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Preparation of ammonium intercalated vanadyl phosphate by redox intercalation and ion exchange

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Abstract

Redox intercalation of NH_4^+ into vanadyl phosphate dihydrate ($VOPO_4 \cdot 2H_2O$) leads to a two-phase $(NH_4)_xVOPO_4 \cdot H_2O$ ($x = 0.2 - 0.9$) compound with interlayer distances of 6.7 and 6.4 Å. Ammonium ions can be incorporated into the interlayer space of $VOPO_4$ also by an ion exchange, starting from alkali-metal redox-intercalated vanadyl phosphate $Me_xVOPO_4 \cdot yH_2O$ (Me = Li, Na, K, Rb). Several phases are formed during the ion exchange, one of them with the interlayer distance corresponding to the original $Me_xVOPO_4 \cdot yH_2O$ phase, the second one corresponding to formed $(NH_4)_xVOPO_4 \cdot H_2O$. In addition, a third phase is formed by the ion exchange when $Li_{0.98}VOPO_4 \cdot 1.98H_2O$ or $Rb_{0.60}VOPO_4 \cdot 1.3H_2O$ are used as starting compounds. An opposite ion exchange of NH_4^+ for Me^+ starting from $(NH_4)_xVOPO_4 \cdot H_2O$ does not proceed.

Keywords: Ammonium ion; Vanadyl phosphate; Intercalation; Ion exchange

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1. Introduction

Vanadyl phosphate dihydrate, $VOPO_4 \cdot 2H_2O$, is a layered compound with a structure derived from an α_I form of $VOPO_4$ [1] containing V^{5+} ions, which can be reduced by a proper reducing agent. During this reduction, a charge compensating cation is introduced into the interlayer space of $VOPO_4$. The structure of the original $VOPO_4$ layers is retained, whereas the interlayer distance usually decreases due to stronger electrostatic interactions between the negatively charged $VOPO_4$ layers and the introduced cations. As suitable reducing agents, iodides were proposed. The redox intercalation then proceeds according to the reaction

$$VOPO_4 \cdot 2H_2O + (x/z)MI_z + yH_2O \rightarrow M_{x/z}VOPO_4 \cdot (2+y)H_2O + (x/2)I_2, \quad (1)$$

where x is the amount of the intercalated cation M, z is the charge or valence of M, and y is the change of the water content in the product. The reaction is reported for alkali metals and some divalent metals as the intercalated cations [2,3]. Such compounds could be prepared in some cases also by solid-state method or hydrothermal method as reviewed in Ref. [4]. Recently, these materials are of interest due to their potential applications in rechargeable batteries [5,6].

Regarding an intercalation of ammonium ions into $VOPO_4 \cdot 2H_2O$, Johnson and Jacobson [3] reported a compound with a formula $(NH_4)_{0.48}VOPO_4 \cdot 2H_2O$ having an interlayer spacing of 6.786 Å. The intercalated cation can be exchanged for another cation [7]. In our previous work, we studied such an ion exchange for alkali metals [8]. The present work deals with an intercalation of various amounts of ammonium ion into $VOPO_4 \cdot 2H_2O$, with an ion exchange of alkali metals intercalated $VOPO_4$ for ammonium ions and with characterization of the products.

2. Experimental

$VOPO_4 \cdot 2H_2O$ was prepared by refluxing V_2O_5 in aqueous H_3PO_4 [9]. Acetone and water were distilled with $KMnO_4$ to remove reducing agents before use. $(NH_4)_xVOPO_4 \cdot yH_2O$ compounds were prepared by shaking 0.25 g of $VOPO_4 \cdot 2H_2O$ in 25 mL of 0.5 M solution of NH_4I in a 12:1 (v/v) acetone/water mixture

