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Aluminum dual doping and oxygen transport pathway in novel $Sr_{11}Mo_{4-x}Al_xO_{23}$ oxide-ion solid electrolytes

ABSTRACT

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Three new electrolytes of composition $Sr_{11}Mo_{4-x}Al_xO_{23-6}$ (x = 0.5, 1.0 and 1.5) were synthesized by wetchemistry procedures (citrate method) as polycrystalline samples. They were crystallographically studied from synchrotron and neutron diffraction techniques. They derive from the $Sr_{11}Mo_4O_{23}$ complex perovskite, which can be rewritten as $Sr_{1.75} \square_{0.25}SrMoO_{5.75}$, highlighting the relationship with double perovskites $A_2B'B''O_6$. From these analyses via Rietveld refinement, a dual doping was found from synchrotron data, where the aluminum is equally allocated at both Sr (B') and Mo (B'') sites. A detailed analysis of the neutron data from Difference Fourier Maps (DFM) unveiled the oxygen delocalization around the Mo site. From the refined crystal structures at room and high temperatures, a Bond Valence Sum Map (BVSM) analysis was useful to find the oxygen pathway in the crystal structure, and the minimum density to allow connections among oxygen atoms. The structural characterization was complemented with thermogravimetric and thermodilatometric analysis. The ionic conductivity was measured from electrochemical impedance spectroscopy (EIS) in wet and dry air and nitrogen atmospheres.

1. Introduction

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The urgent need for changing fossil fuels for alternative energy sources is being tackled by new arising technologies involving new materials. Such materials ought to gather a certain number of characteristics and properties, including low-cost, high efficiency, and stability over time. Fuel cells are essential ingredients of the new energy paradigms, necessary to convert the chemical energy stored in chemical bonds directly into electricity, and this is achieved by different mechanisms. Fuel cells that electrochemically drive the fuel (often H₂ or CH₄) oxidation through a solid oxide interface are our primary goal [1–3]. These fuel cells are called Solid Oxide Fuel Cells (SOFC); they are made up of solid components that would need high temperatures (typically over 750 °C, and as much as 850 °C) to work properly. Such devices exhibit excellent conversion rates and performance, due to the enhanced kinetics associated with the working temperatures. As primary requirement, the solid electrolyte acting as a separator between the two redox semireactions needs to display an excellent ionic conductivity, of either O²⁻ or H⁺ ions. The progress in SOFC research relies

on the development of novel solid ionic conductor materials [3,4].

 ABO_3 perovskite oxides present a crystal structure that may contain oxygen vacancies, enabling the oxide ion motion across the solid; hence, they could satisfactorily work as SOFC electrolytes. An example of this is LSGM [5], the conductivity of which is slightly higher than other well known electrolytes like YSZ and GDC [6,7]. These phases have been extensively characterized and novel compositions and superstructures continue to be explored. The Goldschmidt's tolerance factor is a key parameter for designing and preparing novel perovskite materials with new stoichiometries, based on the size relationship between A and B cations [8–10].

The complex phase $Sr_{11}Mo_4O_{23}$ exhibits a distorted double perovskite-like structure, which has been extensively characterized in our group [11,12]. The resemblance with a double perovskite is highlighted by rewriting its stoichiometry as $(Sr_7)_A(Sr_4Mo_4)_BO_{23}$, where part of the Sr^{2+} atoms are at the A sublattice, and the rest accommodates in the octahedral B sublattice. Given that the ionic radius $r_{Sr}^{2+} = 1.26$ Å is considerably large for an octahedral coordination, the structure is rather deformed, giving rise to a distorted stacking of polyhedra and

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octahedra. This structure bears resemblance to that reported by King et al. [13], where this phenomenon was introduced as a broken corner sharing of the octahedral arrangement. This structure also allows doping with small quantities of an aliovalent cation in the B sublattice, and by exploiting this fact, new materials can be designed and produced with new or better properties than those of the parent compound. Recently, interesting results have been obtained upon Ti and Nb doping [14,15] the parent $Sr_{11}Mo_4O_{23}$ framework.

Following this line, we present the results on new materials obtained by introducing Al^{3+} ions in the $Sr_{11}Mo_4O_{23}$ perovskite, with the aim to introduce additional oxygen vacancies and thus to enhancing the ionic conductivity. We report on a complete crystallographic characterization from synchrotron x-ray and neutron diffraction data, complemented with transport measurements.

