

Synthesis of heavily hydrated La_2NiO_4 through ion exchange of its fluorinated derivative: a new route to the synthesis of oxyhydroxide systems

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Abstract: In this paper we report the synthesis of heavily hydrated La_2NiO_4 . While prior literature work has shown that under normal conditions La_2NiO_4 can incorporate very little water, the results here show that samples with high levels (up to 0.6 H_2O per formula unit) can be achieved by first fluorinating La_2NiO_4 and then performing an ion exchange (OH^- for F^-) under hydrothermal conditions. The success of this work highlights the potential of such anion exchange as a novel route of preparing new metastable hydrated (oxyhydroxide) phases.

Keywords: K_2NiF_4 , La_2NiO_4 , fluorination, hydration, ion exchange

1. Introduction

Materials with the K_2NiF_4 structure have attracted considerable attention following the observation of superconductivity in alkaline earth doped La_2CuO_4 [1-2]. The structure may be classed as an intergrowth between perovskite and rock salt layers (figure 1), and one of the interesting features is the ability to accommodate either anion vacancies or anions excess. In terms of the latter, these extra anions occupy fluorite-type positions within the rock salt layers (figure 1). The ability to accommodate anion excess has also driven researchers to investigate the potential of oxygen excess K_2NiF_4 systems as Solid Oxide Fuel Cells cathodes, with both nickelate ($\text{Ln}_2\text{NiO}_{4+\delta}$; Ln=rare earth) and cobaltate systems ($\text{Ln}_{2-x}\text{Sr}_x\text{CoO}_{4\pm\delta}$) investigated [3-15]. These studies have shown promising potential for these materials in terms of this application. While there have been numerous studies examining the oxygen non-stoichiometry of such systems, there have been only limited studies of the ability of Ln_2NiO_4 systems to accommodate water, with this prior work showing only limited water incorporation (≈ 0.03 H_2O) [16]. Such studies are of interest because these materials have also been attracting significant interest as cathode materials for use in proton conducting ceramic fuel cells. In this work, we have investigated strategies to increase the water content achievable in La_2NiO_4 by the use of an indirect route. In this indirect route, we make use of the fact that K_2NiF_4 type oxides can incorporate F (by $2\text{F}^-/1\text{O}^{2-}$ exchange) leading to oxide fluorides, with relatively large anion contents in the interstitial sites [17-25], and investigate the potential for subsequent OH^-/F^- ion exchange.

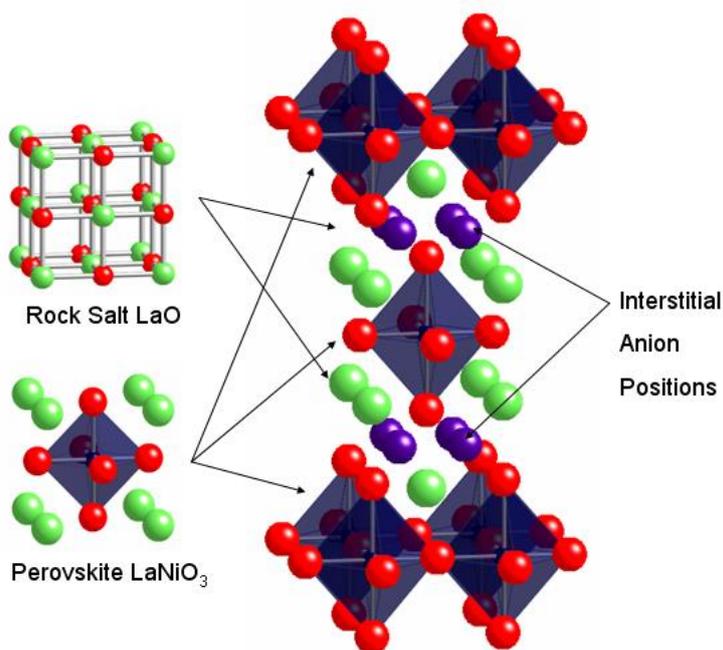


Figure 1. Structure of La_2NiO_4 showing the intergrowth of perovskite and rock salt units, and the location of potential interstitial sites

2. Results and Discussion

X-ray powder diffraction showed the successful synthesis of La_2NiO_4 , which was then used for the fluorination experiments. Successful fluorination of La_2NiO_4 by heating with PVDF was demonstrated by XRD: a large splitting of (020)/(200), (024)/(204), (026)/(206) and (133)/(313) peaks was observed after fluorination, indicating a large increase in the orthorhombic splitting (figure 2). On increasing the fluorination levels to >0.4 moles CH_2CF_2 per mole of La_2NiO_4 , the sample was no longer a single phase, but rather extra peaks are seen, which are due to the higher fluorinate content phase $\text{La}_2\text{NiO}_3\text{F}_2$ [25] (Figure 3).

