



Article Phase Formation in NaH_2PO_4 - $VOSO_4$ - $NaF-H_2O$ System and Rapid Synthesis of $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$

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Abstract: Renewable electricity products, for example, from wind and photovoltaic energy, need largescale and economic energy storage systems to guarantee the requirements of our daily lives. Sodiumion batteries are considered more economical than lithium-ion batteries in this area. Na₃V₂(PO₄)₂F₃, NaVPO₄F, and Na₃(VO)₂(PO₄)₂F are one type of material that may be used for Na-ion batteries. In order to better understand the synthesis of these materials, the phase formation in a NaH₂PO₄– VOSO₄–NaF–H₂O system under hydrothermal conditions was studied and is reported herein. This research focused on the influences of the sodium fluoride content and hydrothermal crystallization time on phase formation and phase purity. The phase transformation between Na(VO)₂(PO₄)₂(H₂O)₄ and Na₃V₂O_{2x}(PO₄)₂F_{3-2x} was also studied. Na₃V₂O_{2x}(PO₄)₂F_{3-2x} with a high degree of crystallinity can be obtained in as short as 2 h via hydrothermal synthesis using a conventional oven at 170 °C without agitation. All compounds obtained in this research were studied mainly using powder X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectrometry, and Fouriertransform infrared spectroscopy.

Keywords: hydrothermal synthesis; sodium vanadium fluorophosphate; battery; phase transformation

1. Introduction

Batteries are more and more important in our daily lives. Besides portable devices like cellular phones and portable computers, they also find applications in hybrid and electronic vehicles. Lithium-ion batteries have been used in many of these cases. The development of this type of material with better quality is still ongoing. However, since lithium is a not-so-accessible material [1], it is also important to find cheaper alternatives for lithium-based cathode materials. It is known that sodium secondary batteries have a lower energy density than lithium ones. However, although they may not be suitable for portable devices, they are a proper choice for large-scale energy storage, which can be used to store "peak" electrical energy from the unstable generation of renewable electricity, for example, from wind energy, photovoltaic energy, and so on. Large-scale energy storage is the key to a reliable, clean electricity supply.

A recent paper reviewed the use of polyanion sodium vanadium phosphates in the next generation of sodium-ion batteries [2]. Polyanion fluorophosphates [3–5] have also been proposed as safer compounds for battery applications and present better working potential. This is related to the structural characteristics of these compounds since the inductive effect derived from phosphate-based functional groups enhances their working potential [6], and, theoretically, the introduction of fluorine into the phosphate-based structure increases the cation insertion voltage [7]. A group of compounds, including Na₃V₂(PO₄)₂F₃ [8–12], Na₃(VO)₂(PO₄)₂F [13], and NaVPO₄F [6], have received much attention as substitutes for lithium-based cathode materials. Their ion insertion/extraction properties are related to the presence of the V³⁺/V⁴⁺ redox couple. They are also safer, made from cheaper raw resources, and show a higher working potential. These compounds are usually synthesized using a two-step solid-state reaction [8], hydrothermal reactions [14], or the sol–gel method [15]. These processes are time-consuming or complicated. Mao et al.



 $\begin{array}{l} \label{eq:citation: Lin, Z. Phase Formation in $$NaH_2PO_4-VOSO_4-NaF-H_2O System $$and Rapid Synthesis of $$Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$. Crystals $$2024, $$14, 43. $$https://doi.org/10.3390/$$cryst14010043$$} \end{array}$

Academic Editor: Yutaka Moritomo

Received: 11 December 2023 Revised: 21 December 2023 Accepted: 26 December 2023 Published: 28 December 2023



