

New protonic solid electrolyte with tetragonal tungsten bronze structure obtained through ionic exchange

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Abstract

Proton exchange reactions have been performed on tetragonal tungsten bronze-like NaNbWO_6 by using nitric acid as an exchanging agent. The characterization of the exchange reaction products has been made by means of chemical analysis, X-ray diffraction, thermal analysis, and IR spectroscopy. The exchange reaction takes place topotactically and the following formula is proposed for the obtained phase of variable composition: $\text{Na}_{1-x}\text{H}_x\text{NbWO}_6 \cdot y\text{H}_2\text{O}$ ($0 < x \leq 0.46$ and $0 \leq y \leq 0.12$). Impedance spectroscopy on the present proton exchanged samples indicated that these samples behaved as solid electrolytes under high humidity. As an example, the compound with the composition $\text{Na}_{0.68}\text{H}_{0.32}\text{NbWO}_6 \cdot 0.1 \text{H}_2\text{O}$ exhibits ionic conductivity of 8×10^{-3} and $1 \times 10^{-2} \text{S cm}^{-1}$ at 70°C and 90°C , respectively.

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1. Introduction

Tetragonal tungsten bronzes (TTB hereafter) have been known since the 19th century [1] although the structure was not determined until 1949 when Magnéli solved the structure of K_xWO_3 within the potassium compositional range $0.475 \leq x \leq 0.57$ [2]. This discovery was followed by the structural determination of a sodium analogous compound [3,4]. Fig. 1 shows the projection of the structure of such a tungsten bronze onto the x – y plane.

The framework is built up by corner-sharing $[\text{WO}_6]$ octahedra. Several types of tunnels run along the z -direction (Fig. 1). Some of them can be either partially or fully occupied by alkali metals. This framework structure with metals in these cavities and the high oxidation state of W ions with possible mixed valency [M(VI) and W(V)] could be ascribed to the origin of the very rich chemistry of M_xWO_3 compounds [5–8].

Ionic conductivity is an interesting property of such M_xWO_3 as a potential candidate of solid electrolyte, and protonic conductivity has been studied in these types of bronzes [9]. However, possible electron conduction due to mixed valency of W ions inhibits the use of these materials as solid electrolytes. In fact, electronic conduction due to mixed valency can be suppressed by means of an appropriate chemical substitution, e.g. by partial replacing of W(V) with Nb(V) [10]. For the system NaNbO_3 – WO_3 , a phase with composition $\text{Na}_6\text{Nb}_6\text{W}_4\text{O}_{30}$, which is $6\text{NaNbO}_3 \cdot 4\text{WO}_3$, with TTB structure was found by Horlin et al. [11]. What is more, a solid solution between those two oxides also seems to exist [5].

In this work we present a study made on NaNbWO_6 , i.e. the 1:1 member of the aforementioned ideal solid solution. This compound has been used to perform cationic exchange reactions in order to substitute Na^+ with H^+ (or H_3O^+). The characterization of exchanged samples and the electrical conductivity measurements indicated that our exchanged Na(H)–Nb–W–O system behaves as a solid electrolyte.

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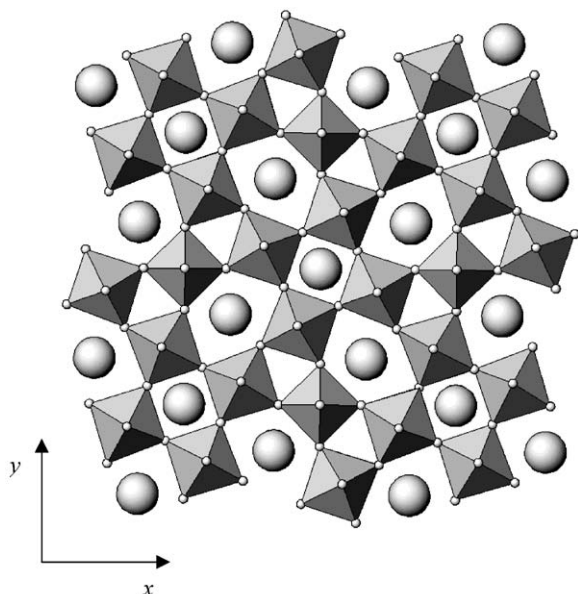


Fig. 1. Schematic representation of sodium tetragonal tungsten bronze Na_xWO_3 structure projected onto the x - y plane. Big circles represent sodium atoms.

