

Electrical conductivity of $MOXO_4$ ($M = V, Nb$; $X = P, As$) compounds intercalated with H_2O and H_3XO_4

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Abstract

Layered compounds with the general formula $MOXO_4 \cdot yH_2O$ ($M = V, Nb$; $X = P, As$) were prepared. The content of water y was controlled by keeping the samples in an atmosphere with various relative humidities (RH). Depending on RH, the formation of several hydrates of niobyl phosphate and arsenate was observed and their basal spacings (d) were determined, namely, $NbOPO_4 \cdot H_2O$, $d = 6.4 \text{ \AA}$, at 11% RH and lower, $NbOPO_4 \cdot 2H_2O$, $d = 7.0 \text{ \AA}$, at 22–33% RH, $NbOPO_4 \cdot 3H_2O$, $d = 7.8 \text{ \AA}$, at 43–84% RH, and $NbOPO_4 \cdot 5H_2O$, $d = 8.0 \text{ \AA}$, at 92% RH and above; $NbOAsO_4 \cdot H_2O$, $d = 6.2 \text{ \AA}$, at 0–16% RH and $NbOAsO_4 \cdot 3H_2O$, $d = 7.9 \text{ \AA}$ at 33% RH and above. As follows from ac and dc conductivity data, $NbOXO_4 \cdot yH_2O$ compounds are practically pure protonic conductors, whereas $VOXO_4 \cdot yH_2O$ compounds are mixed protonic–electronic conductors and the protonic component increases with y . Two intercalates of $MOXO_4 \cdot yH_2O$ with inorganic acids were prepared. A new intercalate of H_3AsO_4 into $VOAsO_4 \cdot yH_2O$ with the formula $VOAsO_4 \cdot 0.5H_3AsO_4 \cdot yH_2O$ ($y = 0.5–0.8$) has the cell parameters $a = 6.37$ and $c = 8.81–9.13 \text{ \AA}$ at 0–22% RH. Above 22% RH, the intercalate decomposes and the parent $VOAsO_4 \cdot yH_2O$ with H_3AsO_4 adsorbed on the surface is formed. Another intercalate with formula $NbOPO_4 \cdot H_3PO_4 \cdot yH_2O$ ($y = 2–4$ at 0–75% RH) has the cell parameters $a = 6.43$ and $c = 9.56–9.70 \text{ \AA}$ at RH from 0% to 5% and $a = 6.48$ and $c = 11.2 \text{ \AA}$ at RH from 33% to 75%. Both intercalates are more conductive than their $MOXO_4 \cdot yH_2O$ hosts and their conductivity increases with increasing RH of the surrounding atmosphere. Like $NbOPO_4 \cdot yH_2O$, also $NbOPO_4 \cdot H_3PO_4 \cdot yH_2O$ can be considered pure proton conductor and its conductivity at 20 °C reaches $5 \times 10^{-3} \text{ S cm}^{-1}$ for $y = 4$.

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1. Introduction

Compounds with the general formula $MOXO_4$ ($M = V, Nb$; $X = P, As$) represent a group of layered materials which are able to accommodate (intercalate) neutral species into the interlayer space. The structure of $MOXO_4$ sheets with a tetragonal symmetry was described for $VOPO_4 \cdot 2D_2O$ [1]. It was confirmed that $VOPO_4 \cdot 2H_2O$ [2,3], $VOAsO_4 \cdot yH_2O$ [4], $NbOPO_4 \cdot yH_2O$ [5], and $NbOAsO_4 \cdot yH_2O$ [6] are isostructural.

The layers of $MOXO_4$ are formed by MO_6 octahedra, which are connected through their equatorial oxygens to four different XO_4 tetrahedra. The oxygen atoms of the XO_4 groups are connected to four different MO_6 and in such a way the layered structure is formed. One of the MO_6 apical oxygen atoms is a vanadyl or niobyl oxygen atom. In the hydrates of $MOXO_4$, a coordinated oxygen atom from water molecules present in the interlayer space occupies the second apical coordination site. The coordination of water oxygen to vanadium or niobium causes an enlargement of the distance between the $(MOXO_4)_\infty$ layers thus forming cavities in which another molecules of water can reside.

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In contrast to pentavalent niobium, vanadium(V) can easily be reduced to vanadium(IV) in the $VOXO_4$ compounds. The reduction causes the formation of a negative charge on the $VOXO_4$ layers which is compensated by a positive charge of species introduced into the interlayer space of $VOXO_4$ during the redox reaction. This phenomenon was utilized to intercalate cations of alkali metals, ammonium, hydronium, and some divalent metals [7]. Lithium-intercalated $VOPO_4$ was also studied from the point of view of its potential applications in batteries [8]. Generally, it was found that intercalations of cations of alkali metals (Li [9], Na [10], K [11], and Rb [12]) or hydronium [11] into $VOPO_4 \cdot 2H_2O$ cause a decrease of conductivity with increasing amount of the intercalated cation.

