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Structure and conductivity of Nd₆MoO₁₂-based potential electron–proton conductors under dry and wet redox conditions†

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Nominal compositions Nd₆MoO₁₂ (3 : 1) and Nd₁₀Mo₂O₂₁ (5 : 2) were prepared by high-temperature synthesis in air from a mechanically activated mixture of Nd₂O₃ and MoO₃. Phase-pure Nd₆MoO_{12-δ} and Nd₆MoO_{12-α} have been obtained at 1600 and 1650 °C, respectively. They are both slightly rhombohedrally distorted derivatives from the cubic fluorite structure. Nd₁₀Mo₂O₂₁ with a lower content of Nd₂O₃ was shown to be a more complex phase based on the rhombohedral phase (*R* $\bar{3}$) in the 1600–1650 °C temperature range. As a result of the formation of a more complex rhombohedral phase, the conductivity of Nd₁₀Mo₂O₂₁ changes dramatically in comparison with Nd₆MoO_{12-δ}. In wet air Nd₆MoO_{12-δ} is a p-type electronic conductor, whereas proton conductivity dominates in Nd₁₀Mo₂O₂₁ over the entire temperature range studied. The electrical conductivity dependence of Nd₆MoO_{12-δ} on the oxygen partial pressure shows a V-type behaviour typical of a transition from a p-type to n-type conductivity mechanism at 800 ≤ *T* ≤ 1000 °C. There is no p-type conductivity contribution in Nd₁₀Mo₂O₂₁ in the same temperature range. The prevalence of electronic conductivity in the samples with nominal composition Nd₆MoO₁₂ in a wide temperature range is due to the fact that Nd and Mo in the fluorite materials are readily reduced. Predominantly Nd³⁺ and Mo⁶⁺ forms exist in more complex rhombohedral phase Nd₁₀Mo₂O₂₁ and it has proton conductivity ~8.5 × 10^{−3} S cm^{−1} at 800 °C. Thus, the loss of dimensional stability is more characteristic of fluorites and rhombohedral phases with small rhombohedral distortion (Nd_{5.4}Zr_{0.6}MoO_{12.3}, Nd₆MoO_{12-δ}) than more complex rhombohedral phases based on (*R* $\bar{3}$) (Nd₁₀Mo₂O₂₁). A comparative high-temperature *in situ* neutron diffraction study under high vacuum of rhombohedral Nd₆MoO_{12-δ} and cubic fluorite Nd_{5.4}Zr_{0.6}MoO_{12.3} showed that the former transforms to the high-temperature cubic fluorite type above ~1140 °C while the latter retains its cubic structure in the studied range up to 1350 °C.

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1. Introduction

A search for solid electrolytes that have high proton conductivity and at the same time are stable to reduction in both dry and wet atmospheres presents serious difficulties. As a rule,

highly conductive oxides are readily reduced.^{1–3} Therefore, in studies of new oxygen ion and proton conductors, attention should be paid to their reduction behaviour, in particular in a wet atmosphere. As shown recently,^{4–6} rhombohedral fluorite-like lanthanum molybdates with La/Mo = 5.4, 5.5 offer the highest proton conductivity among the Ln₆MoO₁₂-based materials studied to date: about 10^{−5} S cm^{−1} at 400 °C in wet air and Ar. Moreover, the La_{5.5}MoO_{11.25} impedance spectrum has no grain boundary contribution, regardless of whether it was measured in a dry or wet atmosphere.^{4,6} Rhombohedral (*R* $\bar{3}$) fluorite-like La_{5.5}MoO_{11.25} is more stable to reduction in a vacuum below 1100 °C in heating–cooling cycles than is Zr doped fluorite Ho_{5.4}Zr_{0.6}MoO_{12.3}.⁶ Given the higher proton conductivity of La_{5.5}MoO_{11.25}, the La₆MoO₁₂-based rhombohedral fluorite-like molybdate can be used under mild reducing conditions in the range of 600–800 °C for a long time.

According to Bartram⁷ and Czeskleba-Kerner *et al.*,⁸ there are also other light-lanthanide Ln₆MoO₁₂ molybdates (Ln = Pr,

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Nd) with an $R\bar{3}$ structure, so it is important to study the conductivity of $\text{Nd}_6\text{MoO}_{12}$ as a potential mixed electron–oxygen ion conductor in a dry atmosphere and an electron–proton conductor in a wet atmosphere. Note that, previously, the Zr-doped neodymium molybdate $\text{Nd}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ with the fluorite structure was shown to be an electron–proton conductor with dominant proton conductivity in a wet atmosphere below 525 °C.⁹

The objectives of this work were to synthesize rhombohedral $\text{Nd}_6\text{MoO}_{12}$ (3:1) and $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ (5:2) with a smaller content of Nd_2O_3 by 3.5%, investigate them as potential mixed electron–proton conductors, and assess their stability to reduction in comparison with $\text{Nd}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$, a previously studied electron–proton conductor with the fluorite structure.⁹ The stabilities of rare-Earth molybdates belonging to two distinct structural types, namely cubic fluorite $\text{Nd}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ and fluorite-like rhombohedral $R\bar{3}$ $\text{Nd}_6\text{MoO}_{12-\delta}$ were investigated under harsh conditions: vacuum at elevated temperatures up to 1100 or 1350 °C using *in situ* neutron powder diffraction. Such conditions (elevated temperatures up to 1100 °C and high vacuum $\sim 10^{-7}$ – 10^{-6} mbar) are similar to prolonged exposure of the molybdates to temperatures from 600 to 800 °C in a moderately reducing medium, *i.e.* under typical operating conditions of SOFCs.

2. Experimental study

Nominal compositions $\text{Nd}_6\text{MoO}_{12}$ and $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ were prepared by the mechanical activation method. After preheating the starting Nd_2O_3 oxide at 1000 °C for 2 h, it was mixed with MoO_3 and co-milled in the SPEX8000 ball mill for 1 h. MoO_3 was activated prior to co-milling in the high energy Aronov ball mill for 4 min. The mechanically activated mixture $3\text{Nd}_2\text{O}_3 + \text{MoO}_3$ was uniaxially pressed at 914 MPa and sintered at 1600 °C for 3 h in air (sample A). To avoid liquid phase formation, another sample (B), also of composition $\text{Nd}_6\text{MoO}_{12}$, was prepared at a higher temperature in two steps: 1200 °C, 40 h + 1650 °C, 3 h. $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ samples were prepared by similar thermal annealing ways. $\text{Nd}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ was synthesized as described elsewhere.⁹

The microstructure of the $\text{Nd}_6\text{MoO}_{12-\delta}$ and $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ ceramics sintered at 1600 °C was examined using scanning electron microscopy (JEOL JSM-6390LA). The density of the as-prepared ceramics synthesized at 1600 °C was measured using hydrostatic weighing in toluene (Table 1).

Thermogravimetric analysis was performed by using the NETZSCH STA 449C system (30–1000 °C, heating rate of 10 K min^{−1}, Al_2O_3 plate) in air. Massive ceramic samples (800–1100 mg) were used to detect a weak weight loss effect. The correction curve of an empty measuring cell was previously measured to remove the effect of an increase in weight due to a decrease in the density of air when heated. Several successive heating steps were performed for samples under investigation which yielded the uncertainty due to all other contributions, *e.g.* drift of the balance, initial measurement conditions, *etc.*, of $\pm 0.02\%$ per heating or cooling cycle.