Copyright: © 2023 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). tried to prepare Na₃V₂(PO₄)₂F₃ at 180 °C for 1 h in a water–glycerol mixed solvent using microwave heating. However, the crystalline phase was obtained only after annealing at 650 °C for 8 h [16]. Burova et al. reported the microwave-assisted hydrothermal synthesis of Na₃V₂O_{2x}(PO₄)₂F_{3-2x}. Different reducing agents were tested [17]. Although the compound can be rapidly crystallized at 180–220 °C in less than 15 min, a microwave hydrothermal reactor with constant stirring is needed, which limits its application on a large industrial scale. Recently, Na₃V₂(PO₄)₂F₃ and NaVPO₄F were prepared via solvothermal synthesis at 240 °C for 12 h and 72 h, respectively, using benzyl alcohol as a solvent. Sodium ethoxide was used as the Na source and 20 M hydrofluoric acid as the F source [18]. Hu and Jiang prepared Na₃V₂(PO₄)₂F₃ via a solvothermal process at 150 °C for 1 day in a mixed solvent of tetraglycol and lactic acid with little water [19]. Bi et al. prepared Na₃(VO)₂(PO₄)₂F at 170 °C for 9 h using sodium fluoride as the sodium and fluorine source, V₂O₅ as the V source, and oxalic acid as a reductive agent [20].

Understanding and controlling the external factors affecting the crystallization process and the overall stability of crystals are very important. In this paper, the crystallization process in a NaH₂PO₄–VOSO₄–NaF–H₂O system under hydrothermal conditions was studied, and the focus was on the influence of the sodium fluoride amount in the precursor and the hydrothermal heating time at the set point temperature on the phase formation and phase purity. Easier and less time-consuming synthetic conditions for preparing highcrystalline Na₃V₂O_{2x}(PO₄)₂F_{3-2x} compounds were obtained, which can be as short as 2 h using a conventional oven at 170 °C without agitation.

2. Experimental Section

2.1. Materials

Sodium dihydrogen phosphate (98–100.5 wt.% NaH₂PO₄; Riedel-de-Haën, Seelze, Germany), vanadyl sulfate hydrate (97 wt.% VOSO₄·3.55H₂O; Aldrich, St. Louis, MO, USA), and sodium fluoride (99 wt.% NaF; Merck, Rahway, NJ, USA) were used as received. The water content in the vanadium source was estimated using thermogravimetry analysis.

2.2. Synthesis

Powder samples were prepared via hydrothermal synthesis in the NaH₂PO₄-VOSO₄· $3.55H_2O-H_2O-NaF$ system, where different amounts of NaF and water were tested (with molar ratios of 1.4/1.0/70-140/0-2.1). In a typical synthesis, 2.44 g of the phosphorous source and 3.36 g of the vanadium source were dissolved in 18.0 g of distilled water. Then, 0.42 g of sodium fluoride was added. This mixture, with the composition of $1.4 \text{ NaH}_2\text{PO}_4$:1 VOSO₄:0.7 NaF:70 H₂O, was homogenized via magnetic stirring for 40 min and then transferred into Teflon-lined stainless-steel autoclaves (with a capacity of 45 mL) and statically treated at 170 °C for different times (from 2 h to 15 days). After that, the autoclaves were cooled down to room temperature under flowing water, and the products were filtered and washed with distilled water. The resulting powders were dried for one day.

2.3. Characterization

Powder X-ray diffraction (PXRD) was recorded at room temperature in a step-scan regime with an X'Pert MPD Philips diffractometer (CuK α X-radiation) at least in the 2 θ range 5–45°. The phases were identified by comparing the powder XRD of products with a simulated one using the Powder Cell program version 2.4 [21]. The cell parameters were also refined using the least squares method in the Powder Cell program. The morphology and crystallite size of the samples were examined using scanning electron microscopy (SEM) with a Hitachi S-4100 (Chiyoda, Japan) or FE-SEM SU-70 microscope. The Na/V/P ratios were analyzed using energy-dispersive X-ray spectrometry (EDS) carried out with a Römteck EDS system attached to the scanning electron microscope. The powder samples were spread on carbon tape, and carbon thin film was deposited via vacuum deposition to cover the powder samples. Fourier-transform infrared (FT-IR) spectra of the powdered samples suspended in KBr pellets were collected in the range of 400–4000 cm⁻¹ using a

Mattson 7000 spectrometer, with a resolution of 2 cm^{-1} . Diffuse reflectance (DR) UV-visible spectra were recorded in air at room temperature with a Jasco V-560 spectrometer in the range of 230–800 nm, using BaSO₄ as the reference material.