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at 40°C. The amount of intercalated NH_4^+ ions was determined by amperometric titration of the released iodine in the filtrate with thiosulfate. Intercalates of $VOPO_4 \cdot 2H_2O$ with alkali metals were prepared by the previously described method [2,3]. $Li_{0.98}VOPO_4 \cdot 1.9H_2O$ was prepared by shaking 5 g of $VOPO_4 \cdot 2H_2O$ with a solution of 50 g of LiI in a mixture of 140 mL of acetone with 20 mL of water at 40°C for 72 h. $NaVOPO_4 \cdot H_2O$ was prepared by refluxing 4 g of $VOPO_4 \cdot 2H_2O$ with a solution of 37.5 g of NaI in a mixture of 200 mL of acetone and 40 mL of water for 72 h [10]. $K_{0.83}VOPO_4 \cdot 2.2H_2O$ was prepared by refluxing 6 g of $VOPO_4 \cdot 2H_2O$ with a solution of 50 g of KI in a mixture of 200 mL of acetone and 50 mL of water for 120 h [11]. $Rb_{0.60}VOPO_4 \cdot 1.3H_2O$ was prepared by shaking 5 g of $VOPO_4 \cdot 2H_2O$ with a solution of 10 g of RbI in a mixture of 140 mL of acetone and 20 mL of water for 76 h. As found previously [12], prolonged reaction of $VOPO_4 \cdot 2H_2O$ with RbI did not lead to a product with higher amount of Rb^+ ions. The products were isolated by filtration, washed with a 1:1 (v/v) acetone/water mixture several times and dried in air at room temperature overnight.

The ion exchange was done in the following way: 1 g of NH_4Cl was dissolved in 40 mL of a 1:1 (v/v) acetone/water mixture. About 0.4 g of alkali-metal intercalated $VOPO_4 \cdot 2H_2O$ was suspended in the solution and shaken at 40°C. The amount of exchanged ions was controlled by the time of the reaction (5 min to several days). The products were isolated by filtration and the solids were washed with the 1:1 (v/v) acetone/water mixture and with redistilled acetone and dried in air at room temperature.

The amount of reduced vanadium(IV) in the samples was checked by cerimetry. About 0.08 g of the sample was dissolved in 10 mL of 0.1 M KOH to which 20 mL of 50% H_2SO_4 was added under stirring. About 10 mL of 0.06 M $Ce(SO_4)_2$ was then added and the solution was titrated with a 0.05 M $(NH_4)_2Fe(SO_4)_2$ solution. The titration was followed using a potentiometric method with platinum electrode and calomel reference electrode.

The contents of vanadium, phosphorus, sodium, potassium, and rubidium were determined by an electron scanning microscope JEOL JSM-5500LV and energy-dispersive X-ray microanalyzer IXRF Systems (detector GRESHAM Sirius 10). The accelerating voltage of the primary electron beam was 20 kV. The composition in the case of Li containing compounds was determined by induction coupled plasma optical emission spectrometry using an Integra XL 2 (GBC Dandenog, Australia) instrumentation. An x_{Me} (Me = Li, Na, K, Rb) value is then given as a molar fraction of Me to $VOPO_4$ as found by EDX or ICP OES. Powder X-ray diffraction data were obtained with a D8-Advance diffractometer (Bruker AXE, Germany) using Co$K\alpha$ radiation with secondary graphite monochromator. Diffraction angles were measured from 7° to 80° (2θ). The amount of water was determined by thermogravimetric analysis using a Netzsch STA 449C apparatus. The measurements were carried out in air between 30°C and 800°C at a heating rate of 5°C min^{-1}.

3. Results and discussions

3.1. Intercalation of NH_4^+ into $VOPO_4 \cdot 2H_2O$

The amount of intercalated NH_4^+ determined by the amperometric titration as a function of time has an exponential course (Fig. 1). The stoichiometric coefficient x in $(NH_4)_xVOPO_4 \cdot yH_2O$ reaches $x = 0.9$ after about 250 min of the reaction. In contrast to original $VOPO_4 \cdot 2H_2O$, ammonium intercalated $VOPO_4$ contains about one molecule of water per formula unit, i.e., the general formula is $(NH_4)_xVOPO_4 \cdot H_2O$ for all x studied. By heating the fully intercalated sample to 250°C, this water is released from the interlayer space and the interlayer distance of the compound decreases to 5.99 Å.