In situ variable temperature neutron diffraction data were collected on a high-resolution powder diffractometer ECHIDNA at the OPAL research reactor (Australian Nuclear Science and Technology Organisation) using neutrons with the wavelength of 2.4395 Å. The as-prepared pellets of $\text{Nd}_6\text{MoO}_{12-\delta}$ and $\text{Nd}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ were suspended in a vacuum furnace on a platinum wire, and diffraction data were collected under dynamic vacuum in the range of 10^{-6} – 10^{-7} mbar on heating at a rate of 20 °C min^{−1} from room temperature to 1300 or 1350 °C and subsequent cooling. At each temperature, on reaching the set point the waiting period of 10 min was used before data collection to ensure isothermal conditions on the sample. The data collection time at each temperature was 1.2–1.4 h with the total experiment time of ~ 17 h.

Electrical conductivity of the samples was studied by impedance spectroscopy. Prior to taking measurements, both faces of the ceramic pellets prepared as described above were covered by Pt paste (Chempure) and fired at 950 °C for 1 h. Given the high density of the ceramics, prehydrated samples were used in subsequent studies. To this end, the electrode samples were immersed in water and held there at room temperature for a month.

Electrical conductivity measurements of $\text{Nd}_6\text{MoO}_{12-\delta}$ and $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ were performed using a P-5X potentiostat/galvanostat combined with a frequency response analyzer module (Elins Ltd, Russia) over the frequency range of 500 kHz to 0.1 Hz at a signal amplitude of 150 mV in the temperature range of 100–900 °C in dry and wet air. A dry atmosphere was created by passing air through KOH and a wet atmosphere – through a water saturator held at 20 °C. The air flow rate is 130 ml min^{−1}. The measurements were made during cooling (or heating) in wet and dry air, with isothermal holding at each temperature for at least 40 min.

Electrical characterization of $\text{Nd}_6\text{MoO}_{12-\delta}$ and $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ was carried out by impedance spectroscopy in the frequency range of

Table 1 Density of the compounds studied

Nominal composition, synthesis temperature	Density determined by hydrostatic weighing, g cm ^{−3}	X-ray density, g cm ^{−3}	Relative density, %	Unit-cell parameters, Å
$\text{Nd}_6\text{MoO}_{12-\delta}$, 1600 °C	6.08 ± 0.01	6.38	95.3	$a = 10.264(5)$ $c = 9.615(5)$
$\text{Nd}_6\text{MoO}_{12-\delta}$, 1650 °C	6.08 ± 0.03	6.366	95.5	$a = 10.272(5)$ $c = 9.618(6)$
$\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$, 1600 °C	6.01 ± 0.06	5.6	—	—

20 Hz to 1 MHz, with a signal amplitude of 200 mV, using a Hewlett-Packard 4284A precision LCR bridge, as a function of the oxygen partial pressure, during reoxidation, after reduction with a mixture of 95% N₂ and 5% H₂, between 800 and 1000 °C. Under these conditions the impedance spectra only showed a single arc, attributed to the electrode reaction, with a single interception with the *x*-axis, or a single point over this axis, which corresponds to the total resistance of the sample.

3. Results and discussion

3.1. Microstructure of Nd₆MoO_{12-δ}

Fig. 1 shows the micrograph of the surface of the Nd₆MoO_{12-δ} sample prepared by firing at 1600 °C for 3 h (sample A). Note that sample A has low open porosity and a rather large grain size: 5–30 μm. The density was estimated using hydrostatic weighing of the sample in toluene and is 95.3% of the theoretical density (Table 1). According to X-ray fluorescence data, the Nd/Mo cation ratio in Nd₆MoO_{12-δ} is 6.26 ± 0.44, in good agreement with the nominal composition.

3.2. TG evaluation of weight loss in Nd₆MoO_{12-δ}-based samples

The Nd₆MoO_{12-δ} (sample A), Nd₆MoO_{12-α} (sample B) and Nd_{5.4}Zr_{0.6}MoO_{12.3} molybdates were characterized by thermogravimetry (TG) to verify whether they contained bound water and interstitial protons, which might be responsible for the proton conduction.

Fig. 2a presents the data obtained for a newly synthesized sample Nd₆MoO_{12-δ} (sample A) in two sequential cycles, each consisting of heating to 1000 °C in air. In the TG curve obtained during the first heating, continuous weight loss can be seen in the range of 100–1000 °C (0.03%), which can be interpreted as the removal of both surface water and hydroxide ions from the pores of the ceramic and structurally bound water and interstitial protons.^{10,11} In the TG curve obtained during the second heating, the weight loss in the sample is almost zero.

A separate TG measurement was done on a Nd₆MoO_{12-δ} pellet immersed in distilled water for 4 weeks and then stored in air for 1 day. Fig. 2b presents the data obtained for the pellet after such treatment in two sequential cycles, each consisting of heating to 1000 °C in air. In this case weight loss was observed in both cycles indicating that not all of the water was removed during the first heating and that additional hydration occurred. Given the high density (95.3%) of the sample, we conclude that the 4-week hydration resulting in structural incorporation of additional water could not be completely removed after a single cycle of heating to 1000 °C.

The weight loss in sample B (Nd₆MoO_{12-α} synthesized at 1650 °C and hydrated for 4 weeks (Fig. 2c)) is smaller than that in sample A, prepared at 1600 °C, which may be due to both the higher density (95.5%) of the former sample and crystal structural distinctions between these samples (see section 3.3). The TG curve obtained during the first heating of the sample contains two broad weight loss regions, in the ranges 200–450 (0.01%) and 550–900 °C (0.01%), due to the removal of the water from the pores of the ceramics and the structurally bound water, respectively. During the second heating, the weight loss in the range of 100–600 °C is near zero, but there is again a weight loss, slightly below 0.01%, corresponding to the removal of the structurally bound water. In this respect, the behavior of sample B is similar to that of sample A, so we believe that it also contains water incorporated into the structure during the hydration process.

As to electron–proton conductor Nd_{5.4}Zr_{0.6}MoO_{12.3} (Fig. 2d), zirconium doping results in a sharper weight loss step related to the water in the pores (~0.02%). The loss of the structurally bound water in the range of 520–1000 °C is of the order of 0.01%, *i.e.* the same as in Nd₆MoO_{12-δ} (sample A) and Nd₆MoO_{12-α} (sample B). During the second heating, the weight loss in Nd_{5.4}Zr_{0.6}MoO_{12.3} is near zero.

It is of interest to note that Nd_{5.4}Zr_{0.6}MoO_{12.3} (Fig. 2d) loses the structurally bound water starting at 520 °C. In the case of the Nd₆MoO_{12-δ} and Nd₆MoO_{12-α} samples, this temperature is higher, between 550 and 590 °C, and this can also be observed, even though the removal of the structurally bound water and interstitial protons is less pronounced.

