

## ***Praseodymium substituted lanthanum orthoniobate: electrical and structural properties***

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### Abstract

The results of ionic transport and structural measurements for the lanthanum orthoniobate doped by praseodymium are presented and discussed. The influence of calcium co-doping on these properties has also been analyzed. The results suggest the predominant protonic conductivity for the investigated system in the whole range of investigated temperatures. The influence of calcium co-doping on phase purity is analyzed.

### Introduction

Lanthanum orthoniobates are materials with high potential applicability due to their relatively high proton conductivity and chemical stability. Therefore, these materials are potential candidates for proton conducting fuel cells (PCFC) or proton conducting electrolyzers (PCE) [1], [2], [3], [4]. During the last decade, lanthanum orthoniobate system's properties have been modified extensively by both substitution and doping. We can distinguish two main reasons for which such a modification is introduced: elevation of the proton conductivity level and change of the phase transition temperature of the system. The mechanism of conduction of protons in lanthanum orthoniobates is described as proton hopping and for such a mechanism, the presence of oxygen vacancies in the

material is crucial [5]. Therefore, the introduction of the acceptor dopant into the system can elevate its ionic conductivity by extra vacancies formation, due to charge compensation. The first, introduced by Haugrud and Norby [6], acceptor dopant was calcium. Then other works followed introducing strontium and magnesium as acceptor dopants [7], [8], [9]. Another approach has been presented by authors who introduced substitution on the lanthanum site by other lanthanides which can exhibit two different valence states 3+/4+ i.e. cerium and praseodymium [10], [11]. Such a substitution can potentially enhance the electron p- or n-type conductivity in the material. Such a modification can be beneficial for other than electrolyte applications e.g. fuel cells electrodes. Apart from the proper level of conductivity, the future applications are determined by other properties such as thermal expansion. In the case of lanthanum orthoniobate, thermal expansion coefficient changes at about 500°C as a result of structural phase transition from monoclinic to tetragonal structure [8]. Therefore, various dopants on a niobium site, e.g. vanadium, antimony or tantalum, have been introduced to change the temperature of phase transition and to obtain material stable in one of two polymorphs [3], [12], [13], [14]. As for Nb site doping also other elements have been investigated e.g. Ge or Ti which could potentially change not only phase transition temperature but also conductivity of the system [15].

In this work, we present the structural and transport properties of praseodymium- and calcium-doped lanthanum niobates. The influence of a dopant on the conductivity of the system has been determined by the means of electrochemical impedance spectroscopy.

## Experimental

Powders of  $\text{La}_{0.9}\text{Pr}_{0.1}\text{NbO}_4$ ,  $\text{La}_{0.9}\text{Pr}_{0.08}\text{Ca}_{0.02}\text{NbO}_4$  and  $\text{La}_{0.88}\text{Pr}_{0.1}\text{Ca}_{0.02}\text{NbO}_4$  were prepared via a two-step solid-state reaction route. Reactants  $\text{La}_2\text{O}_3$  (99.99 % Aldrich, preheated at 900 °C for 4h),  $\text{Pr}_6\text{O}_{11}$  (99.99 % Aldrich),  $\text{CaCO}_3$  (99.99 % Aldrich) and  $\text{Nb}_2\text{O}_5$  (99.99 % Alfa Aesar) were used as starting materials. Precursors were hand milled in agate mortar in isopropanol. Obtained powders were uniaxially pressed at 400 MPa into 12 mm diameter pellets. The green bodies were calcined at 1000 °C for 12 h. After the first step of the synthesis, specimens were ground into powders. Dense pellets were obtained in the second step, in which powders were pressed again and sintered at 1400 °C for 12h. Density measurements of the samples were performed by a vacuum-assisted Archimedes method. The room-temperature powder X-ray diffraction patterns were collected using

Philips X'Pert Pro MPD with Cu K $\alpha$  radiation. Phase identification and Rietveld analysis were performed by using X'Pert Highscore Plus and Fullprof suite software [16], [17]. The microstructure of the 15 nm gold-coated samples was characterized using FEI Quanta FEG 250 scanning electron microscope equipped with EDAX Apollo energy-dispersive X-ray spectroscopy detector. Impedance spectroscopy measurements were performed using Novocontrol Alpha-A frequency analyzer in the frequency range 1 Hz -1 MHz and 1 V amplitude on samples with ink painted platinum electrodes (ESL 5542). The measurements were performed in both wet (3% H<sub>2</sub>O) and dry, hydrogen and synthetic air at the temperature range from 350 °C to 750 °C with 50 °C steps. Results were analyzed by ZView software.

