Newcastle University ePrints

Tabacaru C, Aguadero A, Sanz J, Chinelatto AL, Thursfield A, Perez-Coll D, Metcalfe IS, Fernandez-Diaz MT, Mather GC. [Protonic and electronic defects in the 12R-type hexagonal perovskite \$\text{Sr}_3\text{LaNb}_3\text{O}_{12}\$](#) . *Solid State Ionics* 2013, 253, 239-246.

The definitive version of this article, published by Elsevier BV, 2013, is available at:

<http://dx.doi.org/10.1016/j.ssi.2013.10.031>

Always use the definitive version when citing.

Date deposited: 27 October 2014

This work is licensed under a [Creative Commons Attribution-NonCommercial 3.0 Unported License](#)

ePrints – Newcastle University ePrints

<http://eprint.ncl.ac.uk>

Protonic and electronic defects in the 12R-type hexagonal perovskite
 $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$

C. Tabacaru^a, A. Aguadero^{b,c}, J. Sanz^b, A.L. Chinelatto^{a,d},
A. Thursfield^e, D. Pérez-Coll^a, I.S. Metcalfe^e, M.T. Fernandez-Díaz^f, G.C. Mather^{a*}

^a *Instituto de Cerámica y Vidrio, CSIC, Cantoblanco, 28049 Madrid, Spain*

^b *Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, 28049 Madrid, Spain*

^c *Department of Materials, Imperial College London, South Kensington Campus, London SW7 2AZ, UK*

^d *Departamento de Engenharia de Materiais, Universidade Estadual de Ponta Grossa, Av. Gal. Carlos Cavalcanti, 4748, 84030-900- Ponta Grossa-PR, Brazil*

^e *Department of Chemical Engineering and Advanced Materials, Newcastle University, NE1 7RU, Newcastle upon Tyne, UK*

^f *Institut Laue-Langevin, B.P. 156, F-38042 Grenoble Cedex 9, France*

*e-mail address: mather@icv.csic.es

Tel.: + 34 917355840

Fax.: + 34 917355843

Abstract

The structural properties of the 12R-type hexagonal perovskite $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ (space group $R\bar{3}$) have been examined by neutron diffraction and ^1H magic angle spinning-nuclear magnetic resonance (^1H MAS-NMR). The latter technique supports the presence of protonic species in $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ with bands at 5, 3.4 and 1.3 ppm. The electrical-transport properties of the nominally stoichiometric and acceptor-doped phases $\text{Sr}_3\text{LaNb}_{3-x}\text{M}_x\text{O}_{12-\delta}$ ($\text{M} = \text{Ti}$, $x = 0.1$; $\text{M} = \text{Zr}$, $x = 0.03$) have been analysed in the temperature range 550-900 °C by impedance spectroscopy in a selection of wet- and dry-gas atmospheres. Protons contribute increasingly to transport with decreasing temperature in wet air, as confirmed by an H^+/D^+ isotope effect, representing the first observation of proton conductivity in this structure type. The magnitude of the protonic transport increases with increasing acceptor-dopant concentration (x). A total conductivity value of $1.2 \times 10^{-6} \text{ Scm}^{-1}$ is reached at 650 °C for the Ti-doped phase in humidified air ($p\text{H}_2\text{O} \approx 0.03 \text{ atm}$). The activation energy in wet air at 550-700 °C is slightly lower for the doped compositions (0.93 eV for the Zr-doped phase) in comparison to the nominally undoped material (1.13 eV). The origin of proton transport in the latter may originate from “self doping” of a small amount of Sr on the La sites. Conductivity is dominated by n -type charge carriers in reducing conditions, as confirmed by the observance of a $-1/4$ power-law dependency for $p\text{O}_2 \leq \sim 10^{-8} \text{ atm}$. The activation energy of the title phase in the n -type region measured in 10% H_2 :90% N_2 is 0.96 eV. In dry oxidising atmospheres, p -type charge carriers predominate ($E_a = 1.42 \text{ eV}$) with the p - n transition occurring at $p\text{O}_2 \sim 10^{-4} \text{ atm}$.

Keywords: proton conduction, crystal structure, ^1H MAS NMR, protonic ceramic fuel cell, hydrogen-separation membrane, microwave dielectric

1. Introduction

Perovskites (ABO_3) which are formed by hexagonal close packing (hcp) of the AO_3 layers, as opposed to the more common cubic close packing (ccp), are characterised by face-sharing octahedra with the B cations in close proximity [1]. Different stacking combinations of ccp and hcp layers lead to a rich structural complexity allied to a number of interesting and useful properties involving electric, dielectric and magnetic phenomena [2,3,4,5]. The nomenclature employed to describe the unit cells of the family includes the number of AO_3 layers per cell and a symbol to describe the unit-cell symmetry.

The 12R-type hexagonal perovskite $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ (12 AO_3 layers, rhombohedral symmetry) has recently been reported of interest as a good low-loss microwave dielectric material [6,7]. The $\text{SrO-Nb}_2\text{O}_5\text{-La}_2\text{O}_3$ system has also given rise to a number of proton-conducting oxides, such as $\text{Sr}_3(\text{Sr}_{1+x}\text{Nb}_{2-x})\text{O}_{9-3x/2}$ [8], and the more recently discovered $\text{La}(\text{Sr})\text{NbO}_{4-\delta}$ phase [9]. The low electronegativity (high basicity) of the constituent cations in this system would seem to favour the protonation of lattice oxygen as a determining step in the hydration of oxygen vacancies and the subsequent appearance of proton transport [10].