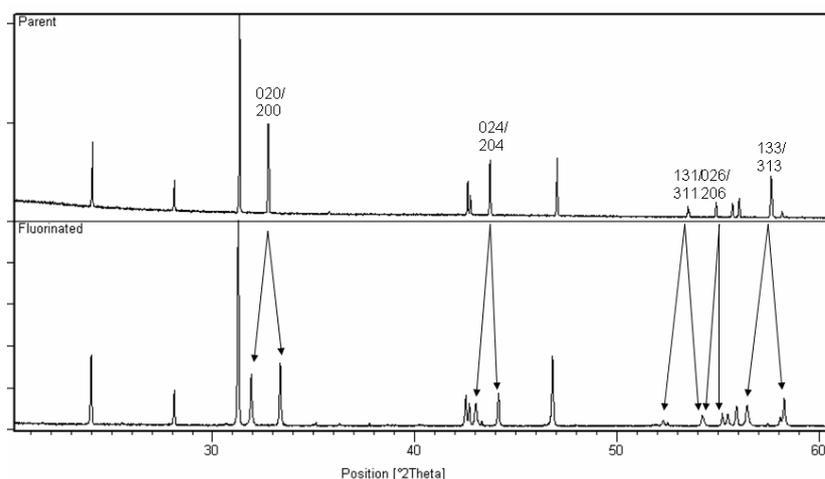


Figure 2. X-ray diffraction pattern of the parent and fluorinated (0.25 PVDF) La_2NiO_4 highlighting the increased orthorhombic peak splitting.

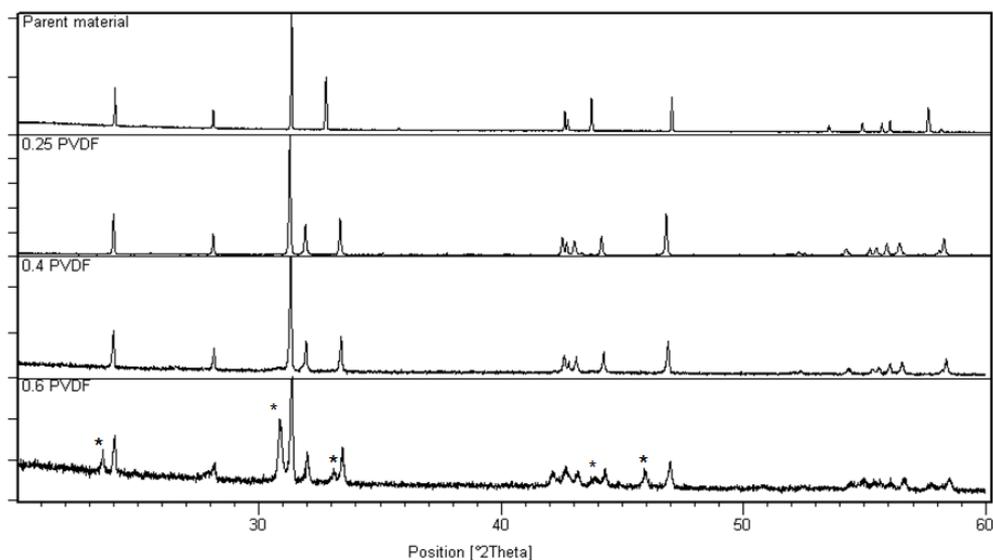


Figure 3. X-ray diffraction patterns of La_2NiO_4 samples fluorinated with different amounts of PVDF. At the higher levels (ratio 1 La_2NiO_4 : 0.6 PVDF (CH_2CF_2)) extra peaks are seen (marked *) which are from a higher F content $\text{La}_2\text{NiO}_3\text{F}_2$ phase [25].

