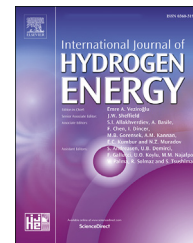




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# Structural peculiarities of $\text{La}_2\text{Ge}_{1-x}\text{Cr}_x\text{MgO}_{6-\delta}$ ( $0 < x \leq 0.5$ ): a superior oxide-ion electrolyte for low-temperature solid-oxide fuel cells

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## HIGHLIGHTS

- A novel series of electrolyte materials over-perform in electrolyte-supported SOFC cells.
- Ge-containing perovskites where both  $\text{Ge}^{4+}$  and  $\text{Cr}^{3+}$  ions can exhibit octahedral and tetrahedral oxygen coordination.
- Oxygen vacancies generated by Cr doping favor oxygen diffusion across the crystal structure.
- A neutron powder diffraction (NPD) study of the perovskite matrix unveils the oxygen diffusion paths.
- The power density of test cells at 600 °C is  $\sim 600 \text{ mW cm}^{-2}$ , a threefold increase compared with LSGM electrolyte.

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## ABSTRACT

The double perovskite  $\text{La}_2\text{MgGeO}_6$  has been modified by substitution of Ge by Cr to introduce oxygen vacancies. A specimen of composition  $\text{La}_2\text{Ge}_{0.55}\text{Cr}_{0.45}\text{MgO}_6$  has been studied by neutron diffraction, in the 300–873 K temperature range. The perovskite structure can be defined in the rhombohedral R3 space group. At 295 K, the unit-cell parameters are  $a = 5.5115(2)$ ,  $c = 13.3485(7) \text{ \AA}$  and  $V = 351.16(3) \text{ \AA}^3$ . This double perovskite exhibits two distinct crystallographic sites for Mg and (Cr,Ge), statistically distributed at the octahedral sites. It presents a conspicuous deficiency at O1 sites, accounting for the excellent ionic conduction properties. The Bond-Valence Energy Landscape (BVEL) map at 873 K shows that oxygen atoms present a higher mobility around the (Ge/Cr) $\text{O}_6$  octahedra than the  $\text{MgO}_6$  ones; therefore, the “bottleneck” points for oxygen mobility are placed between the (Ge/Cr) $\text{O}_6$  octahedra around the  $\text{La}^{3+}$  and  $\text{Mg}^{2+}$  cations. The dark-red samples prepared in air show evidence of oxidation of some  $\text{Cr}^{3+}$  to  $\text{Cr}^{4+}$  to give a polaronic component to a conductivity of  $10^{-2} \text{ Scm}^{-1}$  at 300 °C for  $\text{La}_2\text{Ge}_{0.5}\text{Cr}_{0.5}\text{MgO}_{6-\delta}$ ; Arrhenius plots of conductivity obtained on cooling from 900 °C to 25 °C in air give an activation energy of  $\sim 0.25 \text{ eV}$ . The fuel-cell performance at 600 °C gave a power density of  $606 \text{ mW cm}^{-2}$ , a threefold increase over the output compared with LSGM electrolyte.

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## Introduction

Solid-oxide fuel cells (SOFC) are electrochemical devices that convert the chemical energy of a fuel into electricity in a clean and reversible way [1]. They offer a multi-fuel capability; not only hydrogen or carbon monoxide, but also various hydrocarbon species can be made as fuel by the introduction of internal or simple external fuel reforming reactions [2–7]. SOFCs rely on a solid-oxide electrolyte having a high oxide-ion conductivity  $\sigma_o$ , enabling the chemical transport of  $O^{2-}$  ions from the cathode to the anode, where they recombine with the fuel [8]. This reversible technology affords working in SOEC (solid-oxide electrolyzer cell) mode [9–12], converting electrical energy from solar, wind and nuclear energy [13] and generating  $H_2$  or methanol from steam and/or  $CO_2$  [14].

The key technical issue that has limited the development of this technology is the high operation temperatures [15],  $T_{op} \sim 1000$  °C, which results in higher system costs and performance-degradation rates, as well as slow start-up and shut-down times, the latter dramatically limiting its applicability to portable power and transportation markets [16–18]. Addressing the increasing polarization losses associated with electrolyte conduction and electrode reaction kinetics as  $T_{op}$  is lowered are the key issues limiting lower temperature operation [19,20] and have been the focus of many groups over the past few decades [21–38]. The entire SOFC material set is dependent on the selection of the electrolyte and its chemical and thermo-mechanical stability with respect to the electrodes. The vast majority of SOFCs use a zirconia-based electrolyte, typically yttrium-stabilized zirconia (YSZ) [39,40] or gadolinium-stabilized ceria (GDC) [41–43], because of its superior stability with respect to the catalytic electrolyte. Although a good oxygen-ion conductor above 800 °C, YSZ is far from having the highest conductivity [29].