We found that the fresh products of the intercalation comprise two phases. As an example, the diffractogram of $(NH_4)_{0.52}VOPO_4 \cdot H_2O$ is given in Fig. 2a. The interlayer distance of both phases decreases with x up to 0.5 and remains constant for higher x (Fig. 3). The phase with higher interlayer distance d equal to about 6.7 Å (denoted 1 in Fig. 2a) corresponds to that reported by Johnson [3], the second phase (2 in Fig. 2a) has the interlayer distance around 6.4 Å for $x = 0.5-0.9$. Aging causes a decrease of the amount of the phase 2 in the product. It can be seen in Fig. 2b that the phase with the lower interlayer distance almost extincts in the $(NH_4)_{0.52}VOPO_4 \cdot H_2O$ sample which was aged for

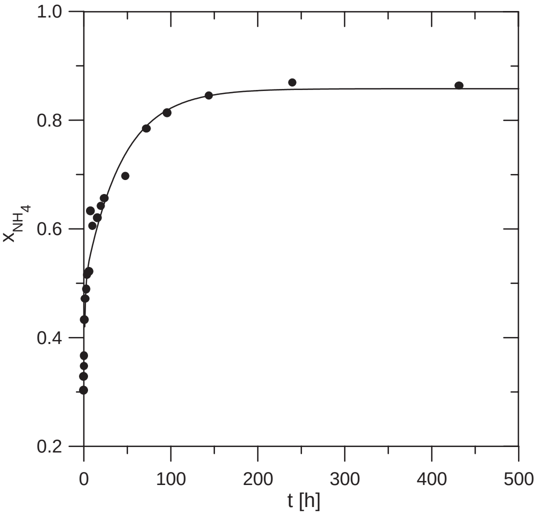

Fig. 1. The amount of intercalated NH_4^+ ions x in $(NH_4)_xVOPO_4 \cdot yH_2O$ as a function of the time of intercalation t.

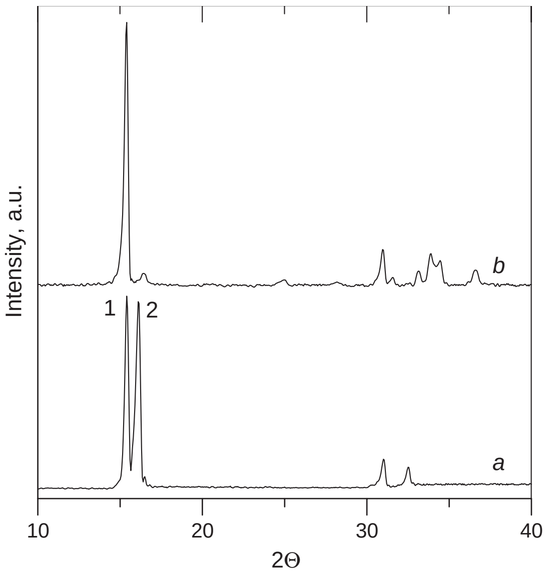

Fig. 2. The influence of aging on $(NH_4)_{0.52}VOPO_4 \cdot H_2O$, (a) as-prepared sample, 1—phase 1, 2—phase 2, and (b) the same sample after 1-year standing.

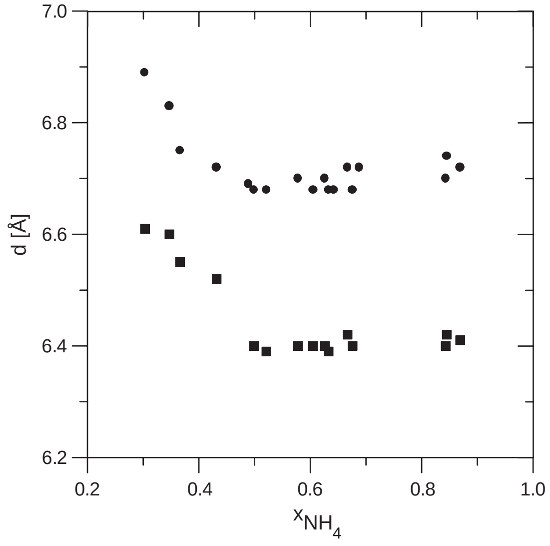

Fig. 3. The change of the interlayer distance d in $(NH_4)_xVOPO_4 \cdot H_2O$ with x.

about 1 year by standing at room temperature. Most probably, the ammonium ions in phase 2 are rearranged to the more thermodynamically stable phase 1. This rearrangement is accompanied with an increase of water content up to $y = 1.4$.

The behavior of $(NH_4)_xVOPO_4 \cdot H_2O$ is most similar to that of $K_xVOPO_4 \cdot H_2O$. The potassium intercalates also contain one molecule of water per formula unit and it comprises also two phases at low amount of potassium. The interlayer distances of these phases are about 0.3 Å higher than that of the ammonium phases and decrease with increasing amount of potassium up to $x = 0.6$ [11]. $(NH_4)_xVOPO_4 \cdot H_2O$ differs from $K_xVOPO_4{\cdot}H_2O$ at higher amount of the intercalated ion, as the latter forms only one phase with constant interlayer distance equal to about 6.4 Å for $x > 0.6$. It was found that the diffractograms of the potassium intercalates do not change even after several years, regardless of the amount of potassium intercalated.