## Results and discussion

Fig. 1 shows the XRD patterns of the synthesized sample powders. All reflections were indexed within the monoclinic LaNbO<sub>4</sub> (ICSD: 01-071-1405) phase [18]. The unit cell parameters of the compounds are summarized in Table 1. In the case of all samples, the unit cell volume is reduced with respect to the LaNbO<sub>4</sub>. In this work, the two dopants, which are introduced into lanthanum (ionic radius 1.16 Å CN=8 [19]) sublattice is praseodymium (Pr<sup>3+</sup>/ Pr<sup>4+</sup>) and calcium with ionic radii of 1.126/0.96 Å and 1.12 Å (CN=8) [19], respectively. The decrease of the unit cell parameters can be attributed to the shorter respective ionic radii for 8-fold coordination, which is in accordance with Vegard's law. Also, no structural or compositional change has been noticed after measurements in reducing atmospheres which is in good agreement with other works on chemical stability of lanthanum orthoniobate in a broad range of oxygen partial pressures [20].

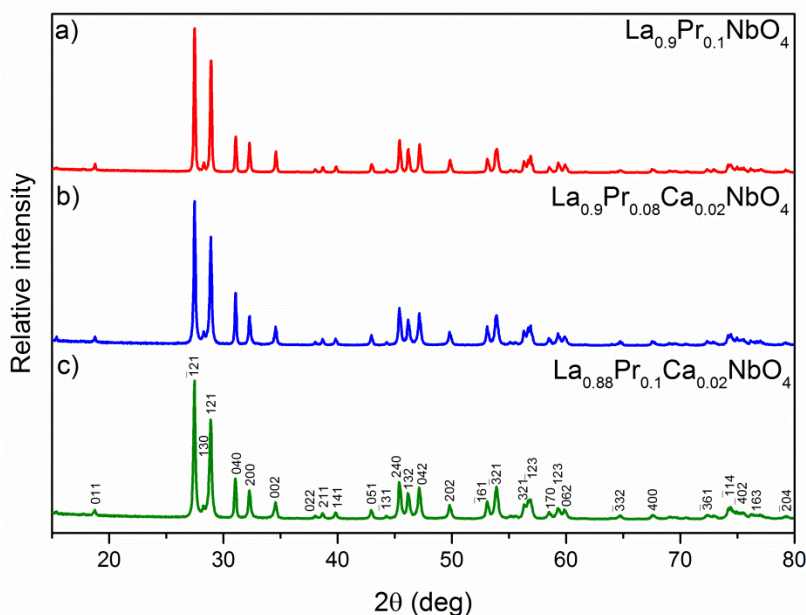


Fig. 1. XRD patterns of a)  $\text{La}_{0.9}\text{Pr}_{0.1}\text{NbO}_4$ , b)  $\text{La}_{0.9}\text{Pr}_{0.08}\text{Ca}_{0.02}\text{NbO}_4$  and c)  $\text{La}_{0.88}\text{Pr}_{0.1}\text{Ca}_{0.02}\text{NbO}_4$  samples.

Table 1. Unit cell parameters of obtained compounds.  $\text{LaNbO}_4$  unit cell data was added for comparison.

	$\text{LaNbO}_4$ [19]	$\text{La}_{0.9}\text{Pr}_{0.1}\text{NbO}_4$	$\text{La}_{0.9}\text{Pr}_{0.08}\text{Ca}_{0.02}\text{NbO}_4$	$\text{La}_{0.88}\text{Pr}_{0.1}\text{Ca}_{0.02}\text{NbO}_4$
a (Å)	5.56470	5.55813(5)	5.55616(11)	5.55436(9)
b (Å)	11.51940	11.50550(11)	11.51210(23)	11.51338(21)
c (Å)	5.20150	5.19813(5)	5.20028(10)	5.19981(8)
V(Å <sup>3</sup> )	332.57	331.55(5)	331.79(1)	331.68(4)
β(°)	94.100	94.115(1)	94.062(1)	94.064(2)

Relative densities of  $\text{La}_{0.9}\text{Pr}_{0.1}\text{NbO}_4$ ,  $\text{La}_{0.9}\text{Pr}_{0.08}\text{Ca}_{0.02}\text{NbO}_4$  and  $\text{La}_{0.88}\text{Pr}_{0.1}\text{Ca}_{0.02}\text{NbO}_4$  were 90, 93 and 94%, respectively. Fig.2 shows the SEM images of sintered  $\text{La}_{0.9}\text{Pr}_{0.1}\text{NbO}_4$  (Fig. 2a),  $\text{La}_{0.9}\text{Pr}_{0.08}\text{Ca}_{0.02}\text{NbO}_4$  (Fig. 2b) and  $\text{La}_{0.88}\text{Pr}_{0.1}\text{Ca}_{0.02}\text{NbO}_4$  (Fig. 2c) samples. For samples containing calcium, an additional phase (cf. darker regions in Fig. 2b) was identified by EDS measurements. The EDS results shows that the secondary phase is enriched in Ca and Nb. It has been previously shown by Syvertsen et al. that limited calcium solubility in lanthanum orthoniobates can induce extra phases formation [21]. One of them is  $\text{Ca}_2\text{Nb}_2\text{O}_7$ , which is believed to be the secondary phase in our the case. However, since the