Proton conduction in oxide materials is exploitable in high-temperature electrochemical devices such as solid oxide fuel cells (SOFCs) and ceramic hydrogen-permeation membranes, which are at the forefront of research efforts to find highly efficient and environmentally friendly energy-conversion technologies based on sustainable resources. Although the most studied and commercially viable electrolytes for SOFCs involve an oxide-ion conducting material with a typical operation temperature above 800 °C, development of a suitable proton-conducting electrolyte with a potentially lower operation temperature (500–700 °C) would be of particular interest [9,10,11]. This temperature range avoids the technological problems and cost associated with the higher working temperatures of contemporary SOFCs, yet also alleviates the catalyst and fuel problems related with the low operating temperature of the polymeric proton-conducting devices.

Here, we have undertaken an electrical-transport study of the $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ hexagonal perovskite, paying particular attention to previously unobserved protonic transport. Structural details and the effects of small amounts of acceptor dopant on the electrical conductivity are also provided. ^1H magic angle spinning nuclear magnetic

resonance spectroscopy (^1H MAS-NMR) has been used to investigate protonic species present in the as-prepared and hydrated materials.

2. Experimental

Compositions of $\text{Sr}_3\text{LaNb}_{3-x}\text{M}_x\text{O}_{12-\delta}$ ($\text{M} = \text{Zr}, \text{Ti}; 0 \leq x \leq 0.1$) were prepared by solid-state reaction from dried precursors of SrCO_3 , Nb_2O_5 , TiO_2 (all Aldrich, 99.9% purity or higher), La_2O_3 (Fluka, 99.9%) and ZrO_2 (Alfa Aesar, 99.7 %) in the appropriate stoichiometric ratios. The reagents were firstly milled in acetone, dried, then fired at 1100°C for 12 hours to allow decarbonisation to take place. Mixtures were subsequently fired at 1250°C for 24 hours with intermediate grinding, prior to milling, drying and sieving. Batches were prepared with milling either conducted by the attrition method in teflon vials with ZrO_2 balls or hand milling with an agate mortar and pestle. The second method was employed to assess the effects of any contamination introduced by attrition milling. Final firing of samples in the form of powders or pressed pellets took place in the range $1400\text{--}1500^\circ\text{C}$ for up to 36 hours; typical sintered pellet dimensions used in electrical measurements were ~ 0.8 cm in diameter and ~ 0.2 cm in thickness. Completeness of reaction and phase purity were confirmed by powder X-ray diffraction (XRD) with a Siemens D5000 diffractometer using $\text{Cu K}\alpha$ radiation.

For Rietveld refinement of the crystal structure, powder neutron-diffraction data were collected on the D1A instrument (Grenoble) over the range $10 \leq 2\theta \leq 160^\circ$. Structural models were refined with the Fullprof program [12]. The microstructure of fracture surfaces and polished surfaces which had previously been thermally etched at 1450°C were analysed by scanning electron microscopy (SEM) with a Zeiss DSM400 instrument.

The densities of sintered pellets were measured by the Archimedes method on displacement of water to be $> 94\%$ of the theoretical values. Porous pellets were also prepared for the purpose of measuring the $p\text{O}_2$ dependence of conductivity at 900°C , and for certain measurements in reducing conditions where stabilisation with the atmosphere was found to be sluggish. For these samples, a porosity correction was made based on Archie's law [13,14]

$$\sigma_{\text{B}}^{\text{app}} = \sigma_{\text{B}}^{\circ} (1 - P)^m \quad (1)$$

where σ_B^{app} is the apparent bulk conductivity, σ_B° is the intrinsic bulk conductivity, P is the porosity of the sample and m is a constant based on geometric considerations ($m \sim 2$). For electrical-conductivity measurements, the pellets were lightly polished with SiC paper then coated with Au paste and fired at 900°C for 1 hour in air to remove the organic content, harden the Au and attach it to the pellet faces. Impedance spectroscopy was performed employing a signal amplitude of 300 mV in potentiostatic mode with either an Autolab PGStat302N instrument operating over the frequency range $\frac{1}{10^6} \leq f \leq 10^6$ Hz or with an Agilent 4294A instrument in the range $40 \leq f \leq 10^6$ Hz, computer controlled with the Sweep software [15]. The temperature dependence of conductivity was determined from data collected on cooling in steps of 50 °C or 100 °C in the temperature range 500 – 900 °C in wet and dry atmospheres of air, O₂, N₂ and 10% H₂: 90% N₂. Dry gases were fed from the bottle through a drying column containing a commercial moisture trap of aluminosilicate- and zeolite-based beads. For wet atmospheres, gases were firstly bubbled through H₂O or D₂O (Apollon Scientific, 99.9%) at room temperature to provide a water content of ~ 0.03 atm [16]. Analysis of impedance spectra was performed with the Zview 2.9c software (Scribner Associates) by fitting the data to appropriate equivalent circuits in order to resolve the impedance response into bulk, grain-boundary and electrode contributions.

