Proton conduction in some acid niobium phosphates

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Proton mobility in \( \text{K}_0.3\text{NbOPO}_4\cdot0.2\text{H}_3\text{PO}_4\cdot1.7\text{H}_2\text{O} \) and in its pristine compound \( \alpha\text{-NbOPO}_4\cdot\text{nH}_2\text{O}(n<3) \) is studied by means of the impedance spectroscopy technique in the temperature range 300–413 K and in the frequency range 1 Hz to 12 MHz. The \( \text{K}_0.3\text{NbOPO}_4\cdot0.2\text{H}_3\text{PO}_4\cdot1.7\text{H}_2\text{O} \) exhibits a greater conductivity at room temperature (1.5 × 10\(^{-5}\) S cm\(^{-1}\)) than \( \alpha\text{-NbOPO}_4\cdot\text{nH}_2\text{O}(n<3) \) (10\(^{-6}\) S cm\(^{-1}\)) due to the presence of \( \text{H}_3\text{O}^+ \) in its interlayer space. This is confirmed by IR spectroscopy which shows a band centered at 1700 cm\(^{-1}\) assigned to deformation vibration of \( \text{H}_3\text{O}^+ \).

1. Introduction

Niobium phosphate \( \alpha\text{-NbOPO}_4\cdot\text{nH}_2\text{O}(n<3) \) is a lamellar solid whose sheets have the \([\text{NbOPO}_4]_\infty\) composition. The interlayer space is defined by two types of water molecules and their nature and situation has been investigated using IR and NMR spectroscopy [1,2].

Polar molecules [3], particularly different types of amines can be intercalated in the \( \alpha\text{-NbOPO}_4\cdot\text{nH}_2\text{O}(n<3) \). This compound also acts as host matrix in the \( \text{H}_3\text{PO}_4 \) and \( \text{H}_2\text{SO}_4 \) intercalation. Several acid derivatives from \( \alpha\text{-NbOPO}_4\cdot\text{nH}_2\text{O}(n<3) \) have been reported [3–5]. The existence of \( \text{H}_3\text{O}^+ \) has been identified in these compounds, although it has not been deeply studied.

Recently a fast ionic conductor (3.6 × 10\(^{-3}\) S cm\(^{-1}\) at 683 K) has been prepared by solid ionic change between the \( \alpha\text{-NbOPO}_4\cdot\text{nH}_2\text{O}(n<3) \) and lithium chloride at 200°C [6].

Our purpose is to prepare a "sandwich" compound of \( \text{H}_3\text{PO}_4 \) combining \([\text{NbOPO}_4]_\infty\) phosphate sheets and this acid. The proton mobility in the resulting compound is compared with the pristine solid \( \alpha\text{-NbOPO}_4\cdot\text{nH}_2\text{O}(n<3) \) that has only water species in its interlayer space.

2. Experimental

2.1. Preparation of the compounds

The synthesis of \( \alpha\text{-NbOPO}_4\cdot\text{nH}_2\text{O}(n<3) \) has been made by the method of Chernorukov [2] and modified by Bruque [1]. 20 g of \( \text{Nb}_2\text{O}_5 \) was dissolved with 140 ml of HF (45%) and 15 ml of \( \text{HNO}_3 \) (60%), after were added 82 ml of \( \text{H}_3\text{PO}_4 \) (85%). This solution was heated in water bath to appear as a white crystalline solid, that was separated by decantation, and later was put in 560 ml of \( \text{HNO}_3 \) 5 M. The suspension was centrifuged, washed with distilled water several times, dried in an oven at 50°C and stored in 76% relative humidity environment.

To prepare \( \text{K}_0.3\text{NbOPO}_4\cdot0.2\text{H}_3\text{PO}_4\cdot1.7\text{H}_2\text{O} \), 0.3 g of \( \text{K}_0.3\text{NbOPO}_4\cdot2.2\text{H}_2\text{O} \) was placed into a teflon vessel (44 ml capacity) from a pressure reactor and 29 ml of \( \text{H}_3\text{PO}_4 \) (85% w/w) was added. The hydrothermal reaction was maintained at 120°C for three days and the white suspension was centrifuged,
washed with distillate water several times, dried in an oven at 50°C stored in 58% relative humidity environment (atmosphere from H2SO4 40%) [7].