secondary reflections of the  $\text{Ca}_2\text{Nb}_2\text{O}_7$  phase are not visible in X-ray data it is assumed that its content does not exceed 2-4 wt. % of the sample. Moreover, it is expected the secondary phase first precipitates along the grain boundaries and then as an inclusion in the bulk of the sample [22–25].

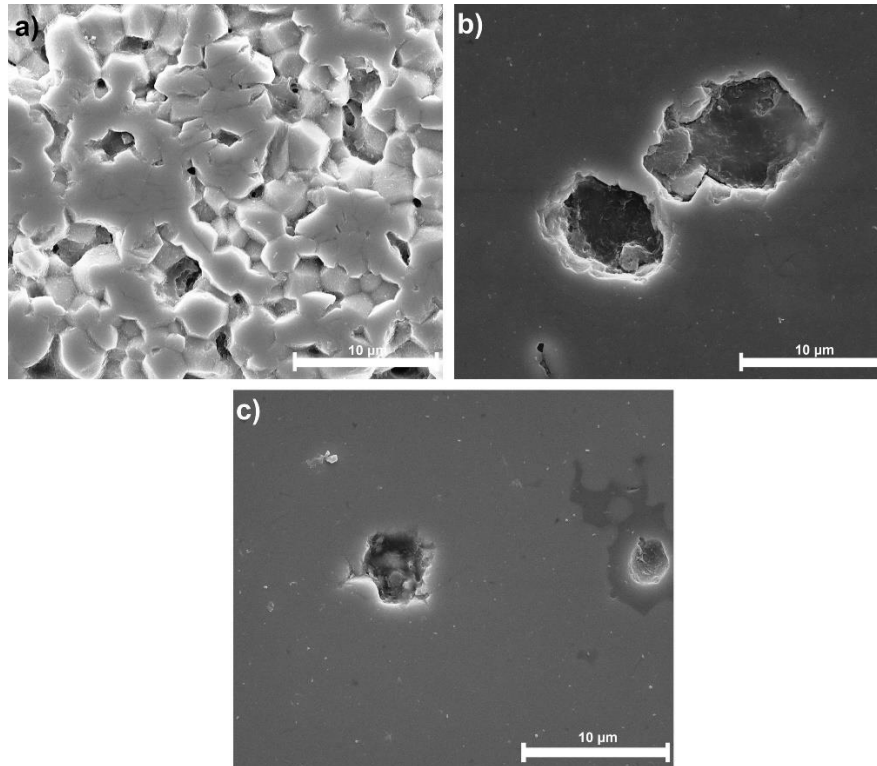


Fig.2. SEM photographs of a)  $\text{La}_{0.9}\text{Pr}_{0.1}\text{NbO}_4$ , b)  $\text{La}_{0.9}\text{Pr}_{0.08}\text{Ca}_{0.02}\text{NbO}_4$  and c)  $\text{La}_{0.88}\text{Pr}_{0.1}\text{Ca}_{0.02}\text{NbO}_4$ .

Impedance spectroscopy measurements were performed to determine the electrical properties of the investigated system. Fig. 3 presents the example of the acquired Nyquist plot for  $\text{La}_{0.88}\text{Pr}_{0.1}\text{Ca}_{0.02}\text{NbO}_4$ . One can see the clear separation of the curve into three semicircles. The brick layer model was used in the analysis of the impedance data in which the highest frequency semicircle is attributed to grain interior, the mid-frequency to grain boundaries, and the lowest frequency to the electrode phenomena [26]. The impedance data were collected at various temperatures to determine the temperature dependence of the conductivity. Fig. 4 depicts the total conductivities (the sum of grain and grain boundary contributions) of the three compounds. For all atmospheres, the sample doped only with praseodymium exhibits the lowest conductivity level but still one order of magnitude higher than that for undoped lanthanum niobate [27]. For all of the samples conductivity increases in wet conditions both in oxidizing and reducing atmospheres. One

can also notice that the increase of total conductivity is in general higher in reducing than in oxidizing conditions. The difference between the conductivities in reducing and oxidizing conditions is pronounced in dry conditions, whereas in the wet atmosphere the change is less distinct. In all of the studied compounds, the highest conductivity was achieved in the wet reducing atmospheres and the lowest in the dry air, what was presented numerically in Table 2.