Compounds containing intercalated phosphoric acid, of general formula $MOPO_4 \cdot xH_3PO_4 \cdot yH_2O$ ($M = V, Nb$), were also prepared [13,14]. H_3PO_4 -intercalated $VOPO_4$ [13] is very unstable and releases H_3PO_4 even at ambient humidity. Chernorukov [14] described preparation and characterization of $NbOPO_4 \cdot 2H_3PO_4 \cdot 5H_2O$, which is stable at ambient conditions and releases water by heating. The lattice parameters ($a = 6.47 \text{ \AA}$, $c = 11.20 \text{ \AA}$) indicate that the compound retains the layered structure of $NbOPO_4$ ($a = 6.41 \text{ \AA}$, $c = 8.04 \text{ \AA}$ for pentahydrate) with enlarged interlayer distance. In aqueous solutions, this compound releases phosphoric acid and transforms to $NbOPO_4 \cdot 3H_2O$. As Beneke and Lagaly [13] pointed out, the washing procedure therefore affects the composition of the product. In spite of the massive work dealing with structural aspects and intercalation behavior of $MOXO_4 \cdot yH_2O$ compounds, only little information is available on their electrical conductivity. Niobyl phosphate hydrate, $NbOPO_4 \cdot yH_2O$ ($y < 3$), is claimed to be a pure protonic conductor [15] with conductivity of $10^{-6} \text{ S cm}^{-1}$ at room temperature. Nevertheless, it is not clear from the paper what hydrate was used for the conductivity measurements. The same authors report higher conductivity ($\sigma = 1.5 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature) for a compound with the formula $K_{0.5}NbOPO_4 \cdot H_3PO_4 \cdot 1.7H_2O$ having the structure of the layers closely related to that of niobyl phosphate. The increased conductivity is caused by an increased concentration of H_3O^+ in the interlayer space of the compound.

While anhydrous $VOPO_4$ is an extrinsic n -type semiconductor [16], we found that $VOPO_4 \cdot 2H_2O$ is a mixed protonic–electronic conductor, with dominant protonic component at room temperature and 58% relative humidity (RH) [17]. The influence of intercalated water on conductivity was investigated by ac/dc measurements in the range 40–200 °C where progressive dehydration ends up with the formation of anhydrous $VOPO_4$. It was shown that $VOPO_4 \cdot H_2O$ is a pure electronic conductor and that its electronic conductivity

is strongly enhanced by the water co-ordinated to vanadium atom. A similar effect was also found for $Rb_xVOPO_4 \cdot yH_2O$ compounds with $x = 0.18$ and 0.28 [12].

Taking into account the importance of hydration on both protonic and electronic conductivity, the lack of information about the dependence of conductivity on hydration at room temperature for vanadium and niobium phosphates, as well as the complete lack of conductivity data for vanadium and niobium arsenates, it was of interest to elucidate the influence of the central atom M , of the anionic group XO_4 and of the water content on the conductivity of isostructural layered compounds with general formula $MOXO_4 \cdot yH_2O$. To this aim the influence of RH of the surrounding atmosphere on hydration and basal spacing was studied, while combined ac/dc-conductivity measurements at controlled RH were carried out to estimate protonic and electronic conductivity under conditions with different RH. In addition to this group of compounds, two of their intercalates with mineral acids, namely an intercalate of $VOAsO_4$ with H_3AsO_4 and an intercalate of $NbOPO_4$ with H_3PO_4 , were also investigated.

2. Experimental section

Generally, the hydrates of $MOXO_4$ were prepared by refluxing M_2O_5 in an aqueous solution of H_3XO_4 . In the case of $M = Nb$, addition of hydrofluoric acid was necessary to facilitate the solubilization of Nb_2O_5 in the reaction mixture. Thus, $VOPO_4 \cdot 2H_2O$ [2], $VOAsO_4 \cdot 3H_2O$ [4], $NbOPO_4 \cdot 3H_2O$ [5,18], and $NbOAsO_4 \cdot 4H_2O$ [6] were prepared according to this method as described in the literature.

Arsenic acid-intercalated vanadyl arsenate hydrate was prepared in the same way as $VOAsO_4 \cdot 3H_2O$ [4]. As distinct from $VOAsO_4 \cdot 3H_2O$, the yellow solid separated from the reaction mixture by filtration was washed with a small amount of cold water and dried in air.

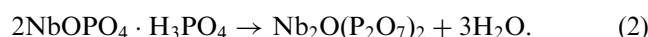
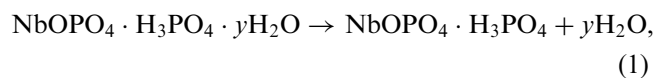
Phosphoric acid-intercalated $NbOPO_4$ was prepared by a modified Chernorukov's method [14]. Instead of metal niobium, 4 g of niobium pentoxide was dissolved in 12 mL of 40 wt% hydrofluoric acid while heating in a water bath. To the solution, 20 mL of 85 wt% phosphoric acid was added and refluxed until a white solid precipitated. The precipitate was separated by filtration, washed with ethanol and dried over P_4O_{10} in vacuum.

Before measurements at desired RH of 11% and above, the samples were kept in closed vessels over saturated solutions of inorganic salts for several weeks [19]. For measurements at 5% RH, 69.4 wt% sulfuric acid solution was used; for measurements at 0% RH, the samples were kept over P_4O_{10} in a desiccator.