An isothermal impedance measurement of a porous pellet of Sr₃LaNb₃O was collected as a function of pO₂ in a similar manner to that reported previously [2,17]. The porous pellet was employed to enhance the equilibration times with the gas ambient. The cell was firstly equilibrated in dry 10% H₂:90% N₂ over a period of 2 days until the sample resistance had stabilised; the gas flow was then switched off and the chamber allowed to equilibrate over several days with the outside air. The pO₂ was measured in intervals of 20 minutes or longer with an yttrium-stabilised zirconia sensor situated adjacent to the sample, and attached to an external voltmeter with Pt electrodes.

¹H MAS-NMR spectra were obtained in an AVANCE 400 Bruker spectrometer, at 400.13 MHz (9.4 T magnetic field) on as-prepared samples and material which had been treated at 600 °C in humidified Ar for 12 hours. MAS-NMR signals were recorded after irradiation of samples with $\pi/2$ pulses (4 μ s), using a frequency filter of 100 kHz. The spinning rate was 10 kHz. The recycling time used between successive experiments was 5s and the number of accumulations amounted to 100. The probe signal was

subtracted from those of analysed samples after the Fourier mathematical conversion to eliminate the background signal. The Winfit (Bruker) software was used for quantitative analysis.

3. Results and discussion

3.1 Phase Formation and Crystal Structure

The XRD powder patterns of $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ (SLN) sintered at 1500 °C showed the formation of monophasic hexagonal perovskite in accordance with published X-ray diffraction data. Moreover, no second phases are discernible in the scanning electron micrographs of SLN. A typical micrograph of a fracture surface is shown in Fig. 1 (a), in which the absence of both cracks and open porosity are apparent. The microstructure is composed of needle-shaped grains with a typical length of around 2-3 μm , as seen in Fig. 1 (b) for a Ti-doped analogue.

Single-phase $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ is consistent with the phase diagram for the $\text{SrO-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ system at 1300 °C based on the results of Averkova et al. [18] but not the later phase relationships reported by Huang et al. [19], who indicate a phase mixture at this composition in the ternary phase diagram at 1500 °C. More recent work also confirms the formation of $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ with a hexagonal 12R-type perovskite structure in which refinements of high-resolution, neutron-diffraction data in space groups $R\bar{3}$ and $R\bar{3}m$ were conducted [7]. The two space groups are barely distinguishable by XRD since the symmetry is determined by subtle movements of the oxygen atoms. It was reported that the lower symmetry space group $R\bar{3}$ leads to an improved refinement [7].

Similarly, here, refinement of $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ was more successfully performed in space group $R\bar{3}$ rather than in $R\bar{3}m$. The refined structural parameters are listed in Table 1, and bond lengths and angles in Table 2. The observed powder neutron diffraction pattern and the difference pattern between observed and calculated data on termination of Rietveld refinement are shown in Fig. 2. The Rietveld refinement indicated that Sr fully occupies the A2 site, with La and the remainder of the Sr occupying the A1 site in approximately equivalent amounts. Rawal et al. [7] also noted a preference of Sr for the A2 site. Correlations of intensity-dependent parameters,

including thermal-vibration factors and occupancies, may not permit any conclusive analysis of small variations in stoichiometry [20]. Nevertheless, refining the occupancy of the A1 site with fixed, common thermal vibration factors for the A-cation sites led to a slightly higher Sr content, as suggested by the greater thermal vibration factor of the A1 site in comparison to that of A2, in spite of the heavier average cation content (Table 1). The extent of Sr over-stoichiometry on the A1 site is likely to be minor and was not readily proved from the performed sequence of refinements; nevertheless, such a phenomenon may have important effects on properties.

A schematic diagram of the unit cell and ion arrangement in $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ is shown in Fig. 3. The structure consists of the stacking of layers of Nb(1)O_6 - Nb(2)O_6 - Nb(1)O_6 perovskite-type corner-sharing octahedra, with B-cation vacancies occurring in planes every fourth layer. The mixed La/Sr-occupied sites are situated within the three-octahedra-thick layers adjacent to the Nb(2)O_6 octahedra, whereas the Sr sites are located adjacent to the B-site-vacancies. The Nb(2)O_6 octahedra in the centre of the layers are fairly regular and undistorted, whereas the Nb(1)O_6 octahedra occupying the outer layers are considerably distorted with Nb(1) displaced along the c axis towards the layers containing cation vacancies (Table 2). The polarisation occurring in successive Nb(1)-containing layers is oppositely aligned, such that antiferroelectric properties may be expected.

The bond-valence concept can be used to provide an indication of the correctness of the structure solution and to estimate the valence state of atoms. The valence of the atom is the sum of the individual bond valences surrounding the atom, which are in turn estimated from the calculated and “ideal” bond lengths [21]. The bond valence values for each cation and anion calculated with the Bond-Str program using parameters given in Ref. [21] are shown in Table 3; for the mixed Sr/La cation site, the average bond valence has been calculated. The deviation from the valence sum rule is < 13% for all ions, supporting the correctness of the structural model. We note that the calculated valences of the oxygens are less than and greater than the formal valence of -2 for O(1) and O(2) species, respectively. This will be discussed in greater detail in section 3.3.