3.3. Room temperature XRD and ND of Nd_{5.4}Zr_{0.6}MoO_{12.3}, Nd₆MoO_{12-δ}, and Nd₆MoO_{12-α}, synthesized at 1400, 1600 and 1650 °C

Fig. 3a presents XRD data for the Nd_{5.4}Zr_{0.6}MoO_{12.3} Zr-doped sample, which has dominant proton conductivity below 525 °C (Fig. 3a, scan 1),⁹ Nd₆MoO_{12-δ} prepared at 1600 °C (sample A) (Fig. 3a, scan 2), and Nd₆MoO_{12-α} (sample B) synthesized by two-step firing at 1200 °C for 40 h and 1650 °C for 3 h (Fig. 3a, scan 3). Clearly, samples A and B are similar in structure to fluorite Nd_{5.4}Zr_{0.6}MoO_{12.3}. At the same time, the structure of sample A and, to a lesser extent, that of sample B has a slight rhombohedral distortion (Fig. 3a, scans 2 and 3). However, unlike in the case of the previously studied rhombohedral La_{5.5}MoO_{11.25}, stable to reduction,⁶ the degree of rhombohedral distortion in the neodymium molybdates is rather low

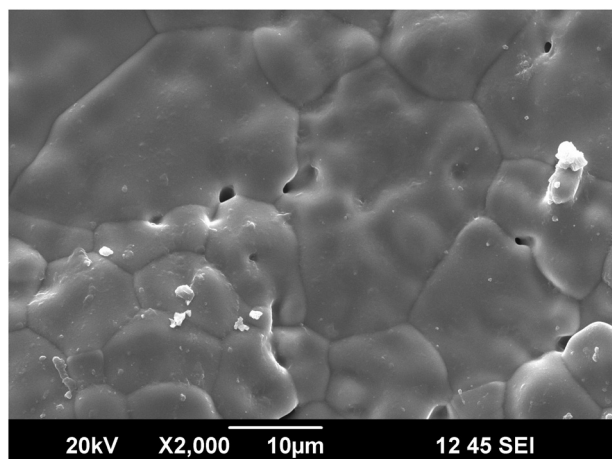


Fig. 1 Microstructure of the Nd₆MoO₁₂ (*T*_{syn} = 1600 °C) sample.

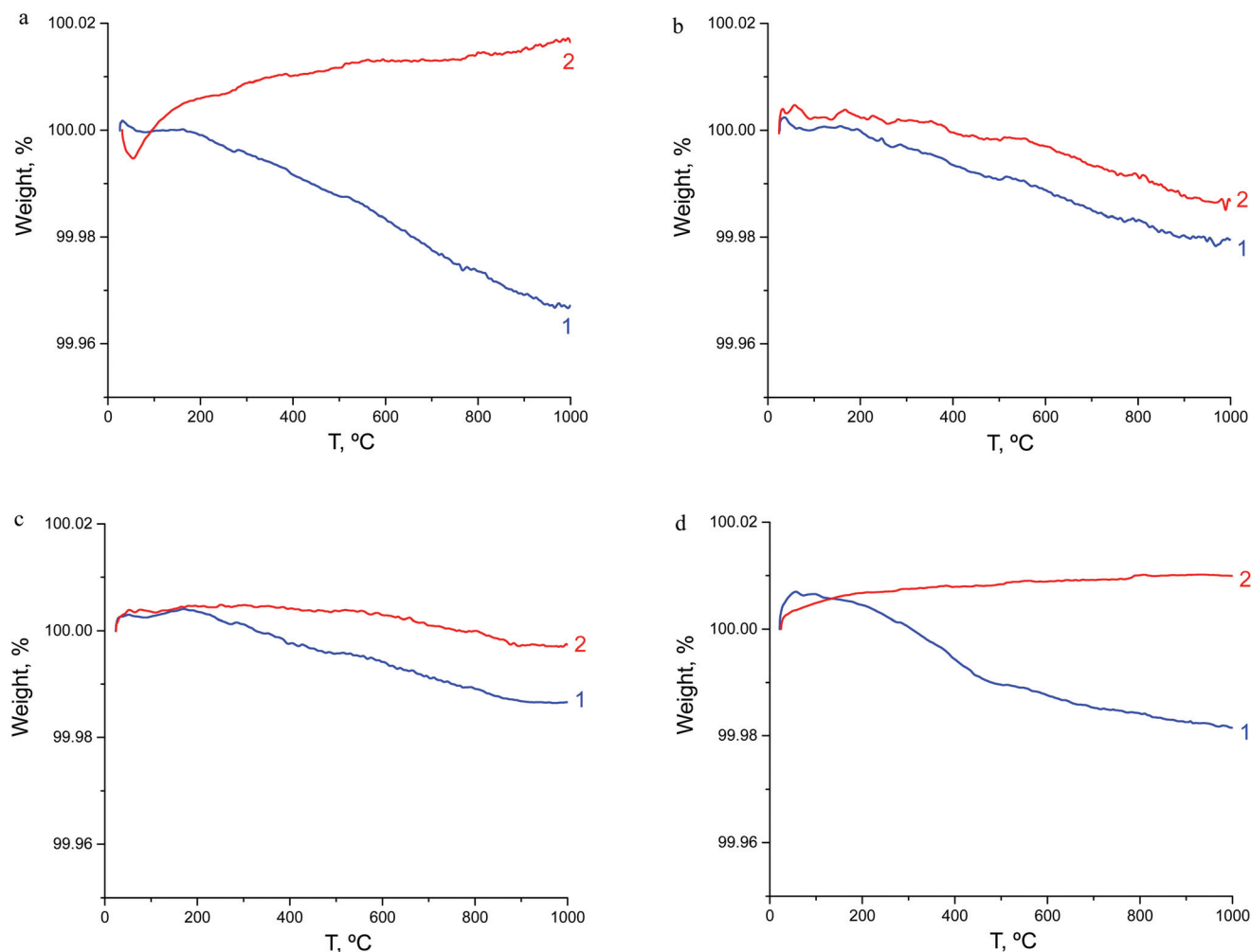


Fig. 2 TG data for (a) newly synthesized $\text{Nd}_6\text{MoO}_{12-\delta}$ (sample A); (b) $\text{Nd}_6\text{MoO}_{12-\delta}$ (sample A) hydrated for 4 weeks; (c) for a $\text{Nd}_6\text{MoO}_{12-\alpha}$ (sample B) hydrated for 4 weeks; (d) for a $\text{Nd}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ hydrated for 4 weeks. (1) 1st heating; (2) 2nd heating.

and decreases with increasing synthesis temperature in air (Fig. 3a, scans 2 and 3; Table 1).

The room-temperature ND data of these samples (Fig. 3b) lend support to the XRD data. Scan 4 in Fig. 3b presents the ND results for the nominal composition $\text{Nd}_6\text{MoO}_{12}$ after annealing at 1400 °C for 3 h in air. It is seen that, after annealing at this temperature, the sample consists of a rhombohedral phase and Nd_2O_3 as an impurity phase. The single-phase $\text{Nd}_6\text{MoO}_{12-\delta}$ sample in the Nd_2O_3 – MoO_3 system can only be obtained at higher temperatures, ~1600 and 1650 °C, in air (Fig. 3b, scans 2 and 3).

3.4. Conductivity of hydrated $\text{Nd}_6\text{MoO}_{12-\delta}$ sample in dry and wet air studied by impedance spectroscopy

Recently neutron diffraction, TGA and Raman studies were used for the investigation of $\text{SrZr}_{0.9}\text{Er}_{0.1}\text{O}_{3-\delta}$ perovskites, a potential candidate for the electrolytic membrane of a hydrogen economy device.¹² The role of hydration/dehydration cycling was shown for the sample with 90% density. This study¹² clearly demonstrated that the presence of secondary

phases (SrO , SrCO_3 , Sr(OH)_3), even limited to traces, at the grain boundary would always lead to premature ageing. Therefore, the study of proton-conducting materials which don't consist of alkaline-Earth elements, is very important. These materials include $\text{Nd}_6\text{MoO}_{12}$ based ceramics.