The possibility to ion exchange (OH^- for F^-) was then analysed for the La_2NiO_4 sample fluorinated with 0.25 monomer moles equivalent of PVDF. The ion exchange was performed under hydrothermal conditions (1M KOH, 200°C) in order to try to ensure a good exchange. After the first exchange experiment, XRD analysis was performed to determine if any change had occurred. As can be seen from the XRD patterns (figure 4) there appeared to be no major change, with the cell parameters (Table 1) increasing slightly after the exchange. In order to determine whether there had indeed been any OH^-/F^- exchange, TGA experiments were performed up to 500°C . The TGA experiments showed a mass loss consistent with 0.13 moles of water being lost on heating. Moreover after the TGA measurement, XRD analysis was performed on the sample, which showed a small decrease in cell volume. Both results are consistent with a partial F^-/OH^- exchange and subsequent loss of the hydroxide as H_2O in the TGA experiments.

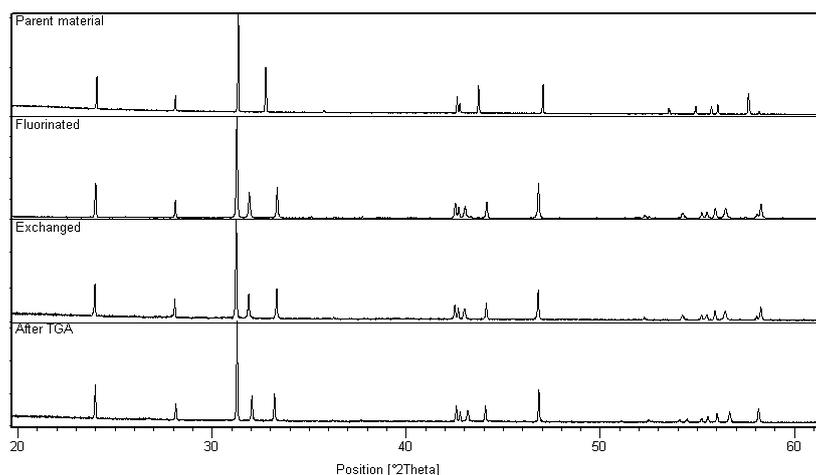


Figure 4. Powder X-ray diffraction patterns for La_2NiO_4 : as prepared, fluorinated, after a single ion exchange, and after subsequent analysis of the ion exchanged sample by TGA

Table 1 Cell parameters for La₂NiO₄: as prepared, fluorinated, after single ion exchange, and after subsequent analysis of the ion exchanged sample by TGA

| | a (Å) | b (Å) | c (Å) | Cell Volume (Å ³) |
|-------------|--------------|-------------|-------------|-------------------------------|
| Parent | 5.45265 (4) | 5.45859 (4) | 12.6699 (1) | 377.10 (1) |
| Fluorinated | 5.36780 (7) | 5.60196 (8) | 12.6887 (2) | 381.55 (1) |
| Exchanged | 5.37093 (10) | 5.6061 (1) | 12.6959 (2) | 382.27 (2) |
| After TGA | 5.38727 (9) | 5.57711 (9) | 12.6690 (2) | 380.65 (1) |

The results therefore showed that, when comparing the first exchanged material with the fluorinated material, there is a significant change, but it does appear that the OH⁻/F⁻ exchange had not gone to completion. TGA studies of non-exchanged samples showed negligible mass loss and no change in cell parameters after the heat treatment, confirming that the water incorporation was a result of the hydrothermal exchange process and was not present in the original fluorinated phase.

The initial results were therefore positive, but suggested that a single exchange was insufficient to completely replace all the F⁻ by OH⁻. The exchange process was therefore repeated several times. The material was deduced to be essentially fully exchanged when, after performing the TGA studies, the XRD analysis showed a pattern similar to the parent material along with similar cell parameters. This showed that the material was essentially fully exchanged after performing the ion exchange 7 times. After this number of exchanges, the TGA results indicated a water content of 0.64 per formula unit for this phase, and hence a composition (assuming Ni²⁺) of La₂NiO₄.0.64H₂O or La₂NiO_{3.36}(OH)_{1.28}. Notably the resulting hydroxide content is higher than that expected from simple exchange for F, and so suggests that additional H₂O incorporation has occurred in addition to the OH⁻/F⁻ exchange. Figure 5 shows the X-ray diffraction patterns of the progression of this material after fluorination, exchange and TGA, and the corresponding cell parameters are given in table 2. The XRD patterns show that after the TGA heat treatment the exchanged product gives an XRD pattern very similar to that of the parent sample. However the cell parameters of these two phases (table 2) do show some small differences, which might suggest that there is still a small amount of F in the sample.

