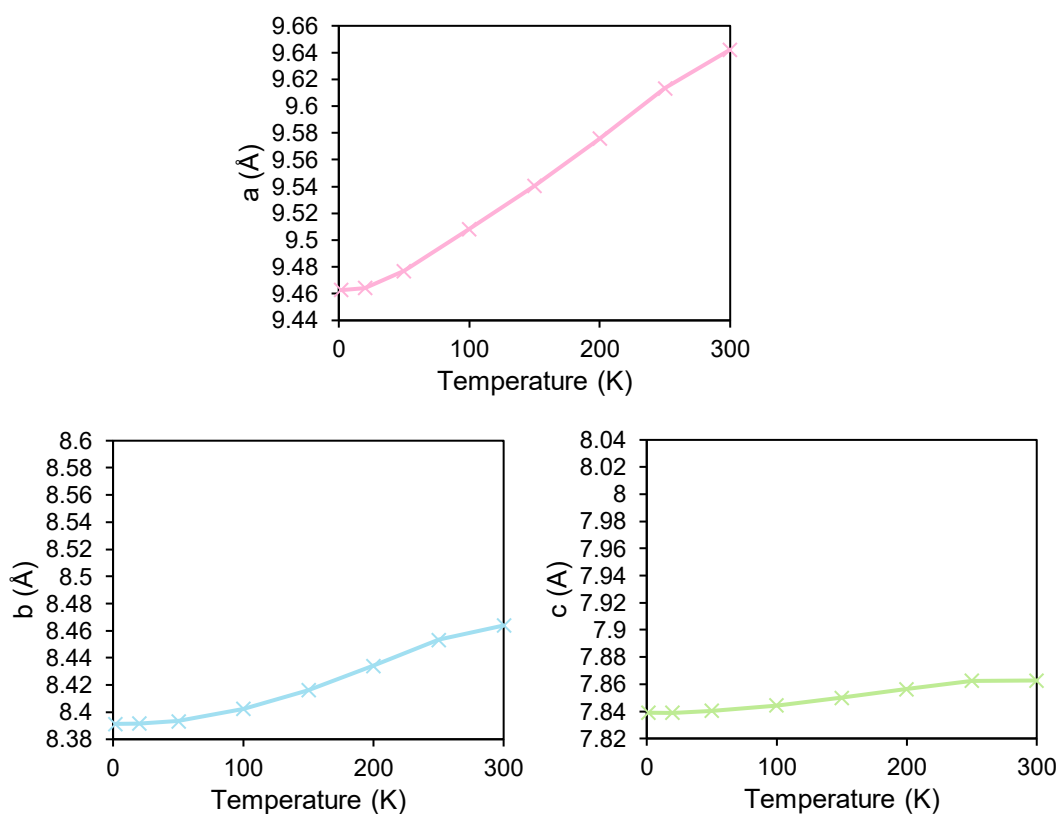


Figure 39 Graphs of lattice parameters against temperature on the same scale to highlight the difference in increasing lattice parameters.

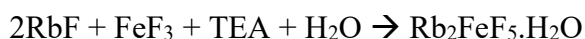
The expansion of the unit cell volume is almost entirely due to the increase in the lattice parameter along the a direction. Lattice parameter c shows an even smaller increase compared to lattice parameter b . Increasing temperature (unless negative thermal expansion occurs) always results in the volume of the unit cell increasing.

4.3 Rb₂FeF₅.D₂O

4.3.1 Synthesis

The compound Rb₂FeF₅.H₂O which is isostructural to Rb₂TiF₅.H₂O was synthesised by a project student, Olivia Hobson, and the sample deuterated so that it could be taken for neutron experiments. This compound was later taken for single-crystal and powder diffraction analysis at NIST Centre for Neutron research in Maryland, USA. Data were collected using the Ge (311) monochromator at $\lambda = 2.0782 \text{ \AA}$ and the Cu (311) monochromator at $\lambda = 1.5401 \text{ \AA}$, with an in-pile collimation of 15°. Rietveld refinement was performed using the FullProf suite of programs.

This compound was synthesised via a similar hydrothermal method used to make the Rb₂TiF₅.H₂O (see equation below). The main difference being that TEA was used instead of DMF as the Fe³⁺ ions were added directly from FeF₃ so a reducing agent was not needed. This meant the sample only needed 24 hours in the oven. The deuterated version of this compound was made via the same method, replacing D₂O with H₂O, which was done in a moisture box to avoid water from the air contaminating the sample. The deuterated version was synthesised so that neutron scattering experiments could be performed and the H positions included. The Rb₂FeF₅.H₂O and Rb₂FeF₅.D₂O samples are treated as identical, so their names are used interchangeably in this section.



The sample produced 2 types of crystals: one needle shaped and the other wider, more cube shaped (see Figure 40).



Figure 40 Microscope photo of $\text{Rb}_2\text{FeF}_5 \cdot \text{D}_2\text{O}$ crystals

4.3.2 Neutron diffraction

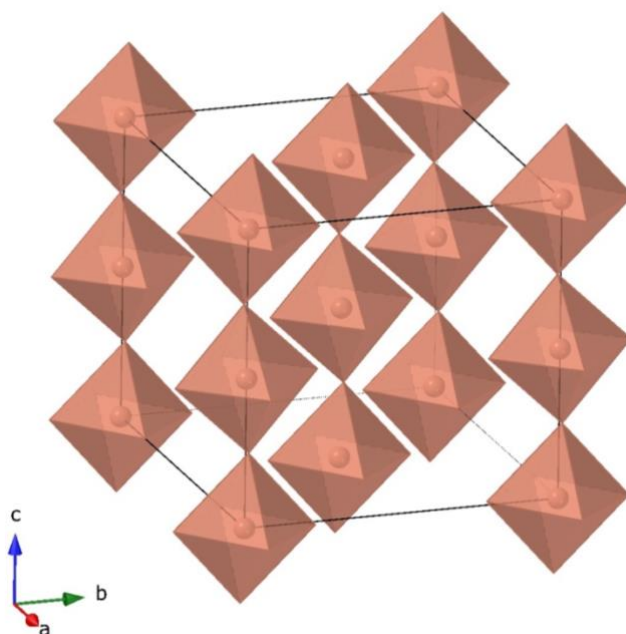


Figure 41 FeF_6 octahedra chains in the structure of $\text{Rb}_2\text{FeF}_5 \cdot \text{D}_2\text{O}$ taken from the CIF files generated from neutron diffraction data (A site cations are omitted for clarity)

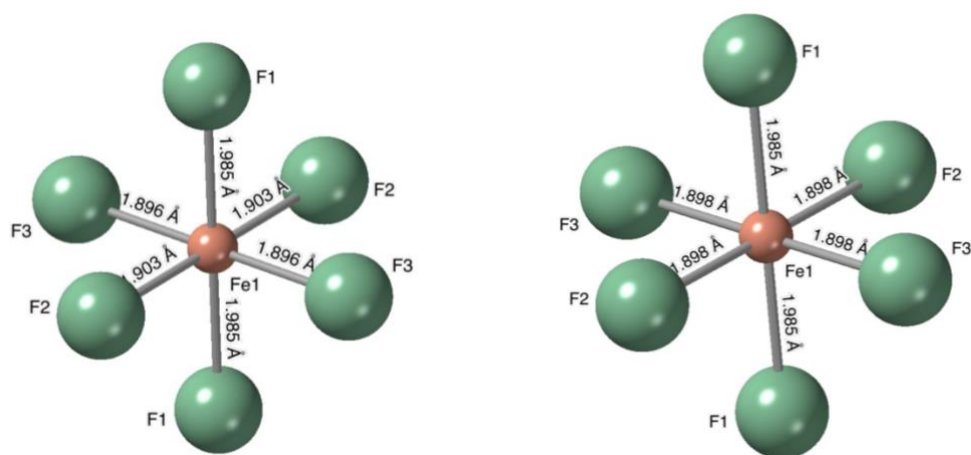


Figure 42 Bond distances in the FeF_6 octahedra of $\text{Rb}_2\text{FeF}_5 \cdot \text{D}_2\text{O}$ at 1.6K (left) and 5K (right) taken from the CIF files generated from neutron diffraction data

Axial Fe-F bonds remained identical at 5K and 1.6K. All equatorial Fe-F bonds at 5K are 1.898 Å. At 1.6K two of these equatorial bonds are slightly shorter at 1.896 Å and the other two are longer at 1.903 Å.

RbDMF_3 normal unit cell at 150K		Rb ₂ FeF ₅ ·D ₂ O at 5K		Rb ₂ FeF ₅ ·D ₂ O at 1.6K	
Ti(1) - F(1)	1.898(3)	Fe(1) - F(1)	1.9853(4)	Fe(1) - F(1)	1.985(3)
Ti(1) - F(2)	1.9601(3)	Fe(1) - F(2)	1.890(4)	Fe(1) - F(2)	1.903(4)
Ti(1) - F(3)	1.9(3)	Fe(1) - F(3)	1.9(5)	Fe(1) - F(3)	1.896(4)

Table 10 Comparison of selected bond distances (Å) from RbDMF_3 single-crystal data and Rb₂FeF₅·D₂O neutron diffraction data

RbDMF_3 normal unit cell at 150K	Rb ₂ FeF ₅ .D ₂ O at 5K	Rb ₂ FeF ₅ .D ₂ O at 1.6K
F(1) - Ti(1) - F(1) 180(0)	F(1) - Fe(1) - F(1) 180(0)	F(1) - Fe(1) - F(1) 180(0)
F(1) - Ti(1) - F(2) 90(0)	F(1) - Fe(1) - F(2) 90(0)	F(1) - Fe(1) - F(2) 90(0)
F(1) - Ti(1) - F(3) 90(0)	F(1) - Fe(1) - F(3) 90.1(3), 89.9(3)	F(1) - Fe(1) - F(3) 89.9(2), 90.0(0)

Table 11 Comparison of selected bond angles (°) from RbDMF_3 single-crystal data and Rb₂FeF₅.D₂O neutron diffraction data

4.3.3 Rietveld Refinements

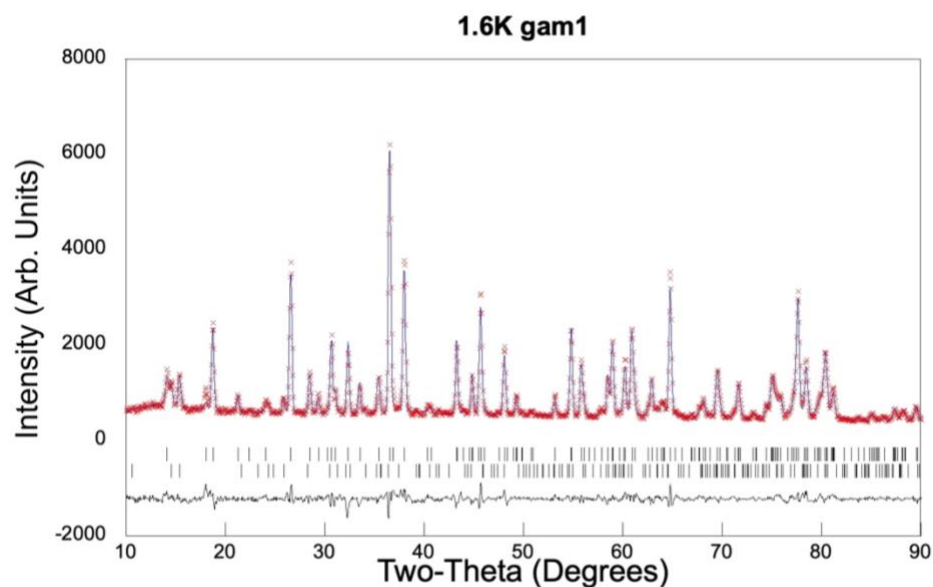


Figure 43 Neutron diffraction data from Rb₂FeF₅.D₂O sample at 1.6K. Observed (red), calculated (blue) and the difference (black). Gam1 BASIREPS applied

The occupancy of deuterium is slightly under 0.5, possibly due to deuterium vacancies in the structure.