2. Experimental

Materials were prepared by wet chemistry procedures. In a first stage, stoichiometric quantities of pure reactants, (NH₄)₆Mo₇O₂₄·4H₂O 99.98% Sigma-Aldrich, anhydrous Sr(NO3)2 99.9% Mallinckrodt, Al (NO₃)₃·9H₂O Sigma-Aldrich 99% were weighed. The solid reactants were dissolved in beakers with a citric acid solution (10%) containing several drops of HNO3 (Merck 65%) to allow complexation and complete dissolution. Resulting solutions were dried forming a viscous gel. Then the gels were placed in a furnace for 2 h at 200 °C until the formation of an organometallic low-density foam. These foams were ground, put into porcelain capsules and then heated at 600 °C to decompose the organic matrix. The resulting powder was then ground in an agate mortar for 30 min, after that put in alumina boats for further heat treatment. The powders were first calcined at 1100 °C and then fired at 1400 °C for 12 h, obtaining the pure Sr₁₁Mo₄O₂₃ oxide and Sr₁₁Mo_{4-x}Al_xO₂₃ phases with minor impurities. They will be labeled as SAMO-n with n being 0, 1, 2 and 3 for doping levels x = 0.0, 0.5, 1.0and 1.5, respectively.

Initial characterizations were made by laboratory X-ray powder diffraction (XRPD). The diffraction patterns were acquired with a Rigaku Ultima IV type II diffractometer with Ka-Cu radiation $\lambda = 1.5418$ Å. A more detailed analysis of the crystal structure and its thermal evolution was performed by synchrotron X-ray powder diffraction (SXRPD) at 25, 200, 400, 600 and 800 °C. SXRPD patterns were collected in the high angular resolution mode (so-called MAD set-up) on the MSPD diffractometer in ALBA synchrotron at Cerdanvola del Vallès, Spain, selecting an incident beam with 38 keV energy, $\lambda = 0.3252$ Å operating at the Bl-04 beamline [16]. The sample was contained within 0.3 mm diameter amorphous quartz capillary that was rotating during the data acquisition. Additionally, neutron powder diffraction (NPD) patterns were collected on the D2B diffractometer, at the Laue-Langevin Institut, Grenoble, France with a wavelength of 1.594 Å. The coherent scattering lengths (b_{coh}) for Sr, Mo, Al and O are 7.02, 6.71, 3.449 and 5.805 fm, respectively. XRPD, SXRPD and NPD patterns were analyzed with the Rietveld method using the FullProf program [17,18]. The software 3DBVSMapper [19] was used to calculate the BVS maps as isosurfaces, from the crystal data obtained from NPD structure refinements. These maps have been calculated with a spatial resolution of 0.1 Å. VESTA software [20] was used to plot BVS maps and crystal structures as well.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves were obtained using a Stanton STA 781 instrument. The temperatures of the peaks were measured with a precision of ± 1 K. Analyses were carried out in an air flow at a heating rate of 1 K·min⁻¹. About 50 mg of powder sample was used in each case.

Measurements of the thermal expansion coefficient (TEC) and electrical conductivity required the use of sintered pellets of 6 mm of diameter, heated in air at 1300 °C for 12 h. Achieved density values are between 90%–95%. Thermal expansion of sintered samples was performed in a Linseis L75HX1000 dilatometer, between 100 and 1000 °C



Fig. 1. Laboratory XRPD of obtained samples $Sr_{11}Mo_{4.x}Al_xO_{23}$ with x = 0.0, 0.5, 1.0 and 1.5. Sample with highest aluminum content has two minor impurities that were assigned to $SrMoO_4$ (dot), and a sodalite of formula $Sr_8[Al_{12}O_{24}](MoO_4)_2$ (asterisks).

in air with a heating rate of 5 °C/min.

Scanning electron microscopy (SEM) images were obtained on a Zeiss LEO1450VP instrument; and samples were placed on adhesive carbon tape coated with gold.

Electrical conductivity was measured by two-probe electrochemical impedance spectroscopy (EIS) from 500 to 900 °C in different atmospheric conditions using a Potentiostat/Galvanostat AUTOLAB PGSTAT 302 from ECO CHEMIE. The frequency range was $0.1-10^6$ Hz. For these measurements, sintered pellets were painted with a uniform layer of Pt paste, and Pt wire contacts were fixed to each layer with the same Pt paste. Finally the whole device was fired at 1100 °C for 1 h.