2.2. Characterization of the products

The chemical composition of these compounds was determined by dissolving the solids (0.1–0.2 g) in hot hydrofluoric acid (48% w/w) (0.5–1 ml). The solution was put into a vessel which contained distillate water and was diluted to 100–150 ml. To this solution, 2 g of boric acid was added in order to eliminate the excess of hydrofluoric acid and to avoid stable niobium complexes with fluorine. The niobium was precipitated in the cold solution (5–10°C) by adding 25 ml of cupferron (3%) in the presence of ashless paper pulp, and then calcinated to Nb2O5 at 1000°C [8]. Phosphorus content was determined by colorimetric analysis as the molybdophosphate complex. Water content was measured by thermal analysis and by static heating at different temperatures.

Thermal analysis (TGA and DTA) was carried out in air on a Rigaku Thermoflex apparatus at a heating rate of 10 K min⁻¹ with calcinated Al2O3 as the internal standard reference.

X-ray diffraction (XRD) studies were carried out on both the oriented aggregates and the powder diffractograms of the samples with a Siemens D-501 automated diffractometer using graphite-monochromated Cu Ko radiation.

Infrared spectra were recorded on a Perkin Elmer 883 spectrometer with a spectral range of 4000–200 cm⁻¹, using dry KBr pellets containing 2% of the product. In some cases, the sample for IR was prepared as oriented aggregates by evaporating aqueous suspensions on a CaF2 crystal. The diffuse-reflectance spectra (UV–VIS–NIR) were recorded on a Shimadzu 3100 spectrophotometer with an integrating sphere of 60 mm diameter coated with BaSO4; pressed tablets of BaSO4 were used as the reference.

For the electrical measurement, pellets were prepared by pressing the powder at 6 MPa. The ac electrical impedance of the pellet was performed using a frequency response analyzer Solartron FRA 1255. The impedance was measured in the range between 1 Hz and 12 MHz. The temperature range was from 300 K to 413 K.

3. Results and discussion

The product obtained K_{0.5}NbOPO₄·0.2H₃PO₄·1.7H₂O is a niobium phosphate with molar ratio P:Nb>1 closely related to that prepared by Chernorukov et al. [4] and Beneke et al. [3], but with potassium in the lattice. Kinomura [5] has described two phosphates similar to that solid, one phosphate with sodium and another phosphate with potassium, whose formulas are: NaNb₂(OH)₂(PO₄)₃·2.5H₂O and KNb₂(OH)₂(PO₄)₂·nH₂O. These compounds are three-dimensional solids with P:Nb = 1.5 whereas the previous phosphate is a layered solid with P:Nb = 1.2.

The chemical composition shows the presence of potassium. This ion came in the structure to replace protons from P–O–H and/or Nb–O–H.

3.1. X-ray diffraction

The X-ray powder diffractograms of α-NbOPO₄·nH₂O (n<3) and the K₀.₅NbOPO₄·0.2H₃PO₄·1.7H₂O are shown in fig. 1. Both compounds are lamellar solids and it can be verified in oriented samples by the greater intensity of the 00l reflections. Moreover the nature of the layers of the hydrated niobium phosphate with interlayer phosphoric acid is identical to the α-NbOPO₄·nH₂O (n<3) because the hk0 reflections of both compounds are very similar. In the K₀.₅NbOPO₄·0.2H₃PO₄·1.7H₂O its sheets have been separated by free interlamellar H₃PO₄ as is shown with a high intensity of a reflection at 13.2 Å (dₐ) and the second order at 6.6 Å whereas the α-NbOPO₄·nH₂O (n<3) has a basal spacing of 8 Å.