3. Results

Clearly, since the target compounds of this study were $Na_3V_2(PO_4)_2F_3$, $NaVPO_4F$, and $Na_3(VO)_2(PO_4)_2F$, the inclusion of a fluorine source in the synthesis precursor was necessary. The focus was on its amount. This study indicated that fluorine has an important influence on phase formation even with a very low content. When a solution with a molar composition of 1.4 NaH_2PO_4 :1 $VOSO_4$:70 H_2O was hydrothermally treated at 170 °C, a mixture containing black large single crystals ((see Figure S1a in supplementary materials) and green powder was obtained after one day (powder XRD in Figure 1b,c). The black large single crystals were identified as $Na(VO)_2(PO_4)_2 \cdot (H_2O)_4$ (Figure 1a,c) [22], while the powder was a mixture of several phases. Besides $Na(VO)_2(PO_4)_2(H_2O)_4$, the rest of the peaks in the powder XRD pattern could not be identified by a single phase. Some peaks evencould not be identified by any existing phases. After 3 days of synthesis, the black single crystals became the main phase, and the powder XRD indicated that the product mainly contained $Na(VO)_2(PO_4)_2(H_2O)_4$ and $Na(VO)PO_4$ (Figure 1a,d,e) [23].



Figure 1. Simulated powder XRD patterns of (a) $Na(VO)_2(PO_4)_2(H_2O)_4$ and (d) $Na(VO)PO_4$. Experimental powder XRD patterns of samples obtained without addition of sodium fluoride: (b) 1-day green powder sample; (c) 1-day black single crystal sample; and (e) 3-day sample (mainly black single crystals).

However, when a small amount of sodium fluoride was added to the above solution, $Na_3(VO)_2(PO_4)_2F$ was precipitated. A solution with a molar composition of 1.4 NaH_2PO_4 :1 $VOSO_4$:0.1 NaF:70 H_2O gave a mixture of $Na_3(VO)_2(PO_4)_2F$ and $Na(VO)_2(PO_4)_2(H_2O)_4$ after being treated at 170 °C for one day (powder XRD in Figure 2c). Black large single crystals could be clearly seen (photo in Figure S1b). After 3 days of synthesis, the amount of black single crystals clearly increased (powder XRD in Figure 2d,e and photo in Figure S1c). In all three target compounds $(Na_3V_2(PO_4)_2F_3, NaVPO_4F, and Na_3(VO)_2(PO_4)_2F)$, the less-F-containing compound is $Na_3(VO)_2(PO_4)_2F$, which has a F/V molar ratio of 0.5. When F was present in the starting mixture, the F-containing phase crystallized. However, when the amount of F was very low (0.1), only a limited amount of V and P sources went to the F-containing phase. After the F source was depleted by the crystallizing F-containing phase, the rest of the V and P sources crystallized compounds without containing F, in this work, $Na(VO)_2(PO_4)_2(H_2O)_4$.



Figure 2. Simulated powder XRD patterns of (a) $Na(VO)_2(PO_4)_2(H_2O)_4$ and (b) $Na_3(VO)_2(PO_4)_2F$. Experimental powder XRD patterns of samples with a F/V molar ratio of 0.1 in the starting mixture and with synthesis time of (c) 1 day, (d) 3-day powder sample with few black single crystals, and (e) 3-day black single crystal sample with a small amount of powder.