3. Results and discussion

3.1. Structural features and refinement

3.1.1. Initial characterizations

Laboratory XRPD patterns at RT of the four samples x = 0, 0.5, 1.0and 1.5 are similar to each other indicating that they are all isostructural, see Fig. 1, and their peaks correspond to a cubic symmetry in the $Fd\overline{3}m$ space group. All the samples were fitted correctly with this cubic model. In the Al-doped samples, minor amount of strontium aluminum molybdenum oxide with Sodalite structure (Sr₈[Al₁₂O₂₄] (MoO₄)₂), defined in the tetragonal $I4_1/acd$ space group, [21] were identified and added to the refinements as a second phase. From the scale factors of the main and impurity phase, the impurity levels were estimated to be 5 and 7 wt% for x = 1.0 and 1.5, respectively. Also for x = 1.5, minor amounts (2%) of SrMoO₄ with scheelite structure were found from a two-phase refinement.

3.1.2. Synchrotron radiation refinement for x = 1

The SXRPD pattern collected at RT confirms the cubic symmetry observed from laboratory XRPD. In this cubic model, the strontium atoms are distributed at three different positions; molybdenum at two, and oxygen at four distinct crystallographic sites. Two out of three Sr atoms (Sr1_{8b} and Sr2_{48f}) belong to the A-site sublattice, while the remaining Sr with the two Mo atoms (Sr3_{32e}, Mo1_{16d} and Mo2_{16c}) correspond to B-site cations, in what would be a conventional perovskite framework. The initial refinement was made considering that the Al cations replace Mo, in the same way that the samples were designed for x = 1, Sr₁₁Mo₃AlO₂₃₋₈. Crystallographically, the dopant was allocated in Mo2 site, according to the crystallographic formula:

 $([Sr1]^{A}_{8b})_{1}([Sr2]^{A}_{48f})_{6}([Sr3]^{B'}_{32e})_{4}([Mo1]^{B''}_{16d})_{2}([Mo2]^{B''}_{16c})_{1}([Al1]^{B''}_{16c})_{1}(O)_{23-\delta}$

This model was successfully used for Ti and Nb-doped phases



Fig. 2. Synchrotron diffraction pattern obtained at room temperature for the composition $x_{Al} = 1.0$, adjusted by Rietveld refinement, featuring equimolar split doping of aluminum.

[14,15]. For Al-doped phase the obtained refinement using this model may also be considered successful; however, minor differences were observed in two reflections, namely (222) and (331). A detailed analysis of structure factors of these reflections made it possible to deduce that Mo1, Mo2 and Sr3 sites are the biggest contributors to those diffraction lines. Thus, from several analyses, described in the Supporting information (SI), it has been possible to infer that the Al-doping is split equally into two sites Sr3 and Mo2, according to:

$Sr_{7}^{A}(Sr3_{3,5}^{B'}Al_{0,5}^{B'})Mo1^{B''}(Mo2_{1,5}^{B'}Al_{0,5}^{B''})O_{23-\delta}$

This structural model successfully fits the SXRPD data, as displayed in Fig. 2. The final refined crystal structure is shown in an inset of this figure. Table 1 summarizes the main crystallographic parameters of this refinement.

This unexpected and unprecedented behavior may be analyzed in terms of ionic radii of the host and dopant ions. The ionic radii of AI^{3+} , Mo^{6+} and Sr^{2+} are 0.535, 0.59 and 1.26 Å, respectively. We found that Al cations have no impediments to replace either Mo or Sr hosts; moreover, the best agreement after the refinement is reached with an equimolar dual doping. A secondary and more desirable effect of Al

substitution is the injection of oxygen vacancies (δ) with respect to Sr₁₁Mo₄O₂₃; the expected δ values should have been 0.75, 1.5, 2.25 for x = 0.5, 1 and 1.5, respectively. It is important to clarify that the undoped phase already has one less oxygen than the non-defective phase (A₁₁B₄O₂₄). The splitting in the Al-doping compensates these oxygen vacancies through the overall charge balance; while the substitution in Mo reduces the charge in +3, in Sr the charge is increased by +1. In the current dual doping situation for x = 1, the δ value is 0.5; therefore, the obtained oxygen vacancies are substantially lower than expected. A hypothesis for this behavior is that the structure does not support a high level of defects and the dual doping constitutes a chemical recourse to the crystal stabilization.

The crystal structure also was analyzed at high temperature (200, 400, 600 and 800 °C). These patterns were also successfully fitted with the model used at RT. Fig. S3 (SI) shows the fitted patterns and Tables S1–S4 summarize the main crystallographic results. At these temperatures, all the crystallographic parameters exhibit an expected increase as temperature rises. A more detailed analysis as a function of temperature was performed from NPD, as will be discussed later.