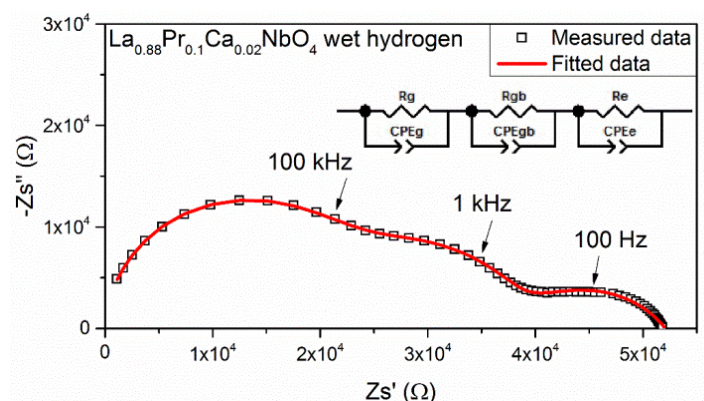


Fig. 3. Nyquist plot of  $\text{La}_{0.88}\text{Pr}_{0.1}\text{Ca}_{0.02}\text{NbO}_4$  measured in wet  $\text{H}_2$  at  $450\text{ }^\circ\text{C}$ .

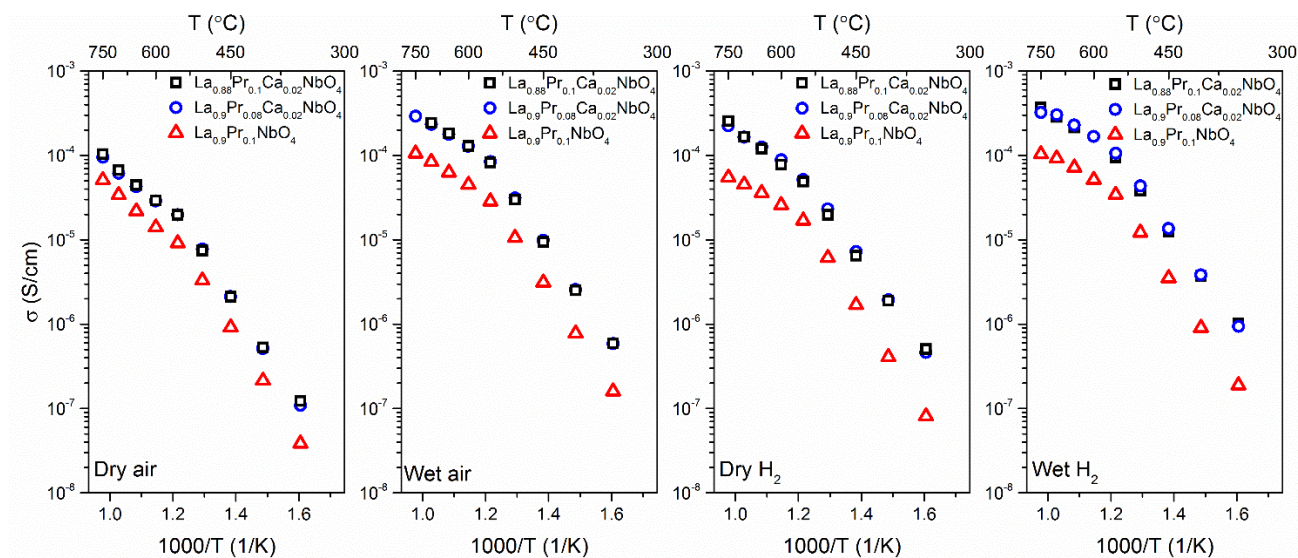


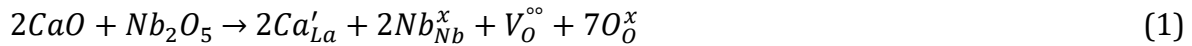
Fig. 4. Total conductivities of  $\text{La}_{0.9}\text{Pr}_{0.1}\text{NbO}_4$ ,  $\text{La}_{0.9}\text{Pr}_{0.08}\text{Ca}_{0.02}\text{NbO}_4$  and  $\text{La}_{0.88}\text{Pr}_{0.1}\text{Ca}_{0.02}\text{NbO}_4$  measured in a) dry air, b) wet air, c) dry  $\text{H}_2$  and d) wet  $\text{H}_2$ .

Table 2. Summary of electrical properties of  $\text{La}_{0.9}\text{Pr}_{0.1}\text{NbO}_4$ ,  $\text{La}_{0.9}\text{Pr}_{0.08}\text{Ca}_{0.02}\text{NbO}_4$  and  $\text{La}_{0.88}\text{Pr}_{0.1}\text{Ca}_{0.02}\text{NbO}_4$ .