Atom	x	y	z	Occupancy
Rb(1)	0.20921(6)	0.2799(4)	0.25(0)	1
Fe(1)	0(0)	0(0)	0(0)	1
F(1)	0(0)	0.0117(8)	0.25(0)	1
F(2)	0.2008(4)	0(0)	0(0)	1
F(3)	0(0)	0.2266(5)	-0.0116(4)	1
O(1)	0.5(0)	0.0364(7)	0.25(0)	1
D(1)	0.5(0)	0.1052(6)	0.1535(5)	1

Table 12 Rb₂FeF₅.D₂O refined atomic coordinates taken from Rietveld refinement data of the neutron diffraction at 1.6K in the Cmc₂m space group with cell parameters: $a = 9.45901(1)$, $b = 8.35054(1)$ and $c = 7.93132(8)$ Å. Chi² value of 2.40

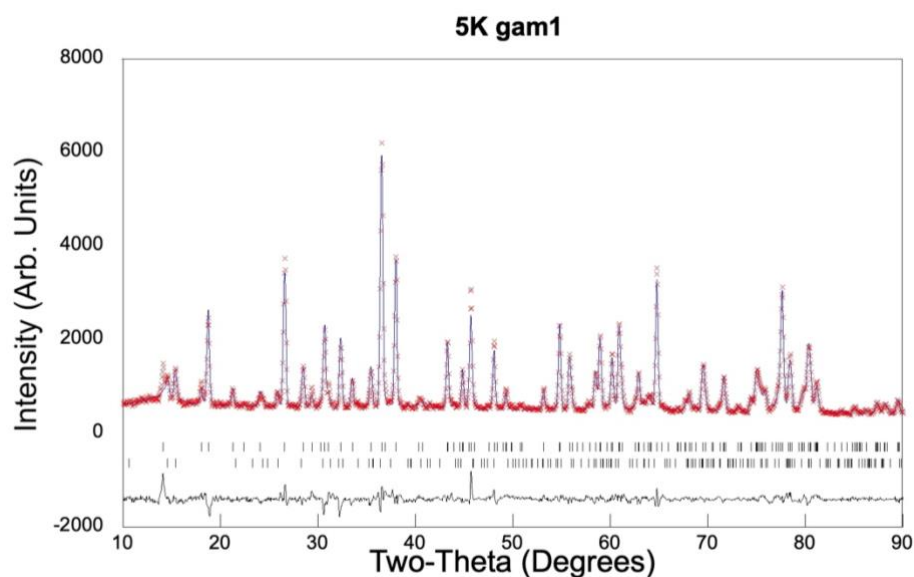


Figure 44 Neutron diffraction data from Rb₂FeF₅.D₂O sample at 5K. Observed (red), calculated (blue) and the difference (black). Gam1 BASIREPS applied

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy
Rb(1)	0.21246(6)	0.2794(4)	0.25(0)	1
Fe(1)	0(0)	0(0)	0(0)	1
F(1)	0(0)	0.0121(8)	0.25(0)	1
F(2)	0.2006(4)	0(0)	0(0)	1
F(3)	0(0)	0.2270(4)	-0.0111(4)	1
O(1)	0.5(0)	0.0315(7)	0.25(0)	1
D(1)	0.5(0)	0.1035(6)	0.1533(5)	1

Table 13 Rb₂FeF₅.D₂O refined atomic coordinates taken from Rietveld refinement data of the neutron diffraction at 5K in the C₂cm space group with cell parameters: $a = 9.46011(1)$, $b = 8.35081(1)$ and $c = 7.93149(8)$ Å. χ^2 value of 2.36

4.3.4 Magnetic Structure

The diffraction patterns at 1.6K and 5K show additional scattering not seen at 10K and higher temperatures. As this additional scattering indicates the formation of a long range magnetic structure, the magnetic structure of the compound could be determined using BASIREPS [73]. The magnetic structure calculated using Gam1 fit the diffraction pattern best. The different BASIREPS and their conditions are listed in the table below; refinements of Gam3, 5 and 7 can be found in the supplementary material.

	Gam1	Gam3	Gam5	Gam7
SYMM	<i>x, y, z</i>	<i>x, y, z</i>	<i>x, y, z</i>	<i>x, y, z</i>
BASR	1 0 0	0 1 0 0 0 1	0 1 0 0 0 1	1 0 0
BASI	0 0 0	0 0 0 0 0 0	0 0 0 0 0 0	0 0 0
SYMM	- <i>x, -y, z+1/2</i>	- <i>x, -y, z+1/2</i>	- <i>x, -y, z+1/2</i>	- <i>x, -y, z+1/2</i>
BASR	-1 0 0	0 -1 0 0 0 1	0 1 0 0 0 -1	1 0 0
BASI	0 0 0	0 0 0 0 0 0	0 0 0 0 0 0	0 0 0

Table 14 BASIREPS conditions for possible magnetic structures

As the temperature increases the magnetization of the sample decreases in intensity as the magnetic spins become misaligned. The graph (see Figure 45) shows that an antiferromagnetic phase transition at 9.4K, after which the magnetic order becomes significantly weaker.

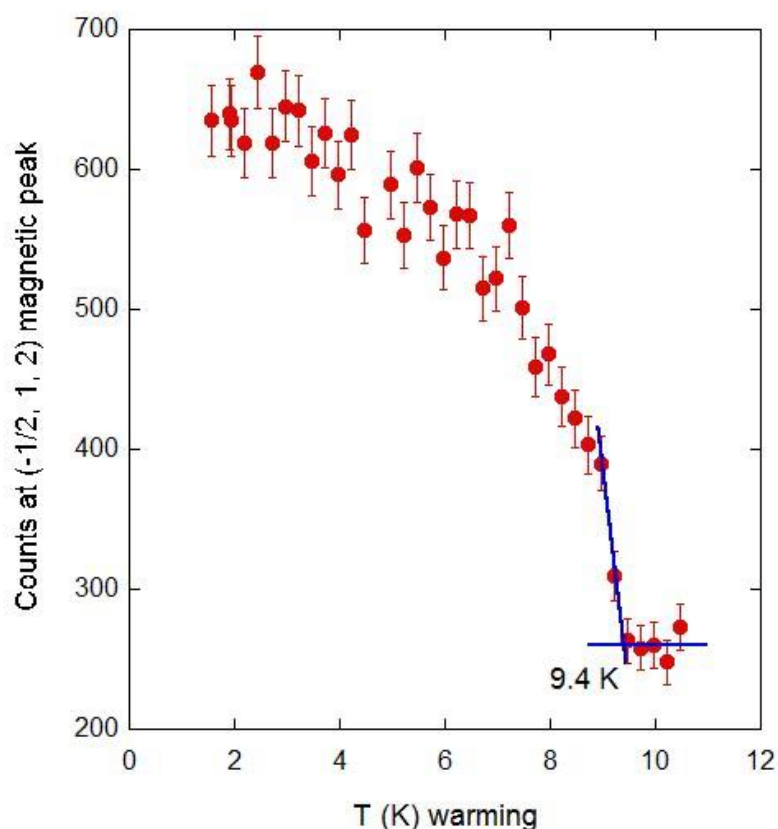


Figure 45 Magnetic scattering intensity as a function of temperature

4.4 Dehydration of $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$

4.4.1 Rb_2TiF_5

The compound $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ was attempted to be dehydrated to obtain Rb_2TiF_5 . Attempts to synthesise Rb_2TiF_5 directly proved unsuccessful so dehydration from $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ offers a relatively low effort way to synthesise.

The structures of these dehydrated compounds are expected to be very similar to their hydrated counterparts as the Rb / Cs – F interactions would be unaffected by the water loss in the molecule. This water loss is also believed to be reversible [9]. The structure of these dehydrated compounds has not been officially characterised or the loss of water from these molecules backed up with data. It was therefore attempted to dehydrate these samples and prove this loss of water through single-crystal XRD, TGA and FTIR analysis.

Dehydration attempt	Reaction conditions	Results	% Transmittance for water peak around 3400 cm ⁻¹ obtained from FTIR
Rb_dehyd_1	180°C, 6 hours	Temperature too high, crystals cracked	<i>N/A</i>
Rb_dehyd_2	130°C, 20 hours	Partially dehydrated	88.9
Rb_dehyd_3	140°C, 24 hours	Partially dehydrated	93.5
Rb_dehyd_4	150°C, 24 hours	Almost fully dehydrated	95.1
Rb_dehyd_5	150°C, 37 hours	Most successful attempt at dehydration	98.3
Rb_dehyd_6	155°C, 46 hours	Unsuccessful	<i>N/A</i>
Rb_dehyd_7	165°C, 2 days	Unsuccessful	<i>N/A</i>
Rb_dehyd_8	140°C, 4 days	Unsuccessful	<i>N/A</i>
Rb_dehyd_9	140°C, 4 days, product ground down first	Unsuccessful	<i>N/A</i>

Table 15 Dehydration attempts and conditions for Rb₂TiF₅·H₂O

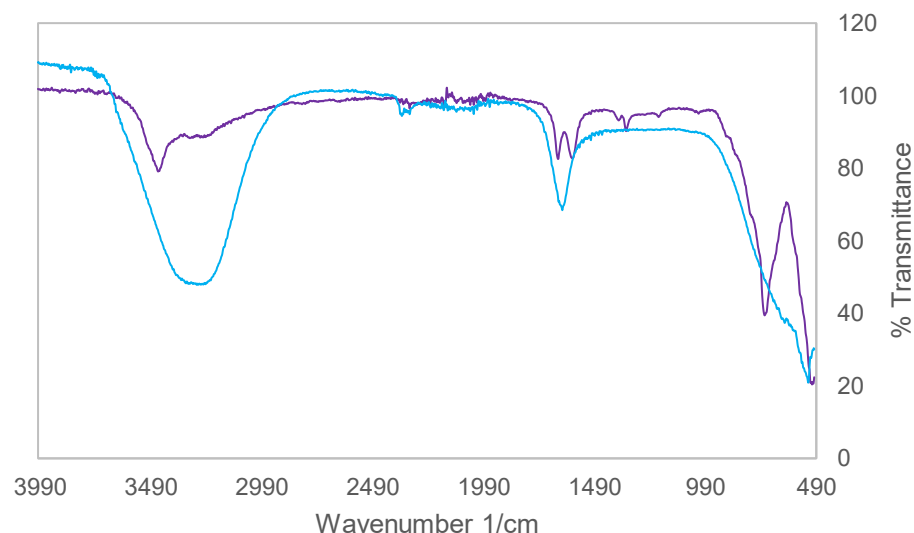


Figure 46 FTIR spectrum of RbDMF_3 (purple) with the spectrum for water (blue) overlaid

Water has a very broad peak at 3275.13 cm^{-1} and a narrow peak at 1635.64 cm^{-1} which represents the hydrogen bonding in water. The RbDMF_3 spectrum shows the presence of the water molecules in the sample with peaks at 3531.66 cm^{-1} , 1597.06 cm^{-1} and 1591.27 cm^{-1} .

4.4.2 Single-crystal X-ray Diffraction

Crystals of Rb_dehyd_1 were taken for single-crystal diffraction to the University of Silesia in Katowice, Poland. The crystals had cracked and finding a crystal good enough for single-crystal diffraction was difficult. It took multiple attempts of mounting and performing pre-experiment scans on different crystals. The selected crystals produced very bad data, indexing reflections at less than 60 % of the crystal. The indexed cell was monoclinic but only on a fraction of reflections were incorporated. No solution could be found with such little bad quality data.

4.4.3 FTIR

For the following dehydration attempts the reaction conditions were made less intense to avoid cracking the crystals. Through each attempt the oven temperature and length of time the crystals spent in the oven was gradually increased. FTIR on both Rb_dehyd_2 and Rb_dehyd_3 crystals showed partial dehydration, so the temperature

and oven time was further increased for Rb_dehyd_3 which was even closer to being fully dehydrated, and then again for Rb_dehyd_5 which showed the best attempt at dehydration. Rb_dehyd_2 had a mass loss of 2.59% but importantly, the Rb sample contains a mixture of products so determining if the water was lost from the desired compound's structure and not from the product of a side reaction is not possible from this data. This number of 2.59% is therefore not reliable and cannot be compared against the experimental mass loss of 5.09% (or theoretical mass loss of 5.58%) stated in the reference paper. The dehydration attempts, Rb_dehyd_3 and Rb_dehyd_4, experienced *gains* in mass which should not be possible. Rb_dehyd_4 had a mass loss of 10.6% which at double the reference paper value seems unreasonable. This high value could be due to an error or loss of product in the measurement process.

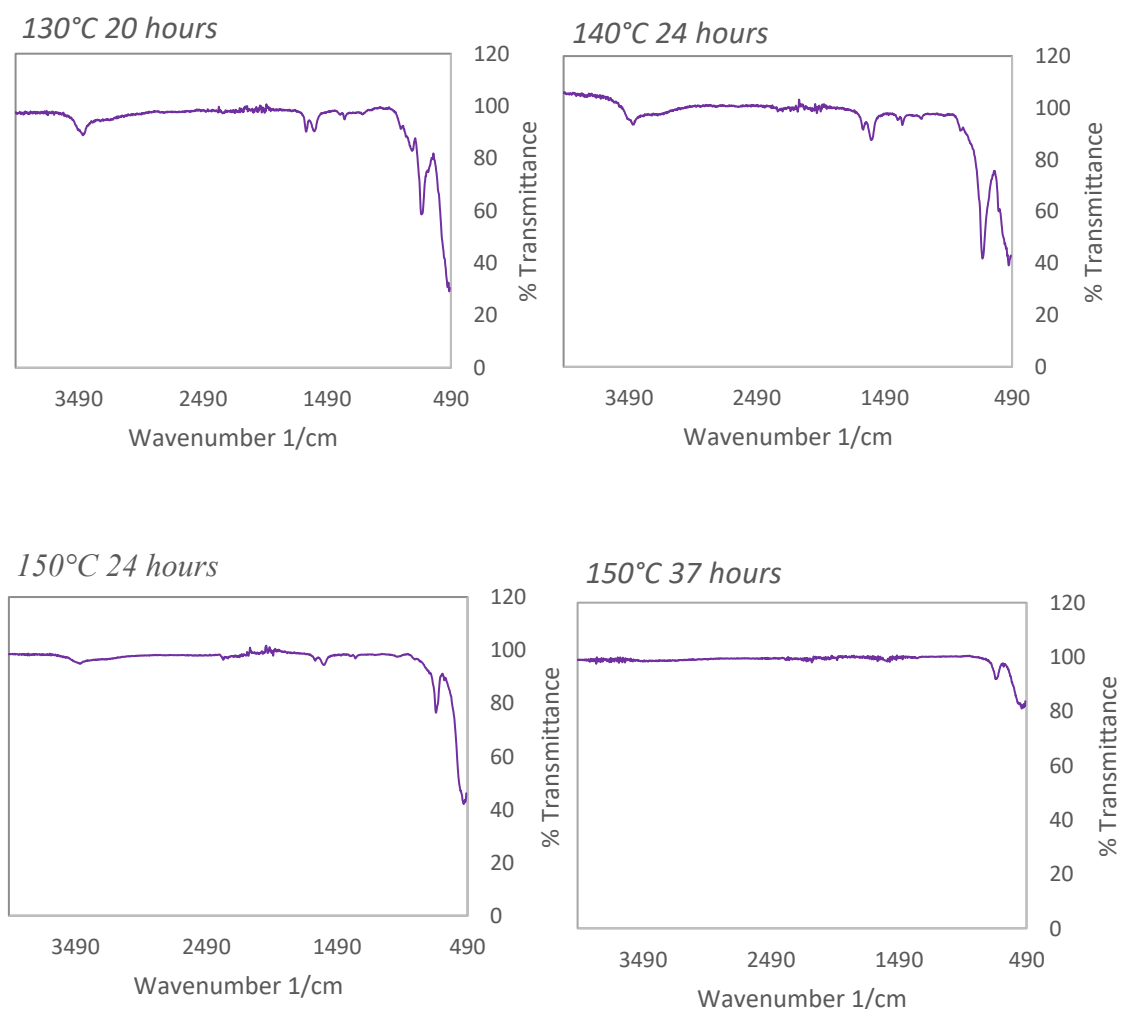


Figure 47 FTIR spectra of Rb_dehyd_2 – Rb_dehyd_5

Dehydration attempts Rb_dehyd_2 - Rb_dehyd_5 were taken for powder X-ray diffraction. Their diffraction patterns show no significant changes compared to the diffraction pattern of RbDMF_3. This is expected as removing the water molecules theoretically should not interfere with the main structure.