Hydration of dense samples before proton conductivity measurements is sometimes necessary.⁶ Prolonged holding (up to 5 h) at each temperature during cooling in the process of measurements under a wet atmosphere is incapable of ensuring equilibration of high-density samples. As a rule, the incorporation of protons into the structure of proton conductors is kinetically hindered. This is clearly demonstrated in Fig. 2a and b for $\text{Nd}_6\text{MoO}_{12-\delta}$ before and after hydration for a month. It is seen that the weight of the as-prepared $\text{Nd}_6\text{MoO}_{12-\delta}$ remains unchanged during the second heating, whereas in the hydrated sample $\text{Nd}_6\text{MoO}_{12-\delta}$ structurally bound water and interstitial protons are present even after the second heating.

Fig. 4a and b shows 300 and 695 °C impedance plots of $\text{Nd}_6\text{MoO}_{12-\delta}$ prepared at 1600 °C (sample A) and then hydrated

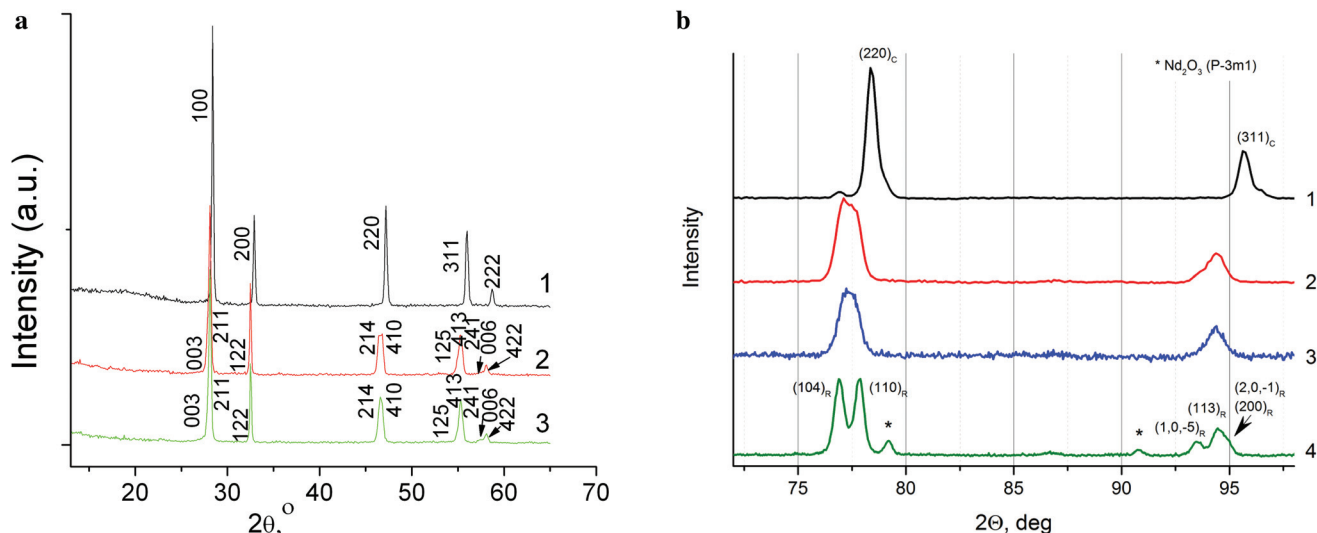


Fig. 3 (a) XRD patterns of (1) $\text{Nd}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$, synthesized at 1400 °C, 3 h; (2) $\text{Nd}_6\text{MoO}_{12-\delta}$, synthesized at 1600 °C, 3 h, (sample A); $\text{Nd}_6\text{MoO}_{12-\delta}$, synthesized at 1200 °C, 40 h + 1650 °C, 3 h (sample B). (b) Room temperature ND patterns of (1) $\text{Nd}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$, synthesized at 1400 °C, 3 h, (2) $\text{Nd}_6\text{MoO}_{12}$, synthesized at 1600 °C, 3 h, (sample A), (3) $\text{Nd}_6\text{MoO}_{12}$, synthesized at 1200 °C, 40 h + 1650 °C, 3 h (sample B), (4) $\text{Nd}_6\text{MoO}_{12}$, synthesized at 1400 °C, which includes admixture Nd_2O_3 (*).

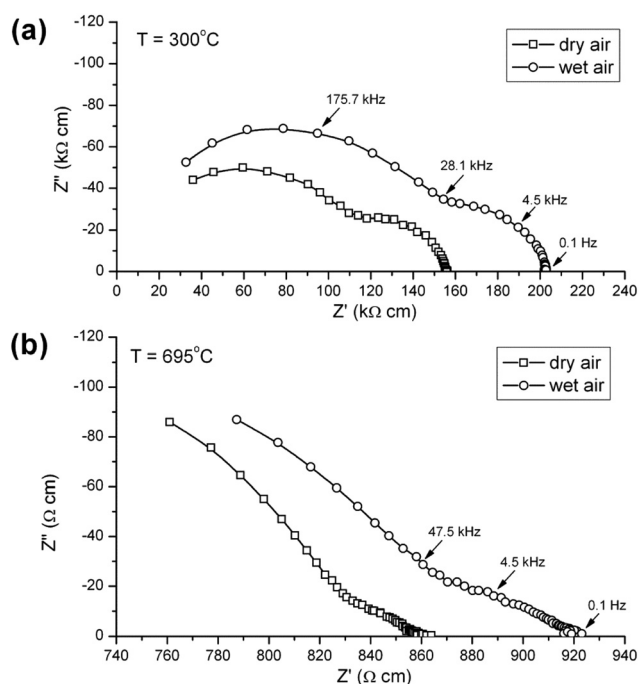


Fig. 4 Impedance plots of $\text{Nd}_6\text{MoO}_{12-\delta}$ ($T_{\text{syn}} = 1600^\circ\text{C}$) at (a) 300 and (b) 695 °C obtained in cooling cycles under a dry and wet atmosphere.

at room temperature for four weeks. Note that during the first heating under a wet atmosphere, there is no grain boundary contribution (not shown here). At the same time, during cooling in wet and dry air the grain boundary contribution is noticeable below 340 °C. In a study of Zr-doped molybdates with the fluorite structure,⁹ there was no grain boundary conductivity after cooling under a dry atmosphere, but a grain

boundary contribution emerged after cooling under a wet atmosphere. Thus, in the case of reduction in the bulk of the material, it is grain boundaries that are “weak links”. Changes in the atmosphere, probably in any sequence, influence the properties of the ceramics, where redox processes take place.