2. Experimental techniques

The parent compound, with nominal composition NaNbWO_6 , was prepared from a mixture containing stoichiometric quantities of high purity Na_2CO_3 (99%), Nb_2O_5 (99.5%) and WO_3 (99.8%). The mixture was heated at 500°C for 24 h and afterwards pressed into disks and heated at 775°C for 24 h. The sample was then allowed to slowly cool down to room temperature, grounded, pressed into pellets and sintered for 24 h at the same temperature.

The exchange $\text{H}^+ \rightleftharpoons \text{Na}^+$ was carried out by treatment of the parent compound (powdery form) with a 5 mol dm^{-3} HNO_3 aqueous solution at 80°C for 12 h under reflux. The solid was afterwards isolated by filtration and washed, first with water and secondly with acetone. Finally the sample was dried in air at 25°C . In a typical experiment, 3 g of parent compound were treated with 150 mL of the above-mentioned acidic solution. In order to obtain samples with a different exchange rate, the exchange treatment was repeated several times with fresh nitric acid, but keeping the same experimental conditions in every treatment.

Metal contents of both parent and exchanged samples were determined by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Perkin-Elmer apparatus. Sodium carbonate, niobium(V) nitrate and tungsten(VI) nitrate were used to prepare standard solutions.

X-ray powder diffraction was used to perform a structural characterization of the parent compound as

well as of the exchanged samples. Experiments were performed on a Philips X'Pert diffractometer using $\text{CuK}\alpha$ radiation. Unit cell parameters were calculated by means of pattern matching by using the Fullprof program [12].

Thermal analysis has been used to detect both the presence of protonic species as well as to determine the stability range of the protonated compounds. Experiments have been carried out on a Seiko Instrument TG/DTA 6200 apparatus within the temperature range 25 – 600°C . The heating and cooling rate were set to $10^\circ\text{C}/\text{min}$ in all the measurements.

Infrared spectra were recorded in KBr pellets using a Perkin-Elmer 599 spectrometer.

Impedance spectroscopy has been used to determine ionic conductivity of both parent and exchanged samples. Measurements were performed in the frequency range 10 – 10^7 Hz on a Hewlett Packard 4192A impedance analyzer. Powder samples were pressed into tablets (12 mm diameter and 1–2 mm thick) and dried at 90°C . The electrical contacts between sample and platinum disk electrodes of the experimental cell were ensured by painting both planar sides of the tablets with a silver paint. The ac impedance spectra of samples were collected at different temperatures in the range from 25°C up to 90°C . Samples were kept under respective maximum humidity during measurements.

3. Results and discussion

3.1. Parent material: synthesis and characterization

Following the synthesis procedure described for the parent material with nominal composition NaNbWO_6 , a white powder was obtained. The analysis of metal content lead to the following formulation $\text{Na}_{0.97(2)}\text{Nb}_{0.99(1)}\text{W}_{1.01(1)}\text{O}_6$ where the oxygen content has been assumed to be the stoichiometric. Sodium, niobium and tungsten contents are coincident with nominal composition if one takes into account the standard deviation. Therefore the parent compound will hereafter be referred to as NaNbWO_6 .

Observed X-ray powder diffraction profile from the parent is shown in Fig. 2, together with profile matching results. All the peaks were successfully indexed and then well fitted by assuming a tetragonal cell with cell dimensions $a = b = 12.105(2) \text{ \AA}$ and $c = 3.8378(7) \text{ \AA}$. Close resemblance of the cell dimensions and observed intensity ratio between previously reported TTB compounds [11] and the present sample indicated that the present sample had the TTB structure. An unindexed small peak ($2\theta = 18.75^\circ$) from an unidentified impurity phase vanished after exchange treatment in an acidic solution (mentioned later). This means that our sample preparation is not yet optimized.

