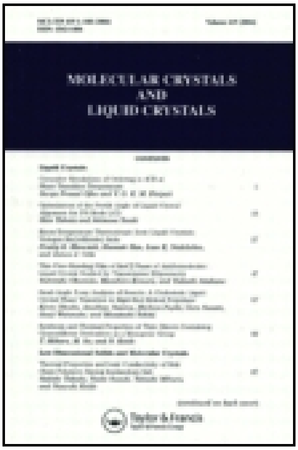

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INTERCALATION OF ALKALI METAL IONS INTO LAYERED $VOPO_4.2H_2O$

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Abstract The intercalates of the $M_xV^{IV}_xV^{V}_{1-x}OPO_4.yH_2O$ (M=Li, Na, H) type were prepared . The structure of products was studied by X-ray diffraction and DTA. The consecutive rise of the stages was observed during intercalation. The decrease of conductivity with increasing content of the guest was observed by the impedance measurements.

INTRODUCTION

Alpha vanadyl phosphate dihydrate is a compound crystallizing in tetragonal structure created by layers of $(VOPO_4)_\infty$ and water molecules in interlayer space. Layers of $(VOPO_4)_\infty$ are formed from corner linked VO_6 octahedra and PO_4 tetrahedra[1,2]. Vanadium (V) atoms can be reduced to vanadium (IV) by proper reducing agent. Charge risen by reduction of vanadium may be compensated by intercalation of some cations into interlayer space. In this way intercalates of $VOPO_4.2H_2O$ with sodium cations were prepared by shaking of solid $VOPO_4.2H_2O$ with ethanolic solutions of NaI[3].

In the present study we used acetone solution of NaI, LiI and hydroquinone (the last one as a source of H^+ ions). Intercalation reaction followed scheme either

$$VOPO_4.2H_2O + x\,MeI \rightarrow Me_xVOPO_4.yH_2O + x/2\,I_2 + (2-y)H_2O, \qquad (1)$$

where Me = Na, Li ; x = 0.25 - 1.00 ; y = 2.0 (for Me = Li) or y = 1 to 2 (for Me = Na), or

$$VOPO_4.2H_2O + x/2\text{hydroquinone} \rightarrow H_xVOPO_4.2H_2O + x/2\text{quinone} \qquad (2)$$

at various temperatures (from 20° to 40°C).

A layered structure of products was determined by X-ray diffraction. A consecutive rise of the stages was observed during intercalation of host by sodium and lithium iodide. A content of water in dependence of content of guest was determined by DTA. A conductivity of prepared samples (in form of pellets) with various content of guest was investigated by impedance spectroscopy.

EXPERIMENTAL

$VOPO_4.2H_2O$ was prepared by a method described in previous paper[4]. Intercalating agents (LiI, NaI, hydroquinone) were commercial (Lachema, Czechoslovakia) and were used without further purification. A 0.5 $mol.l^{-1}$ solution of NaI was prepared by dissolving in acetone-water mixture (10% vol. of water). Solution of LiI (0.4 $mol.l^{-1}$) and hydroquinone (0.35 $mol.l^{-1}$) were prepared in pure acetone. Intercalates were prepared by shaking of 0.5 g solid $VOPO_4.2H_2O$ (with particle size from 0.1 to 0.2 mm) in 20 ml of solution of intercalating agent.

Several reaction mixtures were used for each intercalate,. After a defined time the solid was filtered, thoroughly washed by acetone and dried in a desiccator.

Two methods were used for determination of content of intercalated guest in $VOPO_4.2H_2O$. Amount of iodine in the filtrate after intercalation reaction of MeI with $VOPO_4.2H_2O$ was determined by an amperometric titration with thiosulfate. A content of alkali metal in $M_xVOPO_4.yH_2O$ was then calculated from equation (1). A content of hydrogen in $H_xVOPO_4.2H_2O$ (equation (2)) was determined by cerimetric titration of reduced vanadium in solid product.

DTA and TG analyses were carried out under air at 20-900°C at heating rate $5°C.min^{-1}$.

A method of calculation a relative content of phases from X-ray diffraction data is described in paper[4].

