A convenient hydrothermal route for the synthesis of $M_x$VOPO$_4 \cdot y$H$_2$O ($M = Na$ and $K$)

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Abstract

Monophasic crystals of $M_x$VOPO$_4 \cdot y$H$_2$O ($M = Na$, $K$) could be readily synthesized through a hydrothermal reaction (180°C and 10 h) involving alkali borohydrides as reducing agents.

Keywords: Vanadyl phosphates; Intercalation; Hydrothermal synthesis; Borohydride

1. Introduction

Synthesis of metal intercalated layered vanadium phosphate, $M_x$VOPO$_4 \cdot 2$H$_2$O has been extensively studied for possible applications as ionic conductors, inorganic ion-exchangers and oxidation catalysts. Incorporation of metal ions, in particular alkali metal ions into VOPO$_4$ has been attempted by several groups employing novel chemical routes [1-3]. For alkali metal intercalation, Jacobson et al. [2] employed a redox reaction of VOPO$_4 \cdot 2$H$_2$O with aqueous alkali iodides at room temperature. They obtained a complete range of solid solutions $M_x$VOPO$_4 \cdot (>_<x<1)$H$_2$O (M = Na, K) in polycrystalline form which were not suitable for detailed structural studies. On the other hand, Wang et al. [3] employed a mild hydrothermal reaction and obtained good crystals of only $M_{0.5}$VOPO$_4 \cdot >$H$_2$O; the products however contained other impurity phases. In the above reaction, the authors used VO$_2$ to reduce vanadate ions and alkali hydroxide supplied the required amount of counter cations. Recently, use of borohydride has been demonstrated in preparing alkali intercalated mixed valent vanadates, molybdates and tungstates [4-7] and ultrafine metal-boron powders [8,9] at ambient temperatures. In almost all these reactions the products were amorphous and required further thermal annealing at temperatures $> 350°C$ for crystallization.

In this paper, we report our results that use of alkali borohydrides is effective in directly precipitating single phasic $M_x$VOPO$_4 \cdot >$H$_2$O ($M = Na$, K) powders from aqueous solutions of vanadate acidified with phosphoric acid under refluxing conditions. Under hydrothermal conditions, the same reactions result in good crystals with better yields at lower temperatures and shorter times than reported earlier with single phasic products. The phases were characterized by X-ray powder diffraction, thermal
analysis, scanning electron microscopy, FTIR and Raman spectroscopy.

2. Experimental

In a typical preparation, reagent grade 0.6096 g of NaVO₃ (0.005 mol) was dissolved in 30 ml water and varying amounts of sodium borohydride solid (0.00125 to 0.025 mol) was added with constant stirring while the solution was heated to boiling for 1 h in air. At this stage the solution was brown in colour. When 2 ml of H₃PO₄ (85%) was added to the above solution, a blue precipitate formed immediately which disappeared within a minute resulting in an intensely blue coloured homogeneous solution. The solution was transferred to a 45 ml teflon lined Parr acid digestion reactor and the reaction vessel was heated at 180°C for 10 h under autogenous pressure before cooling to room temperature at 10°C/h. The products were washed off with water followed by acetone and dried in air. We also carried out hydrothermal reactions of V₂O₅ with KBH₄ similar to the conditions described above. The samples appeared to be air stable even after exposing them in air for months and this was further confirmed by chemical analysis. Visual microscopic examination of the crystals prepared from various batches revealed the presence of uniform, green platy crystals which were quite fragile. The above experiments were also carried out under refluxing conditions (~100°C). There is no difference between the X-ray pattern of this product and the sample prepared from hydrothermal conditions. While the products obtained from refluxing conditions were polycrystalline, the hydrothermal reaction yielded well-developed platy crystals.

3. Results and discussion

X-ray powder diffraction patterns showed (Fig. 1) mostly (001) reflections with a layered periodicity of ~0.66 nm for Na₀.₅VOPO₄ • 2H₂O and |0.68 run for K₀.₅VOPO₄ • 1.5H₂O. Chemical analysis of the samples was carried out by a potentiometric titration by dissolving ~100 mg of the sample in a known excess of 0.01 M ferrous ammonium sulphate. Table 1 gives the reactants, the ratio of V⁴⁺/total V, yield on the basis of vanadium, weight loss and composition. Thermal analysis of the samples indicated a weight loss at 200°C due to water molecules. FTIR spectra (Fig. 2) of all the samples show characteristic absorption around 3500-3400, 1640, 1200-980, 640 and 540 cm⁻¹ corresponding to stretching and bending modes of water, V=O stretching, phosphate groups and V-O networks [10,11]. Raman spectra (Fig. 3) could be assigned [12] to P-O stretching in 1200-1000 cm⁻¹ range, a V=O stretch at 1000-990 cm⁻¹, a P-O stretch at 985-975 cm⁻¹ as well as coupling with V-O and P-O bending modes and skeletal vibrations in the range 600-150 cm⁻¹. Scanning electron micrographs (Fig. 4) of the samples showed the formation of platy crystals characteristic of all metal intercalated layered vanadyl phosphates.