The most common oxide-ion electrolytes have an oxygen-deficient, cubic fluorite or perovskite structure with oxygen transport via oxygen vacancies. However, the apatite, scheelite, Ruddlesden–Popper, and mayenite structures provide examples where oxide-ion transport is by interstitial oxide ions [22–37]. Whereas the perovskite  $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{2.81}$  (LSGM) is an example of an oxygen-vacancy conductor [23,24,44], the melilite structure of the competitive phase  $La_{1+x}Sr_{1-x}Ga_3O_{7+x}$  contains mobile interstitial oxide ions [26,27].

However, superior oxide-ion conductivity ( $\sigma_o > 10^{-2} \text{ Scm}^{-1}$ ,  $T < 500$  °C) can be realized if the vacancy movement can happen freely in all three dimensions. A new oxide-ion electrolyte based on the parent double perovskite  $La_2GeMgO_6$  phase [45] has been identified; it is the only Ge-containing perovskite existing at ambient temperature and pressure. The double perovskite  $La_2GeMgO_6$  phase crystallizes in a hexagonal cell (R3 space group) with ordering of Ge and Mg octahedra. The substitution of  $M^{3+}$  cations for  $Ge^{4+}$  introduces oxygen vacancies that can diffuse in all three directions with a low activation energy by an oxygen-vacancy mechanism, because both the  $Mg^{2+}$  and  $Ge^{4+}$  cations are stable in both tetrahedral and octahedral oxygen coordination. Indeed, we obtained superior oxide-ion conductivity ( $\sigma_o > 10^{-2} \text{ Scm}^{-1}$ ,  $T \geq 300$  °C) by substitution of  $Cr^{3+}$  for the  $Ge^{4+}$  ion in the

$La_2Ge_{1-x}Cr_xMgO_{6-\delta}$  ( $0 < x \leq 0.5$ ) series; the  $Cr^{3+}$  ions have a strong octahedral site preference and prevent the ordering of vacancies.

On the other hand, neutron powder diffraction (NPD) is a powerful tool for the determination of subtle structural details, especially in oxides [46–50]. Here we provide with precise structural characterization from (NPD) data of a selected member of the series of composition  $La_2Ge_{0.55}Cr_{0.45}MgO_{6-\delta}$ , including a visualization of the oxide-ions diffusion path, which unveils interesting peculiarities of the different octahedral coordination environments.

## Experimental

$La_2Ge_{1-x}Cr_xMgO_{6-\delta}$  ( $0 < x \leq 0.5$ ) samples were synthesized by solid-state reaction from stoichiometric amounts of  $La_2O_3$ ,  $GeO_2$ ,  $Cr_2O_3$  and  $MgO$  powders, ground and heated for 20 h at 1350 °C. The samples were obtained by slow furnace cooling to room temperature. For conductivity measurements, the resulting powders were made into pellets (typically ~0.2 cm in thickness and ~1 cm in diameter) by pressing the powder with 1 wt % of polyvinyl butyral (PVB) at 5 GPa and firing for 20 h at 1400 °C.

The phase purity of the compounds was confirmed by powder X-ray diffraction (XRD) with a Philips X'pert diffractometer (Cu  $K_\alpha$  radiation,  $\lambda = 1.5418$  Å) in Bragg-Brentano reflection geometry. Neutron powder diffraction (NPD) patterns were collected at 298, 573 and 873 K and for a selected composition  $La_2Ge_{0.55}Cr_{0.45}MgO_{6-\delta}$  at the HRPT diffractometer of the SINQ spallation source (PSI, Paul Scherrer Institute, Villigen, Switzerland). A Rietveld structure refinement was carried out with the Fullprof program. A pseudo-Voigt function was chosen to generate the line shape of the diffraction peaks. The following parameters were refined in the final runs: scale factor, background coefficients, zero-point error, pseudo-Voigt peak profiles corrected for asymmetry parameters, unit-cell parameters and isotropic thermal factors. The scattering factors for La, Ge, Cr, Mg and O were 8.24, 8.185, 3.635, 5.375 and 5.803 fm, respectively.