Aliovalent doping of metal oxides is well known to have a profound impact on defect chemistry and electrical transport. In the case of substitution with a lower-valence cation (so-called acceptor doping), charge compensation involves the creation

of one or more type of positively-charged defect involving mixed-valence states, cation interstitials, oxide-ion vacancies, or protons when the vacancies become hydrated. Solid-solution formation with Ti and Zr dopants on the Nb site in the title phase was explored, principally in this paper to examine the effects of these acceptor dopants on electrical properties in wet and dry oxidising conditions. Compositions were prepared for $\text{Sr}_3\text{LaNb}_{3-x}\text{M}_x\text{O}_{12-\delta}$ in a low dopant-content range of $0 \leq x \leq 0.1$. In the case of Ti, single-phase material was obtained by XRD for compositions throughout the examined series. Scanning electron micrographs, such as that shown in Fig. 1(b) for a polished and thermally etched surface of $\text{Sr}_3\text{LaNb}_{2.9}\text{Ti}_{0.1}\text{O}_{12-\delta}$, confirmed the absence of secondary phases. However, Zr was found to have a rather low solid-solution limit. SrZrO_3 was identified as a second phase in the composition $x = 0.1$ after firing at 1500 °C for 6 h. The minority phase was not observed for $x = 0.03$ after sintering for 36 hours at 1500 °C; nevertheless, a vestige of unidentified material of very low intensity was discernible, even after this treatment. The higher solubility of Ti on the Nb is to be expected based on the closer match of ionic radius to the host cation [22].

3.2 Electrical conductivity

3.2.1 Dry conditions

The total conductivity of SLN in reducing conditions (10% H_2 :90% N_2) was determined from the low-frequency intercept on the Z' axis of the Nyquist plots (inset of Fig. 4), which shows only the resistive contribution ascribable to transport process in the sample. The impedance plots in N_2 , air and O_2 were, instead, dominated by a large, slightly depressed, high-frequency arc, with a poorly resolved lower-frequency response (Fig. 4, main panel). The “non-ideal” behaviour of the large arc was modelled with a single RQ element. The capacitance was estimated according to $C = Q^{1/n} R^{1-n/n}$, giving a value of 7.3 pFcm⁻¹ at 650 °C in dry air (Fig. 4, main panel), typical of a bulk response for samples with $\epsilon \sim 10^{1-2}$ [23]. The low-frequency contribution was not readily resolved into grain-boundary and electrode-material interface responses; however, the estimated capacitances are more typical of electrode behaviour, suggesting that the grain-boundary impedance is low.

The temperature dependencies of conductivity of $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ in a selection of dry atmospheres (total conductivity in 10% H_2 :90% N_2 ; bulk conductivity in N_2 and O_2) are shown in Fig. 5. The much greater conductivity observed in the most reducing conditions of 10% H_2 :90% N_2 is accompanied by a drop in activation energy, from 1.42 eV in O_2 , to 0.96 eV. The lower conductivity observed in N_2 in comparison to O_2 indicates that p -type charge carriers are present in more oxidising atmospheres.

The $p\text{O}_2$ dependence of conductivity of SLN was studied in more detail by performing an isothermal oxidation run at 900 °C. The conductivity was confirmed as n -type as revealed by a linear negative power-law relationship with $p\text{O}_2$ of slope -1/4 in the range $\sim 10^{-19.5} \leq p\text{O}_2 \leq \sim 10^8$ atm, and, at lower $p\text{O}_2$, by a slope better approximated as -1/6 (Fig. 6). The equilibrium loss of oxygen at low $p\text{O}_2$ is expressed in Kröger-Vink notation by the reduction reaction

The following mass-action expression

$$[\text{V}_\text{O}^{\bullet\bullet}]n^2 = K_r p\text{O}_2^{-1/2} \quad (3)$$

gives n and conductivity proportional to $p\text{O}_2^{-1/6}$ when reduction is the major source of defects and charge neutrality is approximated by $n \approx 2[\text{V}_\text{O}^{\bullet\bullet}]$, according to the intrinsic model for defect formation [2,24].

The slope of -1/4 in less reducing conditions is consistent, however, with the electroneutrality condition $[\text{A}'] \approx 2[\text{V}_\text{O}^{\bullet\bullet}]$, where A' is an acceptor centre (extrinsic model) [2,24]. Analogously, the log-log plots of doped and nominally undoped BaTiO_3 are characterised by slopes of -1/4 in reducing conditions, the latter of which has been attributed to small amounts of acceptor impurity on the B site of the perovskite [24]. In the present case, the acceptor centres may also be generated by unavoidable lower-valence impurities on the Nb site. Alternatively, the “self-doping” of the La/Sr (A1) site with a slight excess of Sr would also result in the generation of positive defects as oxygen vacancies. Such off-stoichiometric behaviour would necessarily lead to the exsolution of an equivalent amount of La from the A1 site. Although, no secondary

phase was observed by either of the employed diffraction techniques or by SEM, as discussed in further detail later, ^1H MAS-NMR revealed the possible presence of some surface species which may be attributable to $\text{La}(\text{OH})_3$ that would hardly be detectable with diffraction techniques.