On the basis of chemical and thermal analysis the composition of our phases appeared to be Na₁VOPO₄ • 2H₂O (Table 1) and the X-ray powder
Table 1
Chemical and TG analysis of M_xV^{a+b}V_j,OPO_4•yU_2O

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Amount of V^{4+} (%)</th>
<th>Total vanadium (%)</th>
<th>Yield on the basis of V (%)</th>
<th>TGA wt. loss</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaVO_3 + NaBH_4 + H_3PO_4 + H_2O</td>
<td>10.8</td>
<td>27.0</td>
<td>61</td>
<td>19.0</td>
<td>Na_{0.5}VOPO_4•2.23H_2O</td>
</tr>
<tr>
<td>V_2O_5 + NaBH_4 + H_3PO_4 + H_2O</td>
<td>14.0</td>
<td>26.3</td>
<td>85</td>
<td>17.8</td>
<td>Na_{0.5}VOPO_4•2.09H_2O</td>
</tr>
<tr>
<td>NaVO_3 + NaBH_4 + H_3PO_4 + H_2O</td>
<td>14.0</td>
<td>24.9</td>
<td>46</td>
<td>18.6</td>
<td>Na_{0.5}VOPO_4•2.20H_2O</td>
</tr>
<tr>
<td>NaVO_3 + NaBH_4 + H_3PO_4 + H_2O</td>
<td>14.9</td>
<td>23.0</td>
<td>64</td>
<td>15.9</td>
<td>Na_{0.5}VOPO_4•1.87H_2O</td>
</tr>
<tr>
<td>NaVO_3 + NaBH_4 + H_3PO_4 + H_2O</td>
<td>28.3</td>
<td>28.3</td>
<td>49</td>
<td>3.3</td>
<td>Na_{0.5}VOPO_4•0.35H_2O</td>
</tr>
<tr>
<td>NaVO_3 + NaBH_4 + H_3PO_4 + H_2O</td>
<td>25.4</td>
<td>27.3</td>
<td>75</td>
<td>5.8</td>
<td>Na_{0.5}VOPO_4•0.62H_2O</td>
</tr>
<tr>
<td>NaVO_3 + NaBH_4 + H_3PO_4 + H_2O</td>
<td>13.8</td>
<td>24.8</td>
<td>53</td>
<td>18.2</td>
<td>Na_{0.5}VOPO_4•2.14H_2O</td>
</tr>
<tr>
<td>NaVO_3 + NaBH_4 + H_3PO_4 + H_2O</td>
<td>13.4</td>
<td>25.3</td>
<td>80</td>
<td>13.2</td>
<td>K_{0.5}VOPO_4•1.53H_2O</td>
</tr>
<tr>
<td>V_2O_5 + KBH_4 + H_3PO_4 + H_2O</td>
<td>10.0</td>
<td>24.9</td>
<td>70</td>
<td>16.3</td>
<td>K_{0.5}VOPO_4•1.92H_2O</td>
</tr>
</tbody>
</table>

patterns were comparable to those reported in the literature [2] as well as the simulated X-ray powder diffraction patterns based on the single crystal coordinates given by Wang et al. [3]. In order to prepare a continuous solid solution of Na_{x}VOPO_4•2H_2O (0 ≤ x ≤ 1), we carried out the synthesis by varying the mole ratios of NaVO_3 and NaBH_4. In most cases when the NaBH_4/NaVO_3 ratio is less than one, we invariably got Na_{x}VOPO_4•2H_2O.
where $x \leq 0.5$ (see Table 1). Since the reduction of aqueous vanadate solution by NaBH$_4$ is slow, it is probably difficult to control the formal oxidation state of vanadium in the final compound. We also attempted the preparation of Na$_x$VOPO$_4 \cdot 2$H$_2$O starting from V$_2$O$_5$ rather than NaVO$_3$. In this case we could obtain the phase with considerable yields only for $x \sim 0.5$. K$_{x}$VOPO$_4 \cdot 1.5$H$_2$O were prepared from V$_2$O$_5$ and KBH$_4$ in a method similar to the one described above. In this case also, we obtained only good crystals of K$_{x}$VOPO$_4 \cdot 1.5$H$_2$O.

The chemistry of borohydride reduction of aqueous metallates has been found to be quite complex. Though we were able to vary the amount of metal
ion intercalated into the product (see Table 1), the amount of alkali could not be controlled on the basis of quantitative amounts of borohydride. In earlier studies, metal intercalated VPO’s are invariably synthesized under hydrothermal conditions at temperatures between 180 and 230°C for a period of 2 to 5 days by keeping the pH of the solution between 3 and 4. Use of borohydrides at much lower pH (1-2) appears to be quite effective to reduce vanadium (V) to vanadium (IV). In our experiments, there was no evidence for the formation of the V(III) species even when we used excess borohydride. While the lower pH favoured the formation of layered vanadyl phosphates, the combined use of borohydride as a reducing agent and hydrothermal conditions resulted in the crystallization of $\text{M}_1\text{VOPO}_4 \cdot >\text{H}_2\text{O}$ at lower temperatures and shorter times with better yields. We also carried out the above hydrothermal reactions in the presence of templates such as tetramethyl ammonium hydroxide and tetraphenyl phosphonium chloride. Under our reaction conditions these molecules did not get incorporated into the lattice.

Acknowledgements

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References