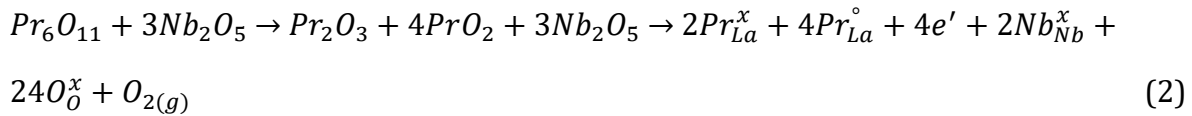


	La <sub>0.9</sub> Pr <sub>0.1</sub> NbO <sub>4</sub>			
	Dry Air	Wet Air	Dry H <sub>2</sub>	Wet H <sub>2</sub>
$\sigma_{tot}$ , 700 °C (10 <sup>-5</sup> S/cm)	3.4	8.4	4.5	9.2
E <sub>a</sub> , <500°C (eV)	1.27 ± 0.02	1.21 ± 0.02	1.25 ± 0.02	1.21 ± 0.02
E <sub>a</sub> , > 500°C (eV)	0.71 ± 0.02	0.55 ± 0.02	0.47 ± 0.02	0.49 ± 0.02
	La <sub>0.9</sub> Pr <sub>0.08</sub> Ca <sub>0.02</sub> NbO <sub>4</sub>			
	Dry Air	Wet Air	Dry H <sub>2</sub>	Wet H <sub>2</sub>
$\sigma_{tot}$ , 700 °C (10 <sup>-5</sup> S/cm)	6.2	23	16	30
E <sub>a</sub> , <500°C (eV)	1.23 ± 0.02	1.16 ± 0.02	1.12 ± 0.02	1.12 ± 0.02
E <sub>a</sub> , > 500°C (eV)	0.69 ± 0.02	0.53 ± 0.02	0.55 ± 0.02	0.49 ± 0.02
	La <sub>0.88</sub> Pr <sub>0.1</sub> Ca <sub>0.02</sub> NbO <sub>4</sub>			
	Dry Air	Wet Air	Dry H <sub>2</sub>	Wet H <sub>2</sub>
$\sigma_{tot}$ , 700 °C (10 <sup>-5</sup> S/cm)	6.7	24	17	29
E <sub>a</sub> , <500°C (eV)	1.20 ± 0.02	1.16 ± 0.02	1.08 ± 0.02	1.06 ± 0.02
E <sub>a</sub> , > 500°C (eV)	0.73 ± 0.02	0.53 ± 0.05	0.68 ± 0.02	0.57 ± 0.02

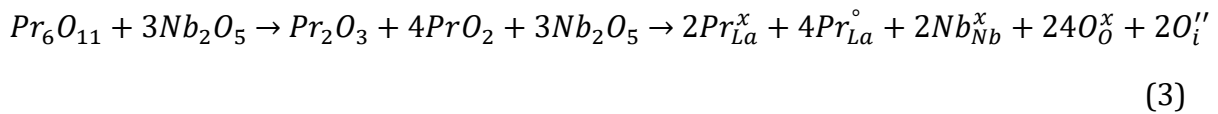
The higher conductivity of calcium-doped samples can be explained by the higher concentration of the oxygen vacancies induced by acceptor doping, which is described by the following reaction:



The influence of Pr on the electrical properties of the material should be analyzed from a broader point of view, because of the change which can be induced by various praseodymium oxidation states in the sample – it can be either isovalent in respect to lanthanum (Pr<sup>3+</sup>) or serve as a donor (Pr<sup>4+</sup>). Two reactions of the incorporation of Pr into lanthanum niobate lattice can be postulated:



or



where the excess positive charge of Pr<sup>4+</sup> can be compensated by the formation of either electron (2) or oxygen interstitials (3). Since the formation of oxygen interstitials requires

more energy than electrons the reaction (2) should dominate. However, it should be noted that reaction (3) can be present to some extent and oxygen interstitials can further react with vacancies via the anti-Frenkel reaction:



This could be the case especially in the Ca-doped compounds, where additional oxygen vacancies are available due to acceptor doping. Another factor to analyze is the preferred oxidation state of Pr in the crystal lattice of lanthanum orthoniobate. One can assume that the more preferred oxidation state of praseodymium is 3+ since the ionic radii difference between  $Pr^{3+}$  and  $La^{3+}$  is much smaller (0.034 Å) than that between  $Pr^{4+}$  and  $La^{3+}$  (0.2 Å). Therefore for 3+ valence, the structure of the material would be much less strained than for 4+. So that, it may be expected that most of the  $Pr^{4+}$  change into  $Pr^{3+}$  either by the generation of holes (5) or recombination with electrons (6):