3.2. Exchanged materials: synthesis and characterization

The parent compound has been treated with dilute nitric acid (5 mol dm^{-3}), as described in the experimental section, yielding pale yellow solids. Results of ICP-AES analyses are listed in Table 1 for some samples, together with amounts of extracted Na with reference to the Na content of the parent material.

While both the niobium and tungsten content remain unchanged upon consecutive treatments with acid, it can be seen that the sodium content decreases with an increase of number of exchange treatments.

Table 1 shows that approximately 30% of sodium has been extracted after only two treatments. However, after nine treatments only a 39% extraction is achieved. We have found that further and lengthy treatments increase the extracted quantity but at a very slow rate. Note that seventeen 12 h treatments are required for achieving a 45% ion extraction. This value of ion extraction can then be regarded as a limit from a practical point of view.

Fig. 3 shows the X-ray diffraction pattern of samples treated with nitric acid up to 17 times for periods of 12 h (a total of 204 h of treatment). The exchanged samples

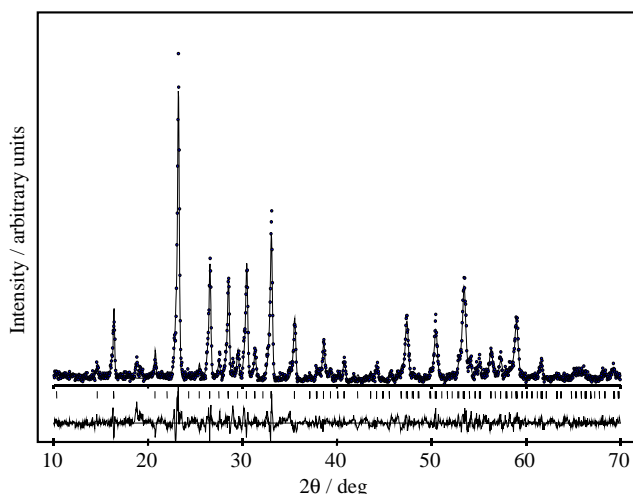


Fig. 2. X-ray powder diffraction pattern of NaNbWO_6 and pattern matching ($a = b = 12.105(2) \text{ \AA}$ and $c = 3.8378(7) \text{ \AA}$).

show similar X-ray powder diffraction patterns, indicating that the host structure is maintained as expected for a topotactic exchange reaction at low temperature. One remarkable difference between parent oxide and exchanged products is the vanishing of the reflection arising from an impurity (marked with an arrow).

Cell parameters remain practically unchanged upon sodium exchange. We have calculated that for a and c parameters the total variation is smaller than 1%. This means that the partial substitution of the large cation Na^+ by the smaller cation H^+ does not affect the rigid framework consisting of $[\text{MO}_6]$ octahedra.

In view of both structural and chemical information we assumed that acidic treatment produces an exchange of cations. Hence a proton quantity equal to the quantity of extracted sodium is incorporated into the TTB structure. Therefore, formulas including proton content can be given (see Table 1). Thermal analysis has been used to confirm the presence of hydrogenated species. The information obtained from both chemical and thermal analysis led us to a more precise knowledge