Rehydration of Rb_dehyd_3 was attempted by adding a few drops of water to the sample and leaving it in a drying cabinet set at 60°C overnight. The % transmittance for the water peak in the sample decreased from 93.5 to 91.9 %. This was not as great a change as expected but the sample likely needed more time to reabsorb the water. Data are not strong enough to comment on the reversibility of dehydration in this sample.

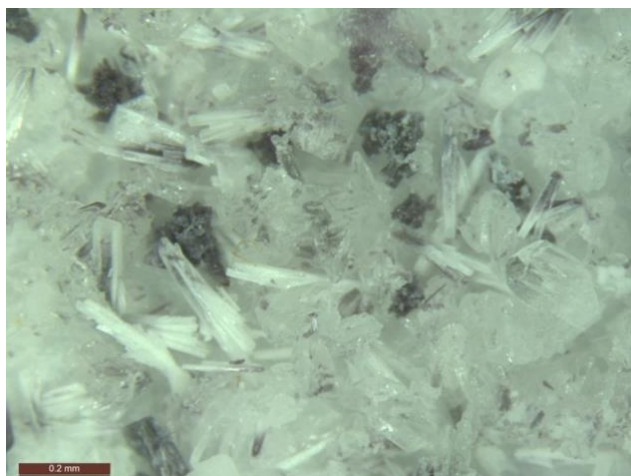


Figure 48 Microscope photo of Rb_dehyd_5 crystals, some crystals appear full or partially white as a result of dehydration

To obtain more dehydrated sample for analysis and to test the limits of the crystal's integrity for dehydration attempts Rb_dehyd_6 - Rb_dehyd_9 used higher temperatures or longer oven time. These stronger conditions proved unsuccessful. A possible explanation for this could be that all the previous dehydration attempts (Rb_dehyd_1 - Rb_dehyd_5) were performed on the same RbDMF_3 batch. For Rb_dehyd_6 - Rb_dehyd_9 however a new RbDMF_3 batch had to be made which for unknown reasons did not respond to dehydration in the same way. Further work needs to be done to confirm if the success of the early dehydration attempts is reproducible or it was just a fluke.

4.5 $\text{Cs}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$

4.5.1 The Structure of $\text{Cs}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$

This structure, like $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$, is orthorhombic and belongs to the $Cmcm$ space group. It has infinite parallel chains of disordered TiF_6 corner-sharing octahedra along the c axis. These TiF_6 octahedra experience Jahn-Teller distortion, resulting in 4 normal Ti-F equatorial bonds and 2 elongated Ti-F bonds in the axial position. The chains in $\text{Cs}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ are slightly less distorted than in $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ due to the larger coordination environment of Cs.

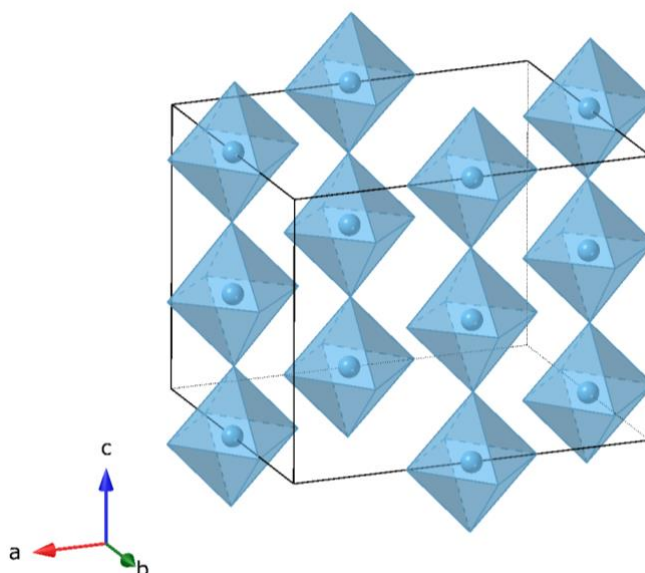


Figure 49 TiF_6 octahedra chains in the structure of $\text{Cs}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ (A site cations are omitted for clarity) [9]

As seen in synthesis of RbDMF , according to Jo et al, CsDMF synthesis should also produce light violet crystals. Big reflections are expected at 30.2° , 35.0° , 28.2° and 26.7° , as well as low angle reflections at 13.3° , 17.3° , 20.2° and 22.2° . The reflections for $\text{Cs}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ appear at slightly lower angles compared to $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ which is attributed to Cs being larger than Rb.

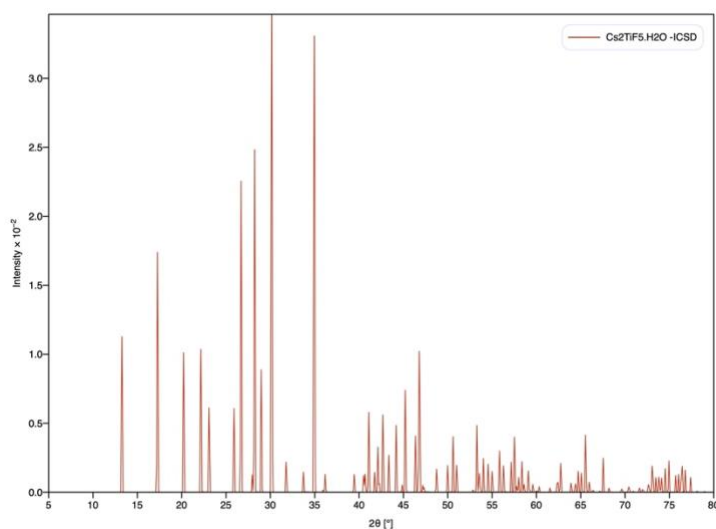


Figure 50 X-ray diffraction pattern of $\text{Cs}_2\text{TiF}_5\cdot\text{H}_2\text{O}$ [9]

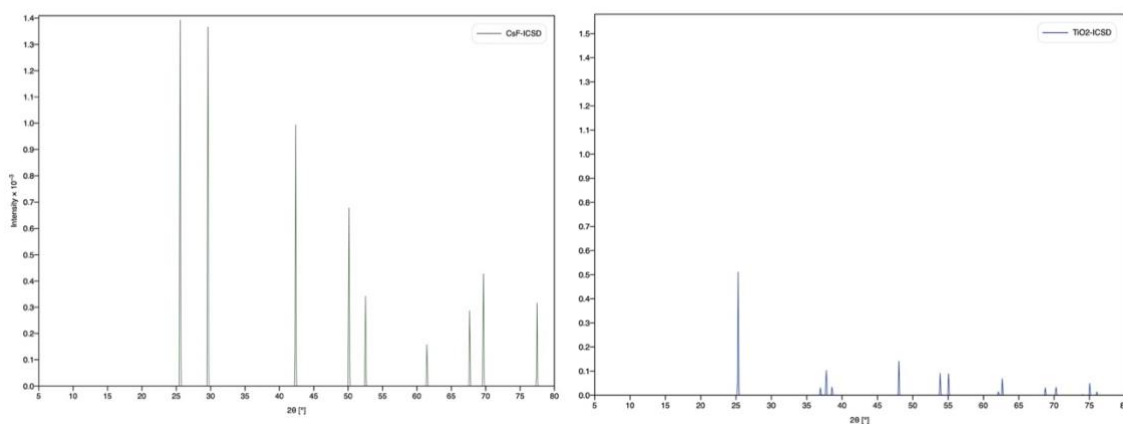


Figure 51 X-ray diffraction patterns of reagents CsF (left) [74] and TiO_2 (right) [72]

4.5.2 Synthesis Results and X-ray Characterisation

Synthesis attempts of $\text{Cs}_2\text{TiF}_5\cdot\text{H}_2\text{O}$ are labelled as CsDMF_1 , CsDMF_2 and CsDMF_3 as outlined in Table 16. Synthesis of this compound proved more difficult than $\text{Rb}_2\text{TiF}_5\cdot\text{H}_2\text{O}$, with the reaction being more sensitive to reagent quantities and length of time in the oven. Even when the optimum synthesis conditions were discovered, on repetition to make up more sample the reaction would sometimes fail to produce a crystalline product for unknown reasons. The crystals also required more work in filtration to separate the crystals from the cloudy white solution.

Synthesis	Reaction conditions	Reagents	Product
CsDMF_1	230°C, 72 hours in oven	CsF (1.519 g, 15 mmol); TiO ₂ (0.1203 g, 1.5 mmol); DMF (1.5 ml); H ₂ O (4 ml)	Cloudy white solution
CsDMF_2	230°C, 72 hours in oven	CsF (1.393 g, 7.5 mmol); TiO ₂ (0.0599 g, 0.75 mmol); DMF (1.5 ml); H ₂ O (4 ml)	Cloudy white solution
CsDMF_3	230°C, 96 hours in oven	CsF (1.393 g, 7.5 mmol); TiO ₂ (0.0599 g, 0.75 mmol); DMF (1.5 ml); H ₂ O (4 ml)	Cloudy white solution containing unidentifiable crystals
CsDMF_4	230°C, 120 hours in oven	CsF (1.393 g, 7.5 mmol); TiO ₂ (0.0599 g, 0.75 mmol); DMF (1.5 ml); H ₂ O (4 ml)	Lesser amount of cloudy white solution containing light purple needle-shaped crystals
CsDMF_5	230°C, 144 hours in oven	CsF (1.393 g, 7.5 mmol); TiO ₂ (0.0599 g, 0.75 mmol); DMF (1.5 ml); H ₂ O (4 ml)	No crystalline product

Table 16 Synthesis attempts and conditions for Cs₂TiF₅.H₂O

The first attempt at synthesising this compound, CsDMF_1, utilized the same approach as in RbDMF_3. The same molar quantities of reagents and reaction conditions were used (see table above).

This synthesis produced a cloudy white solution and not the expected light violet single crystals. One assumption was that the solution was white and cloudy due to unreacted powder reagents. In CsDMF_2 the quantities of CsF and TiO₂ (the powder

reagents) were halved. This change in reagent quantities produced no observable effect and this reaction also produced a cloudy white solution.

A possible theory as to why the solution was still white and cloudy was that the reagents needed more time in the oven to react and form crystals. So, for CsDMF_3 the reagent quantities were kept the same as CsDMF_2 except this time increasing the length of time the sample spent in the oven by 24 hours. A cloudy white solution was produced again, this time containing unidentifiable crystals at the bottom. Efforts to filter out these crystals for analysis were unsuccessful. As increasing the oven time influenced the reaction, for the next synthesis, CsDMF_4, the time was increased by another 24 hours. This reaction produced a lesser amount of cloudy white solution and within this light purple needle-shaped crystals. These crystals were able to be filtered and although a small amount of white residue clung to their surface as seen in the figure below, powder x-ray diffraction and single-crystal diffraction were able to be performed, verifying that these crystals match the structure of the $\text{Cs}_2\text{TiF}_5\cdot\text{H}_2\text{O}$ structure from the reference paper [9].

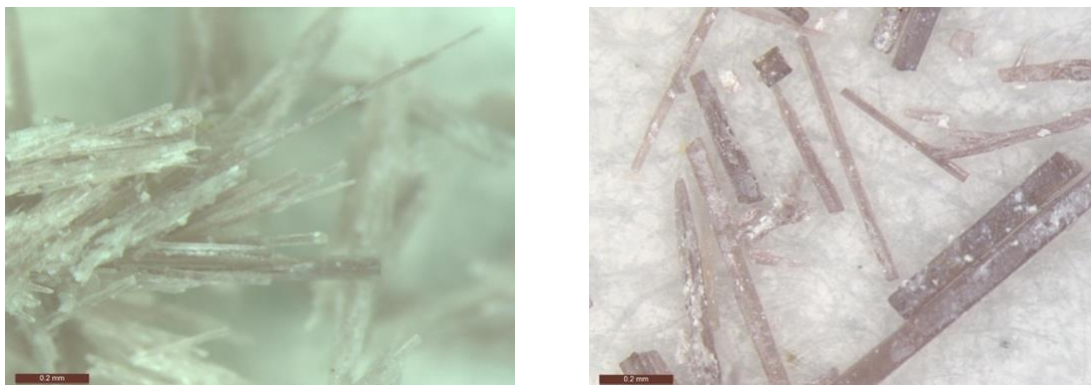


Figure 52 Microscope photos of Synthesis 3 crystals (left) and Synthesis 4 crystals (right)

To see if crystals could be produced with even less white solution stuck to their surfaces the length of the time the sample spent in the oven for CsDMF_5 was increased by a further 24 hours. This failed to produce the expected results and instead formed a murky white solution with no crystalline product. CsDMF_4 was therefore chosen as the optimum method to make this product going forward.