The isothermal study of the $p\text{O}_2$ dependence of conductivity revealed a slightly positive dependence for $p\text{O}_2 > 10^{-3}$ atm, which is further confirmation of contribution of p -type charge carriers to transport in oxidising conditions. However, the significant electrode contribution in dry oxidising conditions (Fig. 4, main panel) may indicate that oxide-ionic conduction also contributes to transport. Unfortunately, a more detailed analysis of the p -type and oxide-ionic behaviour cannot be extracted from these data since our experimental set-up does not permit simultaneous control of $p\text{H}_2\text{O}$ in the isothermal $p\text{O}_2$ runs, such that the presence of water vapour may affect the concentration of contributing charge carriers (see section 3.2.2). Nevertheless, the somewhat larger activation energy in dry O_2 and N_2 (Fig. 5) in comparison to that of dry 10% H_2 :90% N_2 is consistent with the premise that there is a change of transport mechanism, from n -type to one controlled by positive defects (electronic holes and/or oxide-ion vacancies), on progressing from dry reducing to dry oxidising conditions, with the transition occurring at an approximate $p\text{O}_2$ of 10^{-4} atm.

3.2.2. Wet conditions

Arrhenius conductivity plots of $\text{Sr}_3\text{LaNb}_{3-x}\text{M}_x\text{O}_{12-\delta}$ ($x = 0$; $\text{M} = \text{Zr}$, $x = 0.03$; $\text{M} = \text{Ti}$, $x = 0.1$) in dry and humidified air are shown in Fig. 7. The higher conductivity in wet conditions is indicative of a protonic contribution to electrical transport. The second evidence of proton conduction is provided by a clear conductive isotope effect in H_2O - and D_2O -wetted air, as shown in the inset of Fig. 7. The corresponding impedance spectra of SLN at 650 °C are presented in Fig. 8. The conductivity of SLN is higher in air wetted with H_2O in comparison to D_2O by a factor of ~ 1.3 at 550 °C; this value increases with acceptor doping to over 1.6 for the Ti-doped sample. Correspondingly, both the conductivity in wet air and the difference in conductivity between wet and dry regimes increase significantly on doping with lower-valence cations on the Nb site. As is the case for the simple perovskite-like proton conductors, it appears that the acceptor-dopant level directly increases proton conductivity in wet atmospheres through the hydration of oxygen vacancies and the creation of mobile protonic defects according to

As discussed in the above section, the origin of *n*-type transport with a -1/4 power-law dependence with $p\text{O}_2$ (extrinsic model) occurs even in the nominally undoped SLN phase. Hence, a small amount of Sr doping on the La site and/or unavoidable acceptor impurities are likely to be the source of the oxygen vacancies required for hydration (eq. (4)) in the title phase. We note that a similar increase in conductivity in wet with respect to dry oxidising conditions was observed for nominally undoped SLN on preparing with milling steps performed either in an agate mortar or by attrition with ZrO_2 balls, indicating that the acceptor impurities are not introduced via the latter.

The smooth transition to a higher activation-energy regime with increasing temperature, Fig. 7, is also characteristic of many oxide proton conductors [9,25]. This can be understood to result from loss of protonic charge carriers through dehydration at high temperatures due to the exothermicity of the above reaction (eq.(4)), and an increasing contribution of *p*-type and/or oxide-ion charge carriers of higher activation energy. In accordance with the loss of protonic charge carriers with increasing temperature, there is a decrease in the observed isotope effect for all three samples (inset of Fig. 7), to close to zero at 900 °C for the undoped and Zr-doped phases. The greater isotope effect exhibited by the Ti-doped sample ($x = 0.1$) is likely to be attributable to a greater proportion of proton transport in the more heavily doped sample, which is corroborated by the greater difference in conductivity observed between the wet and dry conditions for this phase (Fig. 7). In turn, the undoped and Zr-doped phases are likely to present a lower contribution of proton transport coupled with a greater contribution of *p*-type and/or oxide-ionic conductivity, as reflected in the corresponding activation energies in the wet regime: 1.13, 0.96 and 0.93 eV for the nominally undoped SLN, Zr-doped and Ti-doped samples, respectively. We note that these values were calculated in the lower temperature range, 550-700 °C, in which proton transport may be expected to dominate, and before any discernible inflection to a higher energy activation regime takes place. We observed slightly higher activation energies for all three samples in the D_2O -containing atmosphere ($\Delta \sim 0.06\text{eV}$), which is approximate to the difference one may expect between proton and deuteron hopping [26]. The fact that the activation energies are somewhat higher than the best proton-

conducting perovskites (e.g. 0.54 eV for $\text{BaCe}_{0.95}\text{Nd}_{0.05}\text{O}_{3-\delta}$ [27]), may also provide evidence that a p-type electronic and/or oxide-ionic contribution to the conductivity is additionally present. Nevertheless, some caution is required in drawing firm conclusions as to the relative contributions of different charge carriers to the conductivity in the wet regime. For example, the E_a values for proton conductivity are highly dependent on structure type and can be as high as 2 eV in some close-packed lattices [26], and it may be the case that protons are less mobile in $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ than in state-of-the-art perovskite proton conductors.