The preference of 3+ oxidation state would also explain, why the samples doped with calcium have higher conductivity than  $La_{0.9}Pr_{0.1}NbO_4$  since it indicates the dominance of reactions (2) and (5) or (2) and (6). These routes are more probable than via reactions (3) and (4), which would lead to the annihilation of oxygen vacancies and would be detrimental for ionic conductivity. However, one cannot exclude the possibility that to some extent the praseodymium is still present at 4+ valence state, which would be then compensated by the electrons as in reaction (2). Such phenomenon would explain the difference of total conductivity value for praseodymium solely doped sample with respect to the calcium doped materials.

The observed increase of the conductivity, when gas becomes humid, is a typical feature of a high-temperature proton conductor related to the hydration reaction of an oxide:



Reaction (7) describes the dissolution of protons, which has been observed previously in many  $LaNbO_4$ -based compounds [3,6,11]. It should be noted that hydration reaction requires oxygen vacancies to be present in the material. An increase of the conductivity



of praseodymium doped lanthanum orthoniobate in humid atmospheres indicates that the oxygen defects are present in the structure. This also supports the thesis of Pr undergoing reactions involving electronic defects, such as (2), (5) and (6) and not oxygen interstitials as in (3) and (4).

Based on this analysis and taking (1), (2), (3), (4), (5) into consideration one can assume that electroneutrality equation can be proposed as (8) (where brackets represent concentrations).

$$2[V_O^{\circ\circ}] + [OH_O^\circ] + [Pr_{La}^\circ] + p = [Ca'_{La}] + n \quad (6)$$

Since the  $Pr^{4+}$  concentration may be concerned as low one can assume that in samples containing Ca material is predominantly acceptor doped. Defining  $[Acc]$  as an effective acceptor dopant concentration one can write:

$$[Ca'_{La}] - [Pr_{La}^\circ] = [Acc] \approx const. \quad (7)$$

On the basis of the behavior of the studied material while changing from wet to dry gases and the literature data regarding  $LaNbO_4$  compounds [3], [6], [11] we postulate that material is predominantly a protonic conductor, therefore simplified electroneutrality can be given as:

$$[OH_O^\circ] + 2[V_O^{\circ\circ}] = [Acc] \quad (8)$$

Within this assumption and applying the defect model proposed by Haugsrud and Norby [6] for acceptor doped lanthanum orthoniobate the concentration of protonic defects may be described by the relation:

$$[OH_O^\circ] = K p_{H_2O} \left( \sqrt{1 + \frac{2[Acc]}{K p_{H_2O}}} - 1 \right) \quad (9)$$

where  $K$  is equilibrium constant for reaction (5) and  $p_{H_2O}$  is water vapor partial pressure. One can see that derived concentration of protonic defects does not depend on oxygen partial pressure, which means that if a material is dominated by protons (as it is in wet conditions) its conductivity should be constant and do not change when the gas is changed from oxidizing to reducing conditions. In this study the more pronoun difference is visible while switching the atmosphere from higher to lower  $p_{H_2O}$  than for  $p_{O_2}$  switch (cf. Fig. 4 and Table 2).

The values of the total conductivity for all three compositions do not change much. Nevertheless, at 700°C it is the smallest for  $\text{La}_{0.9}\text{Pr}_{0.1}\text{NbO}_4$  in dry air atmosphere -  $3 \times 10^{-5}$  S/cm (when for co-doped samples is twice higher  $6 \times 10^{-5}$  S/cm) and the highest for co-doped samples in wet hydrogen -  $30 \times 10^{-5}$  S/cm ( $9 \times 10^{-5}$  S/cm). The data presented in Table 2 show that in the case of samples  $\text{La}_{0.9}\text{Pr}_{0.08}\text{Ca}_{0.02}\text{NbO}_4$  and  $\text{La}_{0.88}\text{Pr}_{0.1}\text{Ca}_{0.02}\text{NbO}_4$  the change of conductivity with atmosphere while switching from dry to wet air is more pronounced ( $6 \times 10^{-5}$  S/cm in dry air and  $20 \times 10^{-5}$  S/cm in wet air 700°C), than for the  $\text{La}_{0.9}\text{Pr}_{0.1}\text{NbO}_4$  sample the change is ( $3 \times 10^{-5}$  S/cm and  $8 \times 10^{-5}$  S/cm at 700°C for dry and wet air respectively). Such a difference probably is a result of the different concentration of the oxygen vacancies in the  $\text{La}_{0.98-x}\text{Pr}_x\text{Ca}_{0.02}\text{NbO}_4$  and  $\text{La}_{0.9}\text{Pr}_{0.1}\text{NbO}_4$  samples. Such behavior is consistent with the assumption that the praseodymium in the samples studied in this work holds 3+ valence. For a system with a high content of +4 cations in the structure (e.g.  $\text{La}_{1-x}\text{Ce}_x\text{NbO}_4$ ) the pronounced difference between conductivities in oxidizing and reducing atmosphere was observed by Skinner's group [28], [29]. While the water vapor partial pressure decreases, the proton concentration is reduced and oxygen vacancies start to dominate. The mobility of oxygen vacancies is typically smaller than that of the protons, thus the conductivity is reduced while gas is switched from wet to dry. If the mobility of the minority defects, here electrons and electron holes, is higher than the one of oxygen vacancies they can be an important contribution to the total conductivity. Further derivation of Haugsrud and Norby defect model, as it was presented in our previous work [3], allows determining the dependency of electron and electron holes concentration as a function of  $p_{\text{O}_2}$ , which is  $n \sim p_{\text{O}_2}^{-\frac{1}{4}}$  and  $p \sim p_{\text{O}_2}^{\frac{1}{4}}$ , respectively. Therefore, despite having low concentration, electronic defects can affect the total conductivity, which is visible in the change between conductivities measured in hydrogen and air (cf. Table 2).