3.2. Infrared study

The IR spectra of these compounds are compared in fig. 2. The main zone is located between 1400 and 800 cm⁻¹ where appears the stretching vibration ν₃ corresponding to the phosphate of the layer and the free phosphoric acid in the interlamellar space. The triply degenerate ν₃ stretching in isolate PO₄³⁻ is changed by a lowering of the symmetry due to distortion of the PO₄³⁻ tetrahedron [9,10], passing of symmetry Tₐ to C₂v, or even C₁. Two bands appear
at 1210 cm\(^{-1}\) and 1013 cm\(^{-1}\) due to splitting of the \(\nu_3\) stretching vibration of the \(K_{0.5}\text{NbOPO}_4\cdot 0.2\text{H}_3\text{PO}_4\cdot 1.7\text{H}_2\text{O}\) whereas the \(\alpha\)-\(\text{NbOPO}_4\cdot n\text{H}_2\text{O}\) \((n<3)\) only shows one band at 1145 cm\(^{-1}\). The absorption band at 922 cm\(^{-1}\) in the \(K_{0.5}\text{NbOPO}_4\cdot 0.2\text{H}_3\text{PO}_4\cdot 1.7\text{H}_2\text{O}\) and at 945 cm\(^{-1}\) for \(\alpha\)-\(\text{NbOPO}_4\cdot n\text{H}_2\text{O}\) \((n<3)\) is due to \(\nu_1\) of \(\text{PO}_4^{3-}\), also the low site symmetry makes this band IR-active. The \(\alpha\)-\(\text{NbOPO}_4\cdot n\text{H}_2\text{O}\) \((n<3)\) exhibits a broad band between 690–630 cm\(^{-1}\) with peaks at 685, 665 and 650 cm\(^{-1}\) and is assigned to different \(\nu(\text{Nb}=\text{O})\) stretching vibration. By contrast, the \(K_{0.5}\text{NbOPO}_4\cdot 0.2\text{H}_3\text{PO}_4\cdot 1.7\text{H}_2\text{O}\) only shows in this zone one band at 644 cm\(^{-1}\). This is justified by the different interlayer nature in both solids which influences the environment of the niobium atom.

In these two compounds the \(\nu(\text{Nb}=\text{O})\) stretching is masked by the strong absorption of phosphate groups. The \(\nu(\text{Nb}=\text{O})\) stretching can be observed in niobyl arsenate at 995 cm\(^{-1}\) [4,11,12].
band between 3700 and 2500 cm\(^{-1}\), with a shoulder centered at 2900 cm\(^{-1}\). In the IR spectrum of a film on fluorite, this band is split into a peak 3463 cm\(^{-1}\) and a broad band at 3300 cm\(^{-1}\), and the shoulder appears more definite at 2940 cm\(^{-1}\). The peak at 3463 has a very low wavenumber for \(\nu(\text{OH})\) of free hydroxyl (3700–3650 cm\(^{-1}\)) [13], and so it will be due to \(\nu(\text{OH})\) of weakly linked water [1]. The broad band at 3300 cm\(^{-1}\) is due to \(\nu(\text{OH})\) of hydrogen-bonded water molecules. In the \(\alpha\)-NbOPO\(_4\):\(n\)H\(_2\)O \((n < 3)\) this broad band appears between 3500–3200 cm\(^{-1}\) with a peak at 3615 cm\(^{-1}\).