3.1.3. Neutron radiation refinement for x = 0.5, 1 and 1.5

Room temperature NPD data were initially fitted using the model obtained from SXRPD. For x = 1.0 the equimolar doping of Al into Sr3 and Mo2 sites was successful. The same Al distribution was used for x = 0.5 and 1.5 obtaining satisfactory refinements. The main scope of NPD analysis was to find structural details concerning the oxygen positions and their motion within the lattice. In the parent Sr₁₁Mo₄O₂₃ [12,13], Mo1 is surrounded by six oxygens in octahedral symmetry, whereas around Mo2, oxygen atoms are delocalized or "in constant motion". With regard to the oxygen position around Mo2, in the cubic model there are small differences in the sites occupied by oxygen atoms. In Ba₁₁W₄O₂₃, the delocalization is built by three unique oxygen sites $(O2_{96g}, O3_{96h}$ and $O4_{96g})$ giving a total coordination of 18 partially occupied sites, decomposed into an octahedron and in four differently oriented tetrahedra [22]. In contrast, recently, King et al. reported this delocalization with two oxygen sites ($O2_{96g}$ and $O3_{96h}$). This implies a coordination of 12 partially occupied sites, which may be decomposed into four differently oriented square based pyramids [13]. Alternatively, it may also be described as a stack of three packed layers where the first and third ones have three staggered oxygens corresponding to $O2_{96g}$; and between these layers the remaining six oxygens

Table 1

Crystallographic data for the $Sr_{11}Mo_{4-x}Al_xO_{23-8}$ for x = 1.0 phase from refinement from SXPD data at 298 K.

Sustany auties anago group	$Ed\overline{2} = 7 - 9$	Unit coll peromotores	a = 16,20406,(10)	1 and $V = 4406$ 1E (E)	ÅЗ
System: cubic: space group	$r r a + m z = \delta$	unit-cen parameters.	(l = 10.39400 (10))	a and v = 4400 15 (5)	A

Atom	Wyckoff site	x/a	y/b	z/c	$U_{\rm iso}^*/U_{\rm eq}$	Occupancy	
Sr1	48 <i>f</i>	0.39963(5)	0.12500	0.12500	0.0437(5)	1.00000	
Sr2	8b	0.37500	0.37500	0.37500	0.0358(8)*	1.00000	
Sr3	32e	0.22663(4)	0.22663(4)	0.22663(4)	0.0403(4)*	0.87500 ^a	
A13	32e	0.22663(4)	0.22663(4)	0.22663(4)	0.0403(4)*	0.12500 ^a	
Mo1	16d	0.50000	0.50000	0.50000	0.0154(3)*	1.00000	
Mo2	16c	0.00000	0.00000	0.00000	0.0039(3)*	0.75000 ^a	
A12	16c	0.00000	0.00000	0.00000	0.0039(3)*	0.25000 ^a	
01	96g	0.50073	0.50073	0.61935	0.0349	1.00000	
02	96g	0.08249	0.08249	-0.00021	0.0629*	0.43750 ^a	
03	96h	0.00000	0.07838	-0.07838	0.0676*	0.21876 ^a	
04	96g	-0.02730	-0.02730	0.11232	0.0676*	0.21876 ^a	
SXPD data: $R_p = 9.925$, $R_{wp} = 13.410$, $R_{exp} = 8.701$, $\chi^2 = 2.38$, $R_{Bragg} = 8.707$.							

Anisotropic atomic displacement parameters (Å²) for (SAMO-2) at 298 K.

Atom	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sr1	0.0301 (5)	0.0505 (4)	0.0505 (4)	0.00000	0.00000	-0.0295 (6)
O1	0.04357	0.04357	0.01743	0.00381	0.00858	0.00858

^a Occupation parameters have been fixed in order to avoid coupling of refinement variables.



Fig. 3. DFM calculated from NPD data to recreate the oxygen delocalization effect of O2 and O3 around Mo/Al site (a, b, c). Section of electron density showing that O3 is less occupied than O2 site or that O3 would be able to move more freely through the network than O2, which seems to be more bound to its site (d, e).