The TG analyses were performed using a Netzsch STA 449C apparatus in air between 20 and 600 °C at a

heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$. Powder data were obtained with a D8-Advance diffractometer (Bruker AXE, Germany) using $\text{Cu-K}\alpha$ with a secondary graphite monochromator. Diffraction angles were measured from 7° to 80° (2θ). The temperature measurements from 20 to $250\text{ }^{\circ}\text{C}$ were carried out on a heated corundum plate with a thermocouple [20].

Particular attention was paid to the thermogravimetry analysis of $\text{NbOPO}_4 \cdot \text{H}_3\text{PO}_4 \cdot y\text{H}_2\text{O}$. Expected weight loss during heating comprises two reactions. The first is a removal of interlayer water, the second is a decomposition of $\text{NbOPO}_4 \cdot \text{H}_3\text{PO}_4$ to pyrophosphate. It is difficult to distinguish between these steps in the thermogravimetry curve of $\text{NbOPO}_4 \cdot \text{H}_3\text{PO}_4 \cdot y\text{H}_2\text{O}$, nevertheless, the amount of water y can be calculated from the total weight loss determined at $800\text{ }^{\circ}\text{C}$ according to the following equations:



All conductivity measurements were carried out on pellets, 10 mm in diameter and 1–1.5 mm thick, which were prepared by pressing $\approx 200\text{ mg}$ of material at 40 kNcm^{-2} . The two flat surfaces of the pellet were coated by electrodes made of a pressed graphite powder (Carlo Erba, average particle size $5\text{ }\mu\text{m}$). In order to have good adhesion between pellet and electrodes, the graphite powder was mixed and ground with the sample material in the mass ratio 1:3. Impedance measurements were carried out in the frequency range 10 Hz–1 MHz, at a signal level $\leq 100\text{ mV}$, by a Potentiostat PGSTAT30 Autolab/Eco Chemie equipped with a frequency response analyzer module. Measurements at $20\text{ }^{\circ}\text{C}$ were carried out at controlled RH in a stainless-steel sealed-off cell containing in the lower part a saturated salt solution for RH in the range 11–90%, or a 69.4 wt% sulfuric acid solution for RH = 5%, or P_4O_{10} for RH = 0%. Dc-conductivity was determined by an Amel 554 potentiostat with a dc-load of 0.1 V.

3. Results and discussion

3.1. $\text{MOXO}_4 \cdot y\text{H}_2\text{O}$

In previous papers it was shown that water present in the interlayer region of VOPO_4 and of its rubidium intercalation compounds affects both ionic and electronic conductivity [12,17]. Therefore, before carrying out conductivity measurements, it was of interest to study the hydrated phases formed by MOXO_4 compounds in the RH range from 0% to 100%. In all cases, the water content of a sample equilibrated at a certain RH turned

out to be independent of the sample hydration before equilibration. In contrast to vanadyl arsenate hydrates described in the previous paper [21], the water content of vanadyl phosphate remains the same, $y = 2$, at all RH values. For niobyl arsenate, only two hydrates were observed (Fig. 1): monohydrate ($\text{NbOAsO}_4 \cdot \text{H}_2\text{O}$, basal spacing $d = 6.2\text{ \AA}$) at 0–16% RH and trihydrate ($\text{NbOAsO}_4 \cdot 3\text{H}_2\text{O}$, $d = 7.9\text{ \AA}$) above 33% RH. A more complex system was found for niobyl phosphate (Fig. 1) which forms four different hydrates in the whole range of RH: $\text{NbOPO}_4 \cdot \text{H}_2\text{O}$ ($d = 6.4\text{ \AA}$), stable at RH below 20%, changes to $\text{NbOPO}_4 \cdot 2\text{H}_2\text{O}$ ($d = 7.0\text{ \AA}$) at 22–33% RH and then to $\text{NbOPO}_4 \cdot 3\text{H}_2\text{O}$ ($d = 7.8\text{ \AA}$) at 43–84% RH. Finally, $\text{NbOPO}_4 \cdot 5\text{H}_2\text{O}$ ($d = 8.0\text{ \AA}$) is formed above 92% RH. Hydration data for the four $\text{MOXO}_4 \cdot y\text{H}_2\text{O}$ compounds are summarized in Table 1. It was found that the hydration is reversible. The formation of a particular hydrate depends only on used RH and it is not influenced by the initial degree of its hydration before the storage at particular RH.

The conductivity of $\text{MOXO}_4 \cdot y\text{H}_2\text{O}$ was determined by the impedance technique at $20\text{ }^{\circ}\text{C}$ in the RH range 0–97% with graphite electrodes. Typical impedance plots (Fig. 2) consist of a depressed semicircle pointing at the origin of the complex plane at the high-frequency side and ending with a low-frequency tail associated with the impedance of the electrode–electrolyte interface. The semicircle represents the electrolyte impedance and its extrapolation to the real axis, on the low-frequency side, was used to calculate the so-called ac-conductivity (σ_{ac}). For a mixed protonic–electronic conductor, σ_{ac} is the sum of protonic (σ_{p}) and electronic (σ_{e}) conductivities. The dependence of σ_{ac} on RH for the