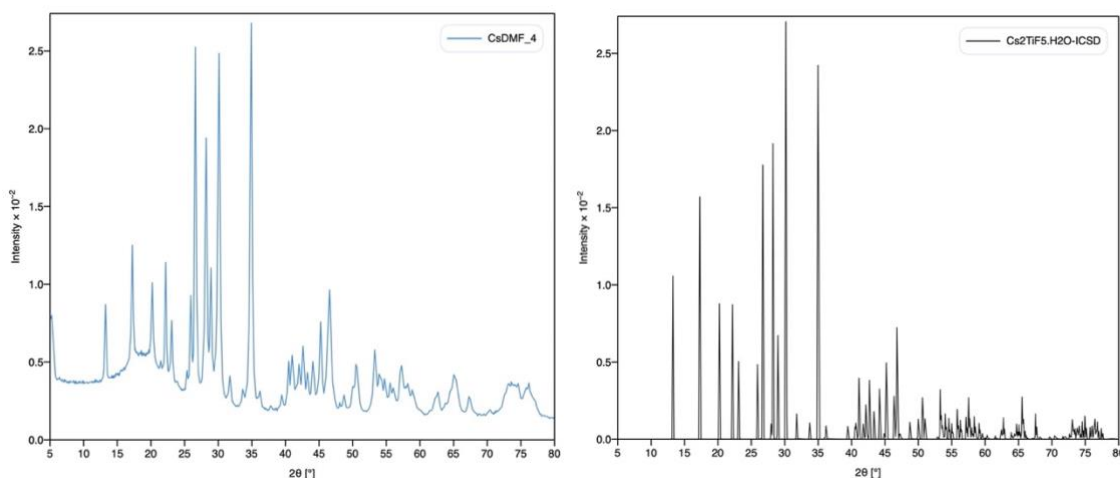


Figure 53 Powder x-ray spectrum of the crystals from CsDMF_4 (left) and reference spectrum (right) [9]

Crystals from the CsDMF_4 sample were ground down and measured on both the X'Pert and Empyrean X-ray diffractometers. The X'Pert in this case produced a pattern with less background so this was the data chosen for analysis. The XRD pattern showed a very strong match up to the reference pattern taken from ICSD. The sample spectra contained all the peaks present in the ICSD pattern, however it did also include some very small peaks, most likely due to impurity. These small impurity peaks were present at 21.4° , 25.2° and 37.9° . These impurity peaks may be from the white residue on the crystals but this was unable to be confirmed.

The sample diffraction pattern was unable to distinguish between peaks where a very small peak is close to a larger peak. This is due to the X'Pert diffractometer's power and resolution limitations. This can be seen at the peak at 28.2° in the sample which has a broader base. This peak is in fact 2 separate peaks, one very small peak at 28.01° and one large peak at 28.2° in the ICSD pattern. This is seen again at 46.5° in the sample pattern which is 2 separate peaks in the ICSD pattern.

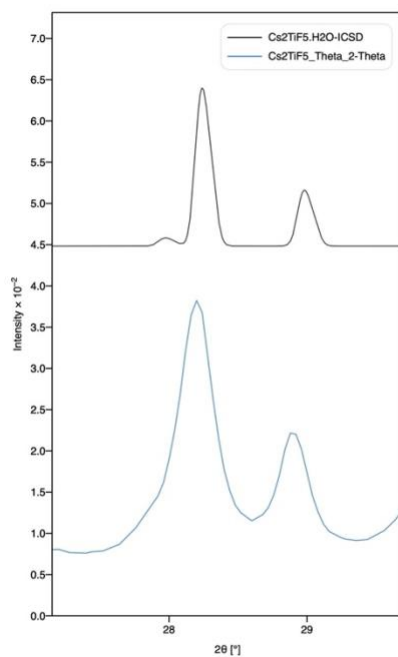


Figure 54 A close-up look at the broad peak in the CsDMF_4 sample at 28.2°

4.5.3 Rietveld Refinements

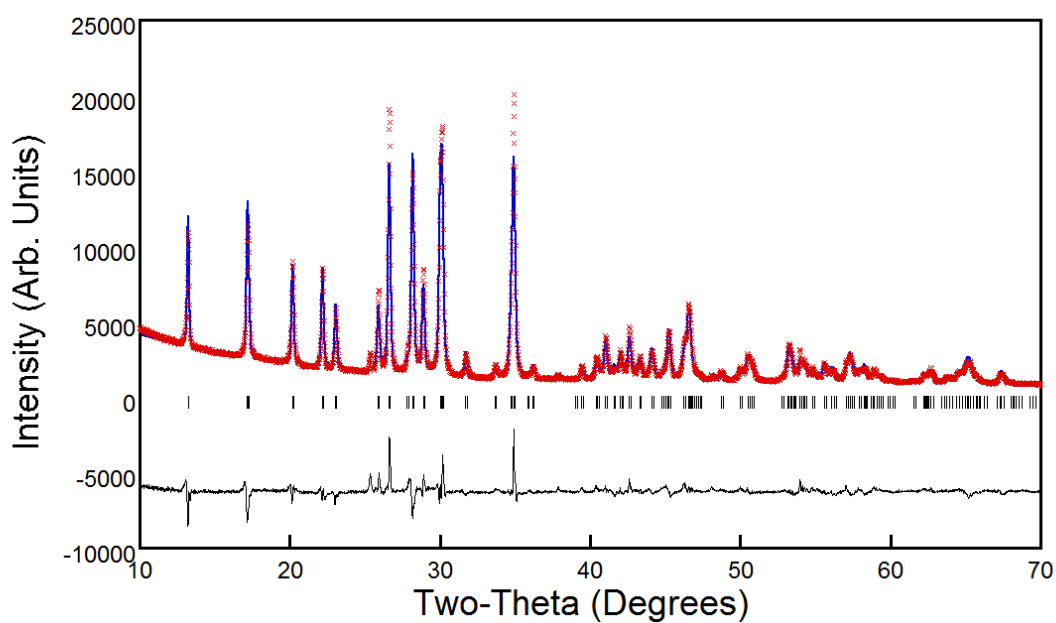


Figure 55 X'Pert powder diffraction data from CsDMF_4 sample. Observed (red), calculated (blue) and the difference (black).

Rietveld refinements of the X'Pert powder X-ray data shows that the desired product was successfully made with no significant impurities, which is highlighted by the low χ^2 value, much lower than seen in the RbDMF_3 Rietveld refinement, indicating a purer sample.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy
Cs(1)	0.28740(2)	0.28701(2)	0.25(0)	1
Ti(1)	0.5(0)	0(0)	0(0)	1
F(1)	0.32801(1)	0(0)	0(0)	1
F(2)	0(0)	0.26399(2)	0.01773(1)	1
F(3)	0.5(0)	0.01749(2)	0.25(0)	1
O(1)	0(0)	0.05255(2)	0.25(0)	1

Table 17 CsDMF_4 refined atomic coordinates taken from Rietveld refinement data of the X'Pert x-ray powder diffraction at 298K in the Cmc₂(1) space group with cell parameters: $a = 10.32487(5)$, $b = 8.79496(4)$ and $c = 8.01500(4)$ Å. χ^2 value of 13.5195

4.5.4 Single-crystal X-ray Diffraction

To confirm the product's space group, look for any signs of phase transitions and to obtain data of a higher resolution, a crystal was selected from the CsDMF_4 sample for single-crystal analysis. The measurements were performed using the in-house diffractometer at the University of Kent with the Cryostat set to 150K.

Unit cell determination

Data were obtained and refined using *CrysAlis*. The data obtained were high quality and did not require any omitting of peaks or changes to unit cell dimensions.

Unit cell data reduction

When reducing the data Cmc₂(1) and Cmc₂(1) were given as viable options for the space group as shown in the figure below. The R_{int} indicates that non-centrosymmetric, Cmc₂(1) is the best fit space group for this crystal. Reducing the data with this space

group however leads to negative electron density which is not possible. The statistics are therefore better if the centrosymmetric space group, Cmc2(1) is chosen. These better statistics could be due to centrosymmetric compounds requiring less peaks for a better fit to data and not based on Cmc2(1) being a better fit overall. As seen in the RbDMF_3 compound piezoelectric or pyroelectric tests are needed to determine with certainty the crystal's space group. For the Cmc2(1) space group an absorption correction was applied in attempts to improve the finalised data.

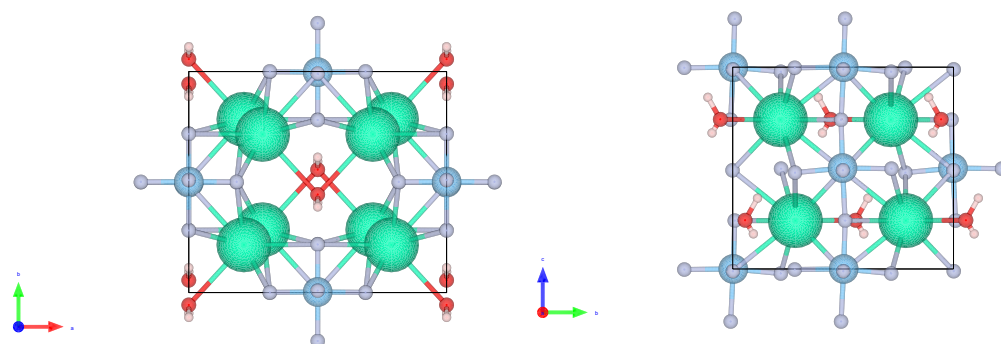


Figure 56 Electron density map of $\text{Cs}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ with the Cmc2(1) space group shown along the c axis (left) and a axis (right)

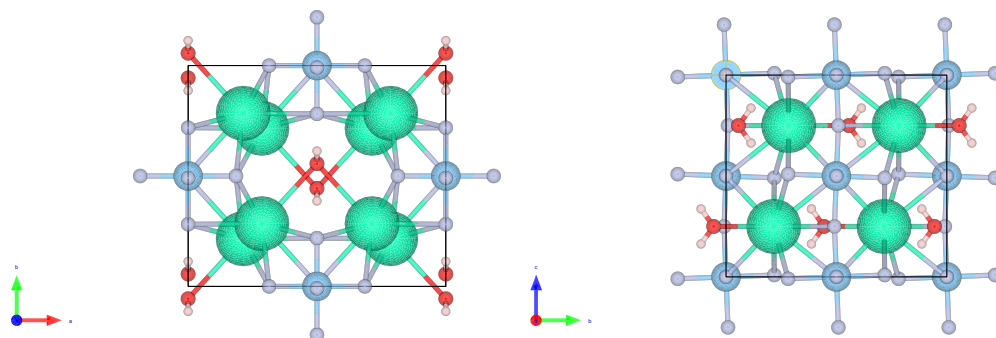


Figure 57 Electron density map of $\text{Cs}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ with the Cmc2(1) space group shown along the c axis (left) and a axis (right)

Both the Cmc2(1) and Cmc2(1) reduced data gave bond distances and bond angles that aligned with the literature values. The bond distances in the Cmc2(1) TiF_6 octahedra

range from 1.89162(9) – 2.08269(11) Å and in Cmc_m 1.89726(10) – 1.91460(9) Å. The bond distances in CsDMF have a wider range than in the RbDMF₃ compound. The bond distances in Cmc₂(1) match up better with those stated in literature, the bond distances in Cmc_m are shorter and match up better to the distances seen in RbDMF₃. The difference in distances is so small that this is not a significant concern. The bond distances can be seen in tables 19 and 21.

The F – Ti – F bond angles in Cmc₂(1) range 86.5291(0) – 173.8982(5)° and in Cmc_m 89.9843(4) – 180(0)°. Both these ranges match up to the literature values of 89.7(6) – 180.0(11)°, with the Cmc_m values being the closest. The variation in bond distances and angles align with values from the reference paper [9], showcasing that the octahedra experience Jahn-Teller distortion.

Sample name		CsDMF_4	CsDMF_4
Determined	chemical	Cs ₂ TiF ₅ .H ₂ O	Cs ₂ TiF ₅ .H ₂ O
formula			
Crystal system		Orthorhombic	Orthorhombic
Space group		Cmc₂(1)	Cmc_m
a (Å)		10.2144(5)	10.2144(5)
b (Å)		8.7496(4)	8.7496(4)
c (Å)		7.9948(4)	7.9948(4)
a		90	90
b		90	90
y		90	90
Z		4	4
V (Å ³)		714.5076	714.5076
Temperature (K)		150	150
R(int)		0.179	0.189
Crystal colour		Light violet	Light violet
Crystal shape		Needle	Needle

Table 18 CsDMF₄ single-crystal crystallographic data from Cmc_m and Cmc₂(1) space groups

CsDMF_4 Cmc _m	
Ti(1) - F(1)	1.91460(9)
Ti(1) - F(2)	1.89726(1)
Ti(1) - F(3)	2.00023(1)

Table 19 CsDMF_4 Cmc_m selected bond distances (Å)

CsDMF_4 Cmc _m	
F(1) - Ti(1) - F(1)	180(0)
F(1) - Ti(1) - F(2)	90(0)
	90.0158(4),
F(1) - Ti(1) - F(3)	89.9843(4)

Table 20 CsDMF_4 Cmc_m selected bond angles (°)

CsDMF_4 Cmc ₂ (1)	
Ti(1) - F(1)	1.93891(9)
Ti(1) - F(2)	1.89817(10)
	2.08269(11),
Ti(1) - F(3)	1.91810(10)
Ti(1) - F(4)	1.89162(9)

Table 21 CsDMF_4 Cmc₂(1) selected bond distances (Å)

CsDMF_4 Cmc ₂ (1)	
F(1) - Ti(1) - F(2)	89.5263(0)
	92.3732(0),
F(1) - Ti(1) - F(3)	86.5291(0)
F(1) - Ti(1) - F(4)	173.8982(5)

Table 22 CsDMF_4 Cmc₂(1) selected bond angles (°)

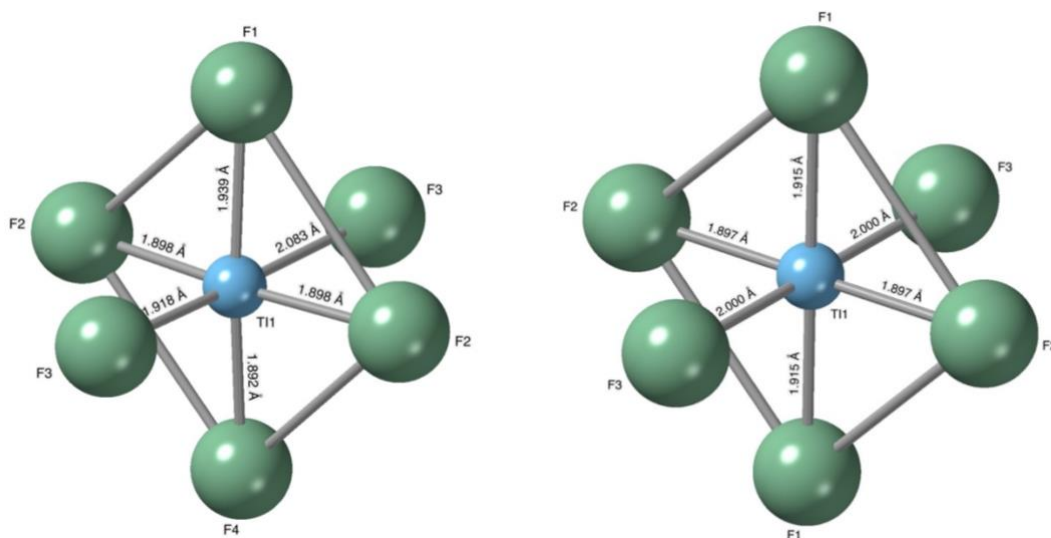


Figure 58 Difference in bond distances in the TiF_6 octahedra from the structure determination of $\text{Cmc}2(1)$ (left) and Cmcm (right)

4.5.5 X-Ray Fluorescence

Fluorine, hydrogen and oxygen are not included in these values as they are too light to be picked up.