 $(O3_{96h})$, like a hexagon centered in Mo2. In a simple way, this arrangement can be visualized as a cuboctahedron. In order to discern between these options in our Al-doped phases, Difference Fourier Maps were calculated without these oxygen atoms. Fig. 3.a, .b and .c illustrates the isosurface of nuclear density (in scattering length) obtained from DFM at level of 0.07 focused around Mo2 site. As shown, the densities correspond to two crystallographic positions ($O2_{96g}$ and $O3_{96h}$) and are in agreement with a cuboctahedral geometry. Besides, if the inner density is analyzed (see Fig. 3.d and .e), $O2_{96g}$ site has a higher intensity than $O3_{96h}$. From this, it is possible to deduce than O3 presents a higher mobility that O2.

Considering the previous analysis, all three Al-doped samples were correctly fitted with two oxygens partially occupying positions around Mo2 site; however, some of the planes do not show an adequate fit, especially the (444) plane. This particular mismatch is also observed with the NPD refinement of Sr₁₁Mo₄O₂₃ informed by King et al. [13] For these reasons, the DFM was calculated again with these refinements in order to observe the mismatch in the nuclear density and, as illustrated in Fig. S4, intermediate densities appear between the six O3_{96h} sites, suggesting the presence of a new partially occupied oxygen position with symmetry corresponding to 96g site. This new position was added as O496g and refined, producing a non-negligible improvement in the pattern matching, see Fig. S5. This enhancement was reproduced in the three Al-doped phases. The Rietveld refinements, along with the crystallographic data, are illustrated in Fig. 4 and Table 2 for x = 1, as a representative member of the series. After refining the structures with a third "extra" oxygen around Mo2, six new positions are generated, close to O3 and forming "bridges" between O3 to O3 and O3 to O2. A schematic view of the crystal structure is shown in the inset of Fig. 4. This oxygen arrangement is not different from those previously reported for Ti and Nb doped Sr₁₁Mo₄O₂₃ phases at both room and high temperatures [14,15].

On the other hand, the unit-cell volume at RT shows a reduction as Al doping increases. As illustrated in Fig. S6, the decrease is linear until to x = 1; beyond this doping level the linearity is lost, and for x = 1.5 a plateau is reached. Hence, it is not possible to increase the Al content and the maximum nominal Al content should be close to 1.3. Unfortunately, this small difference in the Al content cannot be distinguished from NPD.



Fig. 4. Neutron powder diffraction pattern adjusted by Rietveld refinement for Al content of $x_{Al} = 1.0$ at room temperature, with dual doping feature included.

The Rietveld refinements of the structures at higher temperatures from NPD data were also correctly performed using the room temperature model. The Rietveld plots and the crystallographic data are shown in Figs. S7 to S17 and Tables S5–S15, respectively. The thermal evolution of the unit-cell parameters exhibits a similar behavior than that of the undoped phase, [11] showing though a subtle change in the slope around to 500 °C, as displayed in Fig. 5.

Finally, from the structural parameters obtained in the NPD refinements, BVS maps were calculated for the three doped phases at both room and high temperature, with the aim of finding the least energetic (most probable) pathway of O^{2-} ions within the lattice. In all cases, a similar shape of the surfaces was obtained, as illustrated in Fig. 6 for x = 1 at high temperature (HT), as representative of the series. Blue polyhedra (Fig. 6.a) show the oxygen delocalization around the metallic center Mo2, they are thought to be responsible for the ionic conduction via a vacancy driven mechanism. It can be appreciated how each Mo2 polyhedron is shrouded by the isosurface of BVS, and also each polyhedron is connected to another six of the same kind through two contact paths (Fig. 6.b and .c). This contact path is between four Mo2 polyhedra forming a tetrahedron, see Fig. 6. Besides, the interconnection point centered a tetrahedron formed by four Sr3 sites, which are

Table 2

Crystallographic data for the $Sr_{11}Mo_{4-x}Al_xO_{23-\delta}$ for x = 1.0 phase from refinement from NPD data at 298 K.

System: cubic; space group: $F d \overline{3} m$, $Z = 8$. Unit-cell parameters: $a = 16.3072$ (2) Å and $V = 4336.50$ (11) Å ³ .						
Atom	Wyckoff site	x/a	y/b	z/c	$U_{\rm iso}^*/U_{\rm eq}$	Occupancy
Sr1	48 <i>f</i>	0.39875(2)	0.12500	0.12500	0.0424(1) ^a	1.00000
Sr2	8b	0.37500	0.37500	0.37500	0.0615(2)*	1.00000
Sr3	32e	0.22391(1)	0.22391(1)	0.22391(1)	0.0459(6)*	0.87500 ^a
A13	32e	0.22391(1)	0.22391(1)	0.22391(1)	0.0459(6)*	0.12500 ^a
Mo1	16 <i>d</i>	0.50000	0.50000	0.50000	0.0280(6)*	1.00000
Mo2	16c	0.00000	0.00000	0.00000	0.0340(7)*	0.75000^{a}
A12	16c	0.00000	0.00000	0.00000	0.0340(7)*	0.24500^{a}
01	96g	0.49995(2)	0.49995(2)	0.61798(2)	0.0419(1) ^a	1.00000
O2	96g	0.08231(3)	0.08231(3)	-0.00206(7)	0.0639(1)*	0.43750 ^a
O3	96h	0.00000	0.07721(1)	-0.07721(1)	0.141(4)*	0.21876 ^a
04	96g	-0.02446(9)	-0.02446(9)	0.11796(2)	0.141(4)*	0.21876 ^a