The HPO\(_2^–\) group shows a broad and weak band between 2900–2750 cm\(^{-1}\) and other band between 2500–2150 cm\(^{-1}\) [13]. In the case of \(\text{K}_{0.5}\text{NbOPO}_4\cdot0.2\text{H}_3\text{PO}_4\cdot1.7\text{H}_2\text{O}\) a shoulder at 2940 cm\(^{-1}\) can be assigned to \(\nu(\text{POH})\) stretching. Approximately at 2300 cm\(^{-1}\) appears a broad and weak band that in the IR spectrum on fluorite is better defined at 2380 cm\(^{-1}\) and assigned to \(\nu(\text{POH})\) stretching [4]. Finally, there is a weak band at 1624 cm\(^{-1}\) with several shoulders which in the spectrum on fluorite are defined in two peaks at 1700 cm\(^{-1}\) and other at 1620 cm\(^{-1}\) with a shoulder at 1650 cm\(^{-1}\). The band at 1700 cm\(^{-1}\) is due to deformation of H\(_3\)O\(^+\) and/or H\(_2\)O\(^+\) [4], and the band at 1620 cm\(^{-1}\) with shoulder at 1650 cm\(^{-1}\) is attributed to \(\delta(\text{HOH})\) deformation related to the existence of two types of water molecules, free water and niobium coordinated water. In the \(\alpha\)-NbOPO\(_4\):\(n\)H\(_2\)O \((n < 3)\) only two bands appear in this zone at 1635 cm\(^{-1}\) and 1610 cm\(^{-1}\) due to the existence of these types of water molecules.

### 3.3. Thermal analysis

The TGA–DTA curves for both compounds are shown in fig. 3. In the \(\text{K}_{0.5}\text{NbOPO}_4\cdot0.2\text{H}_3\text{PO}_4\cdot1.7\text{H}_2\text{O}\) the TG curve shows two endothermic effects, the first centered at 50\(^\circ\)C associated with a mass loss of 0.7 water molecules, and the second at 90\(^\circ\)C due to the loss of the half niobium coordinated water. This stage connects with the next in which is eliminated the rest of coordinated water and also the water that comes from free H\(_3\)PO\(_4\) according to the reaction:

\[
2\text{H}_3\text{PO}_4 \rightarrow \text{P}_2\text{O}_5 + 3\text{H}_2\text{O}.
\]

This \(\text{P}_2\text{O}_5\) is retained in the structure until high temperatures. A continuous descent in the TG curve until 500\(^\circ\)C does not permit us to discern the third stage of mass loss. In the ATD curve an endothermic effect is observed at 400\(^\circ\)C that is related to the total decomposition of H\(_3\)PO\(_4\) in the interlamellar space. Also the ATD curve presents another endothermic effect at 570\(^\circ\)C without mass loss, tentatively attributed to a structural change.

The X-ray powder diffraction pattern of \(\text{K}_{0.5}\text{NbOPO}_4\cdot0.2\text{H}_3\text{PO}_4\cdot1.7\text{H}_2\text{O}\) heated at 400\(^\circ\)C shows the reflection at 13 Å but with an important diminution of intensity, indicating that at 400\(^\circ\)C the mentioned reaction (eq. (1)) has begun. Here, the IR confirms the decrease of bands due to H\(_2\)O and H\(_3\)PO\(_4\), so the band at 1700 cm\(^{-1}\) \((\delta\text{H}_3\text{O}^+\)\) has disappeared and the shoulder at 2900 cm\(^{-1}\) \((\nu(\text{POH}))\)
is very reduced. When the above phosphate is heated at 700°C there is a lack of the reflection at 13 Å and other sharp reflection at 4.3 Å confirms the transition to an anhydrous phase. This can be related to the endothermic process at 570°C in the DTA curve, which can be assigned to the transition from a 2D towards 3D structure.

About 775°C begins the mass loss for the P₂O₅ remained in the structure, followed by an exothermal process at 827°C without mass loss and an endothermic effect at 957°C. The exotherm at 827°C is assigned to some structural change related to the new position of potassium in the lattice [6].

The endothermic effect at 957°C is attributed to the P₂O₅ loss. In the DTA–TG curve of niobium phosphate with intercalated H₃PO₄ synthesized by Chernorukov (NbOPO₄·2H₃PO₄·5H₂O) [4] also appears mass loss at high temperatures assigned to P₂O₅.