Atom	Weight %	Experimental Atomic %	Theoretical Atomic %
Cs	82.152	62.37	66.67
Ti	17.848	37.63	33.33

Table 23 CsDMF_4 X-ray fluorescence data

The experimental atomic percent for Cs is lower than the calculated theoretical value, and the Ti atomic percentage is higher than the theoretical value. These minor discrepancies could be due to impurities in the sample such as the white powder impurity present in the sample. Overall, the experimental data aligns with the theoretical 2:1 ratio of Cs to Ti in the compound $\text{Cs}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$, supporting that the compound synthesised is close to this formula.

4.5.6 Thermogravimetric Analysis

This graph shows the mass change of CsDMF up to 300°C. It was reported in literature that this compound experiences a weight loss of 3.96% between 120 and 180°C. The compound here shows a slightly higher weight loss of 4.66% which occurs approximately between 100 and 200°C.

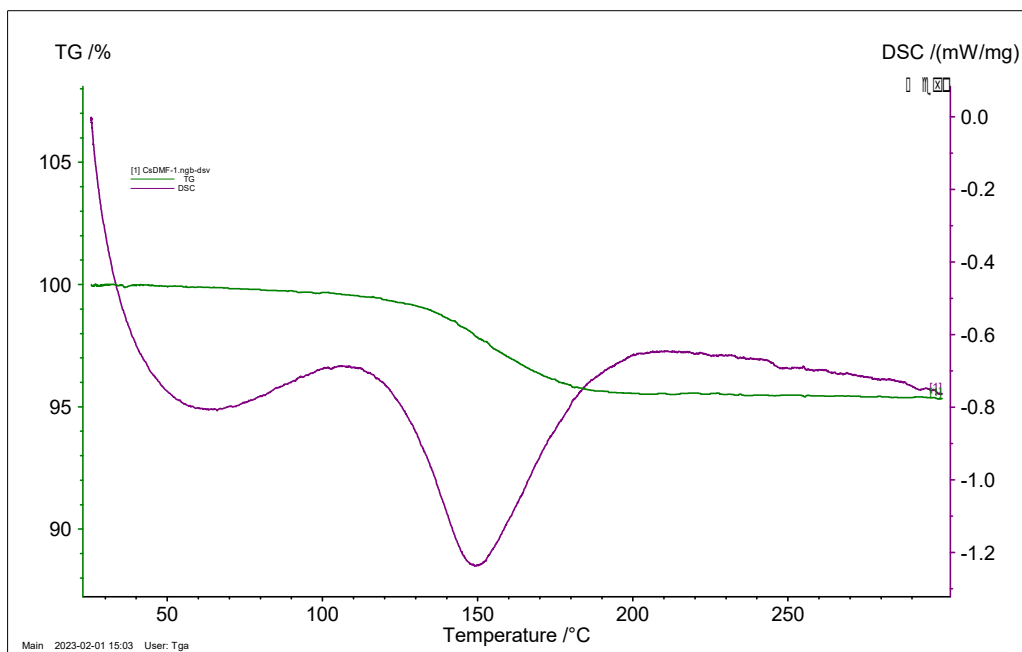


Figure 59 TGA plot showing sample mass % decreasing with increasing temperature

4.6 Cs₂TiF₅.D₂O

The Cs₂TiF₅.H₂O compound was deuterated for neutron diffraction measurements in the same way as described in section 4.2.1.

4.6.1 Rietveld Refinements

Powder diffraction measurements were performed on the D2B beamline (high-resolution two-axis diffractometer). Due to time constraints measurements were only taken at 1.6K and 300K.

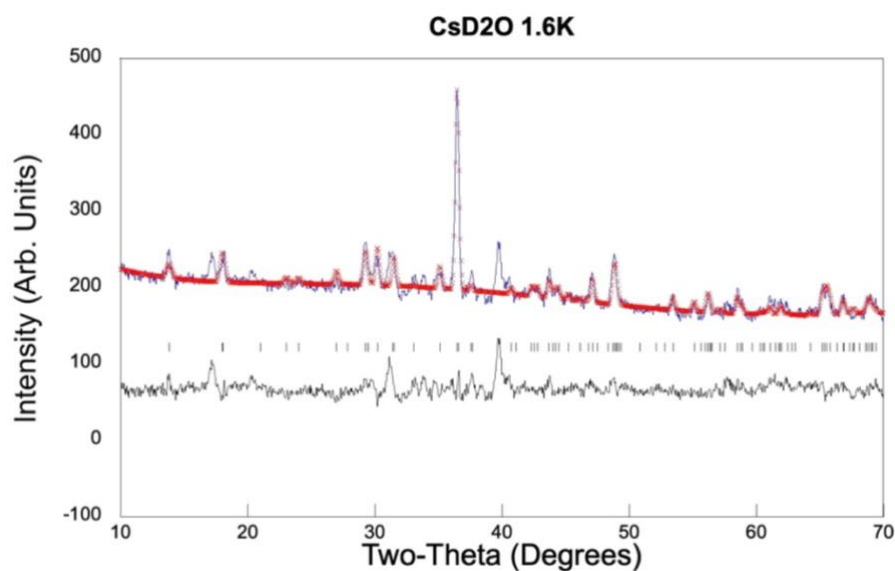


Figure 60 Neutron diffraction data from Cs₂TiF₅.D₂O sample at 1.6K. Observed (red), calculated (blue) and the difference (black).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy
Cs(1)	0.21884(1)	0.78741(1)	0.25(0)	1
Ti(1)	0(0)	0.5(0)	0(0)	1
F(1)	0(0)	0.72992(1)	-0.00912(1)	1
F(2)	0.18081(1)	0.5(0)	0(0)	1
F(3)	0(0)	0.97435(2)	0.75(0)	1
O(1)	0(0)	0.97435(2)	0.75(0)	1
D(1)	0(0)	0.89108(1)	0.67808(1)	1

Table 24 $\text{Cs}_2\text{TiF}_5 \cdot \text{D}_2\text{O}$ refined atomic coordinates taken from Rietveld refinement data of the neutron diffraction at 1.6K in the *Cmcm* space group with cell parameters: $a = 10.158619(1)$, $b = 8.741386(1)$ and $c = 7.976838(2)$ Å. χ^2 value of 3.4303.

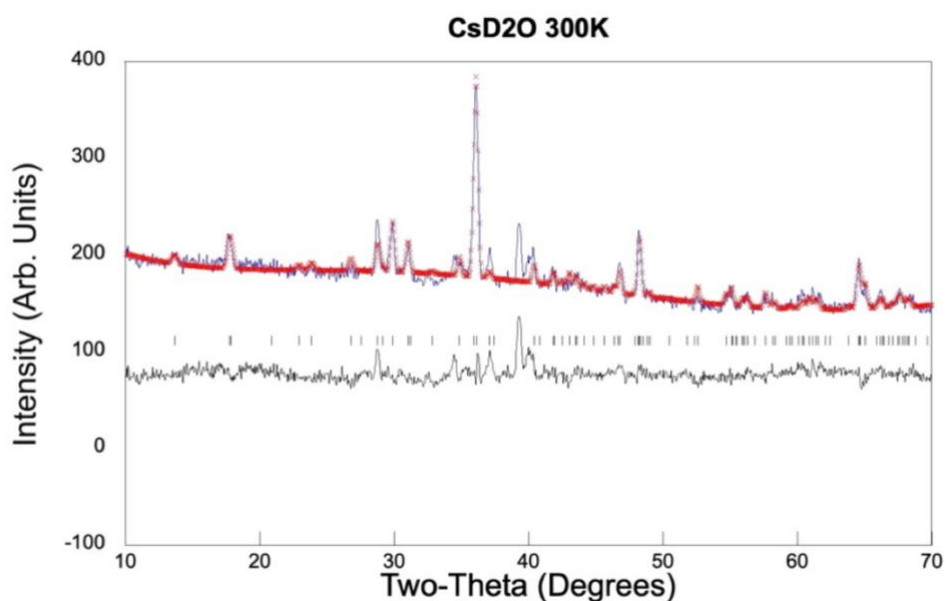


Figure 61 Neutron diffraction data from $\text{Cs}_2\text{TiF}_5 \cdot \text{D}_2\text{O}$ sample at 300K. Observed (red), calculated (blue) and the difference (black).

Atom	x	y	z	Occupancy
Cs(1)	0.21909(1)	0.79113(1)	0.25(0)	1
Ti(1)	0(0)	0.5(0)	0(0)	1
F(1)	0(0)	0.71370(1)	0.00545(1)	1
F(2)	0.18648(1)	0.5(0)	0(0)	1
F(3)	0(0)	0.49923(2)	0.25(0)	1
O(1)	0(0)	0.96603(2)	0.75(0)	1
D(1)	0(0)	0.087001(1)	0.66668(1)	1

Table 25 Cs₂TiF₅.D₂O refined atomic coordinates taken from Rietveld refinement data of the neutron diffraction at 300K in the Cmcm space group with cell parameters: $a = 10.338888(1)$, $b = 8.796904(1)$ and $c = 8.026491(2)$ Å. Chi² value of 2.3769

4.6.2 Magnetic Structure

The diffraction pattern taken at 1.6K shows 2 peaks around 17°, however only one of these peaks is present at the measurement taken at 300K. This additional scattering peak is observed at 17.06° and another can be seen at 31.2°. These peaks correspond to magnetic ordering, which disappear from the diffraction pattern at higher temperatures, suggesting antiferromagnetic order. Additional data are required to fully solve the magnetic structure.

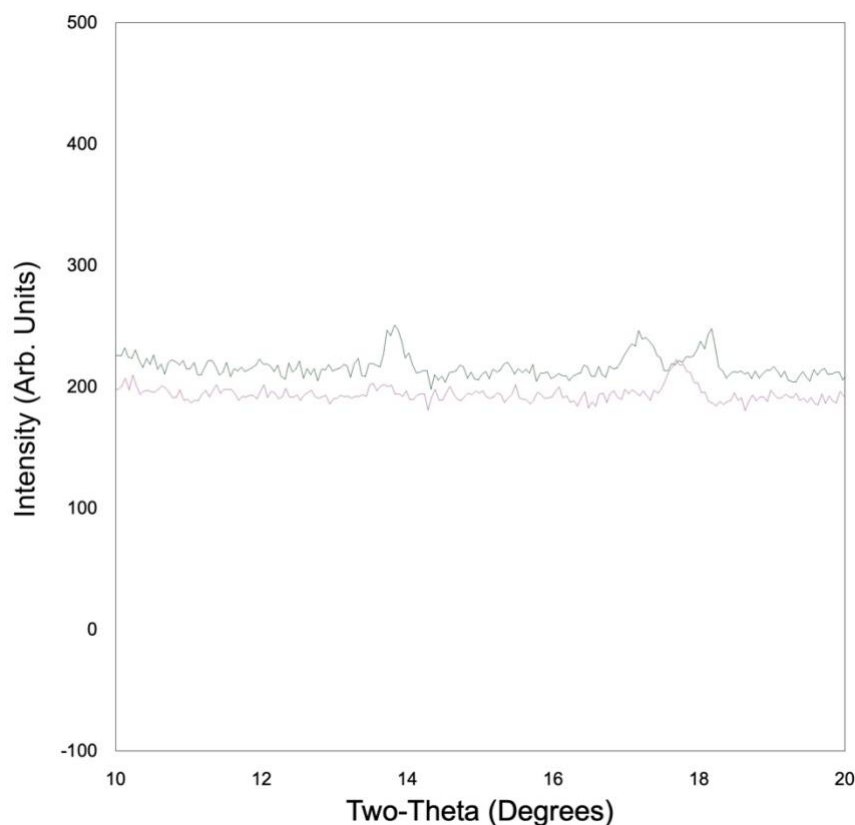


Figure 62 Close-up look at the low angle region of the $\text{Cs}_2\text{TiF}_5\cdot\text{D}_2\text{O}$ neutron diffraction patterns, 1.6K (green) and 300K (purple)

4.7 Dehydration of $\text{Cs}_2\text{TiF}_5\cdot\text{H}_2\text{O}$

4.7.1 Cs_2TiF_5

The compound $\text{Cs}_2\text{TiF}_5\cdot\text{H}_2\text{O}$ was attempted to be dehydrated to obtain Cs_2TiF_5 . Dehydration attempts proved more sensitive to failure compared to dehydration attempts of $\text{Rb}_2\text{TiF}_5\cdot\text{H}_2\text{O}$ with most attempts failing to show any significant decrease in water content. Analysis from the reference paper [9] and TGA analysis on my own sample showed that a mass loss occurs in the compound when heated to 170°C which is likely attributed to water loss.