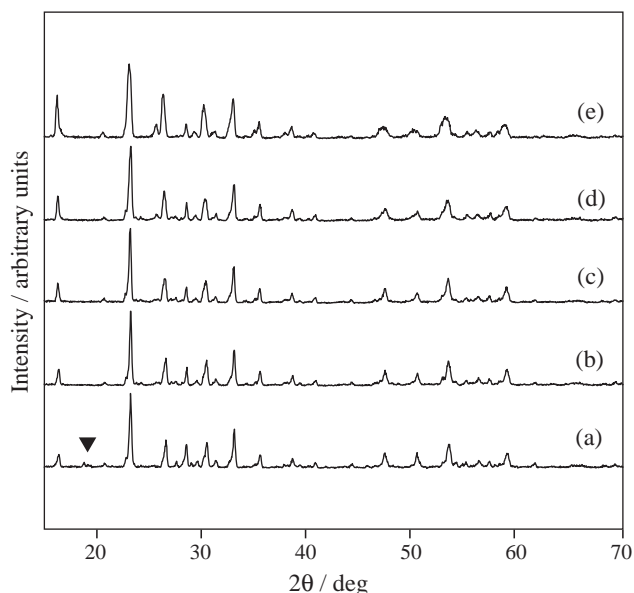


Fig. 3. X-ray diffraction patterns of parent NaNbWO_6 (a) and $\text{Na}_{1-x}\text{H}_x\text{NbWO}_6 \cdot y \text{ H}_2\text{O}$ obtained by protonic exchange reaction with $x = 0.22$ (b), $x = 0.32$ (c), $x = 0.40$ (d), and $x = 0.46$ (e).

Table 1

Composition of some of the samples prepared by exchange reaction with HNO_3 5 mol dm^{-3} at 80°C (only the metallic elements have been analyzed)

Number of exchange treatments	Composition determined by ICP (s.d.'s are given in parenthesis)	Amount of extracted Na^+ (%)	Formula including proton ^a
0	$\text{Na}_{0.97(2)} \text{Nb}_{0.99(1)} \text{W}_{1.01(1)} \text{O}_6$	0	NaNbWO_6
2	$\text{Na}_{0.68(1)} \text{Nb}_{1.00(1)} \text{W}_{1.00(1)} \text{O}_6$	30	$\text{Na}_{0.68}\text{H}_{0.32}\text{NbWO}_6$
9	$\text{Na}_{0.60(1)} \text{Nb}_{0.99(1)} \text{W}_{1.02(1)} \text{O}_6$	39	$\text{Na}_{0.60}\text{H}_{0.40}\text{NbWO}_6$
17	$\text{Na}_{0.54(1)} \text{Nb}_{1.00(1)} \text{W}_{1.00(1)} \text{O}_6$	45	$\text{Na}_{0.54}\text{H}_{0.46}\text{NbWO}_6$

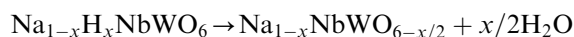
Extracted sodium has been calculated as the difference between sodium content in the parent and in the treated sample.

^aHydrogen content is calculated on the basis of an exchange reaction yielding $\text{Na}_{1-x}\text{H}_x\text{NbWO}_6$.

of the composition of the exchanged compound. Assuming that the oxygen content is that corresponding to the ideal composition of the parent material (NaNbWO_6), the results regarding some selected exchanged products are given in Table 2 using the formula $\text{Na}_{1-x}\text{H}_x\text{NbWO}_6 \cdot y \text{H}_2\text{O}$.

Thermogravimetric analysis of selected protonated products in air showed us that the thermal behavior of protonated samples depends upon the composition. Fig. 4a and b show the typical behavior found for samples with $x \leq 0.40$. Our interpretation is that the first abrupt weight loss, around 80°C, is due to the loss of hydration water. The second and third weight losses would be due to proton loss. On the other hand, the abrupt weight loss at 80°C is absent in the most protonated products ($x > 0.40$). As an example of this different behavior, Fig. 4c shows the thermal behavior of $\text{Na}_{0.54}\text{H}_{0.46}\text{NbWO}_6$. As observed, only the two weight losses attributed to proton loss can be seen. The amount of hydration water (y) for the whole set of prepared samples is presented in Table 2.

We have to note that if the reaction



occurs in two steps, the presence of two different protons could be deduced. A support for this interpretation came from X-ray diffraction. Both anhydrous $\text{Na}_{1-x}\text{H}_x\text{NbWO}_6$ and fully deprotonated $\text{Na}_{1-x}\text{NbWO}_{6-x/2}$ retains the tetragonal tungsten bronze structure. As an example, the X-ray powder patterns of both $\text{Na}_{0.78}\text{H}_{0.22}\text{NbWO}_6 \cdot 0.12 \text{H}_2\text{O}$ and its deprotonation product (nominally $\text{Na}_{0.78}\text{NbWO}_{5.89}$) are shown in Fig. 5. The latter was obtained by heating $\text{Na}_{0.78}\text{H}_{0.22}\text{NbWO}_6 \cdot 0.12\text{H}_2\text{O}$ in air to 600°C.