Further analysis of Arrhenius plots (cf. Fig. 4, Fig. 5) reveals the change of the apparent activation energy related to phase transition from scheelite and fergusonite structure (cf. Table 2).

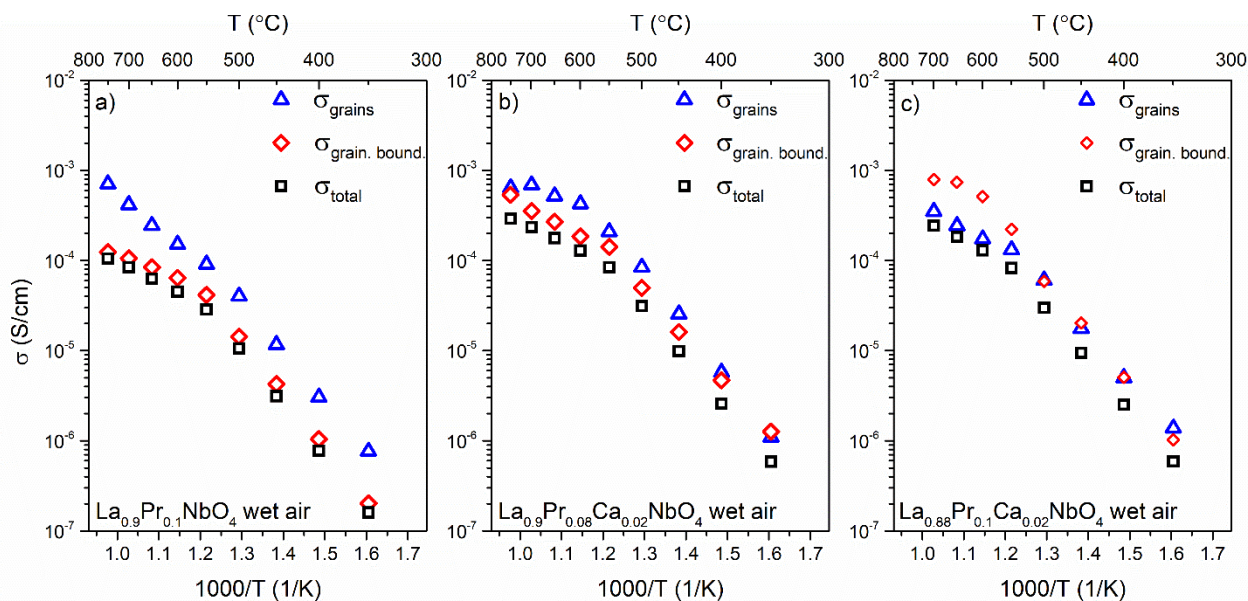


Fig. 5. Temperature dependence of total conductivity, grain conductivity and grain boundary conductivity in wet air for a)  $\text{La}_{0.9}\text{Pr}_{0.1}\text{NbO}_4$ , b)  $\text{La}_{0.9}\text{Pr}_{0.08}\text{Ca}_{0.02}\text{NbO}_4$  and c)  $\text{La}_{0.88}\text{Pr}_{0.1}\text{Ca}_{0.02}\text{NbO}_4$ .