In light of the protonic conductivity in wet atmospheres, and significant n -type transport exhibited in reducing atmospheres, possible hydrogen permeation due to ambipolar protonic and electronic diffusion was assessed with both wet and dry 10% H_2 : 90% N_2 exposed to the feed side of a dense $\text{Sr}_3\text{LaNb}_{2.9}\text{Ti}_{0.1}\text{O}_{12-\delta}$ membrane (thickness, 0.98 mm) at 700 and 850 °C. The adopted experimental procedure was similar to that reported in ref. [28]; Pt was coated on both feed and supply sides prior to measurement. However, in a preliminary examination no hydrogen permeation was detected on stabilising the membrane in these atmospheres for at least 6 hours. It is probable that the level of proton conductivity in the title phases is not sufficient to permit a measurable H_2 flux, or that surface exchange kinetics are very sluggish.

3.3 Analysis of proton content by NMR

The analysis of ^1H MAS-NMR spectra of $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ show the presence of three signals at 5, 3.4 and 1.3 ppm and one complex narrow signal near 1.1 ppm (Fig. 9(a)). The three broader signals become stronger in intensity relative to the sharper signal when samples are treated at 600°C in a wet atmosphere (Fig. 9 (b)). The sharpness of the last signal suggests the presence of monomeric $\text{La}(\text{OH})_3$ species, likely to be residing on the sample surface, and which are not discernible by XRD. As mentioned earlier, the exsolution of a small amount of La as $\text{La}(\text{OH})_3$ is a possibility on considering the ion-site occupancies indicated by the Rietveld refinement. However, any amorphous hydroxide is unlikely to be responsible for the observed proton conductivity since the magnitude of the proton conductivity is directly related to the acceptor-dopant concentration, indicating that the proton transport occurs in the hydrated main phase. The impedance-spectroscopy measurements, in which the bulk response is affected by wet atmospheres, provides supporting evidence of this (Fig. 7).

Accordingly, the three broader signals are most probably attributable to proton sites in the hexagonal perovskite. The band lying at 1.3 ppm with more basic character is likely to be associated to the O(2) species which has a higher calculated oxygen valence state (Table 3) consistent with its surrounding environment of one Nb-O bond and three relatively weaker M-O bonds (M = Sr or La). The bands lying at higher ppm of more acidic character are, in turn, attributable to protons located on the O(1) site, which is of more acidic character having a coordination of two Nb-O and two M-O bonds. The occupation of M sites adjacent to O(1) by both Sr and La cations could be the origin of the splitting of components at 5 and 3.4 ppm, and could also be the reason for the broader linewidth of the 1.3 ppm peak.

4. Conclusions

A study of the electrical-transport properties in the 12R-type hexagonal perovskite $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ has been undertaken. Proton conduction is observed in humidified oxidising atmospheres, in common with a number of other perovskite systems with large cations of low electronegativity. However, to the best of our knowledge, this is the first report of proton conductivity in a hexagonal perovskite structure. An H^+/D^+ conductive isotope effect indicates that transport of protons occurs via the Gröthuss mechanism. It is proposed that the protons are introduced in the nominally undoped phase in the presence of H_2O on the hydration of oxygen vacancies which are created by slight Sr overstoichiometry of the La/Sr A1 site, or by unavoidable acceptor impurities on the Nb site. Accordingly, partially substituting Nb for lower valence cations (Ti^{4+} and Zr^{4+}) significantly increases proton conductivity via a greater nominal oxygen-vacancy concentration. ^1H MAS-NMR spectra provide supporting evidence of proton content in $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$, with bands at 5, 3.4 and 1.3 attributable to protons residing on lattice oxygens.

The electrical conductivity of SLN in reducing conditions in the range $\sim 10^{-8} \leq p\text{O}_2 \leq \sim 10^{-19}$ is *n*-type and consistent with the extrinsic defect model for acceptor-doped systems, as revealed by a power-law conductivity dependence on $p\text{O}_2$ of -1/4. At lower $p\text{O}_2$, a change of slope in the $\log \sigma$ vs $\log p\text{O}_2$ plot to -1/6 is indicative of defect formation (reduction) via the intrinsic model. The conductivity is higher in dry O_2 with respect to N_2 , which suggests a significant contribution of *p*-type charge carriers in dry oxidising conditions.

Although the levels of proton conductivity observed in the presently studied $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ -based materials is low, the possible effects of higher dopant levels and alternative dopants on augmenting protonic and electronic conductivity in this system warrant further investigation.

Acknowledgements

We thank the MINECO (ENE2012-30929) and the EU (ROBANODE, FP7-FCH-JU-2008-1-CP) for financial assistance. D. Pérez-Coll and A Thursfield also acknowledge the financial support of a “Ramón y Cajal” contract (MINECO, CSIC) and of the EPSRC (EP/G012865/1), respectively.