Two-step proton loss has also been observed in other systems. In particular, a similar thermal behavior has recently been shown for several hydrated hydrogen sodium and potassium molybdenum bronzes [13]. It is interesting to note that in the reported cases two different protons exist [14].

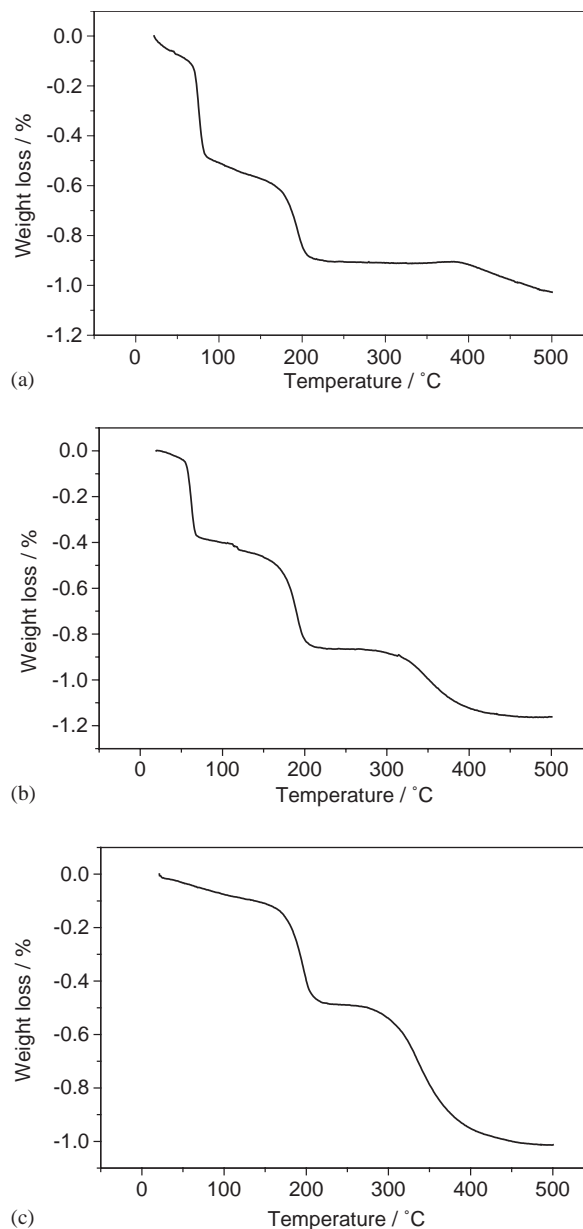


Fig. 4. Thermogravimetric curves of selected $\text{Na}_{1-x}\text{H}_x\text{NbWO}_6$ samples: (a) $x = 0.32$, (b) $x = 0.40$ and (c) $x = 0.46$.

Table 2

Hydration water content per formula unit (y) calculated from the measured weight loss from room temperature to 90°C

Composition	Water of hydration (y)	Experimental weight loss (%) between 90°C and 500°C	Expected weight loss (%) between 90°C and 500°C
NaNbWO_6	—	—	—
$\text{Na}_{0.78}\text{H}_{0.22}\text{NbWO}_6$	0.12	0.45	0.45
$\text{Na}_{0.68}\text{H}_{0.32}\text{NbWO}_6$	0.10	0.60	0.66
$\text{Na}_{0.63}\text{H}_{0.37}\text{NbWO}_6$	0.11	0.71	0.76
$\text{Na}_{0.60}\text{H}_{0.40}\text{NbWO}_6$	0.09	0.73	0.83
$\text{Na}_{0.57}\text{H}_{0.43}\text{NbWO}_6$	—	0.85	0.89
$\text{Na}_{0.54}\text{H}_{0.46}\text{NbWO}_6$	—	0.88	0.95

Experimental weight loss (%) between 90°C and 500°C and the corresponding expected weight loss are also listed. Expected weight loss has been calculated from the sample composition shown in the first column and accordingly to a full deprotonation reaction (see text).