NPD data: $R_p = 2.099$, $R_{wp} = 2.758$, $R_{exp} = 0.840$, $\chi^2 = 10.8$, $R_{Bragg} = 16.251$

Anisotropic atomic displacement parameters (Å²) for (SAMO-2) at 298 K.

Atom	U ¹¹	<i>U</i> ²²	U ³³	U^{12}	<i>U</i> ¹³	U ²³
Sr1	0.03771(2)	0.04482(1)	0.04482(1)	0.00000	0.00000	-0.02144(2)
01	0.05639(1)	0.05639(1)	0.01284(1)	0.00561(2)	0.00372(1)	0.00372(1)

^a Occupation parameters have been fixed in order to avoid coupling of refinement variables.



Fig. 5. Thermal evolution of cell parameter *a*, for all three Al-doped phases, calculated from NPD data using Rietveld analysis.

partially doped by Al atoms. In other words, should any O^{2-} mobility occur, one of the oxygen atoms of the blue polyhedron must enter inside the tetrahedron formed by four Sr3 atoms (depicted in orange in Fig. 6), then, it can come out of any of the three remaining faces of the tetrahedron, to another blue polyhedron. In this way, the O^{2-} ion hops from a crystallographic site to an interstitial, and then back again to another lattice position. There must clearly be an energetic barrier to surpass in order to observe this hopping phenomenon.

From the BVS maps, the minimum infinitely connected value (MinConnected) [23] is obtained. This value indicates the minimum BV value that allows connecting an oxygen to the adjacent one. In this structure, the minimum value is observed in the center of Sr3 tetrahedron and can be associated with the BVS in this interstitial site [23]. It is expected that the O^{2-} to be overbonded in this site; for this reason the BVS value is greater than 2, hence, it can be related to the difficulty for O^{2-} to jump from a Mo2 polyhedron to the next, and consequently with the ionic mobility. Table 3 lists the MinConnected values obtained for each Al composition, at RT and HT. Increasing amounts of Al induce a subtle decrease in the values; however, the major effect is produced with the temperature. All three phases present a not insignificant decrease, suggesting that the structural resistance to the O^{2-} mobility is highly reduced at HT. These crystallographic features are in fair

agreement with the measured conductivity, as described later.

3.2. Thermal analysis (TGA, DTA and thermal expansions measurements)

The thermal analysis in potential component materials for SOFC is a crucial characterization tool to know the thermal stability, resistance (physical and chemical), volume expansion, etc. For this reason the TGA, DTA and thermal expansions measurements were performed in the doped samples.

In previous works, both undoped [11] and Nb [15] and Ti [14] doped phases have shown several minor mass losses from RT to 1000 °C. These losses were assigned to a superficial hydration and carbonation behavior; however, one of the processes involved was found to be reversible. The latter was initially assigned to a loss and uptake of oxygen atoms, although a reversible hydration phenomenon cannot be ruled out. In order to observe this in Al-doped samples, TGA and DTA experiments were performed up to 1000 °C in two consecutive cycles to observe all mass losses during the first one, and just the reversible process in the second one. Fig. S18 shows the first and second cycle for x = 0.5, 1.0 and 1.5. As displayed, after the dehydration and decarbonation processes occurred during the first cycle, the reversible process was the only one remaining, after running the second cycle. This can be explained in terms of oxygen or water loss/uptake. The oxygen elimination implies the reduction of Sr^{2+} or Mo(VI); taking into account chemical stability considerations, the reduction of Mo(VI) to Mo(V) is well known in several perovskites; however, there is not crystallographic evidence of this reduction. On the other hand, considering that strontium is determinant in some way for the chemical nature of the compound, minor mass processes may be attributed to a reversible dehydration (warming) and hydration (cooling) behavior, similar to that observed in SrO, supporting the water loss/uptake process. In spite of this, the introduction of aluminum in the Sr₁₁Mo₄O₂₃ network structure reduces this hygroscopic behavior. While the undoped phase took up to 0.70% [11] of the mass in water, the Al-doped phases took up much less: 0.32, 0.16 and 0.16% for x = 0.5, 1.0 and 1.5, respectively. These values indicate that doping with Al favors hygroscopic inertia for all of the Al-containing compositions.