Fig. 5 shows Arrhenius plots of conductivity for sample A. Note that the plots have a change in slope, typical of electron–proton-conducting oxides, at $\sim 580^\circ\text{C}$. The change in the slope of the Arrhenius plot of conductivity indicates an increase in the contribution of electron conductivity relative to proton conductivity, because above 600 °C molybdenum and neody-

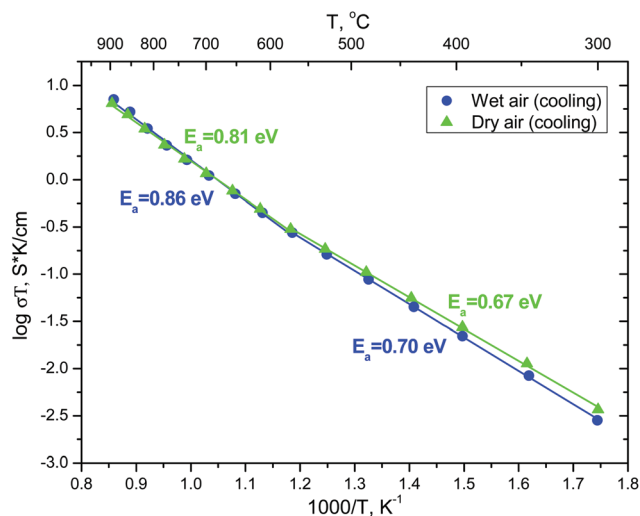


Fig. 5 Arrhenius plots of conductivity for hydrated $\text{Nd}_6\text{MoO}_{12-\delta}$ ($T_{\text{syn}} = 1600^\circ\text{C}$) (sample A) obtained in cooling cycles under a dry and wet atmosphere.

mium are more actively reduced. In the case of the Zr-doped molybdate $\text{Nd}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$, a similar break was observed at 525 °C.⁹ It is of interest to note that the undoped and Zr-doped electron–proton conductors $\text{Sm}_6\text{MoO}_{12}$ and $\text{Sm}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ have a break at 500 and 425 °C, respectively.^{13,14} We observe a similar trend for pure $\text{Nd}_6\text{MoO}_{12-\delta}$ and $\text{Nd}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ samples (580 and 525 °C, respectively). This means that proton conductivity prevails to higher temperatures in the case of undoped rare-Earth molybdates and that the addition of zirconium as a donor dopant reduces the proton conductivity of the material.¹⁵ At the same time, as distinct from the previously studied $\text{La}_6\text{MoO}_{12}$ -based materials,^{4–6} $\text{Sm}_6\text{MoO}_{12}$,¹⁴ and Zr-doped molybdates^{9,13,14,16} the proton conductivity of $\text{Nd}_6\text{MoO}_{12-\delta}$ is not observed in an all temperature range study. Measurements on the hydrated sample during both wet and dry cooling showed no proton contribution.

The unusual results on the conductivity of $\text{Nd}_6\text{MoO}_{12-\delta}$ can be understood in terms of distinctive features of their structure. $\text{Nd}_6\text{MoO}_{12}$ was reported to have a rhombohedral ($R\bar{3}$) structure, but this was inferred from the data obtained at 1400 °C using pure Mo, rather than MoO_3 , as a starting reagent, and the synthesis was performed under controlled gaseous atmospheres.⁸ In this study, the synthesis was carried out in air and, the nominal $\text{Nd}_6\text{MoO}_{12}$ sample obtained at 1400 °C had a rhombohedral structure, but the ND data indicated that it contained 5% Nd_2O_3 (Fig. 3b, scan 4). Firing at higher temperatures, 1600 and 1650 °C, in air (samples A and B, respectively) yielded single-phase samples with a slight rhombohedral distortion, which was found to decrease with increasing air firing temperature, so that they approached the fluorite structure (Fig. 3a and b, scans 2 and 3). We believe that after synthesis at 1600 and 1650 °C, $\text{Nd}_6\text{MoO}_{12-\delta}$ and $\text{Nd}_6\text{MoO}_{12-\alpha}$, similar in structure to fluorite, contain Nd and Mo cations in different valence states. The presence of $\text{Nd}^{3+}/\text{Nd}^{2+}$ and $\text{Mo}^{6+}/\text{Mo}^{5+}$ variable valence cations in ceramics with the nominal composition $\text{Nd}_6\text{MoO}_{12}$ would unavoidably lead to high electronic conductivity. According to the TG data in Fig. 2b, water is rather tightly bound in the structure of the hydrated sample A. Even after the second heating to 1000 °C, some water persists in this sample. Thus, the proton conductivity exists in $\text{Nd}_6\text{MoO}_{12-\delta}$ and is due to the ability of $\text{Nd}_6\text{MoO}_{12-\delta}$ (sample A) to retain strongly bound water and interstitial protons up to 1000 °C.

It is worth mentioning a report by López-Vergara *et al.*,⁵ who showed that lanthanum molybdate with $\text{La}/\text{Mo} = 5.4$ ($\text{La}_{5.4}\text{Mo}_\text{Q}$) rapidly quenched in air from 1500 °C had the fluorite structure ($Fm\bar{3}m$), whereas a slowly cooled sample of the same composition ($\text{La}_{5.4}\text{Mo}_{0.5}$) had a rhombohedral structure. Data obtained under reducing conditions indicate that the cubic polymorph exhibits higher n-type conductivity and somewhat lower ionic conductivity than that of the rhombohedral polymorph. Under oxidizing conditions (in air), a slight increase in p-type conductivity was observed and to a greater extent for a cubic polymorph.

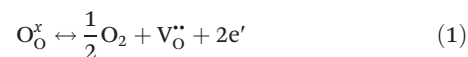
Thus, the tendency of rhombohedral distortion to decrease with increasing synthesis temperature under oxidizing con-

ditions (in air) leads to the formation of $\text{Nd}_6\text{MoO}_{12-\delta}$, in which p-type electron conductivity prevails in air. This is due to the presence of $\text{Nd}^{3+}/\text{Nd}^{2+}$ and $\text{Mo}^{6+}/\text{Mo}^{5+}$ variable valence cations in ceramics. The process is more pronounced in neodymium molybdate than in the lanthanum molybdate-based polymorphs $\text{La}_{5.4}\text{Mo}_\text{Q}$ and $\text{La}_{5.4}\text{Mo}_{0.5}$ ⁵ or in $\text{La}_{5.5}\text{MoO}_{11.25}$,⁶ due to the variable valence of Nd. Because of this, we cannot detect proton conduction in $\text{Nd}_6\text{MoO}_{12-\delta}$ and, most likely, there will be no characteristic ionic conductivity plateau in the plot of conductivity against oxygen partial pressure. Recall that the Zr-doped neodymium molybdate $\text{Nd}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ with the fluorite structure was shown to be an electron–proton conductor with dominant proton conductivity in a wet atmosphere below 525 °C.⁹ Zr doping really stabilized $\text{Nd}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ against reduction although this solid solution has a fluorite structure.

3.5. Effect of oxygen partial pressure on the total conductivity of $\text{Nd}_6\text{MoO}_{12-\delta}$ prepared at 1600 °C at $800 \leq T \leq 1000$ °C

The electrical conductivity dependence of $\text{Nd}_6\text{MoO}_{12-\delta}$ with the oxygen partial pressure (Fig. 6) shows a V-type behaviour typical of a transition from a p-type to n-type conductivity mechanism. For very low oxygen partial pressures, is also observed a change of trend, with the value of the conductivity tending to a constant value.

As mentioned before, the redox behaviour of this material is controlled by Mo and Nd oxidation states. Therefore, considering Mo^{6+} and Nd^{3+} the equilibrium states of these aliovalent ions at high oxygen partial pressure, during reduction are expected to undergo the following reactions:



where each symbol agrees with the Kröger–Vink notation.