Lanthanum orthoniobates doped on La-site with rare earth elements have been analyzed in the past by Solis and Serra [23]. In the referenced work the authors analyzed the properties of  $\text{La}_{0.995}\text{Ca}_{0.005}\text{Pr}_{0.1}\text{NbO}_4$ . They found the domination of protonic conductivity both in reducing and oxidizing conditions, shown by e.g. H-D isotope exchange experiment, and weak dependence of conductivity on oxygen partial pressure in oxidizing conditions indicating hole contribution to total conductivity. Direct comparison between the results of our and their studies is difficult due to several major differences such as: methods of electrical characterization (DC in the reference and AC in this study), conditions (different atmosphere in the case of oxidizing conditions: oxygen and air) and acceptor dopant concentration (0.5 mol% and 2 mol% of Ca), however some comparisons can be made. Results presented in this work and in [20] are in good agreement. In both cases, strong conductivity dependence on the water vapor content is observed both in oxidizing and reducing conditions indicating that material is predominantly a high-temperature proton conductor. Moreover, the  $p_{\text{O}_2}$ -dependency measured by Solis and Serra in dry oxidizing conditions showed  $\frac{1}{4}$  slope, which is in good agreement with defect model presented here. The major difference between results in this work and the one of Solis and Serra is the conductivity measured in wet hydrogen. In our work, the conductivity in this condition shows the highest values, whereas in the

reference it is much lower. The difference stems most probably from the method of conductivity characterization. In the case of AC measurements, we predominantly achieve higher conductivity values than in DC. This is due to the resistance of electrode processes, such as mass transport, charge transfer or double layer formation, which is present in a DC measurement, whereas in impedance spectroscopy it can be cut-off from the final result.

Fig. 5 presents the temperature dependence of the two components of the lanthanum orthoniobates doped on L total conductivity – grain boundary and grain interior (bulk) conductivities - for three compositions. In the  $\text{La}_{0.9}\text{Pr}_{0.1}\text{NbO}_4$  samples, grain boundary conductivity is much lower than the bulk conductivity, which means that the main limiting factor of the conductivity, especially in the temperature range above  $500^\circ\text{C}$ , is the blocking grain boundaries. This phenomenon is common for all lanthanum orthoniobates substituted both on lanthanum and niobium sites [3], [7]. In the case of samples co-doped by praseodymium and calcium the conductivity of both grain boundaries and bulk is similar but for the  $\text{La}_{0.88}\text{Pr}_{0.1}\text{Ca}_{0.02}\text{NbO}_4$  sample in the temperature range above  $500^\circ\text{C}$ , where the grain boundary conductivity becomes higher than the bulk one. The probable cause of such a characteristics is the secondary phase present in calcium co-doped samples. The precipitants forming in the grain boundaries can extensively change their electrical properties. The reason why such behavior is more apparent for the sample  $\text{La}_{0.88}\text{Pr}_{0.1}\text{Ca}_{0.02}\text{NbO}_4$  and not for  $\text{La}_{0.9}\text{Pr}_{0.08}\text{Ca}_{0.02}\text{NbO}_4$  is that the former has the higher total substituting atoms content which may lead to higher secondary phase content.

Summing up all the measured samples exhibit proton conductivity which is reflected in the rise of the total conductivity level in higher water partial pressure. The electron component of the conductivity plays a role only in dry atmospheres as a result of the high mobility of the minority electronic defects.

## Conclusions

Dense samples of praseodymium doped ( $\text{La}_{0.9}\text{Pr}_{0.1}\text{NbO}_4$ ) and praseodymium and calcium doped ( $\text{La}_{0.9}\text{Pr}_{0.08}\text{Ca}_{0.02}\text{NbO}_4$  and  $\text{La}_{0.88}\text{Pr}_{0.1}\text{Ca}_{0.02}\text{NbO}_4$ ) lanthanum orthoniobates were successfully prepared. The  $\text{La}_{0.88}\text{Pr}_{0.1}\text{Ca}_{0.02}\text{NbO}_4$  sample contained a small amount of the secondary phase. Unit cell parameters at room temperature of the studied compounds



were determined. It has been presented that substitution of lanthanum by praseodymium and co-doping by calcium, causes the decrease of unit cell volume. Temperature dependence of electrical conductivity of the  $\text{La}_{0.9}\text{Pr}_{0.1}\text{NbO}_4$  and  $\text{La}_{0.98-x}\text{Pr}_x\text{Ca}_{0.02}\text{NbO}_4$  samples in different atmospheres was investigated. It has been shown that all investigated samples exhibit protonic conductivity in the wide range of temperatures. The higher conductivity of calcium-doped samples can be explained by the higher concentration of the oxygen vacancies induced by acceptor doping. The electron component of the conductivity plays a role only in dry atmospheres as a result of the high mobility of the minority electronic defects.

Analysis of electrical properties in respect to defect chemistry of the studied materials suggests that the majority of praseodymium ions exist in +3 valence state.

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