After the first deprotonation step, the compounds are stable up to temperatures ranging between 300°C and 400°C. The second proton loss and then stability of the protonated compound seems to depend on the sodium (or proton) content, as can be seen in Fig. 4a–c. The most stable protonated compound is that with high sodium content (Fig. 4a).

As can be seen in Table 2, there is a firm agreement between the experimental weight loss measured between 90°C and 500°C and the corresponding expected value. The expected weight loss has been calculated from sample composition and accordingly to the above-mentioned deprotonation reaction.

DTA curves of the protonated compounds $\text{Na}_{1-x}\text{H}_x\text{NbWO}_6 \cdot y \text{H}_2\text{O}$ up to $x = 0.4$ exhibit two endothermic minima centered at about 75°C and 200°C (Fig. 6a and b). These two peaks correspond to the processes of dehydration and first deprotonation,

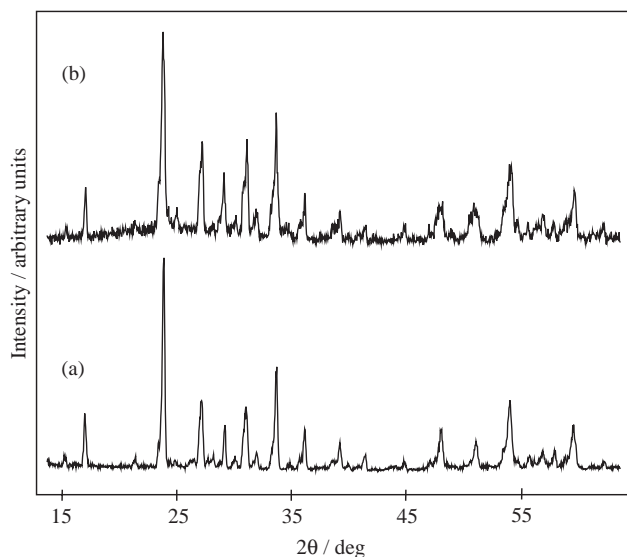


Fig. 5. XRD patterns of (a) $\text{Na}_{0.78}\text{H}_{0.22}\text{NbWO}_6 \cdot 0.12 \text{H}_2\text{O}$ and (b) its corresponding deprotonated (nominally $\text{Na}_{0.78}\text{NbWO}_{5.89}$). The latter is obtained by heating $\text{Na}_{0.78}\text{H}_{0.22}\text{NbWO}_6 \cdot 0.12 \text{H}_2\text{O}$ in air to 600°C.

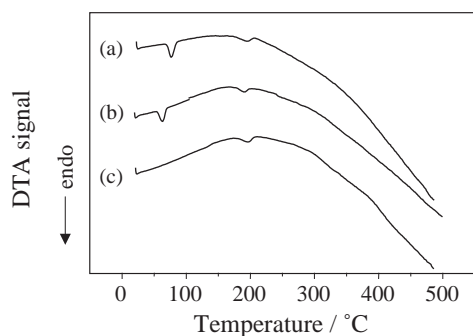


Fig. 6. Differential thermal analysis of $\text{Na}_{1-x}\text{H}_x\text{NbWO}_6$ with (a) $x = 0.32$, (b) $x = 0.40$ and (c) $x = 0.46$.

respectively. Concerning the low temperature process, e.g. loss of hydration water, a shift to lower temperatures is observed when the amount of proton, x , increases, which may be attributed to a weaker association of water molecules in the structure. Finally, for $x \geq 0.40$ no hydration water is detectable and the DTA curve shows only the endothermic process at around 200°C (Fig. 6c). The second proton loss detected by TGA is not clearly observed in DTA, likely because the loss occurs in a very wide temperature interval. As expected, no relevant feature has been detected either in the TG curve or in the DTA curve of the non-protonated NaNbWO_6 , i.e. the starting bronze (not shown).