The structures of Na₃(VO)₂(PO₄)₂F (Figure 3b) and Na(VO)₂(PO₄)₂(H₂O)₄ (Figure 3c) are related. In the structure of $Na_3(VO)_2(PO_4)_2F$, the two VO_5F octahedra share the F, forming a $V_2O_{10}F$ dimer (Figure 3a). When the F in the $V_2O_{10}F$ dimer does not exist, the V becomes five coordinated and the $V_2O_{10}F$ dimer becomes two separated VO₅; therefore, the 3D network disintegrates and becomes a 2D vanadyl phosphate layer (Figure 3c). These layers also shift ca. a/2 along the *a*-axis, and the distance between layers (along the *c*-axis) slightly increases (from ca. 6.42 to 6.84 Å). The powder XRD pattern of the obtained Na₃(VO)₂(PO₄)₂F in this condition resulted in a unit cell of a = 6.365, c = 10.825 Å, and V = 438.6 Å³, clearly showing unit cell expansion along the *c*-axis. Highly crystalline Na₃(VO)₂(PO₄)₂F gave a = 6.386, c = 10.683 Å, and V = 435.7 Å³. Burova et al. reported the unit cell expansion after the replacement of apex O with F in vanadium octahedra (a = 6.38643, c = 10.62375 Å, and V = 433.3 Å³ for Na₃(VO)₂(PO₄)₂F; a = 6.39455, c = 10.6988 Å, and V = 437.5 Å³ for Na₃V₂O_{0.8}(PO₄)₂F_{2.2}) [17]. With the structural relationship between Na₃(VO)₂(PO₄)₂F and Na(VO)₂(PO₄)₂(H₂O)₄ in mind, the expansion along the c-axis may also happen in the presence of a high number of vacancies in the F position due to the low amount of F in the starting solution.



Figure 3. The V₂O₁₀F dimer (**a**) in Na₃(VO)₂(PO₄)₂F structure (**b**) and structural representations of Na(VO)₂(PO₄)₂(H₂O)₄ phase (**c**).

The powder XRD pattern (Figure 4a) of the sample obtained after one day at 170 °C with a F/V molar ratio of 0.7 in the precursor solution is very similar to those of $Na_3(VO)_2(PO_4)_2F$, $NaVPO_4F$, and $Na_3V_2(PO_4)_2F_3$. The structures of these three compounds are very similar. Their structures are composed of a V₂O_{11-x}F_x dimer connected via PO₄ tetrahedra. The differences rely on the replacement of apex O with F in the vanadium octahedra (Figure S2). This replacement results in different optimized sodium positions in these three structures and, therefore, space groups. The space group of compounds $Na_3(VO)_2(PO_4)_2F$ and $NaVPO_4F$ [24] is I4/mmm, while that of $Na_3V_2(PO_4)_2F_3$ is P42/mnm, although Bianchini et al. reported that the space group Amam more accurately described their $Na_3V_2(PO_4)_2F_3$ [25]. In order to study the detailed relationship between the sample in this work and these three compounds, the powder XRD patterns of $Na_3(VO)_2(PO_4)_2F$ and $Na_3V_2(PO_4)_2F_3$ were simulated using the PCW program [21] using unit cell parameters, the atomic coordinates, and space group data from the ICSD database (the space group I4/mmm for Na₃V₂(PO₄)₂F₃). The simulated powder XRD pattern of NaVPO₄F was very similar to that of Na₃(VO)₂(PO₄)₂F. Only the cell volume of NaVPO₄F slightly increased. Close inspection of the pattern in Figure 4a shows the presence of a small peak at $20 \ 23.5^{\circ}$ in the experimental one, which belongs to the (211) diffraction of $Na_3V_2(PO_4)_2F_3$ (Figure S3). The powder XRD pattern of $Na_3(VO)_2(PO_4)_2F$ should not have this diffraction. However, the pattern (Figure 4a) does not have clear diffraction at $20 \ 30.8^{\circ}$, which belongs to the (301) diffraction of the $Na_3V_2(PO_4)_2F_3$ phase. Furthermore, the broadening of the peak at 16.6° is clear, which may be due to the overlap of diffraction from different space groups (I4/mmm and $P4_2$ /mnm). Therefore, the obtained material should be between $Na_3(VO)_2(PO_4)_2F$ and $Na_3V_2(PO_4)_2F_3$, and a higher F content than that of $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$ is expected because $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$ does not have both peaks at ca. 23.5 and 30.8° [17]. The higher F content than that of $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$ is surprising because the F/V ratio in the starting mixture is only 0.7, which is even not enough for the formation of NaVPO₄F, not to mention the formation of $Na_3V_2(PO_4)_2F_3$. Since the structures of these three phases are very similar, their intergrowth with each other is not unexpected. The pattern in Figure 4a was indexed with P4₂/mnm, giving a = 9.041, c = 10.655 Å, and V = 870.9 Å³ (Figure S4). SEM observation indicated the formation of crystallites with a particle size of mainly sub-micrometers (Figure 5a). Chemical analysis (EDS) confirmed the presence of F (Figure S5) and a Na:V:P ratio of 1.1:1.2:1, which suggests the presence of vacancies at P sites and proton substitutions at Na sites.