In agreement with eqn (1), during the reduction process, we expect to increase the electron concentration to compensate

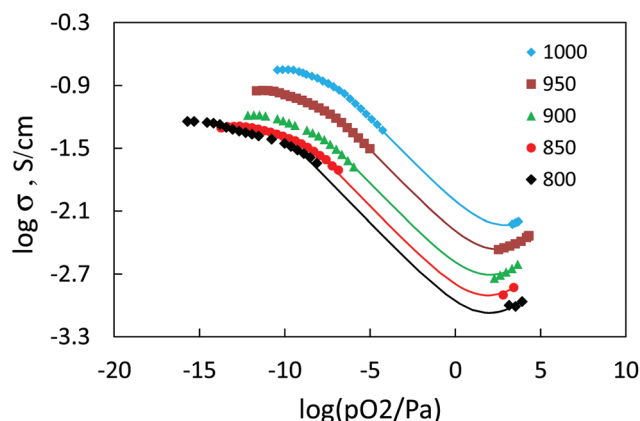


Fig. 6 Electrical conductivity of $\text{Nd}_6\text{MoO}_{12-\delta}$ ($T_{\text{syn}} = 1600$ °C) (sample A) as a function of the oxygen partial pressure, for temperatures between 800 and 1000 °C. Fitting lines calculated using eqn (5).

for the formation of oxygen vacancies, and these electrons will reduce Mo and Nd to the +5 and +2 states, respectively (eqn (2) and (3)). These localized electrons, together with the band-band transfer, described by eqn (4), are responsible for the electrical conductivity of this material.



Combining eqn (1) and (4), assuming the electronic formation to compensate for the oxygen vacancy formations, the typical 1/6 and -1/6 slope, respectively, for p-type and n-type conductivities is obtained, and it is possible to write the dependence of the conductivity on the oxygen partial pressure as:

$$\sigma = \sigma_n^* \cdot pO_2^{-1/6} + \sigma_p^* \cdot pO_2^{1/6} \quad (5)$$

where pO_2 is the oxygen partial pressure and σ_n^* and σ_p^* are, respectively, the n and p-type conductivity at $pO_2 = 1$ Pa. Fitting lines in Fig. 7 were calculated using eqn (5).

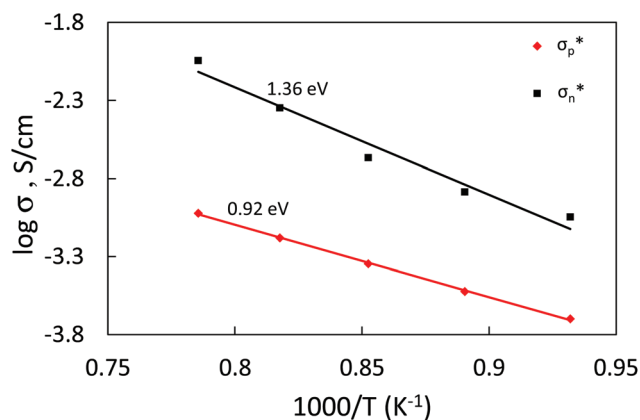


Fig. 7 Arrhenius plot of fitting parameters σ_n^* and σ_p^* in agreement with eqn (5).

Fig. 7 is an Arrhenius type plot of the σ_n^* and σ_p^* fitting parameters found for each measured temperature, which enables the calculation of the activation energy for both electrical conductivity mechanisms. The value obtained for the p-type conductivity (0.92 eV) is in agreement with the obtained values calculated from air measurements, and with this method it was also possible to obtain the activation energy for the n-type conductivity (1.36 eV). For very low oxygen partial pressure the conductivity stops to obey eqn (5), and tends to reach a constant value. This behaviour suggests that as all Mo and Nd ions became reduced, a concentration limit of localized electrons is achieved.

3.6. *In situ* neutron diffraction study of the structure of $Nd_6MoO_{12-\delta}$ and $Nd_{5.4}Zr_{0.6}MoO_{12.3}$ under high vacuum at $800 \leq T \leq 1350$ °C

In situ neutron diffraction data collected for $Nd_6MoO_{12-\delta}$ synthesized at 1600 °C (sample A) and $Nd_{5.4}Zr_{0.6}MoO_{12.3}$ under dynamic vacuum (Fig. 8a and b, respectively) confirmed that $Nd_{5.4}Zr_{0.6}MoO_{12.3}$ has a cubic fluorite structure which was found to be stable in the used temperature range (Fig. 8b). $Nd_6MoO_{12-\delta}$ was confirmed to be rhombohedral up to ~1140 °C. Above this temperature it transformed to a cubic structure. The result is consistent with the report by López-Vergara *et al.*,⁵ who showed that lanthanum molybdate with La/Mo = 5.4 (La_{5.4}Mo₅Q) rapidly quenched in air from 1500 °C had the fluorite structure (*Fm3m*), whereas a slowly cooled sample of the same composition (La_{5.4}Mo₅O_{12.5}) had a rhombohedral structure.

The transitions from the low-temperature cubic phase to the rhombohedral phase and to the high-temperature cubic phase in the Ln_6WO_{12} ($Ln = Y, Ho, Er, Yb$) tungstates were studied previously using *in situ* synchrotron X-ray diffraction study in air.^{17,18} In air at 1240 °C, the onset of an irreversible first-order low temperature fcc-to-rhombohedral transform-

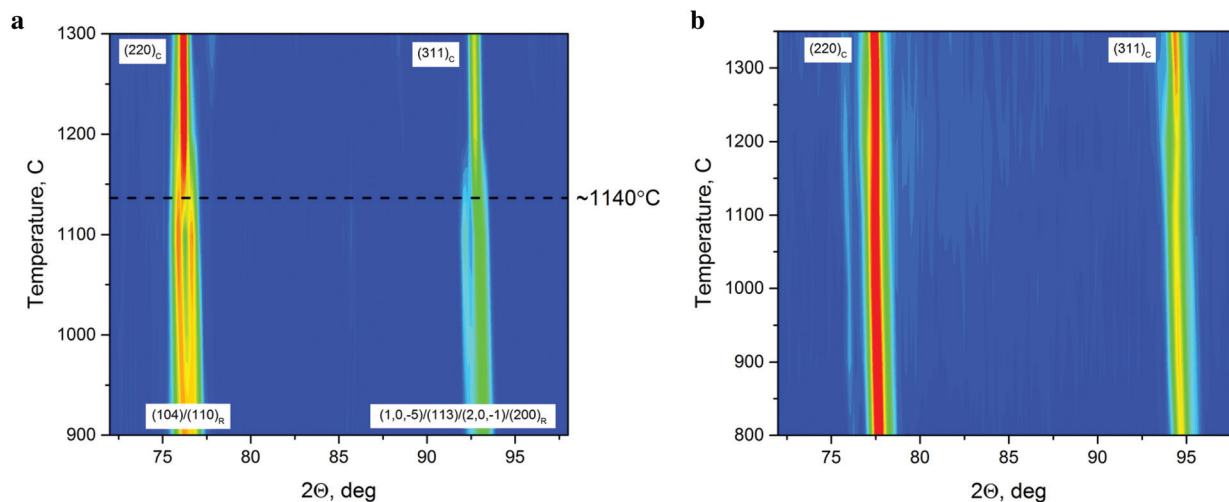


Fig. 8 (a) *In situ* neutron diffraction data obtained for $Nd_6MoO_{12-\delta}$ (sample A) in a vacuum furnace. (b) *In situ* neutron diffraction data obtained for $Nd_{5.4}Zr_{0.6}MoO_{12.3}$ in a vacuum furnace.

ation in $\text{Ln}_6\text{WO}_{12}$ ($\text{Ln} = \text{Y}, \text{Ho}, \text{Er}, \text{Yb}$) was observed.¹⁷ At higher temperature $T > 1650^\circ\text{C}$ rhombohedral-to-fcc phase transformation begins in the $\text{Ln}_6\text{WO}_{12}$ ($\text{Ln} = \text{Y}, \text{Ho}, \text{Er}, \text{Yb}$).¹⁸ This transformation was characterized as a first-order reconstructive, thermally activated process.¹⁸ A similar picture is observed when $\text{Nd}_6\text{MoO}_{12-\delta}$ is heated under vacuum (Fig. 8a). The low temperature fcc-to-rhombohedral transformation transition occurs at $\sim 800^\circ\text{C}$. At a higher temperature of $\sim 1140^\circ\text{C}$, we observe the rhombohedral-to-fcc phase transformation.