The presence of OH groups in the proton-exchanged materials has been investigated by means of infrared spectroscopy. We have recorded the IR spectra of $\text{Na}_{1-x}\text{H}_x\text{NbWO}_6 \cdot y \text{H}_2\text{O}$ and their deprotonated products, nominally $\text{Na}_{1-x}\text{NbWO}_{6-x/2}$ (Fig. 7). NaNbWO_6 (spectrum a) shows a broad and strong absorption centered around 800 cm^{-1} , which is likely to be due to the internal modes of the $[\text{Nb}/\text{WO}_6]$ octahedra. This absorption band is present in all the Na–Nb–W oxides investigated here. $\text{Na}_{0.60}\text{H}_{0.40}\text{NbWO}_6$ shows a broad absorption between 3200 and 3500 cm^{-1} and a weak but sharper absorption around 1630 cm^{-1} (spectrum b). These could be assigned to the stretching and bending modes of water, respectively [15,16]. No absorption bands other than the strong absorption around 800 cm^{-1} are observed on the protonated product in wave numbers lower than 1200 cm^{-1} . Metal hydroxides and hydroxo-complexes show absorption due to M–OH bending in this region [15]. Therefore, we can probably discard the possibility that the proton in $\text{Na}_{0.60}\text{H}_{0.40}\text{NbWO}_6$ occurs as a “free” OH group. Spectrum c shows the IR spectrum of the corresponding deprotonated compound, nominally $\text{Na}_{0.60}\text{NbWO}_{5.80}$. The absorption bands due to O–H interaction are absent, and the spectrum is quite similar to that shown for NaNbWO_6 , as expected.

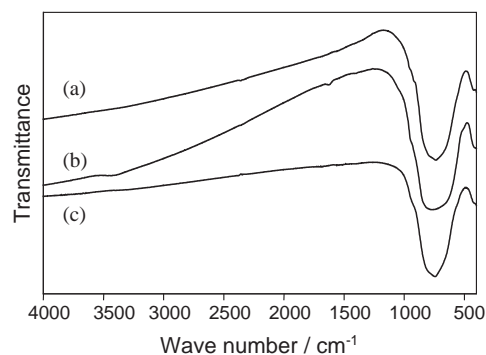


Fig. 7. Infrared spectra of (a) NaNbWO_6 , (b) $\text{Na}_{0.60}\text{H}_{0.40}\text{NbWO}_6 \cdot 0.09 \text{H}_2\text{O}$, and (c) its corresponding deprotonated (nominally $\text{Na}_{0.60}\text{NbWO}_{5.80}$) recorded in KBr pellets.

3.3. Ionic conductivity

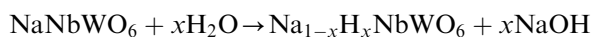
The study of the electrical behavior by means of impedance spectroscopy was made under controlled atmosphere. Parent and acid treated samples were dried at 90°C in order to start in all cases from the anhydrous phase. The conductivity of parent and exchanged samples were measured while keeping the sample under a saturated water vapor environment in order to hydrate the samples in a similar way. Measurements were made at four different temperatures, at 25°C, 50°C, 70°C and 90°C. Measurement results are presented in Table 3 for some selected samples.

For exchanged compounds, the conductivity was low at room temperature. However, it increased with temperature. At 90°C the conductivity reached values between 10^{-3} to 10^{-2} S cm⁻¹.

Two carriers could be responsible for the observed electrical behavior, sodium or proton. A clue about the role of each species was found when the conductivity of some samples was performed under dry air. For all protonated compounds, conductivity values at 90°C under dry air were found to be lower by two to three orders. This points to proton as the main carrier under a water-saturated atmosphere. Note that well-known fast sodium ion conductors are not known to be improved by the presence of water. Mobile ions in the case of the best sodium solid electrolytes are Na⁺ ions, but not hydrated-Na⁺. However, the contribution of sodium ions to the observed high ionic conductivity cannot be fully discarded.