Figure 4. Powder XRD patterns of samples with a F/V molar ratio of 0.7 and synthesis times of 1 day (a) and 3 days (b) and those of samples with a F/V molar ratio of 2.1 and synthesis times of 1 day (c) and 3 days (d).



Figure 5. SEM images of samples with a H_2O/V molar ratio of 70, a F/V molar ratio of 0.7 (**a**), and 2.1 (**b**) in starting mixture and synthesized at 170 °C for 1 day.

When the F/V molar ratio in the precursor was low, the products depended on the synthesis time. The powder XRD patterns indicate that the 3-day sample contained a lot of $Na(VO)_2(PO_4)_2(H_2O)_4$ (Figure 4b and Figure S6). The samples with both F/V molar ratios of 0.1 and 0.7 contained more $Na(VO)_2(PO_4)_2(H_2O)_4$ after a longer synthesis time. Unlike the sample obtained with a F/V molar ratio of 0.1, the $Na(VO)_2(PO_4)_2(H_2O)_4$ obtained with a F/V molar ratio of 0.7 was in powder form.

With the structural relationship in mind, an attempt to transform $Na(VO)_2(PO_4)_2(H_2O)_4$ to $Na_3(VO)_2(PO_4)_2F$ via sodium fluoride treatment was carried out, and the powder XRD patterns are shown in Figure 6. By tumbling (~20 rpm) 0.1 g of sample in 5 mL of H₂O containing 0.13 g of sodium fluoride for 2 days, the diffractions of $Na(VO)_2(PO_4)_2(H_2O)_4$ significantly decreased, while small peaks at 23.5 and 30.8° appeared in the powder XRD pattern (Figure 6b). In fact, due to the excess sodium fluoride used, it transformed into a compound more similar to $Na_3V_2(PO_4)_2F_3$.



Figure 6. Simulated powder XRD patterns of $Na(VO)_2(PO4)_2(H_2O)_4$ (green line) and $Na_3V_2(PO_4)_2F_3$ (red line). Experimental powder XRD patterns of (a) start powder sample (blue line) and (b) powder sample after tumbling in sodium fluoride solution for 2 days (black line).

When the F/V molar ratio was 2.1 in the starting mixture, a compound similar to $Na_3V_2(PO_4)_2F_3$ precipitated after 1 day of synthesis (Figure 4c). The peak at 16.6° was much sharper. The product did not show a uniform habit (Figure 5b). A longer synthesis time resulted in an increase of the fluorine content in the product, indicated by the higher peaks at 23.5 and 30.8° (Figure 4d). The water content in the starting mixture also influenced the product. With double the amount of water in the starting mixture, the powder XRD pattern of the 1-day sample even shows a (101) peak (ca. 12.9°) of the $Na_3V_2(PO_4)_2F_3$ phase (Figure S7c). However, the 3-day sample seems very similar to the 1-day sample. At a F/V molar ratio of 0.7, doubling the water content in the starting mixture could eliminate the formation of $Na(VO)_2(PO_4)_2(H_2O)_4$ (Figure S8d). However, the water content in the starting mixture did not have strong influence on their morphologies. Their SEM images are very similar (Figure S9).