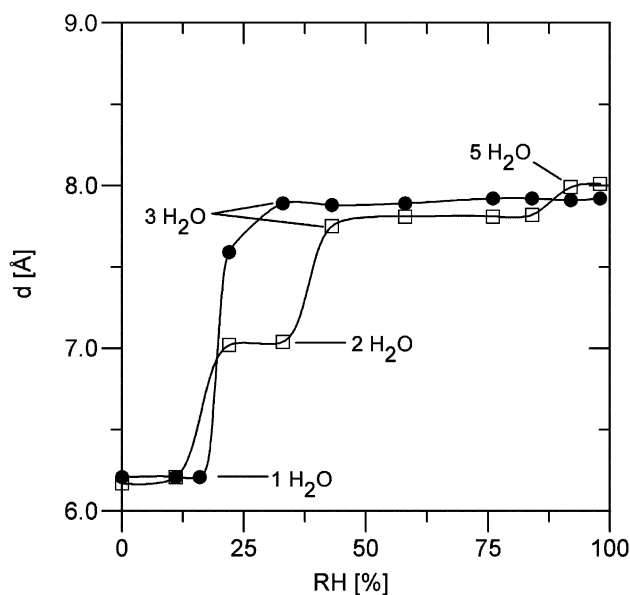


Fig. 1. Basal spacing d of $\text{NbOPO}_4 \cdot y\text{H}_2\text{O}$ (squares) and $\text{NbOAsO}_4 \cdot y\text{H}_2\text{O}$ (circles) as a function of relative humidity (RH). Numbers in the figure denote content of water y .

Table 1
Interlayer distance (d) and water content (y) of $MOXO_4 \cdot yH_2O$ compounds

M	X	d (Å)	Y	RH range (%)
V	P	7.41	2	0–100
V ^a	As	4.18	0	0
		7.33	2	11–43
		8.03	3	43–76
		10.48	5	76–100
Nb	P	6.4	1	0–20
		7.0	2	20–33
		7.8	3	43–84
		8.0	5	92–100
Nb	As	6.2	1	0–16
		7.9	3	33–100

^adata taken from [20].

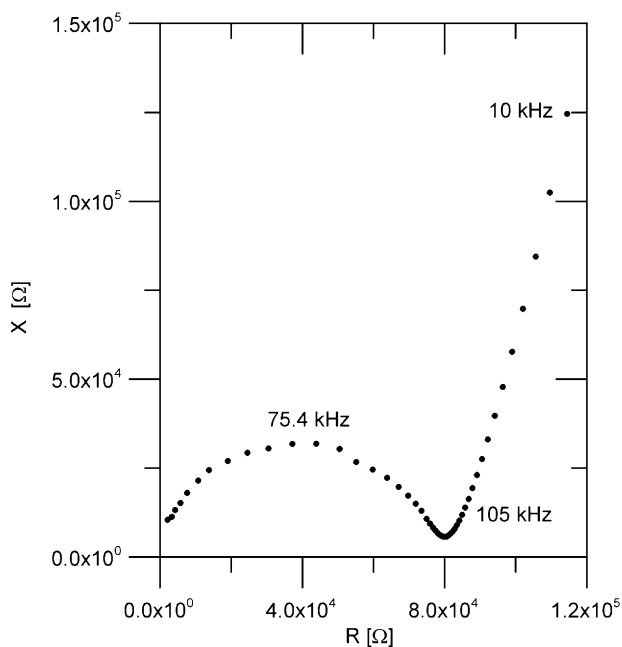


Fig. 2. Impedance plot for $NbOPO_4 \cdot 3H_2O$ at 20 °C and 53% RH.

four $MOXO_4$ compounds is shown in Fig. 3. As a general trend, σ_{ac} rises with RH going from a minimum of $\approx 10^{-9} \text{ S cm}^{-1}$ for $NbOAsO_4 \cdot H_2O$ to a maximum of $3 \times 10^{-5} \text{ S cm}^{-1}$ for $VOAsO_4 \cdot 5H_2O$. At RH close to 0%, the conductivity of $VOXO_4$ is higher than the conductivity of the corresponding $NbOXO_4$ by more than an order of magnitude, but this difference decreases with increasing RH so that, around 100% RH, σ_{ac} lies in the range $1\text{--}3 \times 10^{-5} \text{ S cm}^{-1}$ for all four compounds.

Proton transport in hydrated materials is generally water assisted and an increasing hydration results in an

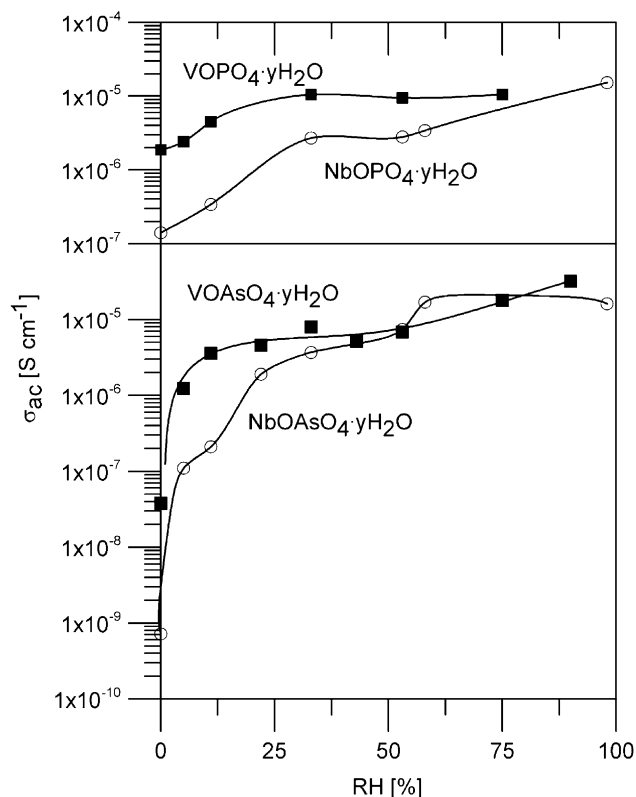


Fig. 3. Ac-conductivity (σ_{ac}) of $MOXO_4 \cdot yH_2O$ compounds as a function of RH at 20 °C.