We must note that an enhancement of conductivity through acidic treatment does not seem to be clear. This is due to the fact that no proton is nominally present in the parent material but its behavior is quite similar to that observed for the exchanged compounds. In fact, the ionic conductivity at 90°C is also high (10^{-3} S cm⁻¹). Our hypothesis to explain this behavior is based on both the readiness shown by the parent NaNbWO₆ to exchange Na⁺ for H⁺ and its behavior under a water-saturated atmosphere. When the parent material was left in a closed container in the presence of a high amount of

liquid water for several days, we detected that it is hygroscopic. After a couple of days, the powder converted itself into a sort of paste. Under this condition it could possibly undergo an exchange reaction if water acts as a weak acid. Thus we propose the following hydrolysis reaction



as responsible for the relatively high conductivity shown by the parent material under a water-saturated atmosphere.

To demonstrate the hydrolysis hypothesis, 100 mg of parent material were stirred in 0.015 dm⁻³ pure water at room temperature in a sealed polypropylene container for two weeks. The solid was separated and the sodium content of the liquid was analyzed by means of flame emission spectrometry. The result indicated that during the treatment with water, ca. 30% of total sodium is exchanged.

It seems clear that high humidity enhances proton conduction in the present samples. However, a more detailed investigation on both the nature and the environment of charge carriers is needed. If bulk proton conduction occurs, proton content should have an influence on ionic conductivity. But we can observe (Table 3) that only minor changes occur in the conductivity values as proton content increases. Another possibility is that proton motion occurs within adsorbed water layers. In fact, it is very well-known that water molecules may be adsorbed from the gas phase on the surface of some oxides [17–19]. This may enable proton conduction in the adsorbed layer as was reported some time ago for the case of silica gel [20,21] and more recently, for hydrated tin oxide and hydrated zirconia [22–24].

To clarify the origin of the high proton conductivity, a NMR study of these types of compounds is now under progress. To date, preliminary results indicate that bulk proton plays a role in the high proton conduction. On the other hand, no mobile sodium has been detected by this technique. The complete study will be published elsewhere.

Table 3

Conductivity as a function of both composition and temperature for previously dehydrated samples but measured under a water-saturated atmosphere

Treatment (number)	Composition	Conductivity (S cm ⁻¹)			
		25°C	50°C	70°C	90°C
0	NaNbWO ₆	2×10^{-5}	1×10^{-4}	2×10^{-4}	1×10^{-3}
1	Na _{0.78} H _{0.22} NbWO ₆ · 0.12 H ₂ O	8×10^{-6}	2×10^{-4}	6×10^{-4}	1×10^{-3}
2	Na _{0.68} H _{0.32} NbWO ₆ · 0.10 H ₂ O	3×10^{-5}	4×10^{-3}	8×10^{-3}	1×10^{-2}
5	Na _{0.63} H _{0.37} NbWO ₆ · 0.11 H ₂ O	1×10^{-5}	8×10^{-3}	1×10^{-2}	2×10^{-2}
9	Na _{0.60} H _{0.40} NbWO ₆ · 0.09 H ₂ O	1×10^{-5}	6×10^{-3}	9×10^{-3}	4×10^{-2}
13	Na _{0.57} H _{0.43} NbWO ₆	1×10^{-6}	4×10^{-3}	2×10^{-2}	2×10^{-2}

Hydrogen content has been estimated as being identical to the extracted sodium quantity.

4. Conclusions

NaNbWO₆ has been used as a parent compound to perform proton exchange reactions with nitric acid. Hereby, a series of exchanged compounds that retain the parent tetragonal structure has been obtained. The series with variable composition Na_{1-x}H_xNbWO₆ ($x > 0$) exhibits high ionic conductivity when it is placed in a water-saturated atmosphere. At 90°C, conductivity values close to 10⁻² S cm⁻¹ are obtained. Hence these compounds may be potentially useful as a new proton conducting solid electrolyte.

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