With a F/V molar ratio of 2.1 and a H_2O/V molar ratio of 140, a compound similar to Na₃V₂(PO₄)₂F₃ could be precipitated in 2 h at 170 °C, the powder XRD pattern of which is shown in Figure 7, and the system was stable for at least 3 days. To the best of our knowledge, this is the shortest time to obtain $Na_3V_2(PO_4)_2F_3$ ever published, except the synthesis via microwave heating at 180–220 °C with different reducing agents reported by Burova et al. [17]. However, fast pure phase formation also depends on the F content in starting mixture. With a F/V molar ratio of 0.7 and H_2O/V molar ratio of 140, the 2-h sample still contained Na(VO)₂(PO₄)₂(H₂O)₄ (Figure S10), while 5-h synthesis resulted in a pure phase of $Na_3V_2O_2(PO_4)_2F$. These results imply that the formation mechanism of $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$ depends on the F concentration in the precursor. At high F concentrations, the target phase forms directly, while at low F concentrations, the target phase partly forms via phase transformation. SEM analysis indicated the formation of aggregate submicron crystallites (Figure 8). Chemical analysis (EDS) confirmed the presence of F (Figure S11). Previously, $Na_3V_2(PO_4)_2F_3$ has also been prepared under hydrothermal conditions [26]. First, V₂O₅ powder in phosphoric acid was reduced with an aqueous solution of hydrazine. Then, sodium fluoride was added, and the mixture was hydrothermally treated at 180 °C for 64 h and slowly cooled down (10 °C/h) to room temperature [26]. The present work reports a process at a lower temperature, with a much shorter time, and without controlling the cooling step, which is significantly different from the processes described in the literature. This process is also stable for at least 3 days.



Figure 7. Powder XRD patterns of samples with a F/V molar ratio of 2.1 in starting mixture and synthesized at 170 °C for 2 h (a), 5 h (b), 1 day (c), and 3 days (d).



Figure 8. SEM images of samples with a H_2O/V molar ratio of 140 in starting mixture and synthesized at 170 °C for 2 h with a F/V molar ratio of 2.1 (**left**) and 5 h with a F/V molar ratio of 0.7 (**right**), respectively.

The materials obtained under different experimental conditions had slightly different cell parameters. Table 1 collects the cell parameters calculated from the powder XRD patterns of the obtained products using the Pī space group for Na(VO)₂(PO₄)₂(H₂O)₄, I4/mmm for samples without peaks at ca. 23.56 and 30.8°, and P4₂/mmm for samples with peaks at 23.56 and 30.8°. The cell volume seemed to increase with an increasing synthesis time. This is in accordance with the increase in F after a longer synthesis time. The structural data indicate that the replacement of O with F should expand cells (2.017 Å of V-F vs. 1.617 Å of V-O in an equivalate place). These data point out that although the vanadium source in the starting solution is V⁴⁺, Na₃V₂(PO₄)₂F₃ can still be formed.

Table 1. Synthesis conditions and unit cell parameters calculated from the powder XRD patterns of obtained products using Pī for space group $Na(VO)_2(PO_4)_2(H_2O)_4$ phase, I4/mmm for samples without peaks at ca. 23.56 and 30.8°, and P4₂/mnm for samples with these peaks.