increasing conductivity. Therefore, the dependence of σ_{ac} on RH can be ascribed to some extent to changes of bulk and/or surface hydration. However, the fact that at low RH $VOAsO_4$ is significantly more conductive than $NbOAsO_4$ cannot simply be attributed to its hydration: at 0% RH, $VOAsO_4$ is anhydrous and cannot conduct protons. This leads to the conclusion that differences in σ_{ac} must be related to some extent to different contributions of electronic and protonic conductivity in σ_{ac} .

According to Ref. [22] and our previous works [12,17], the electronic conductivity can be estimated by passing a dc-current by means of proton blocking electrodes, such as graphite electrodes in the absence of hydrogen. At the steady state, the dc-conductivity is only due to electronic carriers ($\sigma_{dc} = \sigma_e$), while the ac-conductivity is still the sum of both protonic and electronic components ($\sigma_{ac} = \sigma_e + \sigma_p$). The ratio σ_{dc}/σ_{ac} gives therefore the contribution of the electronic component. As mentioned in the Introduction, it was already shown that $VOPO_4 \cdot 2H_2O$ is an electronic–protonic mixed conductor even at RH as low as 5% [12]. Combined ac/dc-measurements were carried out on hydrates of $VOAsO_4$ and $NbOXO_4$ at 5% and 53% RH. The values of the σ_{dc}/σ_{ac} ratio reported in Table 2 show that while the hydrates of $VOAsO_4$ and $VOPO_4$ are mixed electronic–protonic conductors, the hydrates

Table 2
Ratio of steady state dc- and ac-conductivities (σ_{dc}/σ_{ac}) for MOX
 $O_4 \cdot yH_2O$ compounds at 5% and 53% relative humidities

X	RH (%)	σ_{dc}/σ_{ac}	
		$M = V$	$M = Nb$
P	5	$\approx 0.54^a$	0.016
	53	0.11 ^b	0.004
As	5	0.63	0.001
	53	0.07	0.001

^aEstimated from [12].

^bFrom [16].

of $NbOAsO_4$ and $NbOPO_4$ can be considered with a good approximation as pure proton conductors, the contribution of σ_e being in all cases lower than 2% of σ_{ac} even at 5% RH. It is also evident that for $VOXO_4 \cdot yH_2O$ the contribution weight of σ_e decreases with increasing RH and therefore with the material hydration. Consequently, the increase of σ_{ac} with RH is mainly due to the concomitant increase of σ_p . In the specific case of vanadyl phosphate, σ_p changes must be ascribed to changes in surface hydration, since the content of bulk water is independent of RH.

3.2. $MOXO_4 \cdot xH_3XO_4 \cdot yH_2O$

As follows from the diffraction patterns of $VOAsO_4 \cdot 0.5H_3AsO_4 \cdot yH_2O$ taken at RH from 0% to 22%, the cell parameter $a = 6.37 \text{ \AA}$ is the same for all these RH and is identical with that of the parent $VOAsO_4 \cdot yH_2O$ allowing us to presume that the structure of the layers of vanadyl arsenate is retained in $VOAsO_4 \cdot 0.5H_3AsO_4 \cdot yH_2O$.

The content of water y in $VOAsO_4 \cdot 0.5H_3AsO_4 \cdot yH_2O$ kept at 0% RH is very low ($y < 0.5$) and remains practically the same also for the sample kept at 11% RH (Fig. 4). With an increase of RH to 22%, y increases to 0.8. This change of y , when going from 0% to 22% RH, is accompanied by only a small increase of the basal spacing d . This behavior can be explained by a formation of a pillared structure. At low RH, the H_3AsO_4 molecules form pillars in the interlayer space of $VOAsO_4 \cdot 0.5H_3AsO_4 \cdot yH_2O$ with empty cavities between them. With increasing RH of the surrounding atmosphere, these cavities are gradually filled with water molecules without a change of the basal spacing. With a further increase of RH to 33%, a rapid increase of y to 2 is observed whereas the basal spacing decreases to a value corresponding to $VOAsO_4 \cdot 2H_2O$. It indicates that the H_3AsO_4 molecules in the interlayer space are replaced by water molecules and free H_3AsO_4 is then adsorbed on the surface of the crystallites. The presence of H_3AsO_4 in the sample kept at 33% RH was