Dehydration attempt	Reaction conditions	Results	% Transmittance for water peak around 3400 cm^{-1} obtained from FTIR
Cs_dehyd_1	180°C, 6 hours	Temperature too high, crystals cracked	N/A
Cs_dehyd_2	130°C, 20 hours	Not successful	62.6
Cs_dehyd_3	140°C, 24 hours	Not successful	84.2

Table 26 Dehydration attempts and conditions for CsDMF_4

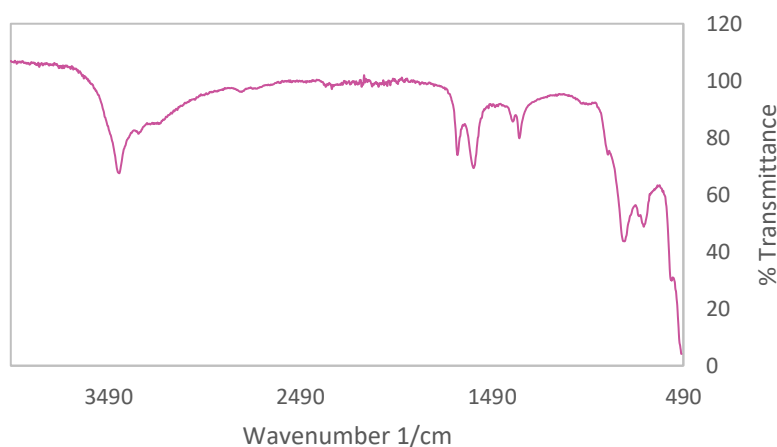


Figure 63 FTIR spectra of CsDMF_4 before dehydration

4.7.2 Single-crystal X-ray Diffraction

Crystals of Cs_dehyd_1 were taken for single-crystal diffraction to the University of Silesia in Katowice, Poland. The crystals appeared white and powdery, they had cracked because of too intense reaction conditions, same as Rb_dehyd_1.

Despite the poor quality data from one of the crystals, analysis was still possible and the unit cell was determined. The Ewald sphere shown below of the Cs_dehyd_1 crystal along the c axis shows broad arcs, almost forming concentric rings. Along the

other directions the reflection spots appear more defined and less broad. This shows that the crystal selected was very dry and powdery, giving data that looks closer to powder x-ray diffraction.

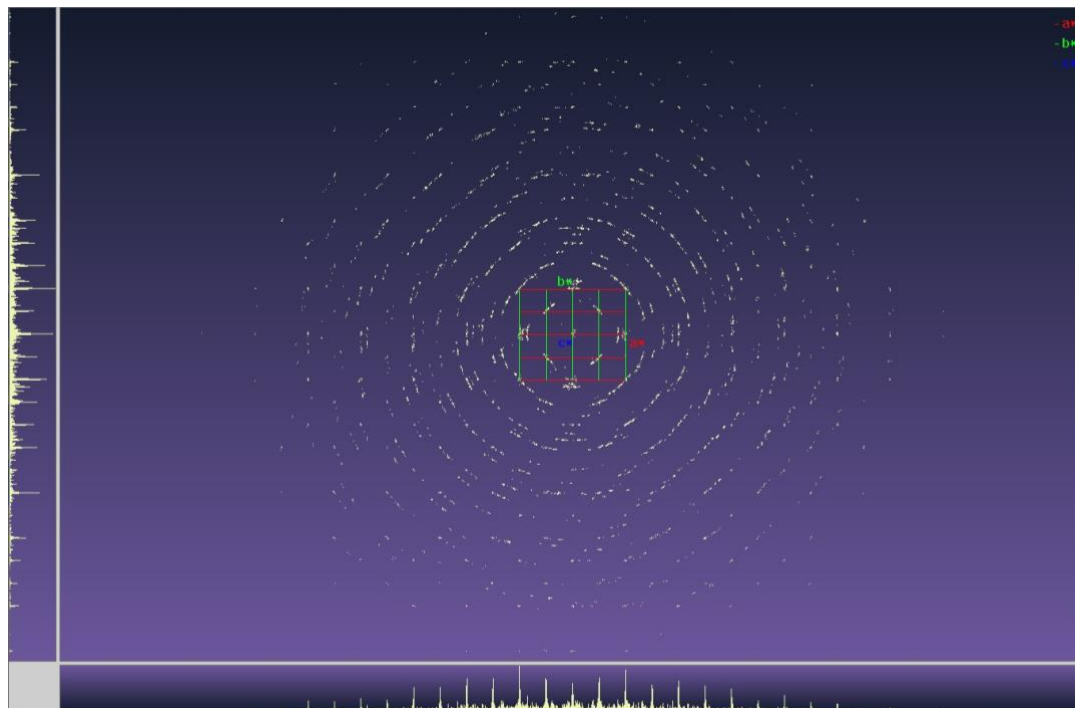


Figure 64 Ewald sphere of Cs_dehyd_1 along the c axis

Data reduction revealed that the Cs_dehyd_1 crystal had cracked into 5 different crystals, each with varying degrees of water occupancy. This explains the water occupancy levels of 1.104 in this crystal which does makes sense as the molecule had been heated at high temperatures. These multi-crystals can be seen in the Ewald sphere where 2 lines of dots overlap and cross each other. Each of these lines belongs to a different crystal with different lattice parameters and water occupancy levels. It was therefore not possible to determine by how much the sample had been dehydrated.

In attempts to reduce and determine the crystal structure the software automatically expanded the initial unit cell to $Z = 4$ as larger cells have higher symmetry. The finalised unit cell indexed at $a = 10.2181(8)$, $b = 8.7361(8)$, $c = 7.9873(3)$ and $\alpha = 89.987(5)$, $\beta = 89.968(5)$, $\gamma = 89.993(7)$.

Cmcm and Cmc2(1) were suggested as space groups for this sample. The R_{int} values for both options were worse compared to the hydrated compounds which was unsurprising considering the bad data collected. Both space groups were used for data reduction in attempts to determine their structure. The obtained electron density maps appeared the same as CsDMF_4, with water molecules still present and no observable differences in structure.

4.7.3 FTIR

The subsequent dehydration attempts used the same reaction conditions as seen for the Rb compound in section 4.4.

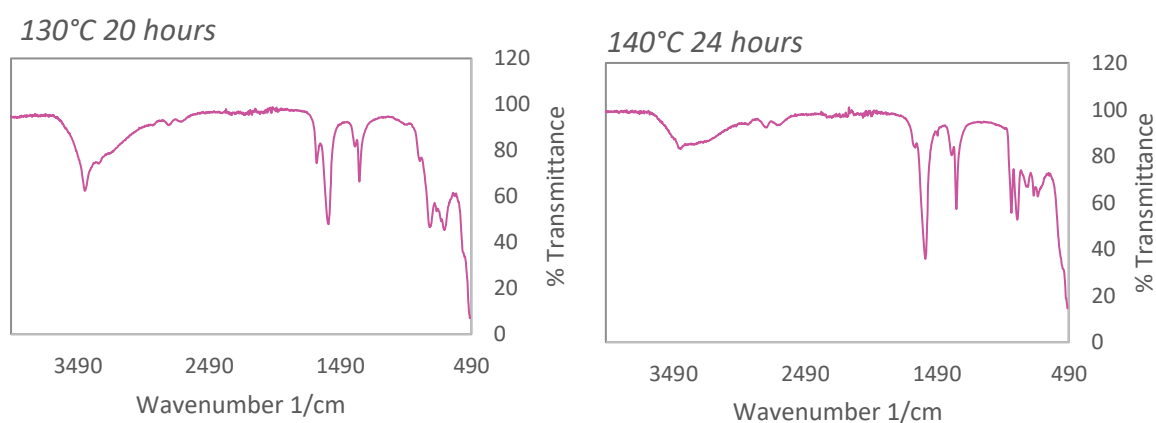


Figure 65 FTIR spectra of Cs_dehyd_2 (left) and Cs_dehyd_3 (right)

The FTIR for Cs_dehyd_2 shows no significant change to the peaks corresponding to the presence of water molecules. A mass loss of 0.0067 g (15.73 %) was observed following dehydration; however, the underlying cause remains unknown. The mass loss quoted from the reference paper [9] is 3.96 % for Cs compound. For Cs_dehyd_3 a visible change in the major peak corresponding to water was observed, but this did not match up to the high mass loss calculated. Rb_dehyd_2 became partially dehydrated under the same conditions. The conditions used in Cs_dehyd_3 were on the upper end of the limit before the crystal would crack. Further attempts to dehydrate the sample were made but the FTIR spectra showed no significant change.

Synthesis using PVP

As discussed in the synthesis chapter PVP (see Figure 14) has mainly been utilised in nanoparticle synthesis so its applications to other areas is yet to be investigated. It has been used in conjunction with DMF, which as discussed is an effective reducing agent in itself. The reducing capabilities of PVP when applied to solid state synthesis both with and without DMF are explored further in this project.

5.1 Rb₂TiF₅.H₂O

5.1.1 Synthesis Results and X-ray Characterisation

Within this chapter synthesis attempts are labelled RbPDMF_1 and RbPDMF_3 for PVP *with* DMF, and RbPVP_2 for solely PVP synthesis. RbDPVP_1 (see Table 27) utilized the same method as seen in RbDMF_3 with PVP (0.2006 g, 0.019 mol dm⁻³) added. The aim of this reaction was to evaluate how adding PVP affected synthesis and the crystal product. The reaction successfully produced light purple / clear crystals (see Figure 66) which were later confirmed using single-crystal X-ray diffraction to match the expected lattice parameters for Rb₂TiF₅.H₂O. The crystals were however coated in small clusters of white and grey granules which were assumed to be PVP. This is something that has been observed in the synthesis of silver nanoparticles where PVP forms a paste containing silver nanoparticles within. Efforts were made to wash as much of the PVP as possible using acetone, but many clumps remained. As PVP is an organic compound this did not interfere with X-ray analysis.

Synthesis	Reaction conditions	Reagents	Product
RbDPVP_1	230°C, 72 hours in oven	RbF (1.567 g, 15 mmol); TiO ₂ (0.1203 g, 1.5 mmol); DMF (1.5 ml, 0.019 mol dm⁻³); PVP (0.2006 g, 1.8 mmol) H ₂ O (4 ml)	Clusters of pale granules coating shards of light purple / clear crystals
RbPVP_2	230°C, 72 hours in oven	RbF (1.567 g, 15 mmol); TiO ₂ (0.1203 g, 1.5 mmol); PVP (0.2006 g, 1.8 mmol) H ₂ O (4 ml)	Light beige clusters with very thin shards of clear crystals within
RbDPVP_3	230°C, 72 hours in oven	RbF (1.567 g, 15 mmol); TiO ₂ (0.1203 g, 1.5 mmol); DMF (1.5 ml, 0.019 mol dm⁻³); PVP (0.0133 g, 0.12 mmol) H ₂ O (4 ml)	No crystalline product

Table 27 Dehydration attempts and conditions for Rb₂TiF₅.H₂O using PVP and/or DMF

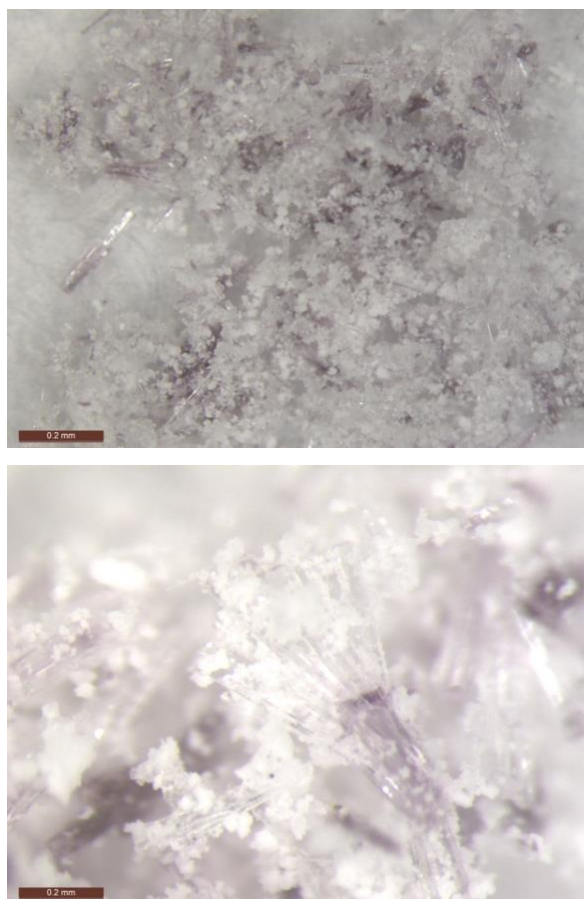


Figure 66 Microscope photo of (RbPDMF_1) product using PVP with DMF

The powder X-ray diffraction of RbPDMF_1 is shown in Figure 67. Powder x-ray diffraction and partial single-crystal analysis verified that these light purple crystals match the structure of the $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ structure from the reference paper [9].