Sample	F/V	H ₂ O/V	Time	Cell Parameters (Å; °; Å ³)
1 *	0.1	70	24	a = 6.365, c = 10.835, and V = 439.0 a = 6.293, b = 6.294, c = 6.834, α = 107.04, β = 92.34, γ = 90.13, and V = 258.6
2 *	0.1	70	72	a = 6.365, c = 10.825, and V = 438.6 a = 6.293, b = 6.294, c = 6.834, α = 107.04, β = 92.34, γ = 90.13, and V = 258.6
3	0.7	70	24	a = 9.039, c = 10.680, and V = 872.6
4 *	0.7	70	72	a = 6.382, c = 10.634, and V = 433.1 a = 6.292, b = 6.298, c = 6.834, α = 107.16, β = 92.44, γ = 90.12, and V = 258.5
5	2.1	70	24	a = 9.043, c = 10.655, and V = 871.3
6	2.1	70	72	a = 9.041, c = 10.655, and V = 870.9
7	0.7	140	2	a = 6.378, c = 10.636, and V = 432.7
8	0.7	140	5	a = 6.382, c = 10.661, and V = 434.2
9	0.7	140	24	a = 6.385, c = 10.685, and V = 435.6
10	0.7	140	72	a = 6.386, c = 10.683, and V = 435.7
11	2.1	140	2	a = 6.384, c = 10.608, and V = 432.3
12	2.1	140	5	a = 6.392, c = 10.636, and V = 434.6
13	2.1	140	24	a = 9.041, c = 10.655, and V = 870.9
14	2.1	140	72	a = 9.044, c = 10.655, and V = 871.5

* Samples 1, 2, and 4 contain two phases.

To grasp further information on the obtained material, diffuse reflectance UV-vis spectra of selected samples were recorded and are shown in Figure 9. One of the main differences between these two phases is the oxidation state of vanadium. In the $Na_3(VO)_2(PO_4)_2F$ phase, vanadium is in a V^{4+} state, while in Na₃V₂(PO₄)₂F₃, it is in a V^{3+} state. However, the spectra of the materials in this work are very similar, with an absorption maximum at ca. 655 nm and a weak shoulder at 400-450 nm. Absorption in this region is related to the sample's color (blue and green) and, hence, to the vanadium oxidation state present in the sample. It is known that V^{3+} can display both a green and blue color [27], and its UV spectrum can have absorption bands with maxima at ca. 400-415 nm and 590-645 nm. However, the d-d transitions of V(IV) can also generate bands around these regions and exhibit the green color of the final product [28]. The colors of the samples in this work were light green to dark green. The UV-vis spectrum of VOSO₄ gives an adsorption band at ca. 760 nm and a shoulder at ca. 630 nm, while that of VCl₃ has two adsorption bands at ca. 600 and 400 nm [29]. Previous work reported that Na₃(VO)₂(PO₄)₂F gave a maximum adsorption band at 765 nm [28,30]. In order to understand this difference, a sample with starting composition 6 in Table 1 was prepared using VCl₃. However, its UV-vis spectrum was very similar to that of sample 10. In this case, high-resolution powder XRD of sample 10 was recorded, and the presence of very weak peaks at 23.56 and 30.8° was confirmed. Therefore, it seems the samples obtained in this system always contain mixed valence of V^{3+} and V^{4+} .



Figure 9. DR UV-vis spectra of selected samples (see Table 1).

Figure 10 shows the FT-IR spectra of typical samples crystallized in the I4/mmm (sample 9) and P4₂/mnm (sample 13) space groups. FT-IR peak positions of selected samples are collected in Table S1. The peaks between 1000 and 1200 cm⁻¹ were due to the vibrations of the (PO₄)³⁻ tetrahedra [13]. The strong peak at 1060 cm⁻¹ is attributed to the asymmetric stretching vibration of (PO₄)³⁻. The peaks at ca. 920 and 950 cm⁻¹ are due to the vibrations of the short vanadyl V=O bond and stretching vibration of the V-F bond, while those at ca. 555 and 670 cm⁻¹ can be attributed to the asymmetric bending vibration and symmetric stretching mode of P-O bonds, respectively [31,32]. The clear difference is in the peak at ca. 795 cm⁻¹; the sample with P4₂/mnm does not have this peak. However, its origin is not clear yet. The peak positions between 1100 and 1200 cm⁻¹ are also different. Similar to Qi's previous report [31], all samples have a peak at ca. 920 cm⁻¹, even Na₃V₂(PO₄)₂F₃. A similar case was reported for its lithium counterpart [33]. Qi et al. [31] studied the Na storage behavior of these two materials in Na-ion batteries, and their performance was very similar. We expect the mixture of them will have very similar performance.