A rectangular pellets (with dimensions 8x3x2 mm) obtained by pressing of dry and powder intercalates was used in a.c. measurements. Impedance was measured in direction of preferable orientation of layers of intercalate. A conductivity of the samples was calculated from impedance data, which show typical arc shape curve in Nyquist plot.

RESULTS AND DISCUSSION

A dependence of content of guest species in the intercalated compounds on reaction time shows exponential character with velocity of reaction increasing with temperature. The reaction rate increases with decreasing ion radius. Reaction is finished when x reaches value of 1, i. e. only vanadium(IV) is present.

Content of water in the intercalate remains constant in intercalates with lithium and hydrogen. On the contrary, the sodium intercalate $Na_xVOPO_4.yH_2O$ releases water (up to y=1), when stoichiometric coefficient x becomes bigger than 0.5. This behavior is probably caused by bigger Van der Waals radius of sodium ion in comparison with Li^+ or H^+. The sodium ions fill cavities among molecules of water in interlayer space at the beginning of the reaction. When amount of sodium reaches value x=0.5, all available cavities are filled and the sodium ions begin to squeeze out loosely bonded molecules of water.

A consecutive rise of phases with different basal spacing was observed during the reaction of $VOPO_4.2H_2O$ with alkali metal ions. The basal spacing of the phases lessens with increasing stoichiometric coefficient due to stronger interaction between guest cations and $VOPO_4$ layers with reduced vanadium.

Relative content w of these phases in intercalates was computed from intensities of diffraction lines. Temperature has no effect on the phase composition as follows from values found at various temperatures (Fig. 1).

In case of intercalation of sodium ion, three phases were observed. The relative content w of the phase with basal spacing c=1.337 nm reaches maximum for stoichiometric coefficient x=0.33. Content of the phase with basal spacing c=1.3063 nm is biggest for x=0.5. The last phase with basal spacing c=1.133 nm is the only product when reaction is finished. The observed phases correspond to stages S3, S2 and S1 as were defined e.g. by Hibma[5].

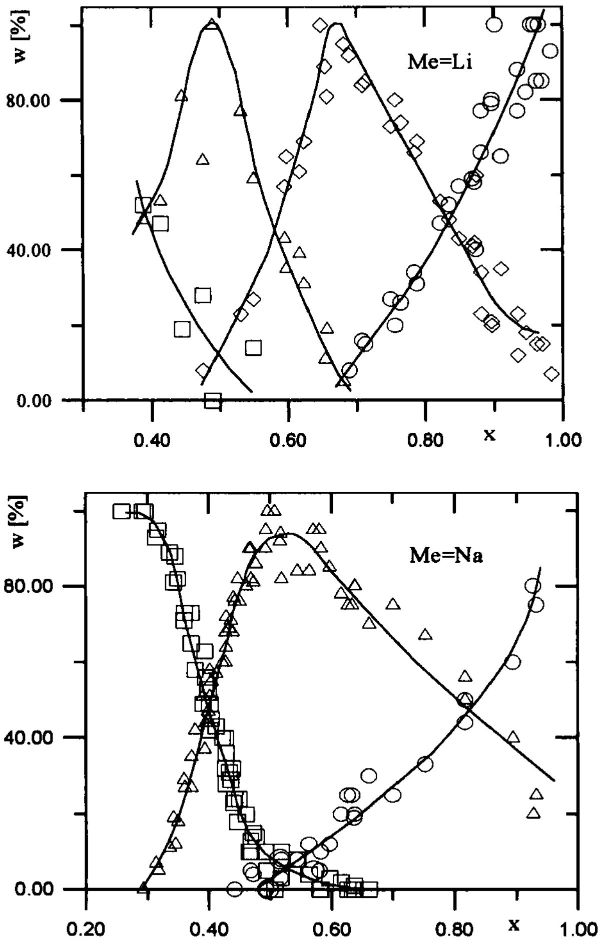

FIGURE 1 Dependence of the relative content w of the stages 3 (squares), 2 (triangles), 1 (open circles) and 3/2 (diamonds) on stoichiometric coefficient x of metal ions in Me$_x$VOPO$_4$.yH$_2$O