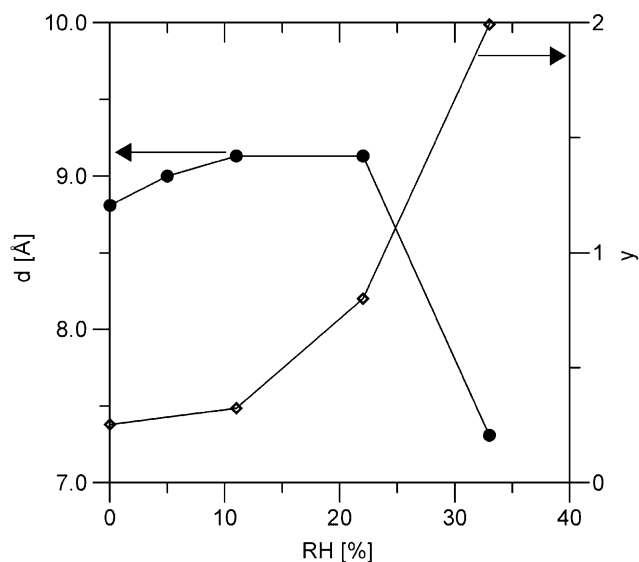


Fig. 4. Basal spacing d (circles) and content of water y (diamonds) of $VOAsO_4 \cdot 0.5H_3AsO_4 \cdot yH_2O$ as a function of RH.

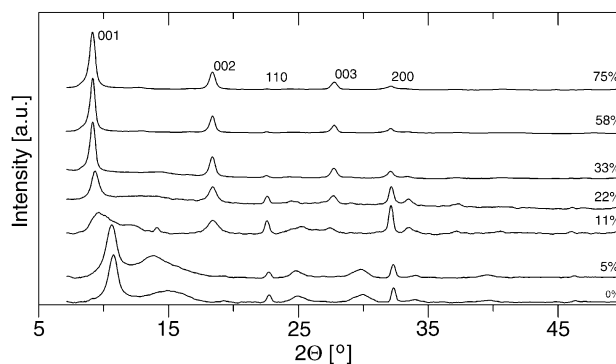


Fig. 5. Diffraction patterns of $NbOPO_4 \cdot H_3PO_4 \cdot yH_2O$ at various RH.

confirmed by a thermogravimetric measurement, where a weight decrease corresponding to the release of water ($y = 2$) is followed by a weight decrease due to a decomposition of H_3AsO_4 .

Following the method described by Chernorukov [14] for the preparation of $NbOPO_4 \cdot 2H_3PO_4 \cdot 5H_2O$, we were able to prepare a compound with P/Nb ratio of 2 instead of P/Nb = 3. That is, the formula of the compound we prepared can be written as $NbOPO_4 \cdot H_3PO_4 \cdot yH_2O$. As it is obvious from the diffractograms of this compound, taken at various RH (Fig. 5), two different phases with different basal spacings are formed. At low RH (0–5%) the basal spacing is around 9.6 Å (Fig. 6). An increase of RH causes a formation of a new phase. The low-humidity phase disappears in the sample kept at 22% RH and the basal spacing $d = 11.2 \text{ \AA}$ of the high-humidity phase remains the same for $RH > 22\%$. The broadening of the (001) lines at 11% RH is associated with crystal disordering occurring

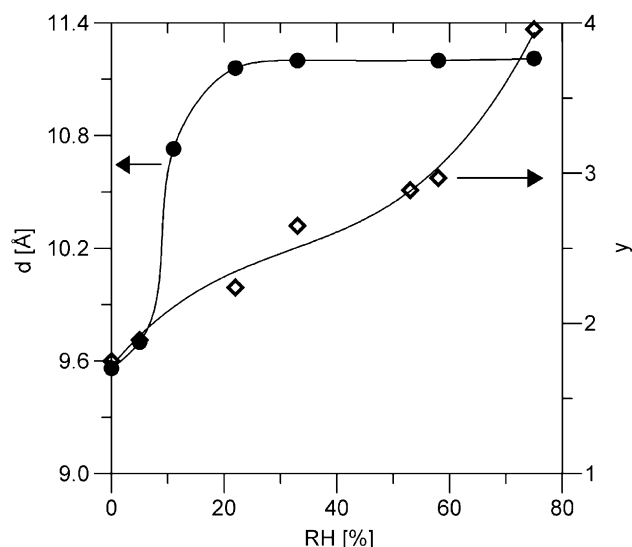


Fig. 6. Basal spacing d (circles) and content of water y (diamonds) of $\text{NbOPO}_4 \cdot \text{H}_3\text{PO}_4 \cdot y\text{H}_2\text{O}$ as a function of RH.

Table 3
The lattice parameters of the $\text{NbOPO}_4 \cdot \text{H}_3\text{PO}_4 \cdot y\text{H}_2\text{O}$ samples

RH (%)	a (Å) ^a	c (Å)
0	6.425	9.56
5	6.43	9.70
33	6.477(1)	11.215(2)
58	6.476(2)	11.203(4)
Heated to 70 °C	6.435(4)	9.096(3)

^aThe difference in precision of the values of the cell parameters is given by a different quality of the diffraction patterns. For the samples at 0% and 5% RH, the a parameter was calculated as an average from the (110) and (200) reflections, the c parameter is given by the (001) reflection. For the samples at 33% and 58% RH and for the sample heated to 70 °C, the a and c cell parameters were calculated from all observed diffraction peaks.

during the phase transition. Distinct (110) and (200) reflections observable in the diffractograms of both phases confirm that the tetragonal $(\text{NbOPO}_4)_\infty$ layers are preserved. The lattice parameters of the tetragonal cell are given in Table 3. In contrast to the basal spacing, the content of water y increases in the whole range of RH from slightly less than 2–4 for RH = 0% to 75%.