3.2. Ion exchange

The ability to exchange alkali-metal ions for NH_4^+ was studied for Li^+, Na^+, K^+, and Rb^+ redox-intercalated $VOPO_4 \cdot 2H_2O$. During the ion exchange, intermediate phases with the general formula $(NH_4)_{1-x}Me_xVOPO_4 \cdot yH_2O$ are formed, where Me = Li, Na, K, or Rb. As found by cerimetry, the vanadium(IV)/vanadium(V) ratio remains the same during the ion exchange, i.e., there is no reduction or oxidation of vanadium. All the products of the ion exchange were green powders. An opposite ion exchange, i.e., a reaction of $(NH_4)_xVOPO_4 \cdot H_2O$ with alkali-metal salt solutions, was unsuccessful.

3.3. $Li_{0.98}VOPO_4 \cdot 1.9H_2O + NH_4^+$

The ion exchange of the lithium ions in $Li_{0.98}VOPO_4{\cdot}1.9H_2O$ for the ammonium ions is completed after 20 days (Fig. 4a). The change is most rapid within first 6 h of the reaction, when the Li content decreases from $x_{Li} = 1$ to 0.67. During the ion exchange, two phases with different interlayer distances are formed (Fig. 5). One of them is the original Li compound, the second one corresponds to a newly formed ammonium compound. The situation becomes more complex after 4 days of the reaction, when a third phase with the

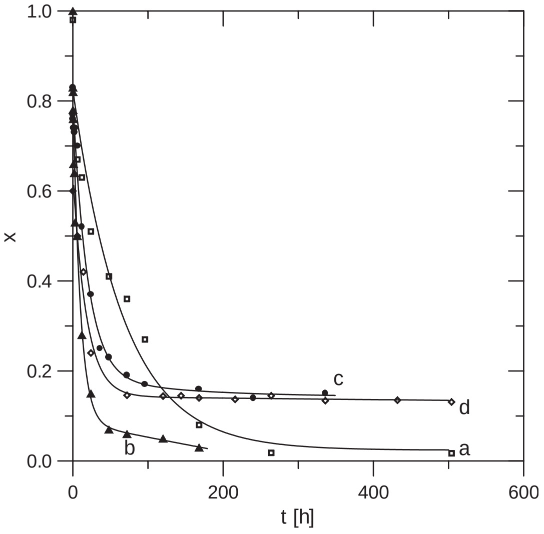

Fig. 4. The amount of alkali-metal ions in the products x_{Me}, where Me is Li (a), Na (b), K (c), and Rb (d), as a function of the time of the ion exchange t.

interlayer distance of about 7.3 Å is formed. This phase disappears in the almost fully exchanged sample (with traces of lithium only, $x_{\mathrm{Li}} = 0.017$), where only a phase corresponding to $\mathrm{NH_4VOPO_4} \cdot y\mathrm{H_2O}$ is present ($d = 6.768$ Å). The interlayer distance of the Li phase remains roughly the same during the ion exchange, around 6.4 Å. The interlayer distance of the $\mathrm{NH_4^+}$ phase is around 6.7 Å for $x_{\mathrm{Li}} > 0.2$, forming a plateau in Fig. 6, and increases for fully $\mathrm{NH_4^+}$ intercalated sample to 6.77 Å. The lattice parameters of the tetragonal cell for the starting $\mathrm{Li_{0.98}VOPO_4} \cdot 1.9\mathrm{H_2O}$ and for the final product of the ion exchange ($x_{\mathrm{Li}} = 0.017$) are given in Table 1. These parameters indicate that the structure of the $\mathrm{VOPO_4}$ layers is retained during the ion exchange. The amount of water y decreases with decreasing amount of lithium x_{Li} almost linearly from $y = 1.9$ for $x_{\mathrm{Li}} = 0.98$ to $y = 1$ for $x_{\mathrm{Li}} = 0.017$.