The X-ray pattern matches all the characteristic peaks expected from the reference [9]. The pattern displays the same feature seen in RbDMF_3 where 3 peaks in the 17.5° - 18.5° region are overlapping. The main difference is a small impurity peak present at 25.5° .

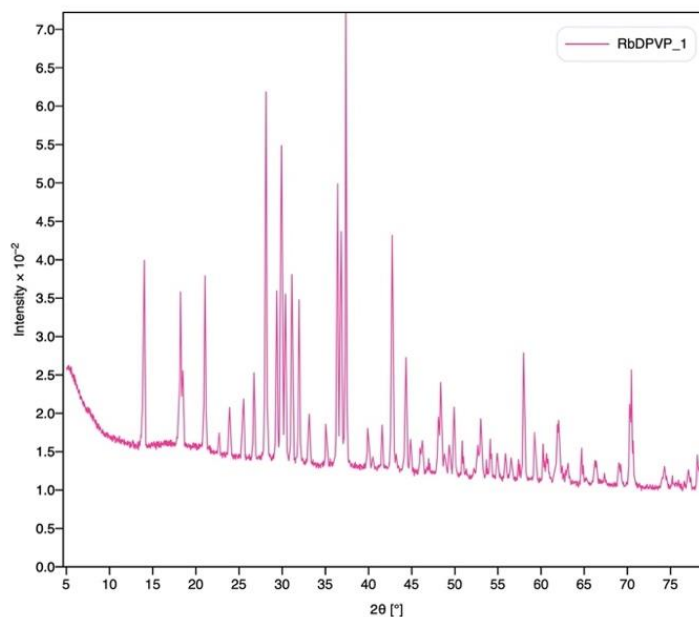


Figure 67 Powder X-ray diffraction pattern of RbDPVP_1

This reaction was repeated using less PVP (0.0133 g, 0.12 mmol) to see if using less would reduce the amount of clusters of PVP surrounding the crystals. The reaction failed to produce any crystalline product for reasons that are unclear as the reaction works both with and without PVP so unclear why using a small amount of PVP could cause the reaction to fail.

To investigate how effective PVP could act as the sole reducing agent the same reaction was repeated, this time without any DMF. RbPVP_2 produced clumps of light beige granules which on further inspection contained thin shards of clear crystals. Despite the differences in colour and appearance of the crystals, they too matched the expected lattice parameters for $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ when analysed using single-crystal X-ray diffraction.

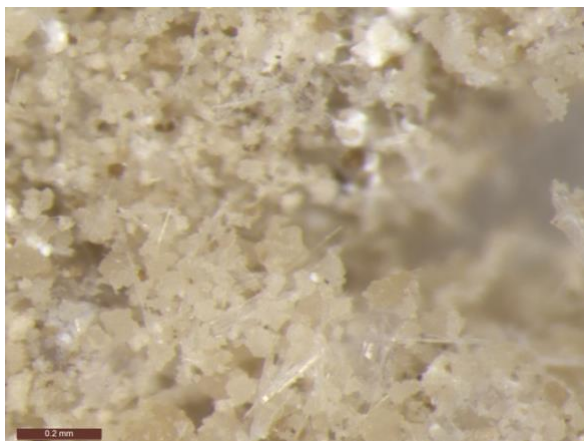


Figure 68 Microscope photo of (RbPVP_2) product using only PVP

The pattern for RbPVP_2 appears almost identical to that of RbDPVP_1 with the same features and impurities mentioned before. The pattern has a higher background which is most likely due to the amorphous scattering of from the PVP. The pattern does show another peak at 21.6° which is not present in RbDPVP_1, RbDMF_3 or the $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ reference spectrum. An experimental reference pattern for PVP was measured. Its pattern shows a very large broad peak in the low angle region, the only sharp peaks it shows are small peaks at 7.4° , 21.6° and 23.9° . The 21.6° peak in the RbPVP_2 pattern matches this PVP characteristic peak.

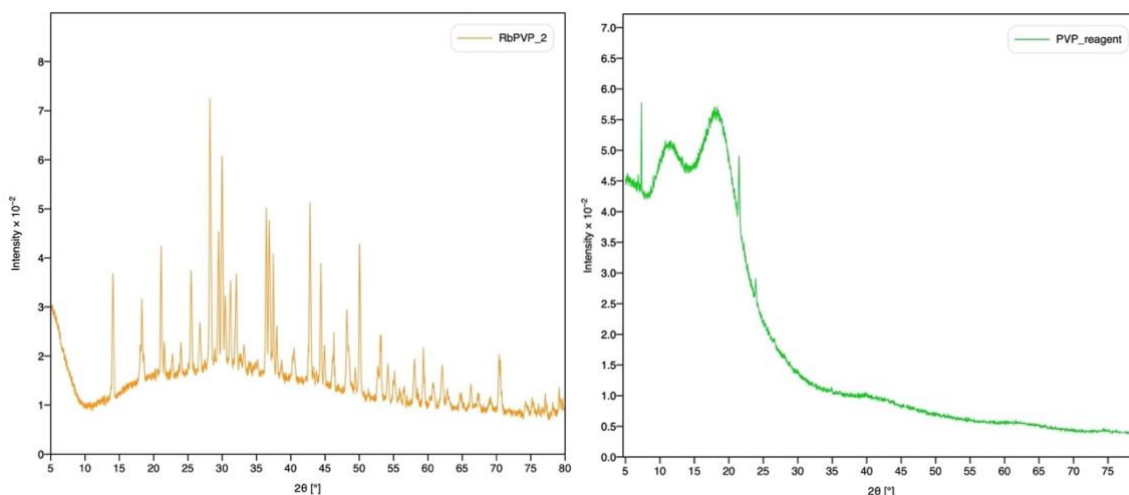


Figure 69 Powder X-ray diffraction pattern of RbPVP_2 (left) and PVP reagent (right)

Attempts to synthesise $\text{Cs}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ using PVP / PVP with DMF were unsuccessful. As seen in the previous section efforts to synthesise $\text{Cs}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ using DMF required longer time in the oven when compared to the synthesis of $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$. Following the same approach, after the first attempt to synthesise $\text{Cs}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ using PVP failed the oven time was increased for the next few attempts. The following attempts all failed however for unclear reasons. As $\text{Cs}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ appears to be a trickier compound to synthesise, being more sensitive to reaction conditions perhaps the reason why the reaction failed lies somewhere in the quantities of reagents. Maybe the quantities of reagents were not favourable to the successful production of $\text{Cs}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ crystals.

5.1.2 Single-crystal X-ray Diffraction

Crystals from RbDPVP_1 and RbPVP_2 were analysed using single-crystal X-ray diffraction in the same way as described for RbDMF_3, however only pre-experiment scans were performed as this, combined with powder X-ray diffraction data, was enough to conclude the desired compound had been made. For the RbPVP_2 crystal the pre-experiment scan indexed 78% of the unit cell, the lattice parameters it obtained match those obtained from RbDMF_3. This was considered high enough quality data to confirm the crystal's identity and not need to perform a full scan. For RbDPVP_1 the pre-experiment scan highlighted that the chosen crystal was long and twinned. Although the pre-experiment scan was unable to identify a unit cell (over 20 lattice parameter values were predicted) this, plus the powder X-ray diffraction data was enough to be confident that the crystals were $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$. These results reiterate the ability for PVP to act as a reducing agent, even by itself, to reduce the notoriously difficult Ti^{4+} to Ti^{3+} .

Synthesis using Triethylamine

As discussed in the synthesis chapter triethylamine (see Figure 15), like PVP has been used in nanoparticle synthesis as both a stabilizing agent and reducing agent. Its ability to act as a reducing agent for other solid state applications is yet to be investigated.

6.1 $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ and $\text{Cs}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$

6.1.1 Synthesis Results and X-ray Characterisation

Triethylamine produced products with a different appearance to those synthesised using DMF and/or PVP. It proved difficult to tell if the reaction had been successful on first observations. Further analysis proved otherwise, showcasing that crystals can look different. Synthesis of both $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ and $\text{Cs}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ were attempted utilizing triethylamine as the sole reducing agent. The same method and reaction conditions used for the successful synthesis of RbDMF_3 were replicated here with the triethylamine replacing the DMF.

Synthesis	Reaction conditions	Reagents	Product
RbTRI_1	230°C, 72 hours in oven	RbF (1.567 g, 15 mmol); TiO ₂ (0.1203 g, 1.5 mmol); triethylamine (1.5 ml) ; H ₂ O (4 ml)	White clumpy sludge
CsTRI_1	230°C, 72 hours in oven	RbF (1.567 g, 15 mmol); TiO ₂ (0.1203 g, 1.5 mmol); triethylamine (1.5 ml) ; H ₂ O (4 ml)	White powder and cloudy liquid

Table 28 Synthesis attempts and conditions for $\text{Rb}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ and $\text{Cs}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$ using triethylamine

CsTRI_1 produced an uncrystallised product which caused speculation that the molar ratio for this reaction was incorrect. As seen before syntheses involving CsF are more sensitive to specific reaction conditions to be successful.



Figure 70 Microscope photo of RbTRI_1

RbTRI_1 produced a product that on first inspection appeared to be a white clumpy sludge. After filtration and leaving the product to dry overnight in a drying cabinet set to $< 50^{\circ}\text{C}$ a crystalline product was more visible. Under the microscope very thin, clear shards were in the sample amongst granules.

Crystals produced from RbDMF_3 and PVP did indeed have some crystals appear a light violet colour, but there were still many crystals which appeared clear, suggesting that both the light violet and clear crystals are the product but perhaps in different phases. Confirming that even though light violet crystals were expected here, it does not mean the reaction was unsuccessful.

The RbTRI_1 X-ray powder diffraction pattern displays all the characteristic peaks expected in $\text{Rb}_2\text{TiF}_5\cdot\text{H}_2\text{O}$, plus the impurity peak at 25.3° which is also present in RbDMF_3. The peak at 29.9° is more intense than in the reference pattern, which is also seen in RbDMF_3. An additional, unknown impurity peak is present at 38.7° .

In the region of 36.2° - 38.1° the sample shows 4 peaks; 2 of which are broad and probably contain multiple peaks that are hard to distinguish. The reference pattern shows only 3 peaks.

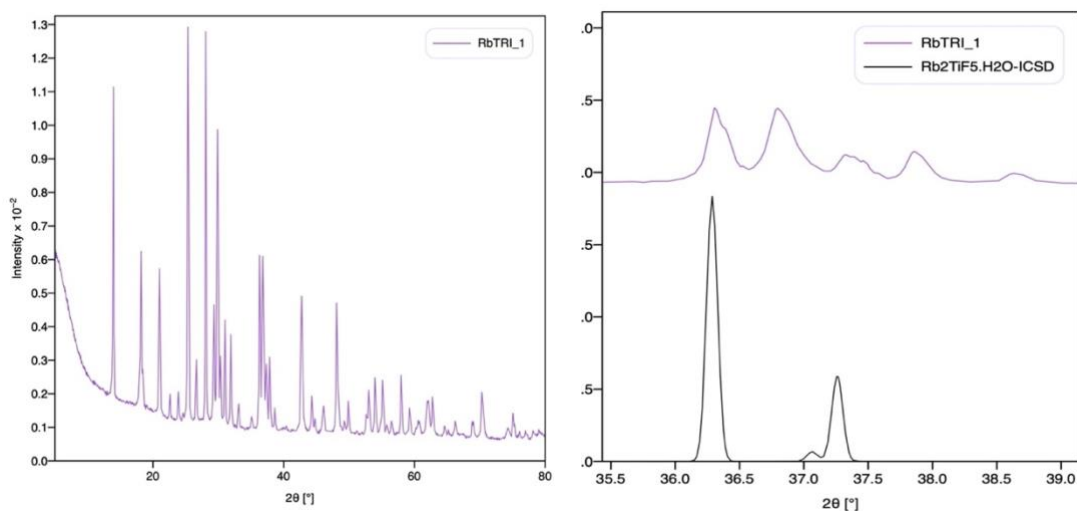


Figure 71 Powder X-ray diffraction pattern of RbTRI_1 crystals (left) and a close up look at the peaks in the region of 36.2° - 38.1° compared against the reference pattern (right) [9]

6.1.3 Single-crystal X-ray Diffraction

The lattice parameters obtained from this sample via single-crystal X-ray diffraction were almost identical to those obtained from RbDMF_3, confirming both crystals are Rb₂TiF₅.H₂O. (Atom positions for H are not accurate as X-rays were used)

Atom	x	y	z	Occupancy
Rb(1)	0.28389(1)	0.78236(1)	0.75(0)	1
Ti(1)	0.5(0)	0.5(0)	0.5(0)	1
F(1)	0.30178(1)	0.5(0)	0.5(0)	1
F(2)	0.5(0)	0.27422(2)	0.50857(2)	1
F(3)	0.5(0)	0.50819(2)	0.75(0)	1
O(1)	0.5(0)	0.03985(2)	0.75(0)	1
H(1)	0.5(0)	-0.4127(2)	0.75(0)	1
H(2)	0.5(0)	1.31464(2)	0.75(0)	1

Table 29 RbTRI_1 atomic coordinates taken from single-crystal data measured at 150K

Sample name		RbTRI_1	RbDMF_3 original
Determined	chemical	Rb ₂ TiF ₅ .H ₂ O	Rb ₂ TiF ₅ .H ₂ O
formula			
Crystal system		Orthorhombic	Orthorhombic
Space group		Cmcm	Cmcm
a (Å)		9.5171(6)	9.5161(6)
b (Å)		8.4119(6)	8.4187(5)
c (Å)		7.8470(5)	7.83171(5)
a		90	90
b		90	90
γ		90	90
Z		4	4
V (Å ³)		628.21(7)	627.42(7)
Temperature (K)		150	150
R(int)		0.064	0.059
Crystal colour		Clear	Clear
Crystal shape		Needle	Needle

Table 30 Single-crystal crystallographic data comparison of RbTRI_1 and RbDMF_3 original unit cell

Conclusion

In this project we proved that Ti^{3+} compounds could be synthesised hydrothermally using unconventional reducing agents. $\text{Rb}_2\text{TiF}_5\cdot\text{H}_2\text{O}$ was successfully synthesised using DMF, PVP and TEA. $\text{Cs}_2\text{TiF}_5\cdot\text{H}_2\text{O}$ was synthesised via DMF only.