Fig. 7 shows thermal expansion profiles of Al-doped ceramic in terms of $\Delta L/L_0$ as a function of temperature. Samples show no abrupt changes within the whole temperature range; nevertheless they do exhibit an increase in their thermal expansion coefficient (TEC), as the



Fig. 6. (a) BVS maps shown in wireframe style, denoting connection between blue (Mo/Al) polyhedra, which is reached by an oxygen atom passing through a triangular face formed by Sr/Al atoms. (b) Detail of the isolated "unit" responsible for conduction from green (Mo/Al) polyhedra to the one in the middle, shown within a red isosurface, and (c) exiting to another green polyhedra. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3

MinConnected values extracted from BVS maps for all Al-doped phases at both room and high temperatures.

Minimum infinitely connected field value (v.u.)						
Phase		Temperature				
Name	x_{Al}	25 °C	900 °C			
SAMO1 SAMO2 SAMO3	0.5 1.0 1.5	- 2.468 - 2.556 - 2.558	- 2.377 - 2.451 - 2.458			



Fig. 7. Thermodilatometric analysis of Al-doped samples, calculated TEC values are displayed together for both low and high temperature regions.

abscissa values increase. Additionally, for all Al contents, a slight increase in the TEC (change in the slope) is observed from 500 to 700 °C, which may be related to the reversible process observed in TGA experiments. TEC values in the operating temperature range are 17.4×10^{-6} , 17.5×10^{-6} and $17.0 \times 10^{-6} \mathrm{K}^{-1}$ for x = 0.5, 1.0 and 1.5, respectively. These values are comparable with those calculated from the unit-cell parameters plotted in Fig. 5: 16.3×10^{-6} (600–900 °C), 16.6×10^{-6} (700–900 °C) and 16.5×10^{-6}

(700–900 °C) for x = 0.5, 1.0 and 1.5, respectively, showing a good agreement between both techniques. TEC values below 500 °C are compatible with the ones reported for the most common compounds used in SOFC [24]; however, above 500 °C these values are higher. Hence, if SAMO materials are considered as electrolytes, both cathode and anode oxides should be selected to present similar expansion behavior.

3.3. Conductivity measurements

Thermal evolution of conductivity was characterized by means of impedance spectroscopy measurements. Fig. 8.a shows the representative impedance spectrum for SAMO-2 sample at 500 °C. Each experimental spectrum was modeled using an equivalent circuit with two components (see Fig. 8.a). The first arc at higher frequencies (red line) is attributed to the sample contributions. On the other hand, the second contribution (blue line) is assigned to the electrode interface (sample/Pt paint). The samples do not show separately bulk and grain boundary arcs in all the temperature range. On the other hand, the sintering degree reached in the pellets was observed from SEM images. Fig. 8.b shows the SEM images of the face and a transversal cut of the SAMO-2 pellet.

Experimental conditions included two chief conditions: negligible (pure N2), and rich (analytical air) partial oxygen pressure atmospheres. In addition, saturated water vapor was added as a secondary component, to establish whether the material had, if any, proton conductivity. In all cases the measurements were performed at temperatures ranging from 950 to 400 °C at intervals of 50 °C, with heat rates of -5 °C/min.

It was found that essayed atmospheres played an almost negligible role on the measured spectra, so that the obtained conductivity values were remarkably close to each other. These values are plotted in Figs. S19–S21. In order to analyze the Al-doping effect, Fig. 9 illustrates the logarithm of conductivity multiplied by temperature versus the inverse of temperature (Arrhenius plots) in dry air for the three Al-doped samples. Taking into account the initial hypothesis, where a high number of oxygen vacancies would be introduced by substituting Mo⁶⁺ by Al³⁺ ions, the observed increase in conductivity values as Al content increases was subtle, which was far lower than expected for such a dramatic decrease in site charge $|\Delta q| = 3$. However, as we previously described, the dual doping of Al³⁺ into Mo⁶⁺ and Sr²⁺ sites leads to a