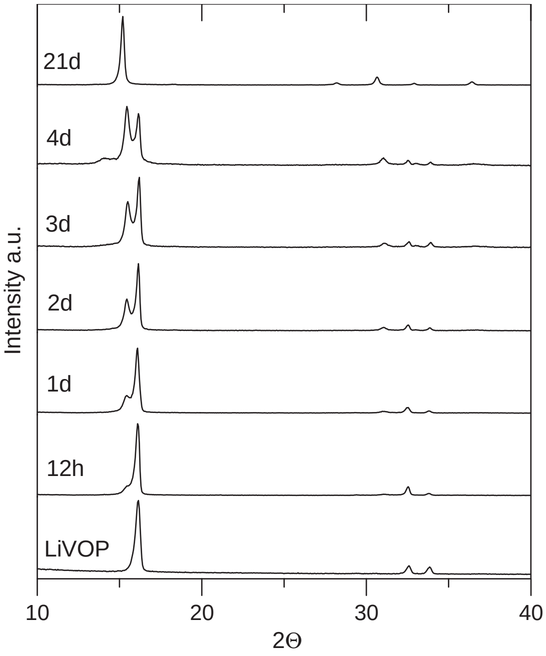

Fig. 5. The diffractograms of the phases formed during the ion exchange of $\mathrm{Li^+}$ in $\mathrm{Li_{0.98}VOPO_4} \cdot 1.9\mathrm{H_2O}$ for $\mathrm{NH_4^+}$. LiVOP—original $\mathrm{Li_{0.98}VOPO_4} \cdot 1.9\mathrm{H_2O}$, duration of the ion exchange from 12 to 504 h.

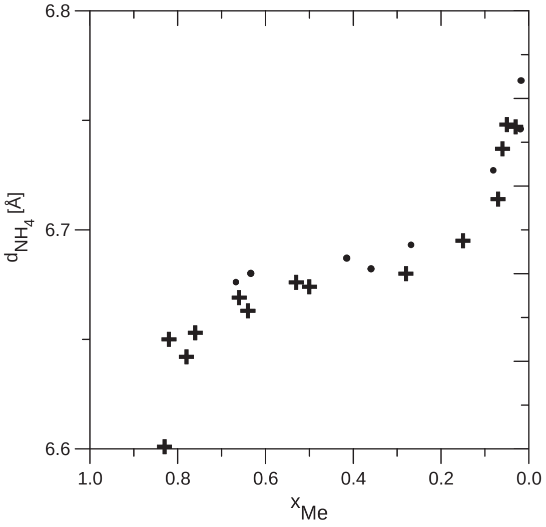

Fig. 6. The change of the interlayer distances of the ammonium phases d during the ion exchange of $\mathrm{Li^+}$ in $\mathrm{Li_{0.98}VOPO_4} \cdot 1.9\mathrm{H_2O}$ (circles) and $\mathrm{Na^+}$ in $\mathrm{NaVOPO_4} \cdot \mathrm{H_2O}$ (crosses) for $\mathrm{NH_4^+}$ as a function of x_{Me} (Me = Li, Na).

3.4. $\mathrm{NaVOPO_4} \cdot \mathrm{H_2O} + \mathrm{NH_4^+}$

During the ion exchange of sodium in $\mathrm{NaVOPO_4 \cdot H_2O}$ for $\mathrm{NH_4^+}$, only two phases are present, corresponding to the original $\mathrm{NaVOPO_4} \cdot \mathrm{H_2O}$ and newly formed $(\mathrm{NH_4})_x\mathrm{VOPO_4} \cdot y\mathrm{H_2O}$. From the diffractograms, a decrease of the intensity of the peak corresponding to the sodium phase and an increase of the intensity of the peak of the ammonium phase can be seen (Fig. 7). The amount of $\mathrm{NH_4^+}$ ions in the solid as a

Table 1
X-ray diffraction data for the selected phases

Starting material	x_{Me}	a (Å)	c (Å)
$\mathrm{Li_{0.98}VOPO_4} \cdot 1.9\mathrm{H_2O}$	0.98	6.344(3)	12.786(4)
	0.017	6.321(1)	13.543(1)
$\mathrm{NaVOPO_4} \cdot \mathrm{H_2O}$	1.00	6.278(1)	11.314(1)
	0.07	6.333(8)	13.43(2)
	0.05	6.329(6)	13.52(2)