The final exchanged sample was analysed further by variable temperature XRD (figure 6) and these data were compared with the TGA-MS data (figure 7). The TGA data shows that the water is lost around 300°C, and the high temperature of this mass loss is consistent with the presence as lattice hydroxide rather than surface water, for which the loss should have occurred around 100°C. The variable temperature XRD shows significant changes on heating. At 300°C there is an intermediate phase which shows both the parent and the exchanged material. However, at the next temperature examined (400°C), there is only 1 phase due to the complete loss of water from the lattice, resulting in conversion back to the non-hydrated parent material. Since the hydroxide is only stable up to ≈300 °C, it is unlikely that such hydrated systems could be used as cathode materials in solid oxide fuel cells using standard ceramic proton conductors, such as doped Ba(Ce/Zr)O₃. However, there is the potential that they could be exploited for use in lower temperature fuel cell systems, such as alkaline fuel cells.

Overall the results show that this indirect fluorination followed by ionic exchange route can be exploited to synthesise heavily hydrated La₂NiO₄. Considering the ready ability of other K₂NiF₄ phases, e.g. La₂CuO₄, and n=2 Ruddlesden Popper phases, e.g. Sr₃Fe₂O_{7-x}, to incorporate F, it is possible that this method might be similarly exploited to prepare heavily hydrated (oxyhydroxide) phases of other systems.

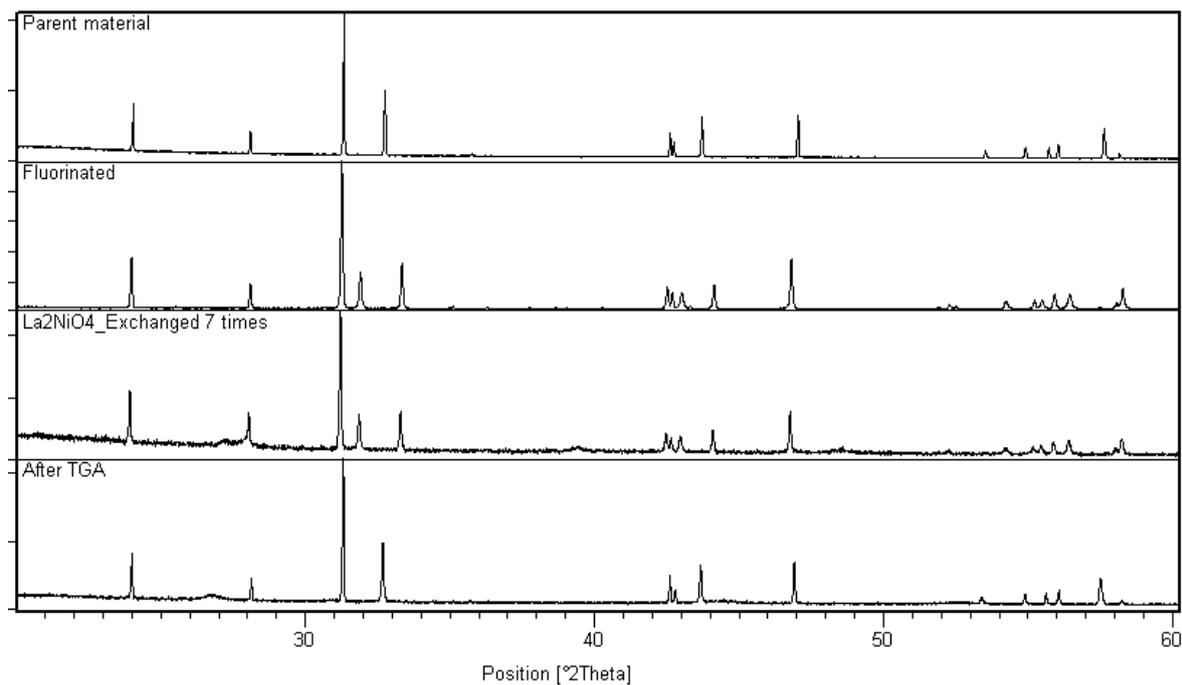


Figure 5. Powder X-ray diffraction patterns of La_2NiO_4 : as prepared, fluorinated, after ion exchange 7 times, and after subsequent analysis of the ion exchanged sample by TGA.