The α-NbOPO₄·nH₂O (n<3) is stable to over 400°C due to the absence in this compound of free H₃PO₄ in its interlamellar space. The α-NbOPO₄·nH₂O (n<3) shows an approximately trihydrate composition at room temperature when it is placed in an atmosphere of high relative humidity, and the hydration is diminished when the compounds pass to a less wet environment. In the TG curve two stages of dehydration appear when the temperature increases. In the first stage it is lost between 1.8–1.9 water molecules per unit formula, which are eliminated in several steps as it is observed by the endothermic effects at 40 and 70°C associated to another centered at 95°C. About 120°C the α-NbOPO₄·nH₂O (n<3) gets the monohydrate composition, at this point the second stage begins and it is possible to observe two little endothermic effects which are separated at 140 and at 230°C.

3.4. UV–VIS–NIR diffuse reflectance spectra

Fig. 4 displays the diffuse reflectance spectra of these compounds. These phosphates are white according to a d⁰ electronic structure for Nb (V). As consequence they do not exhibit d–d transitions in the visible zone, so only L→M charge transfer bands in the UV region and vibrational bands in the NIR region are detected [12].

In all solids the charge transfer band is more intense than the vibrational bands of the ν(XO–H) (X=H, P, Nb), δ(H₂O) and hydrogen bonding systems. The near-infrared region for these phosphates shows two wide bands: (i) a band around 6900–7000 cm⁻¹ due to overtones and combinations of the different O–H stretching and (ii) a band around 5100–5200 cm⁻¹ related to the ν(XO–H) + δ(H₂O) and/or ν(XO–H) + δ(H₃O⁺) combination vibrations (X=H, P, Nb).

3.5. Conductivity measurements

In K₀.₅NbOPO₄·0.2H₃PO₄·1.7H₂O the liquid structure of the interlayer by hydrogen bond H₃PO₄–H₂PO₄ together with the hydration water molecules can be an adequate system for the mobility of the proton. This is confirmed by IR spectroscopy where a band is detected around 1700 cm⁻¹ assigned to deformation vibration of H₃O⁺. It has been made by conductivity measurements in the K₀.₅NbOPO₄·0.2H₃PO₄·1.7H₂O and α-NbOPO₄·nH₂O (n<3) as the reference matrix. The Nyquist plot for these compounds is given in fig. 5. The results of conductivity versus temperature for the α-NbOPO₄·nH₂O (n<3) in fig. 6 reveal a typical
behaviour of a proton conductor with its highest conductivity of $5 \times 10^{-6}$ S cm$^{-1}$ near 100°C: conductivity increases with the temperature although at temperatures higher than 373 K hydration water is lost and proton conductivity suddenly decreases. The parent solid $\alpha$-NbOPO$_4$$\cdot$nH$_2$O ($n < 3$) exhibits less conductivity at room temperature than $K_0.5$NbOPO$_4$$\cdot$0.2H$_3$PO$_4$$\cdot$1.7H$_2$O due to the absence of H$_3$O$^+$ in its interlayer space.

Table 1 shows the conductivity data for $K_0.5$NbOPO$_4$$\cdot$0.2H$_3$PO$_4$$\cdot$1.7H$_2$O. The capacity values are approximately constant indicating that this compound shows the same mechanism for mobility of the proton below 100°C. The conductivity of this compound is approximately $10^{-5}$ S cm$^{-1}$ near room temperature, a high value although less than the conductivity for HUO$_2$PO$_4$$\cdot$4H$_2$O, $4 \times 10^{-3}$ S cm$^{-1}$ at 25°C, one of the phosphates of greatest conductivity known to date.

### Table 1

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<th>$C$ (F cm$^{-1}$)</th>
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<td>$2.8 \times 10^{-10}$</td>
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### 4. Conclusions

With the impedance spectroscopy technique applied to the layered niobium phosphate $\alpha$-NbOPO$_4$$\cdot$nH$_2$O ($n < 3$) and $K_0.5$NbOPO$_4$$\cdot$0.2H$_3$PO$_4$$\cdot$1.7H$_2$O we have shown the influence of their different liquid-like interlayer structure on the proton mobility.
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