These compounds were characterised using X-ray and neutron diffraction techniques, both are orthorhombic and belong to the *Cmcm* space group. The TiF_6 octahedra in $\text{Cs}_2\text{TiF}_5\cdot\text{H}_2\text{O}$ showed the greatest Jahn-Teller distortion which aligns with literature observations to date. No significant structural changes occurred when water molecules were removed from the structure of $\text{Rb}_2\text{TiF}_5\cdot\text{H}_2\text{O}$.

Neutron diffraction confirmed that $\text{Cs}_2\text{TiF}_5\cdot\text{H}_2\text{O}$ is magnetic, which has not yet been reported but higher quality data is needed to solve the magnetic structure. $\text{Rb}_2\text{TiF}_5\cdot\text{H}_2\text{O}$ did not show additional scattering, but it is possible that the diffractometer was not powerful enough to pick up on this.

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Supplementary Material

Compound	Reducing agent / solvent used	Successful (Y) / Failed (N)	Reasons for failure
Rb ₂ TiF ₅ ·H ₂ O	DMF PVP DMF + PVP Triethylamine	Y Y Y Y	-
Cs ₂ TiF ₅ ·H ₂ O	DMF	Y	-
Rb ₁ Cs ₁ TiF ₅ ·H ₂ O	DMF	?	
Rb _{0.5} Cs ₁ TiF ₅ ·H ₂ O	DMF	?	White product formed but unable to analyse, product turned into sludge / was destroyed when touched
Rb _{1.5} Cs _{0.5} TiF ₅ ·H ₂ O	DMF	?	
Rb ₂ TiF ₅ ·D ₂ O	DMF + D ₂ O	Y	-
Cs ₂ TiF ₅ ·D ₂ O	DMF + D ₂ O	Y	-
K ₂ TiF ₅ ·H ₂ O	DMF	Unclear	Unclear
Rb ₂ FeF ₅ ·H ₂ O	TEA	N	
Rb ₂ TiF ₆	TEA	Y	
CsFe ₂ F ₆	TEA	N	Unclear
K ₂ TiF ₅	DMF	N	Unclear
Rb ₂ TiF ₅	TEA	N	Unclear
Cs ₂ TiF ₅	TEA	N	Unclear
KFe ₂ F ₅	TEA	N	Unclear
K ₂ CrF ₅	TEA	N	Unclear. Product may have contained unreacted reagents
Rb ₂ CrF ₅	TEA	N	XRD of product showed broad peaks and multiple phases present, unable to identify compound
Rb ₂ FeF ₅	TEA	N	Crystalline product formed but was destroyed during filtration
K ₂ TiOF ₄	TEA	N	
Cs ₂ KTiF ₆	DMF	N	No crystalline product formed
RbCuFeF ₆	TEA	N	Unclear
Cs ₂ TiF ₆	TEA	N	Unclear
RbZnTiF ₆	DMF	N	Product formed white clumps of ZnF ₂ and TiO ₂
RbNiTiF ₆	DMF	N	No product formed
RbCuTiF ₆	DMF	N	Unclear

Table A1 List of every compound synthesised and success rates

Magnetic Structure of $\text{Rb}_2\text{FeF}_5\cdot\text{D}_2\text{O}$

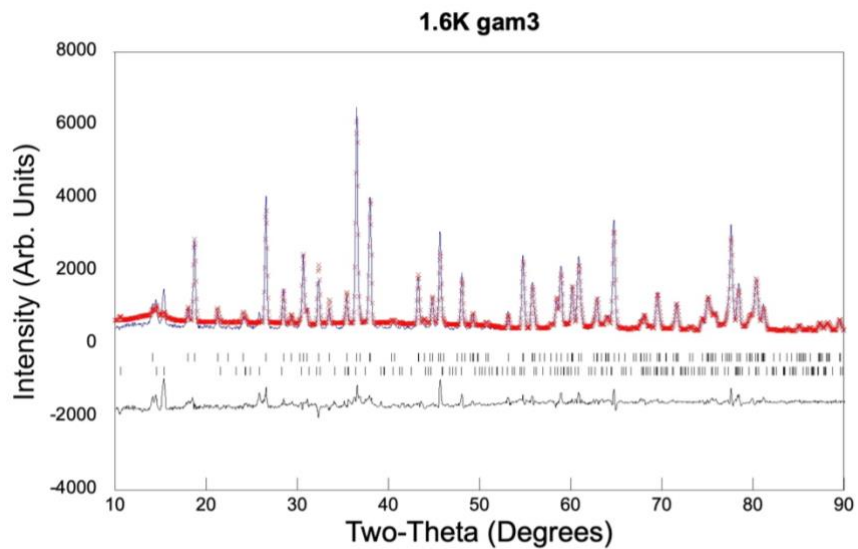


Figure A1 Neutron diffraction data from $\text{Rb}_2\text{FeF}_5\cdot\text{D}_2\text{O}$ sample at 1.6K. Observed (red), calculated (blue) and the difference (black). Gam3 BASIREPS applied

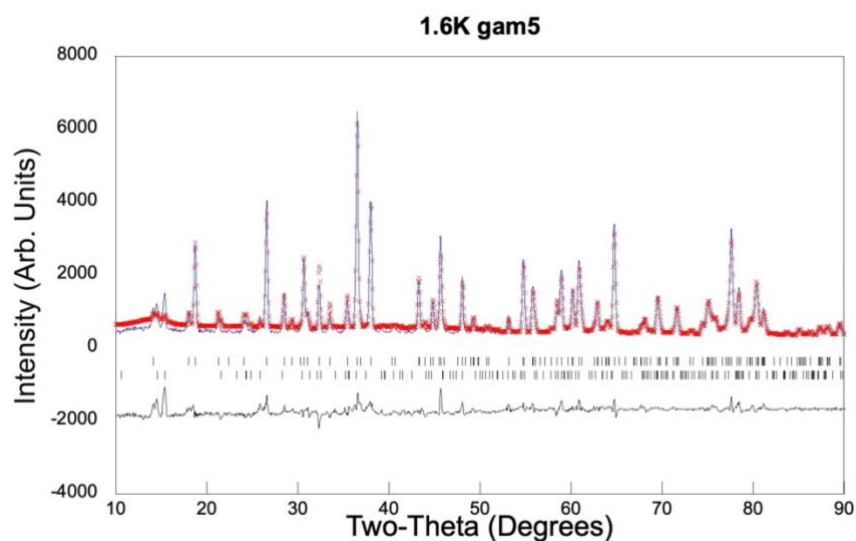


Figure A2 Neutron diffraction data from $\text{Rb}_2\text{FeF}_5\cdot\text{D}_2\text{O}$ sample at 1.6K. Observed (red), calculated (blue) and the difference (black). Gam5 BASIREPS applied

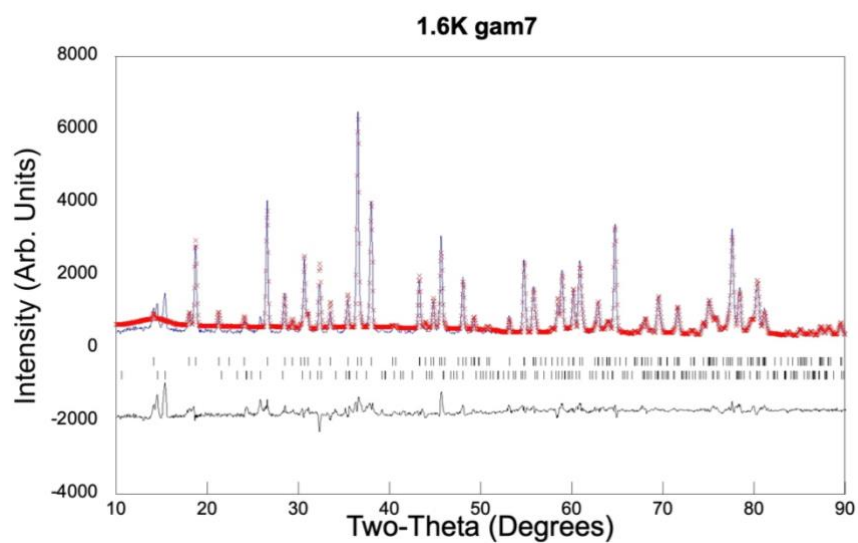
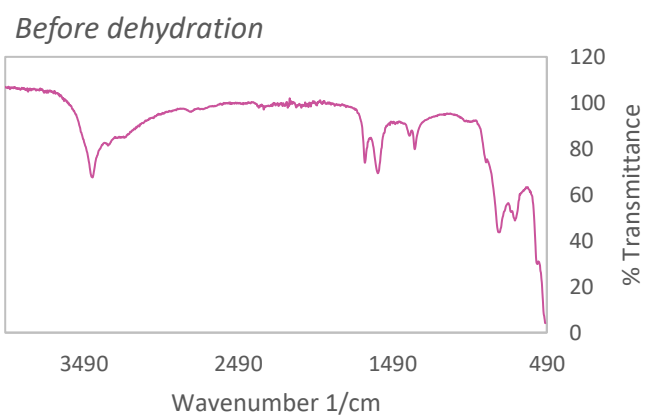


Figure A3 Neutron diffraction data from $\text{Rb}_2\text{FeF}_5\cdot\text{D}_2\text{O}$ sample at 1.6K. Observed (red), calculated (blue) and the difference (black). Gam7 BASIREPS applied

$\text{Cs}_2\text{TiF}_5\cdot\text{H}_2\text{O}$



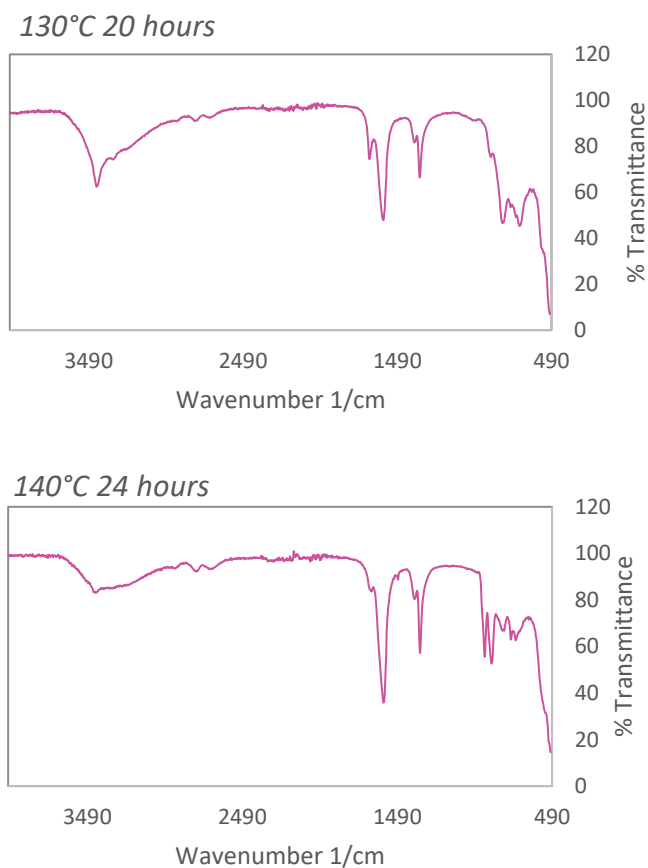


Figure A4 FTIR of further dehydration attempts of $\text{Cs}_2\text{TiF}_5 \cdot \text{H}_2\text{O}$

Atom	x	y	z	Occupancy
Cs1	0.28607(1)	0.28395(1)	0.23961(1)	1
Ti1	0.5(0)	0.00256(1)	0(0)	1
F1	0(0)	0.28098(8)	-0.00276(8)	1
F2	0.31437(1)	0.00088(1)	-0.01094(1)	1
F3	0.5(0)	0.00915(2)	0.23981(2)	1
F4	0.5(0)	0.21778(2)	-0.02247(2)	1
O1	0(0)	0.05612(2)	0.24151(2)	1
H1	0(0)	0.0936(2)	0.17414(2)	1
H2	0(0)	0.11239(2)	0.35069(2)	1

Table A2 $\text{CsDMF}_4 \text{Cmc}2(1)$ atomic coordinates taken from single-crystal data

Atom	x	y	z	Occupancy
Cs1	0.21619(1)	0.2161(1)	0.25(0)	1
Ti1	0.5(0)	0(0)	0(0)	1
F1	0.5(0)	0.21866(1)	0.00929(2)	1
F2	0.31426(1)	0(0)	0(0)	1
F3	0.5(0)	-0.00893(2)	0.25(0)	1
O1	0.5(0)	0.44398(2)	0.25(0)	1
H1	0.5(0)	0.38681(2)	0.16326(2)	1

Table A3 CsDMF_4 Cmc atomic coordinates taken from single-crystal data

Rb₂TiF₅.H₂O

Atom	x	y	z	Occupancy
Rb(1)	0.2835(5)	0.2820(6)	0.25(0)	1
Ti(1)	0.5(0)	0(0)	0(0)	1
F(1)	0.3006(4)	0(0)	0(0)	1
F(2)	0.5(0)	0.0109(7)	0.25(0)	1
F(3)	0.5(0)	0.2255(4)	-0.0086(4)	1
O(1)	0(0)	0.0358(7)	0.25(0)	1
H(1)	0.0320(9)	0.0920(8)	0.1540(7)	1

Table A4 RbDMF_3 atomic coordinates taken from single-crystal data measured at 150K