The complete loss of interlayer water leads to a phase with $d = 9.1$ Å. Diffractograms collected as a function of temperature showed that the more hydrated the starting sample, the easier the formation of dehydrated $\text{NbOPO}_4 \cdot \text{H}_3\text{PO}_4$. In particular, while for $y = 4$ the basal spacing decreases from 11.2 to 9.1 Å in the range from room temperature to 50 °C, for $y = 2$ the basal spacing approaches 9 Å at temperatures as high as 200 °C. At temperatures higher than 200 °C, a decomposition of interlayer H_3PO_4 begins and finally Nb_2O

$(\text{P}_2\text{O}_7)_2$ is formed as confirmed by powder XRD (PDF No. 28-0715 [23]). The cell parameters of a dehydrated compound, prepared by heating the 75%-RH sample to 70 °C for 3 h (Table 3), indicate that the structure of the NbOPO_4 layers is retained in the H_3PO_4 intercalate too.

Fig. 7 shows the ac-conductivity, at 20 °C, of $\text{VOAsO}_4 \cdot 0.5\text{H}_3\text{AsO}_4 \cdot y\text{H}_2\text{O}$ and $\text{NbOPO}_4 \cdot \text{H}_3\text{PO}_4 \cdot y\text{H}_2\text{O}$ as a function of RH. In the RH range 0–22% the H_3PO_4 intercalate is 10–100 times more conductive than the H_3AsO_4 intercalate. This seems to be a consequence of the higher concentration of the intercalated acid and of the larger hydration of the interlayer region. However, when RH is increased to 33%, the conductivity of the H_3AsO_4 intercalate becomes higher than that of the H_3PO_4 intercalate. This is concomitant with the deintercalation of H_3AsO_4 , which is retained as free hydrated acid on the surface of the vanadyl arsenate microcrystals and makes the intergrain region highly conductive. On the other hand, the less steep dependence on RH observed for the conductivity of $\text{NbOPO}_4 \cdot \text{H}_3\text{PO}_4 \cdot y\text{H}_2\text{O}$ reflects the gradual increase of hydration of interlayer H_3PO_4 (y from 1.7 to 4). As expected, combined ac/dc measurements gave in all cases a $\sigma_{\text{dc}}/\sigma_{\text{ac}}$ ratio $\leq 2 \times 10^{-4}$, thus indicating that the H_3PO_4 intercalate can be considered as a pure protonic conductor.

The ac-conductivity of $\text{NbOPO}_4 \cdot 3\text{H}_2\text{O}$ and that of $\text{NbOPO}_4 \cdot \text{H}_3\text{PO}_4 \cdot y\text{H}_2\text{O}$ pellets, with $y = 1.8, 2.2, 2.8$ and 4.0, was also determined in the temperature range 20–95 °C. Plots of $\log(\sigma_T)$ vs. $1/T$ are shown in Fig. 8. All conductivity data were parameterized by using the Arrhenius equation ($\sigma_T = \sigma_0 \exp(-E_a/RT)$). E_a and σ_0 values are listed in Table 4. Let us discuss the conductivity changes determined by intercalation of H_3PO_4 and by hydration of $\text{NbOPO}_4 \cdot \text{H}_3\text{PO}_4$ in terms of variation of E_a and σ_0 . According to the hopping model [24], σ_0 depends on the carrier concentration C ,

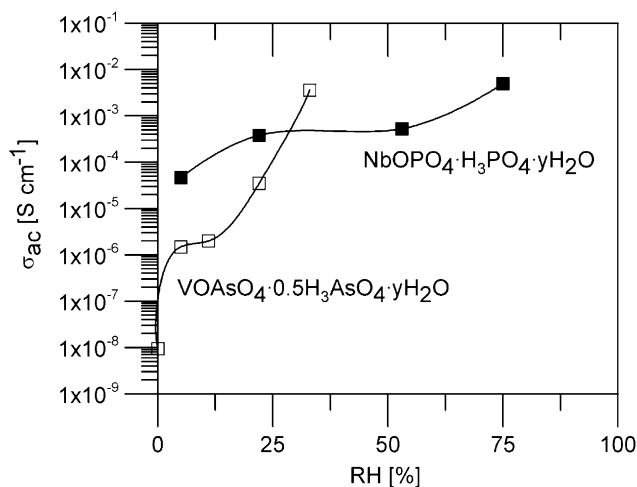


Fig. 7. Ac-conductivity (σ_{ac}) of $\text{VOAsO}_4 \cdot 0.5\text{H}_3\text{AsO}_4 \cdot y\text{H}_2\text{O}$ and $\text{NbOPO}_4 \cdot \text{H}_3\text{PO}_4 \cdot y\text{H}_2\text{O}$ as a function of RH at 20 °C.