Table 1. Structure refinement data for $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ Space group $R\bar{3}$; $a = 5.66093(5)$ Å, $c = 27.2015(3)$ Å; $R_p = 2.84$ %; $R_{wp} = 3.65$ %; $\chi^2 = 4.61$

<i>atom</i>	<i>site</i>	<i>x/a</i>	<i>y/b</i>	<i>c/z</i>	<i>occupancy</i>	<i>U</i> $\times 100/\text{\AA}^2$
Sr/La(1)	6c	0	0	0.28609(9)	0.5/0.5	0.89(5)
Sr(2)	6c	0	0	0.1388(1)	1.0	0.82(4)
Nb(1)	6c	0	0	0.42436(9)	1.0	0.40(3)
Nb(2)	3a	0	0	0	1.0	0.40(3)
O(1)	18f	0.1161(4)	0.7866(4)	0.62709(7)	1.0	1.04(3)
O(2)	18f	0.1075(3)	0.7726(3)	0.45409(6)	1.0	0.95(3)

Table 2. Selected bond lengths (Å) and angles (deg) for $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$

	<i>distance to O(1) in Å</i>	<i>distance to O(2) in Å</i>
Nb(1)	$2.155(3) \times 3$	$1.861(2) \times 3$
Nb(2)	$1.992(2) \times 4$	
	$1.992(3) \times 2$	
Sr/La(1)	$2.874(3) \times 3$	$2.600(3) \times 3$
	$3.113(2)$	
	$3.113(3) \times 2$	
	$2.564(2)$	
	$2.564(3) \times 2$	
Sr(2)	$3.178(3) \times 3$	$2.539(1)$
		$2.539(2) \times 2$
		$2.604(3) \times 3$
O(1)-Nb(1)-O(1)	$82.4(2) \times 2$	O(1)-Nb(2)-O(1) $93.5(2) \times 4$
O(1)-Nb(1)-O(2)	$87.7(1) \times 3$	O(1)-Nb(2)-O(1) $93.5(1) \times 2$
O(1)-Nb(1)-O(2)	$85.4(1) \times 3$	O(1)-Nb(2)-O(1) $86.5(2) \times 6$
O(1)-Nb(1)-O(1)	$82.4(1)$	O(1)-Nb(2)-O(1) $180.0(2) \times 3$
O(2)-Nb(1)-O(2)	$102.5(2) \times 2$	
O(1)-Nb(1)-O(2)	$165.2(2) \times 3$	
O(2)-Nb(1)-O(2)	$102.5(1)$	

Table 3. Calculated valence states in $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$

<i>atom</i>	<i>coordinating species</i>	<i>formal valence state</i>	<i>calculated valence state</i>
Nb(1)	3×O(1); 3×O(2)	5	4.98(1)
Nb(2)	6×O(1)	5	4.82 (1)
Sr/La(1)	6×O(1); 3×O(2)	2.5	2.269(6)
Sr(2)	6×O(2)	2	1.767(4)
O(1)	1×Nb(1); 1×Nb(2); 2×La/Sr(1)	-2	-1.784(7)
O(2)	1×Nb(1); 2×Sr(2); 1×La/Sr(1)	-2	-2.026(8)

Figure Captions

1. Scanning electron micrograph of (a) a fracture surface of $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ and (b) a polished, thermally etched surface of $\text{Sr}_3\text{LaNb}_{0.9}\text{Ti}_{0.1}\text{O}_{3-\delta}$.
2. Observed and difference neutron powder diffraction profiles. Vertical bars indicate the expected positions of Bragg peaks.
3. Schematic diagram of the $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ structure.
4. Impedance spectra of $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ in dry air at 650 °C (main panel, numbers refer to the approximate value of $\log_{10}$ of the frequency in Hz) and in dry 10% H_2 : 90% N_2 at 900 °C (inset).
5. Temperature dependencies of total conductivity (dry 90% N_2 : 10% H_2) and bulk conductivity (dry N_2 and dry O_2) for $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$.
6. Total conductivity of $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ as a function of oxygen partial pressure at 900 °C (initial atmosphere, dry 10% H_2 : 90% N_2).
7. Temperature dependence of the bulk conductivity of $\text{Sr}_3\text{LaNb}_{3-x}\text{M}_x\text{O}_{12-\delta}$ in dry and wet air shown with open and filled symbols, respectively. The inset shows the magnitude of the conductive isotope effect as a function of temperature employing conductivity data collected in D_2O -wetted air.
8. Impedance spectra of $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ in wet air at 650°C showing conductive isotope effect. Numbers refer to the approximate value of $\log_{10}$ of the frequency in Hz.
9. ^1H MAS-NMR spectra of (a) as-prepared $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ and (b) $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ treated in a wet Ar atmosphere at 600 °C for 12 hours.