Table 2 Cell parameters of La_2NiO_4 : as prepared, fluorinated, after 7 ion exchanges, and after subsequent analysis of the ion exchanged sample by TGA

| | a (Å) | b (Å) | c (Å) | Cell Volume (Å ³) |
|-------------------|-------------|-------------|-------------|-------------------------------|
| Parent | 5.45265 (4) | 5.45859 (4) | 12.6699 (1) | 377.10 (1) |
| Fluorinated | 5.36780 (7) | 5.60196 (8) | 12.6887 (2) | 381.55 (1) |
| Exchanged 7 times | 5.3699 (2) | 5.6047 (2) | 12.6939 (4) | 382.04 (3) |
| After TGA | 5.4649 (1) | 5.4716 (1) | 12.6559 (2) | 378.44 (2) |

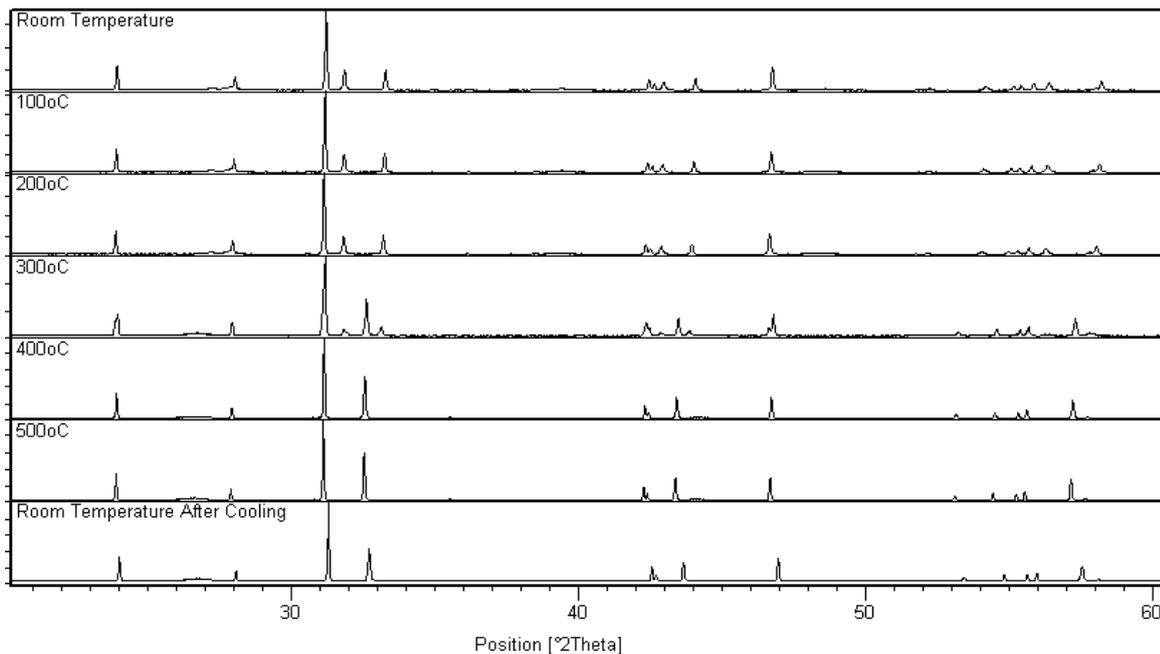


Figure 6. Variable temperature XRD patterns of 7 times exchanged fluorinated La_2NiO_4 , showing significant changes due to loss of H_2O on heating. The final pattern after cooling resembles that of the as-prepared parent La_2NiO_4 phase.