Single test cells were fabricated by an electrolyte-supported technique. A 300- $\mu\text{m}$ -thick  $La_2Ge_{0.5}Cr_{0.5}MgO_{6-\delta}$  (LGCM) disk was used as the electrolyte, commercial  $NiO-Ce_{0.8}Gd_{0.2}O_{2-\delta}$  (GDC) was used as the anode and  $SrCo_{0.8}Fe_{0.2}O_3$  (SCFO) was the cathode.  $NiO$ -GDC and SCFO were made into a paste with a commercial binder (V-006, Heraeus). SCFO was screen printed onto one side of the disk and fired at 1100 °C in air for 1 h.  $NiO$ -GDC was finally screen printed onto the other side of the disk and fired at 1100 °C in 5% $H_2/N_2$  for 1 h. The working electrode area of the cell was 0.24  $\text{cm}^2$  (0.6 × 0.4 cm). Pt gauze with a small amount of Pt paste in separate dots was used as current collector at both the anodic and the cathodic sides for ensuring electrical contact. The cells were tested in a vertical tubular furnace with air directly supplied to the cathode surface and hydrogen to the anode surface. The performance measurements were carried out at 550, 600, and 650 °C. The fuel-cell tests were performed with an AUTOLAB 302 N Potentiostat/Galvanostat by changing the voltage of the cell from the OCV (“Open Circuit Voltage”) to 0.1 V with steps of 0.050 V, holding 40 s at each

step. Current density was calculated by the recorded current flux through the effective area of the cell ( $0.24 \text{ cm}^2$ ).

## Results and discussion

As synthesized  $\text{La}_2\text{Ge}_{1-x}\text{Cr}_x\text{MgO}_{6-\delta}$  ( $x = 0.2, 0.3, 0.35, 0.4, 0.45, 0.5$ ) powders are dark red in color; however, undoped  $\text{La}_2\text{GeMgO}_6$  powder is off-white in color. The XRD patterns of all the compounds of the series are shown in Fig. S1 at the Supporting Information. Rietveld refinement of the XRD profile of nominal  $\text{La}_2\text{Ge}_{0.5}\text{Cr}_{0.5}\text{MgO}_{6-\delta}$  is illustrated in Fig. 1, exhibiting an excellent agreement with the profile generated in the space group R3.

A NPD investigation was essential to unveil subtle details of this double perovskite, since neutrons are sensitive to oxygen positions, yielding information on the octahedral tilting and the presence of oxygen vacancies. This was studied in a selected sample with  $\text{La}_2\text{Ge}_{0.55}\text{Cr}_{0.45}\text{MgO}_{6-\delta}$  composition. The crystal structure was defined according to the model reported for the parent  $\text{La}_2\text{GeMgO}_6$ <sup>45</sup>. In the R3 (No 146) space group, hexagonal description, the two La sites, Ge and Mg occupy the 3a (0,0,z) Wyckoff sites, whereas the two types of O are located at 9b (x,y,z) sites. Cr is statistically distributed at Ge positions. A conspicuous oxygen deficiency was identified at O1 atoms. Table 1 summarizes the main structural parameters after the Rietveld refinement of the structure. Minor impurities of  $\text{MgO}$ ,  $\text{La}_2\text{O}_3$  and  $\text{La}(\text{OH})_3$  were also included in the refinement. Fig. 2a shows the quality of the neutron fit, and Fig. 2b illustrates the crystal structure, highlighting the alternation of (Ge,Cr)O<sub>6</sub> and MgO<sub>6</sub> octahedra in the three directions.

The NPD patterns collected above room temperature ( $T = 573, 873 \text{ K}$ ) could be refined in the same space group R3, showing no evidence of phase transitions or degradation of the samples. The Supplementary Information includes Tables S2 and S3, and Figure S2a and S2b with the atomic parameters and Rietveld plots at  $T = 573$  and  $873 \text{ K}$ , respectively. Fig. 3

displays the thermal evolution of the unit-cell volume and the  $a$  and  $c$  parameters; a monotonous expansion is observed as the sample is warmed up, as expected.

On the other hand, in order to evaluate the oxygen mobility of this ionic conductor, the BondValence Energy Landscape (BVEL) was calculated. Starting from the determined atomic parameters, this methodology enables obtaining the most probable oxygen diffusion pathway across the lattice based upon bond-valence considerations [51]. Fig. 4 shows the obtained BVEL map at  $873 \text{ K}$ . In a more detailed analysis, it is possible to observe that the oxygen atoms present a higher mobility around the (Ge/Cr)O<sub>6</sub> octahedra than the MgO<sub>6</sub> ones, as shown in Fig. 5. Thus, the “bottleneck” points for oxygen mobility are placed between the (Ge/Cr)O<sub>6</sub> octahedra around the  $\text{La}^{3+}$  and  $\text{Mg}^{2+}$  cations. These points with high electrostatic energy for the  $\text{O}^{2-}$  diffusion can be quantified from BVEL through the percolation energies, tabulated in Table S4 at the SI document. Although these values cannot be related to the band gap energy obtained from *ab-initio* calculations or other experimental studies, they allow establishing some predictions about the ionic conductivity. For example, it is possible to note that at higher temperatures the mobility within the  $a$ - $b$  plane is preferable over that along  $c$  direction. By contrast, at room temperature there are not substantial differences in percolation energies, suggesting that the  $\text{O}^{2-}$  mobility is energetically isotropic in the three directions. These are in agreement with the thermal evolution of the unit-cell parameters, which show a higher increase along  $c$  than in the  $a$ - $b$  direction (see Fig. 3).