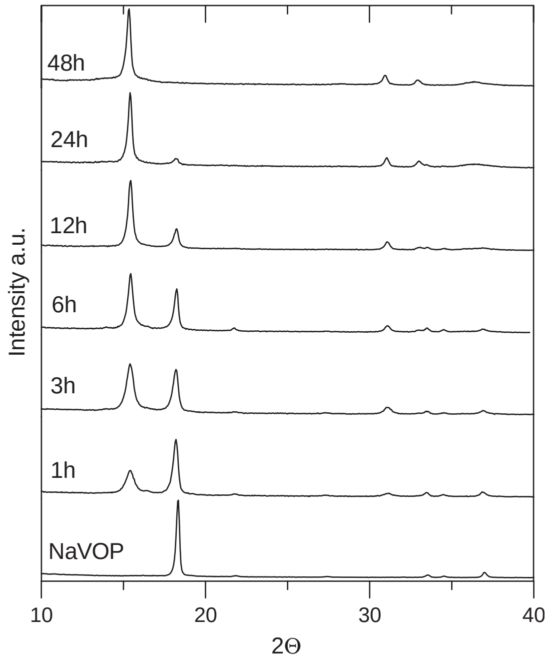

Fig. 7. The diffractograms of the phases formed during the ion exchange of $\mathrm{Na^+}$ in $\mathrm{NaVOPO_4} \cdot \mathrm{H_2O}$ for $\mathrm{NH_4^+}$. NaVOP—original $\mathrm{NaVOPO_4} \cdot \mathrm{H_2O}$, duration of the ion exchange from 1 to 48 h.

function of the reaction time has an exponential shape (Fig. 4b). The reaction is faster than the reaction of $Li_{0.98}VOPO_4 \cdot 1.9H_2O$ and the amount of sodium x_{Na} decreases under 0.1 after 1 day of the reaction.

The interlayer distance of the sodium phase ranges 5.64–5.68 Å and does not follow any distinct trend. The interlayer distance of the ammonium phase increases with the time of the reaction (Fig. 6) and the dependence of d on x_{Me} for $Me = $ Na is practically identical with that for $Me = $ Li. Like in the ion exchange with the lithium compound, a plateau can be observed in Fig. 6 for $x_{Na} = 0.2-0.6$ indicating a formation of an intermediate ammonium phase with $d = 6.68$ Å. In this intermediate phase, both Na^+ and NH_4^+ cations coexist in the interlayer space of $VOPO_4$. The concentration of the larger ammonium cations is lower than in the pure ammonium phase; nevertheless, all vanadium atoms are reduced and the excess of the negative charge on the $VOPO_4$ layers is compensated by the sodium cations. Electrostatic interactions thus formed are responsible for the lower interlayer distance of the intermediate phase compared to that of the pure ammonium phase. For the samples with $x_{Na} < 0.1$, the interlayer distance increases up to $d = 6.75$ Å for $x_{Na} = 0.03$ (the starting mixture shaken for 7 days). The tetragonal structure of the host layers is retained during the ion exchange as follows from the lattice parameters of the starting compound and the product with $x = 0.05$ (Table 1). The amount of water y is not influenced by the ion exchange and is roughly equal to 1.

3.5. $K_{0.83}VOPO_4 \cdot H_2O + NH_4^+$

As can be seen from Fig. 4c, the ion exchange of K^+ in $K_{0.83}VOPO_4 \cdot H_2O$ for NH_4^+ is more rapid than the ion exchange with lithium intercalated $VOPO_4$ but the reaction stops at around $x_K = 0.15$. Similar to the $NaVOPO_4 \cdot H_2O$ ion exchange, two phases are formed during the contact of $K_{0.83}VOPO_4 \cdot H_2O$ with an NH_4Cl solution (Fig. 8). Within the first 6 h of this reaction, a slight decrease of the amount of potassium x_K in the samples was observed, from $x_K = 0.77$ for time of the reaction $t = 5$ min to $x_K = 0.70$ for $t = 6$ h. No peak corresponding to an ammonium phase was observed during this time. Between 6 h and 1 day of the reaction, a sudden decrease of x_K was observed from $x_K = 0.70$ for $t = 6$ h to 0.52 for $t = 12$ h and then to 0.37 for 1 day of the reaction. This process is accompanied by the formation of the ammonium phase with $d = 6.77$ Å. Then the interlayer distance of this phase slightly increases with increasing extent of the ion exchange. The interlayer distance of the potassium phase keeps constant ($d = 6.36 \pm 0.01$ Å) up to $x_K = 0.3$. For the lower content of potassium, the interlayer distance drops to 6.31 ± 0.01 Å. Most probably, the ammonium ions enter the interlayer space of the potassium phase and replace some of the K^+ ions at the beginning of this ion exchange without changing the interlayer distance of the original K^+ phase. When a certain degree of the ion exchange is achieved, the concentration of the ammonium ions in the interlayer space reaches a value at which the NH_4^+ ions are able to move away the $VOPO_4$ layers and the ammonium phase is formed. Unfortunately, the products after the ion exchange of K^+ and Rb^+ could not be indexed due to a poor quality of the diffractograms. As in the case of the $NaVOPO_4 \cdot H_2O$ ion exchange, the content of water remains practically constant, about one molecule of water per formula unit.