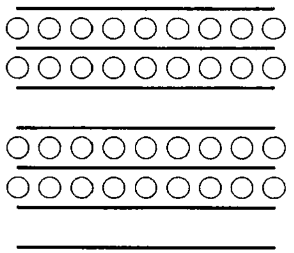

FIGURE 2 Schematic drawing of stage 3/2. Lines are (VOPO$_4$)$_\infty$ layers, circles are atoms of intercalated lithium. Molecules of water are omitted

Similar staging was observed in case of intercalation by lithium ions with stages S3 ($\underline{c}$=1.3361 nm), S2 ($\underline{c}$=1.3200 nm) and S1 ($\underline{c}$=1.2821 nm). In addition a new phase was observed ($\underline{c}$=1.3055 nm), having a maximum of its content at stoichiometric coefficient $\underline{x}$=0.66, i. e. between stage S2 and S1. It seems to be most probable explanation of this facts, that it is a stage in which two full galleries vary with one empty gallery. If we define a stage numbering as a ratio of a number of the all galleries (empty and full ones) to a number of the full galleries in each sequence, we can mark this new sequence as S3/2. This definition of stages does not change marking of other "classical" stages. Considering the stage 3/2 as a sequence of two stages 2 and one stage 1, one can calculate a "theoretical" basal spacing of stage 3/2 as an average of two S2 basal spacings and one S1 basal spacing by a formula $c_{3/2}=(2c_2+c_1)/3$, where indices refer to the stages.

XRD measurements of proton intercalated host does not show any staging in course of reaction of hydroquinone with $VOPO_4.2H_2O$.

Intercalation of all three cations into $VOPO_4.2H_2O$ causes a decrease of conductivity of intercalates prepared (an example for $Na_xVOPO_4.yH_2O$ is given in figure 3). This decrease depends linearly on content of guest up to value of stoichiometric coefficient $\underline{x}$ about 0.5. Dependence of conductivity of intercalates with higher content of guest on $\underline{x}$ is slighter.

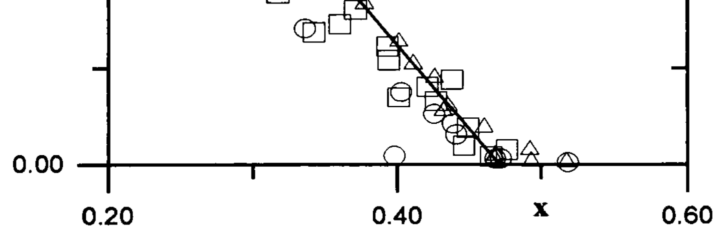

FIGURE 3 Dependence of conductivity $\underline{s}$ on stoichiometric coefficient $\underline{x}$ in $Na_xVOPO_4.yH_2O$ prepared at 20°C (squares), 30°C (triangles) and 40°C (circles)

The decrease of conductivity is probably joined with reduction of vanadium atoms in the layers of $(VOPO_4)_\infty$. Reduction of vanadium(V) to vanadium(IV) brings a negative charge to the layers which is compensated by intercalated cations. As it was described in previous work[4], conductivity in parent $VOPO_4.2H_2O$ is caused by positively charged carriers moving between layers of $(VOPO_4)_\infty$ and the only possible carrier is proton in this case. It is interesting therefore that the intercalation of protons does not increase conductivity. This is possible to explain by anchoring of protons intercalated to the reduced vanadium atoms. Anchored protons are not mobile and have not significant influence on conductivity. The same mechanism inhibits mobility of alkali metal ions in $Me_xVOPO_4.yH_2O$. A stronger electrostatic interaction causes a more rigid arrangement in the interlayer space which is in a good agreement with the decrease of basal spacings of intercalates in comparison with $VOPO_4.2H_2O$.

The reduction of vanadium atoms in $(VOPO_4)_\infty$ during intercalation of cationic guests leads to diminishing of acidity of layers. Consequently, the concentration of protons in interlayer space is lowered. As conductivity depends linearly on amount of carriers (related also linearly to amount of guest through acidity given by ratio of vanadium(V) to vanadium(IV)), the dependence of conductivity vs. stoichiometric coefficient is also linear. This explanation of conductivity mechanism is valid for stoichiometric coefficient $0<\underline{x}<0.5$.

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