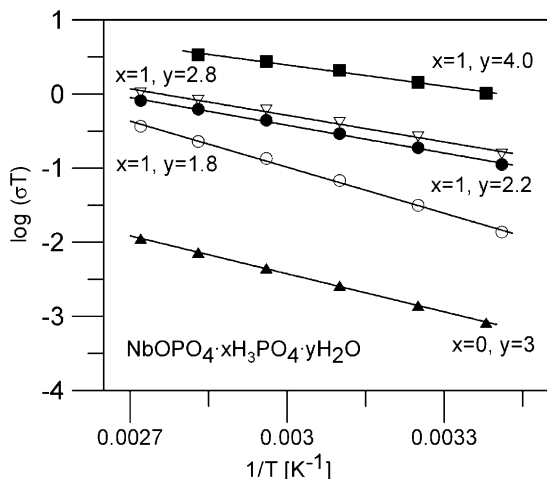


Fig. 8. Arrhenius' plots for the indicated $\text{NbOPO}_4 \cdot \text{H}_3\text{PO}_4 \cdot y\text{H}_2\text{O}$ compounds.

Table 4
Parameters of the Arrhenius equation (activation energy, E_a , and pre-exponential factor, σ_0) for $\text{NbOPO}_4 \cdot \text{H}_3\text{PO}_4 \cdot y\text{H}_2\text{O}$ compounds

x	y	E_a (J mol ⁻¹)	σ_0 (S cm ⁻¹ K)
0	3.0	32.84	2.72
1	1.8	39.62	5.22
1	2.2	23.81	3.31
1	2.8	22.80	3.29
1	4.0	19.50	3.47

the activation entropy ΔS and the hopping frequency ν_0 between sites separated by a distance d :

$$\sigma_0 = (z^2 F^2 / R) \alpha \nu_0 d^2 C \exp(\Delta S / R),$$

where z , F and R have the usual meaning, and α is the reciprocal of the number of all possible hop directions. Table 4 shows that for $\text{NbOPO}_4 \cdot \text{H}_3\text{PO}_4 \cdot y\text{H}_2\text{O}$ both E_a and σ_0 decrease with increasing y from 1.8 to 2.8, so that the corresponding conductivity enhancement is only determined by the decrease of E_a . The simultaneous decrease of E_a and σ_0 is not surprising because, according to the so-called compensation law [25], E_a and ΔS are expected to change in the same direction. On the other hand, the higher conductivity of $\text{NbOPO}_4 \cdot \text{H}_3\text{PO}_4 \cdot 2.8\text{H}_2\text{O}$ and $\text{NbOPO}_4 \cdot \text{H}_3\text{PO}_4 \cdot 4\text{H}_2\text{O}$ in comparison with that of $\text{NbOPO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{NbOPO}_4 \cdot \text{H}_3\text{PO}_4 \cdot 2.8\text{H}_2\text{O}$, respectively, is determined by both a lower E_a and a higher σ_0 . Although the present data do not allow one to identify for certain the factor(s) responsible for these changes, the increase of σ_0 upon H_3PO_4 intercalation is reasonably due to an increase of the effective carrier concentration of protonic carriers.

4. Conclusion

This work compares, for the first time, the conductivity of isostructural compounds with general formula MOXO_4 ($M = \text{V}, \text{Nb}$; $X = \text{P}, \text{As}$). The influence of the central atom M , of the anionic group XO_4 and of the water content on the electrical properties was elucidated and the conclusions suggested in this work could be used also for an assessment of conductivity behavior for other similar phosphates and arsenates of transition metals. The vanadyl compounds are mixed protonic–electronic conductors, whereas niobyl compounds are practically pure protonic conductors. As a consequence of the increasing contribution of protonic conductivity with increasing hydration, all $\text{MOXO}_4 \cdot y\text{H}_2\text{O}$ compounds have similar ac-conductivity at high RH. On the other hand, owing to the contribution of electronic conductivity, the $\text{VOXO}_4 \cdot y\text{H}_2\text{O}$ compounds are more conductive than $\text{NbOXO}_4 \cdot y\text{H}_2\text{O}$ at low RH.

The intercalates of NbOPO_4 and VOAsO_4 with H_3PO_4 and H_3AsO_4 , respectively, were also prepared and investigated. $\text{VOAsO}_4 \cdot 0.5\text{H}_3\text{AsO}_4 \cdot y\text{H}_2\text{O}$ is a new compound, while $\text{NbOPO}_4 \cdot \text{H}_3\text{PO}_4 \cdot y\text{H}_2\text{O}$ differs from that described by Chernorukov [14] in the amount of intercalated H_3PO_4 and can be considered as a new compound too. $\text{NbOPO}_4 \cdot \text{H}_3\text{PO}_4 \cdot y\text{H}_2\text{O}$ is stable in the RH range from 0% to 75% and due to the presence of interlayer H_3PO_4 , is more conductive than $\text{NbOPO}_4 \cdot y\text{H}_2\text{O}$ by two orders of magnitude over the whole RH range. The room temperature conductivity approaches $10^{-4} \text{ S cm}^{-1}$ at RH as low as 5% and is high enough to envisage the use of this material as a solid proton electrolyte for hydrogen or oxygen sensors working in a dry environment as recently shown for the composite $\text{SiO}_2\text{-Zr}(\text{HPO}_4)_2\text{-H}_3\text{PO}_4$ [26].

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