3.7. Structure and mixed electron–proton conductivity of $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$

Due to the fact that in $\text{Nd}_6\text{MoO}_{12-\delta}$ with small rhombohedral distortion synthesized at 1600°C , electron conduction dominated over the whole studied temperature range, it was necessary to find the conditions for the synthesis of the phase-pure rhombohedral phase based on $\text{Nd}_6\text{MoO}_{12}$. For this, the nominal composition of $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ with a smaller content of Nd_2O_3 by 3.5% was synthesized in air in the temperature range of $1600\text{--}1650^\circ\text{C}$.

The microstructure of the $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ sample, synthesized at 1600°C , 3 h is presented in Fig. S1.† The crystallographic (calculated) density of $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ ($R\bar{3}$) (excluding superstructural lines, $Z = 3$) is 5.6 g cm^{-3} . This value is significantly lower than that measured using hydrostatic weighing in toluene (6.01 g cm^{-3}) (Table 1). Apparently, $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ has a more complex structure than does rhombohedral ($R\bar{3}$) $\text{Nd}_6\text{MoO}_{12-\delta}$. It may be similar in structure to $\text{La}_{5.5}\text{MoO}_{11.25}$,⁶ but at the present stage its structure type cannot be identified with certainty. Because of this, Table 1 presents only the experimental density data obtained for $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ by hydrostatic weighing.

The X-ray diffraction data (Fig. 9) and neutron diffraction (Fig. 9, inset) showed that in this case it was possible to obtain

a more complex rhombohedral phase based on ($R\bar{3}$) by air-annealing at 1600 and 1650°C . The structure of $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ seems to be more complex, because Fig. 9 shows additional, unindexed lines: 35, 6; six weak lines in the range $48\text{--}51.5; 66.3; 87^\circ$ in 2θ pointed by asterisks. An attempt to index all the lines of $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ in the space group $R\bar{3}$ was unsuccessful, unlike in the case of $\text{Nd}_6\text{MoO}_{12}$. Note that the complex rhombohedral structure remains the same in the interval $1600\text{--}1650^\circ\text{C}$ (Fig. 9, scans 1 and 2).

$\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$, synthesized at 1600°C , 3 h, was pre-hydrated for a month at room temperature and studied by impedance spectroscopy (Fig. 10) over a heating–cooling cycle in wet air, and then, separately, with cooling in dry air. Arrhenius plots of conductivity for $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ are presented in Fig. 10. As a result (Fig. 10), the contribution of proton conduction in $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ was observed in wet air, which persists at least below 900°C . Heating hydrated $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ under a wet atmosphere demonstrates the highest possible proton conductivity of $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$, whereas during cooling the same sample contains less structurally bound water and protons. Because of this, the temperature dependence of conductivity obtained during heating differs from that obtained during cooling. After a heating–cooling cycle in wet air, the sample was heated and cooled in dry air. As a result, the amount of structurally bound water decreased and the conductivity was lower than that after cooling in wet air.

There is no contribution of the p-type conductivity at high oxygen partial pressures, *i.e.* in air, in the complex rhombohedral $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ phase based on ($R\bar{3}$), and we can observe the appearance of the proton contribution. We did not observe grain boundary contribution in complex rhombohedral $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ under a dry atmosphere on cooling in the all temperature range study (Fig. 11).

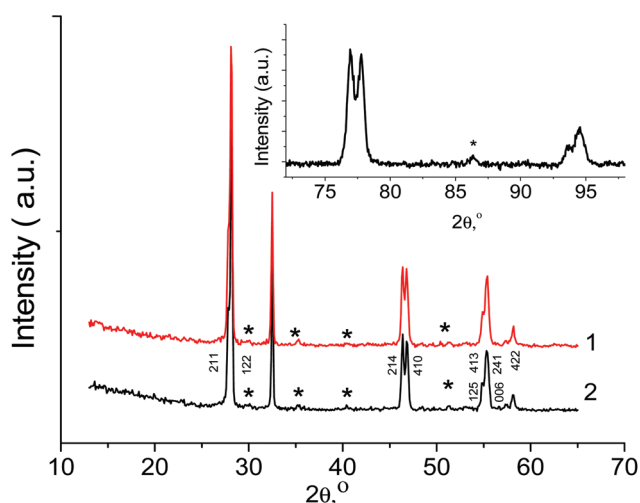


Fig. 9 XRD patterns of (1) $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$, synthesized at 1600°C , 3 h; (2) $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$, synthesized at 1200°C , 40 h + 1650°C , 3 h. Inset: ND of $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$, synthesized at 1200°C , 40 h + 1650°C , 3 h ($\lambda = 2.4395\text{ \AA}$; asterisks show additional lines, which are not appropriate for pure rhombohedral phase).

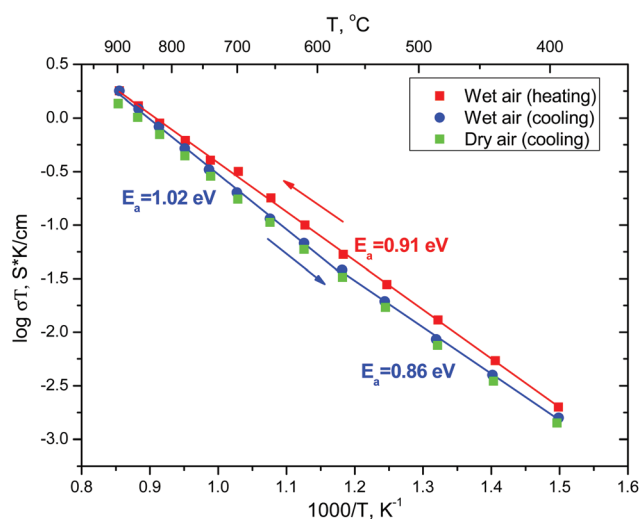


Fig. 10 Arrhenius plots of conductivity for hydrated $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ ($T_{\text{syn}} = 1600^\circ\text{C}$) obtained in heating–cooling cycles under a wet atmosphere and on cooling under a dry atmosphere.