References

- [1] L. Katz, R. Ward, *Inorg. Chem.* 3 (1964) 205-211.
- [2] M.J. Rampling, G.C. Mather, F.M.B. Marques, D.C. Sinclair, *J. Eur. Ceram. Soc.* 23 (2003) 1911-1917.
- [3] R. Rawal, A. Feteira, N.C. Hyatt, D.C. Sinclair, *J. Am. Ceram. Soc.* 89 (2006) 332-335.
- [4] B.B. Van Aken, T.T.M. Palstra, A. Filippetti, N.A. Spaldin, *Natur. Mater.* 3 (2004) 164-170.
- [5] J.F. Vente, P.D. Battle, *J. Solid State Chem.* 152 (2000) 361-373.
- [6] L. Fang, H. Zhang, Q. Yu, H. Su, B. Wu, X. Cui, *J. Am. Ceram. Soc.* 92 (2009) 556-558.
- [7] R. Rawal, A.J. McQueen, L.J. Gillie, N.C. Hyatt, E.E. McCabe, K. Samara, N. McN. Alford, A. Feiteira, I.M. Reaney, D.C. Sinclair, *Appl. Phys. Lett* 94 (2009) 192904
- [8] R. Glöckner, A. Neimann, Y. Larring, T. Norby, *Solid State Ionics* 125 (1999) 369-376.
- [9] R. Haugsrud, T. Norby, *Nat. Mater.* 5 (2006) 193-196.
- [10] K.D. Kreur, *Annu. Rev. Mater. Res.* 33 (2003) 333-359.
- [11] E. Fabbri, D. Pergolesi, E. Traversa, *Chem. Soc. Rev.* 39 (2010) 4355-4369
- [12] J. Rodríguez-Carvajal, *Physica B* 192 (1993) 55-69.
- [13] M.C. Steil, F. Thevenot, M. Kleitz, *J. Electrochem. Soc.* 144 (1997) 390-398.
- [14] D. Pérez-Coll, E. Sánchez-López, G.C. Mather, *Solid State Ionics* 181 (2010) 1033-1042.
- [15] J.C.C. Abrantes, Sweep Control, Software Package, ESTG/IPVC, 2003.
- [16] L. Haar, J.S. Gallagher, G.S. Kell, *NBS/NRC Steam Tables*, Hemisphere Publishing Corp., New York, 1984.
- [17] J.C. Pérez-Flores, C. Ritter, D. Pérez-Coll, G.C. Mather, F. García-Alvarado, U. Amador, *J. Mater. Chem.* 21 (2011) 13195-13204.
- [18] O.E. Averkova, A.A. Evdokimov, V.P. Sirotinkin, A.N. Pokrovskii, *Russ. J. Inorg. Chem.* 31 (1986) 1410-1412.
- [19] Z.K. Huang, D.S. Yan, T.Y. Tien, I.W. Chen, *Mater. Lett.* 11 (1991) 286-290.

-
- [20] L.B. McCusker, R.B. Von Dreele, D.E. Cox, D. Louër, P. Scardi, *J. Appl. Cryst* 32 (1999) 36-50.
- [21] D. Altermatt, I.D. Brown, *Acta. Cryst. B* 41 (1985) 244-247.
- [22] R.D. Shannon, *Acta. Cryst. A* 32 (1976) 751-767.
- [23] J.T.S. Irvine, D.C. Sinclair, A.R. West, *Adv. Mater.* 2 (1990) 132-138.
- [24] N.H. Chan, R.K. Sharma, D.M. Smyth, *J. Am. Ceram. Soc.* 64 (1981) 556-562.
- [25] H. Iwahara, *Solid State Ionics* 52 (1992) 99-104.
- [26] T. Norby, M. Widerøe, R. Glöckner, Y. Larring, *Dalton Trans.* (2004) 3012-3018.
- [27] J.F. Liu, A.S. Nowick, *Solid State Ionics* 50 (1992) 131-138.
- [28] G.C. Mather, D. Poulidi, A. Thursfield, M.J. Pascual, J.R. Jurado, I.S. Metcalfe, *Solid State Ionics* 181 (2010) 230-235.

Fig. 1. Scanning electron micrograph of (a) a fracture surface of $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ and (b) a polished, thermally etched surface of $\text{Sr}_3\text{LaNb}_{0.9}\text{Ti}_{0.1}\text{O}_{3-\delta}$.

Fig. 2. Observed and difference neutron powder diffraction profiles. Vertical bars indicate the expected positions of Bragg peaks.

Fig. 3. Schematic diagram of the $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ structure.

Fig. 4. Impedance spectra of $Sr_3LaNb_3O_{12}$ in dry air at 650 °C (main panel, numbers refer to the approximate value of $\log_{10}$ of the frequency in Hz) and in dry 10% H_2 : 90% N_2 at 900 °C (inset).

Fig. 5. Temperature dependencies of total conductivity (dry 90% N_2 : 10% H_2) and bulk conductivity (dry N_2 and dry O_2) for $Sr_3LaNb_3O_{12}$.

Fig. 6. Total conductivity of $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ as a function of oxygen partial pressure at 900 °C (initial atmosphere, dry 10% H_2 : 90% N_2).

Fig. 7. Temperature dependence of the bulk conductivity of $\text{Sr}_3\text{LaNb}_{3-x}\text{M}_x\text{O}_{12-\delta}$ in dry and wet air shown with open and filled symbols, respectively. The inset shows the magnitude of the conductive isotope effect as a function of temperature employing conductivity data collected in D_2O -wetted air.

Fig 8. Impedance spectra of $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ in wet air at 650°C showing conductive isotope effect. Numbers refer to the approximate value of $\log_{10}$ of the frequency in Hz.

Fig. 9. ^1H MAS-NMR spectra of (a) as-prepared $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ and (b) $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$ treated in a wet Ar atmosphere at 600°C for 12 hours.