Figure 10. FT-IR spectra of selected samples (see Table 1). The peak positions are collected in Table S1.

4. Conclusions

The hydrothermal crystallization in NaH₂PO₄–VOSO₄–NaF–H₂O was studied. A rapid synthesis of Na₃V₂O_{2x}(PO₄)₂F_{3-2x} was achieved after 2 h at 170 °C in the 1.4 NaH₂PO₄–1.0 VOSO₄–140 H₂O–2.1 NaF system, and the fluorine content increased with the synthesis time. The phase formation was confirmed using powder XRD. The materials were further characterized using SEM, EDS, and UV–vis and FT-IR spectroscopy indicating the presence of mixed valence of V³⁺ and V⁴⁺. No other crystalline phase was found in the resulting product. It is expected that pure phases of different representatives of sodium vanadium fluorophosphates can be steadily formed by fine-tuning the synthesis time and vanadium source and maybe adding a reducing agent.

Supplementary Materials: The following supporting information can be downloaded at https: //www.mdpi.com/article/10.3390/cryst14010043/s1, Figure S1: Photos of samples without adding sodium fluoride and 1 day's synthesis (a), with a F/V molar ratio of 0.1 in starting mixture and 1 day's synthesis (b) and 3 days' synthesis (c).; Figure S2: Structure representations of Na₃V₂(PO₄)₂F₃ (top left), Na₃(VO)₂(PO₄)₂F (top right) and sodium positions in the structure (bottom); Figure S3: Powder XRD patterns of simulated ones for $Na_3(VO)_2(PO_4)_2F$ (a) and $Na_3V_2(PO_4)_2F_3$ (b); and for a sample with a F/V molar ratio of 0.7 in starting mixture and synthesized at 170 °C for 1 day (c); Figure S4: Cell parameter fit using space group P42/mnm; Figure S5: Energy dispersive X-ray spectrometry of a sample with a F/V molar ratio of 0.7 in starting mixture and synthesized at 170 °C for 1 day; Figure S6: Powder XRD patterns of simulated ones for Na(VO)₂(PO₄)₂(H₂O)₄ (blue) and $Na_3(VO)_2(PO_4)_2F$ (red); and for a sample with a F/V molar ratio of 0.7 in starting mixture and synthesized at 170 °C for 3 day (black); Figure S7: Powder XRD patterns of samples with a F/V molar ratio of 2.1 and synthesized at 170 °C for 1 day (a); 3 days (b); and with double amount of water and synthesized at 170 °C for 1 day (c); 3 days (d); Figure S8: Powder XRD patterns of samples with a F/V molar ratio of 0.7 and synthesized at 170 °C for 1 day (a); 3 days (b); and with double amount of water and synthesized at 170 °C for 1 day (c); 3 days (d).; Figure S9: SEM of samples with a F/V molar ratio of 0.7, a H₂O/V molar ratio of 70 (left) and 140 (right) in starting mixture and synthesized at 170 °C for 1 day; Figure S10: Powder XRD patterns of samples with a F/V molar ratio of 0.7 in starting mixture and synthesized at 170 $^{\circ}$ C for 2 h (a), 5 h (b), 1 day (c) and 3 days (d); Figure S11: Energy dispersive X-ray spectrometry of samples with a H_2O/V molar ratio of 140 in starting mixture and synthesized at 170 °C for 2 h with a F/V molar ratio of 2.1 (left) and 5 h with a F/V molar ratio of 0.7 (right), respectively; Table S1: FT-IR peaks of selected samples (See sample number in Table 1).

Funding: The Portuguese Foundation for Science and Technology/MCTES, UIDB/50011/2020, UIDP/50011/2020, and LA/P/0006/2020.

Data Availability Statement: The data presented in this study are available in this article and its supplementary materials.

Acknowledgments: The author acknowledges the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020, and LA/P/0006/2020, financed by national funds through the Portuguese Foundation for Science and Technology/MCTES.

Conflicts of Interest: The author declares no conflicts of interest.

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