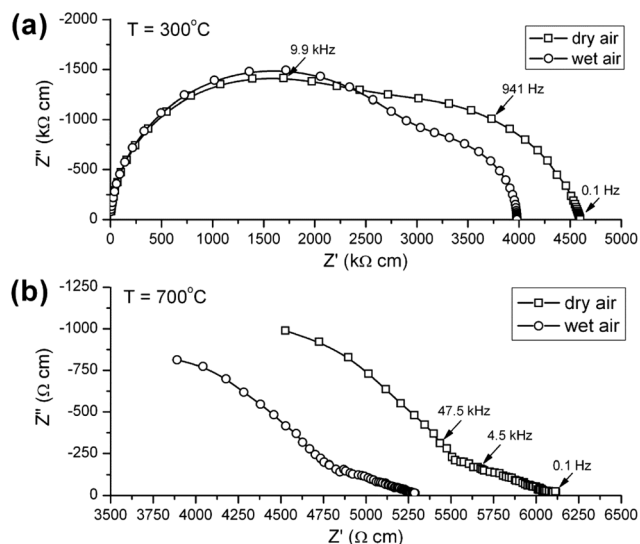


Fig. 11 Impedance plots of $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ ($T_{\text{syn}} = 1600\text{ }^{\circ}\text{C}$) at (a) 300 and (b) 700 $^{\circ}\text{C}$ obtained in cooling cycles under a wet and dry atmosphere.

Thus, like $\text{La}_{5.5}\text{MoO}_{11.25}$,⁶ the complex rhombohedral phase based on ($R\bar{3}$), $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$, obtained by high-temperature annealing in the 1600–1650 $^{\circ}\text{C}$ temperature range is stable under reducing conditions up to 900 $^{\circ}\text{C}$, and Nd and Mo cations are retained in the form of Nd^{3+} and Mo^{6+} predominantly, which agrees with the earlier data.^{7,8} Proton conductivity of $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ is $8.5 \times 10^{-3} \text{ S cm}^{-1}$ at 800 $^{\circ}\text{C}$, and $8 \times 10^{-4} \text{ S cm}^{-1}$ at 600 $^{\circ}\text{C}$, respectively. However, prolonged isothermal exposure of the rhombohedral phases $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ and $\text{Nd}_6\text{MoO}_{12-\delta}$ at low oxygen partial pressures at $\sim 1100\text{ }^{\circ}\text{C}$ is undesirable, because it can lead to the destruction of ceramics due to the phase transition of rhombohedral phase – fluorite, as illustrated by neutron diffraction data (Fig. 8a).

4. Conclusions

The high-temperature synthesis of $\text{Nd}_6\text{MoO}_{12-\delta}$ in air from a mechanically activated mixture of Nd_2O_3 and MoO_3 has been studied for samples, synthesized at 1400, 1600, and 1650 $^{\circ}\text{C}$ using ND and XRD at room temperature. The results demonstrate that firing at 1400 $^{\circ}\text{C}$ in air leads to the formation of a well-crystallized rhombohedral ($R\bar{3}$) $\text{Nd}_{6-x}\text{MoO}_{12-\gamma}$, with Nd_2O_3 as an impurity phase ($\sim 5\%$). Firing at higher temperatures (1600 and 1650 $^{\circ}\text{C}$) leads to the formation of phase-pure $\text{Nd}_6\text{MoO}_{12-\delta}$ and $\text{Nd}_6\text{MoO}_{12-\alpha}$ with a small rhombohedral distortion, which are more similar to fluorite. Raising the firing temperature from 1600 to 1650 $^{\circ}\text{C}$ reduces the rhombohedral distortion. $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ (it has a smaller content of Nd_2O_3 by 3.5%) with a more complex rhombohedral structure based on ($R\bar{3}$) was synthesized in the 1600–1650 $^{\circ}\text{C}$ temperature range. $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ has a more complex structure than does rhombohedral ($R\bar{3}$) $\text{Nd}_6\text{MoO}_{12}$. It may be similar in structure to $\text{La}_{5.5}\text{MoO}_{11.25}$,⁶ but at the present stage its structure type

cannot be identified with certainty. On the whole, $\text{Nd}_6\text{MoO}_{12-\delta}$ and $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ seem to be two distinct compounds, with no solid solution range between them, at least from 1600 to 1650 $^{\circ}\text{C}$.

We have performed a comparative study of $\text{Nd}_6\text{MoO}_{12-\delta}$ and fluorite $\text{Nd}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ in the 800–1300 $^{\circ}\text{C}$ temperature range under vacuum. *In situ* neutron diffraction data collected for $\text{Nd}_6\text{MoO}_{12-\delta}$ synthesized at 1600 $^{\circ}\text{C}$ (sample A) and $\text{Nd}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ under dynamic vacuum confirmed that $\text{Nd}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ has a cubic fluorite structure which was found to be stable in the used temperature range (800–1300 $^{\circ}\text{C}$). $\text{Nd}_6\text{MoO}_{12-\delta}$ was confirmed to be rhombohedral up to $\sim 1140\text{ }^{\circ}\text{C}$. Above that temperature it transformed to a cubic structure.

The weight loss of single-phase $\text{Nd}_6\text{MoO}_{12-\delta}$ and $\text{Nd}_6\text{MoO}_{12-\alpha}$, synthesized at 1600 and 1650 $^{\circ}\text{C}$, respectively, has been studied by TG in ambient air. The as-synthesized samples and hydrated samples with the same composition have been shown to experience a stable weight loss. Even two successive heating-cooling cycles between 25 and 1000 $^{\circ}\text{C}$ do not completely remove strongly bound water and interstitial protons from hydrated $\text{Nd}_6\text{MoO}_{12-\delta}$.

Electrochemical characterization by impedance spectroscopy of $\text{Nd}_6\text{MoO}_{12-\delta}$ has shown that a grain boundary contribution emerges below 340 $^{\circ}\text{C}$ after cooling under a wet and dry atmosphere. We believe that the loss of dimensional stability under reducing conditions in the $\text{Nd}_6\text{MoO}_{12-\delta}$ samples and $\text{Nd}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ solid solution,⁹ which results in a grain-boundary contribution, limiting their conductivity under wet and/or dry atmospheres is due to partial reduction of Mo^{6+} and Nd^{3+} in the rare-Earth molybdates with a fluorite-like slightly distorted rhombohedral and a fluorite structure, respectively. It is known that the process is most manifest in the fluorite phases than rhombohedral phases.⁶ As evidence there is no grain boundary contribution in more complex rhombohedral $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ under a dry atmosphere on cooling in an all temperature range study.

Proton conductivity has not been detected in $\text{Nd}_6\text{MoO}_{12-\delta}$ using impedance spectroscopy in the all temperature range study. The prevalence of electronic conductivity in $\text{Nd}_6\text{MoO}_{12-\delta}$ in a wide temperature range is due to the presence of oxidized and reduced forms of Nd and Mo in the fluorite-like structure with a small rhombohedral distortion. However proton contribution of $\text{Nd}_6\text{MoO}_{12-\delta}$ was confirmed by TG measurements.

With decreasing Nd_2O_3 concentration, the electronic/proton conductivity ratio in $\text{Nd}_{6-x}\text{MoO}_{12-\delta}$ ($x = 0, 1$) decreases. Then we observed that proton contribution in complex rhombohedral $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ and proton conductivity of $\text{Nd}_{10}\text{Mo}_2\text{O}_{21}$ is $8.5 \times 10^{-3} \text{ S cm}^{-1}$ at 800 $^{\circ}\text{C}$, and $8 \times 10^{-4} \text{ S cm}^{-1}$ at 600 $^{\circ}\text{C}$, respectively.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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