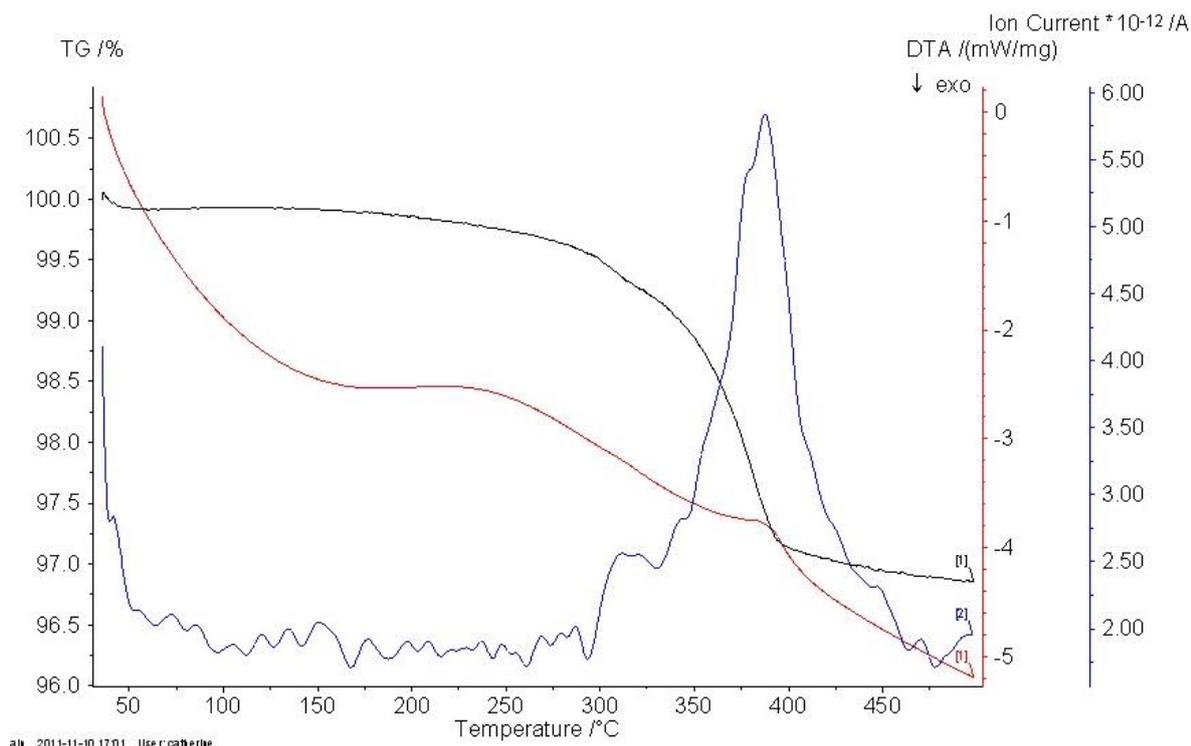


Figure 7. TGA trace of fluorinated La_2NiO_4 after 7 times ion exchange, showing weight loss in black, Differential thermal analysis (DTA) line in red and mass spectroscopy trace illustrating water release in blue.

3. Experimental

High purity La_2O_3 and NiO were used to prepare the La_2NiO_4 sample. The starting materials were ground together in the correct stoichiometric ratio and heated to 1100°C for 12 hours. The samples were then reground and further heated to 1300°C for another 12 hours.

Powder X-ray diffraction experiments were performed using a Bruker D8 diffractometer with $\text{Cu K}\alpha_1$ radiation in order to determine phase purity.

The La_2NiO_4 sample was fluorinated using polyvinylidene fluoride (PVDF), a method that has been previously shown to be a highly versatile route to the incorporation of F into both perovskite and K_2NiF_4 systems [22]. In this method, the parent material La_2NiO_4 was ground with PVDF in the correct molar ratios of La_2NiO_4 :PVDF to achieve the required F content. For PVDF the ratio was based on the monomer equivalent i.e. CH_2CF_2 . These samples were then placed in a furnace in a fume cupboard with a slow heating rate ($1.5^\circ\text{C}/\text{min}$) to 400°C for 24hrs with an intermediate regrind. The subsequent (OH^-/F^-) ion exchange was performed by immersing the fluorinated material in 1M KOH in a hydrothermal vessel (model 4749 Parr digestion vessel with 23 ml capacity) and heating for 2 days at 200°C . After this time, the sample was filtered and washed with copious amounts of distilled water.

Water contents were determined using thermogravimetric analysis (Netzsch STA 449 F1 Jupiter Thermal Analyser). The samples were heated to 500°C at 10°C per minute to eliminate any water present.

4. Conclusions

Whereas direct methods of water incorporation lead to only low levels of water in La_2NiO_4 , higher levels of water incorporation could be achieved via indirect methods. The latter involve the initial synthesis of a fluorinated precursor followed by OH^-/F^- exchange under hydrothermal conditions, and led to high levels of H_2O incorporation (0.64 molecules per formula unit, and hence a composition $\text{La}_2\text{NiO}_4 \cdot 0.64\text{H}_2\text{O}$ or $\text{La}_2\text{NiO}_{3.36}(\text{OH})_{1.28}$). The success of this work highlights the potential of anion exchange as a novel route of preparing new metastable hydrated (oxyhydroxide) phases.

Acknowledgments: We thank the University of Birmingham for funding (studentship for CAH).

Abbreviations

The following abbreviations are used in this manuscript:

PVDF: Polyvinylidene Fluoride

XRD: X-ray diffraction

TGA: Thermogravimetric analysis

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