Fig. 8. a) Impedance spectrum of SAMO-2 at 500 °C, as representative of the series. The lines represent the different components of the spectrum which was used in the fits; the sample and sample/electrode components are drawn in red and blue colors, respectively. b) SEM images of the face and a transversal cut of the SAMO-2 pellet as is illustrated in the scheme. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

lower induction of vacancies. On the other hand, as is observed in Fig. 9, there is no improvement with respect to the undoped phase [11]. This unexpected behavior may also be assigned to the dual doping, but considering the polarizing power in terms of charge over ionic ratio (q/ r_i). If Al³⁺ (q/ r_i = 5.6) only substitutes the Mo⁶⁺ (q/ r_i = 10.2) there would not be an increase in the polarizing power in the site Mo2. But Al³⁺ are also partially allocated at Sr3 sites replacing Sr²⁺ ions (q/



Fig. 9. Ln(σT) vs 1/T for different x values in comparison with Sr_{11}Mo_4O_{23} [11].

 $r_{\rm i}$ = 1.6), thus producing a big increase in the polarizing power of this Sr3 site. Considering that the O^2- mobility occurs through the Sr3 tetrahedron, as revealed from BVS maps, it is possible to infer that the dual Al doping has the effect of hindering the oxygen hopping.

Then, the activation energy can be calculated from the Arrhenius plots in Fig. 9. The linear regression yields the following activation energy values: 0.63 eV, 0.71 eV and 0.70 eV, for Al contents x = 0.5, 1.0 and 1.5, respectively. These values, and that reported for the undoped phase ($E_a = 0.63 \text{ eV}$) [11] show that the Al induces a subtle increase in the E_a .

The best value at 800 °C for SAMO-3 is $1.3 \times 10^{-2} \, \text{S cm}^{-1}$. This value is lower than that observed for electrolytes such as LSGM $(0.14 \, \text{S cm}^{-1})$ [5], La₂Mo₂O₉ $(0.13 \, \text{S cm}^{-1})$ [25] and GDC($8.5 \times 10^{-2} \, \text{S cm}^{-1}$) [6]. However, the obtained value is comparable to the reported for YSZ $(2.1 \times 10^{-2} \, \text{S cm}^{-1})$ [7]. Thus, the SAMO family presents promising features, although a significant conductivity enhancement would be needed to compete with state-of-the art electrolytes in SOFC.

Summarizing, the Al-doping effect can be analyzed from two opposite points of view. First, the increase in oxygen vacancy level and, in second term, the increase in the polarizing power in the Sr3 sites. As the aluminum content increases along x = 0.5, 1.0 and 1.5, the effect of the oxygen vacancies is dominating, but when compared with the undoped phase, it would seem that the polarizing power becomes more significant. Anyway, the most important fact is the discovery of the pathway and the chemical effect of the dopant, which allows us to design new solid electrolyte materials in a more rational way.

4. Conclusions

Three aluminum doped phases of Sr₁₁Mo₄O₂₃ with x = 0.5, 1.0 and 1.5 were successfully synthesized by wet chemistry procedures. The undoped phase also was synthesized and heat-treated at the same final temperature (1400 °C) of the Al-doped phases; all showed a cubic symmetry. Synchrotron XRPD refinements revealed that Al³⁺ ions are allocated in both Sr3 and Mo2 sites in equal amount. NPD was useful to unveil the oxygen delocalization around Mo2 site. From DFM of NPD data it was possible to model oxygen delocalization with three partially occupied oxygen positions, namely O2_{96g}, O3_{96h} and O4_{96g}. Additionally, for the final RT and HT structures, a Bond Valence Sum Map analysis was used to calculate and shed some light about the oxygen pathway in the crystal structure, and the MinConected value allowed deducing the structural resistance to the O²⁻ jump. Thermal

analysis techniques TGA, DTA and TD showed that, when doped with increasing amounts of Al, the samples exhibited improved water tolerance and adequate compatibility to be used as electrolyte in SOFC. Ionic conductivity was measured from impedance spectroscopy in wet and dry conditions using air and nitrogen atmospheres, showing the same behavior regardless of the atmospheric condition. This is important due to two facts; first that there would not be a proton conductivity mechanism and second, that the presence of water is not detrimental for the conductivity of any of the samples, knowing that water is a by-product of the SOFC reaction exhaust gas. Finally, the conductivity measurements are comparable to those of the parent compound, which is accounted for by the crystallographic details: the understanding of the conduction paths for oxide ions enables future improvements of these materials.

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Appendix A. Supplementary data

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