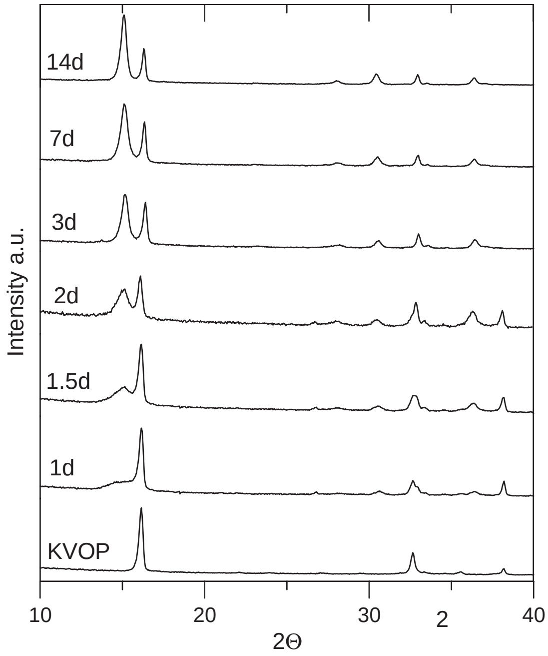

Fig. 8. The diffractograms of $(NH_4)_{1-x}K_xVOPO_4 \cdot H_2O$ phases formed during the ion exchange. KVOP—original $K_{0.83}VOPO_4 \cdot H_2O$, duration of the ion exchange from 1 to 14 days.

3.6. $Rb_{0.60}VOPO_4 \cdot 1.3H_2O + NH_4^+$

The redox intercalation of rubidium into $VOPO_4 \cdot 2H_2O$ proceeds only to $x_{Rb} = 0.60$ in a single intercalation step, i.e., a compound with formula $Rb_{0.60}VOPO_4 \cdot 1.3H_2O$ is formed [12]. Therefore, we used this compound for the ion exchange of Rb^+ for NH_4^+. The exchange is very rapid at the beginning (Fig. 4d) and the amount of rubidium decreases to $x_{Rb} = 0.146$ within 3 days. Further ion exchange is very slow and the rubidium ions are present in the samples even after 28 days of the reaction ($x_{Rb} = 0.134$). All the samples contained about one molecule of water per formula unit after the ion exchange. Similar to the ion exchange with the potassium intercalate, there is no ammonium phase within first 5 days of the reaction although the amount of rubidium decreases to $x_{Rb} =$

0.144. The interlayer distance of the rubidium phase remains constant ($d = 6.43 \pm 0.01$ Å) during this period. After 5 days, two new phases are formed with the interlayer distances of 6.83–6.86 and 6.68–6.70 Å. As in the case of the potassium compound, the ammonium ions replace the rubidium ions in the interlayer space of the original $Rb_{0.60}VOPO_4 \cdot 1.3H_2O$. As the Rb^+ ions are larger than the K^+ ions, more Rb^+ can be replaced with NH_4^+ without a need to enlarge the interlayer distance compared to the situation observed for the exchange of potassium.

A three-phase compound formed after 7 days of the shaking, with $x_{Rb} = 0.14$, was tested for aging. The diffractogram does not change after 1-month standing of the solid in air at room temperature. The same compound was also stirred in the 1:1 (v/v) acetone/water mixture at room temperature for 1 week. The phase with the highest interlayer distance disappeared after this treatment and only one ammonium phase with $d = 6.72$ Å and the rubidium phase with $d = 6.48$ Å were observed in the diffractogram.

Acknowledgments

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