### Transport properties and thermal stability

Owing to the absence of an oxide-ion vacancy, the parent  $\text{La}_2\text{GeMgO}_6$  perovskite does not show any measurable oxide-ion conductivity even at higher temperatures. The oxide-ion conductivity ( $\sigma_o$  vs  $T$  ( $^\circ\text{C}$ )) and Arrhenius plot ( $\ln(\sigma_o)$  vs  $1000/T$  ( $\text{K}^{-1}$ )) for different  $\text{La}_2\text{Ge}_{1-x}\text{Cr}_x\text{MgO}_{6-\delta}$  ( $0 < x \leq 0.5$ )

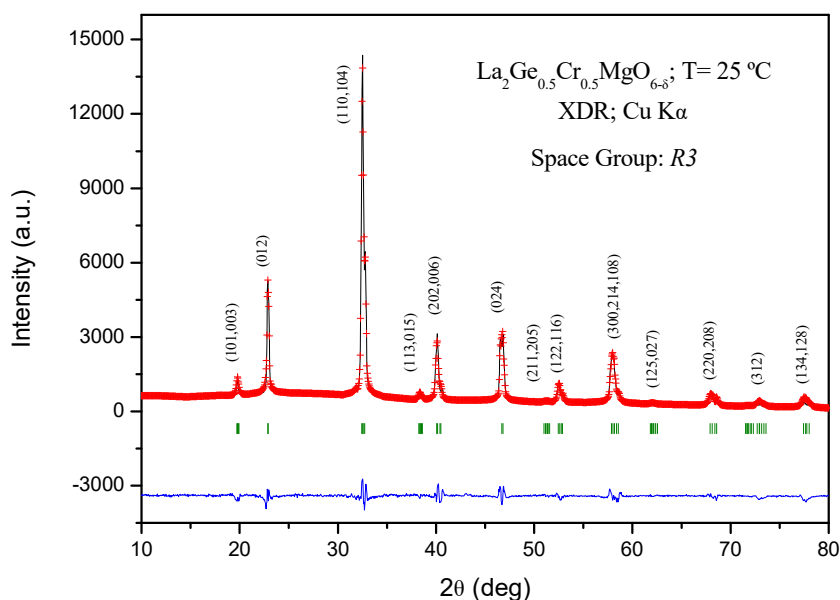
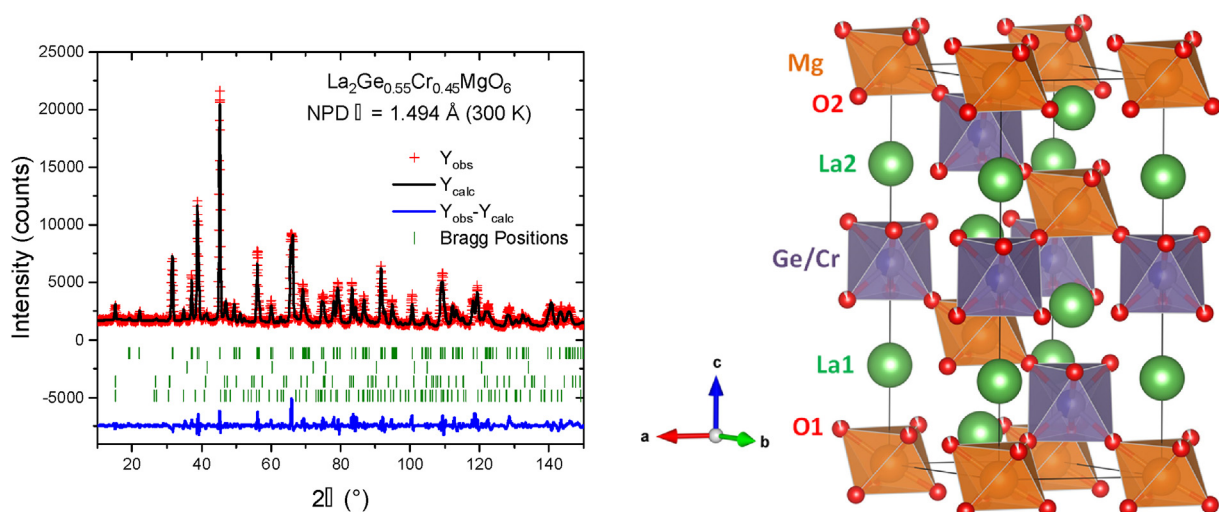


Fig. 1 – XRD Rietveld plot for  $\text{La}_2\text{Ge}_{0.5}\text{Cr}_{0.5}\text{MgO}_{6-\delta}$ , defined in the R3 space group.

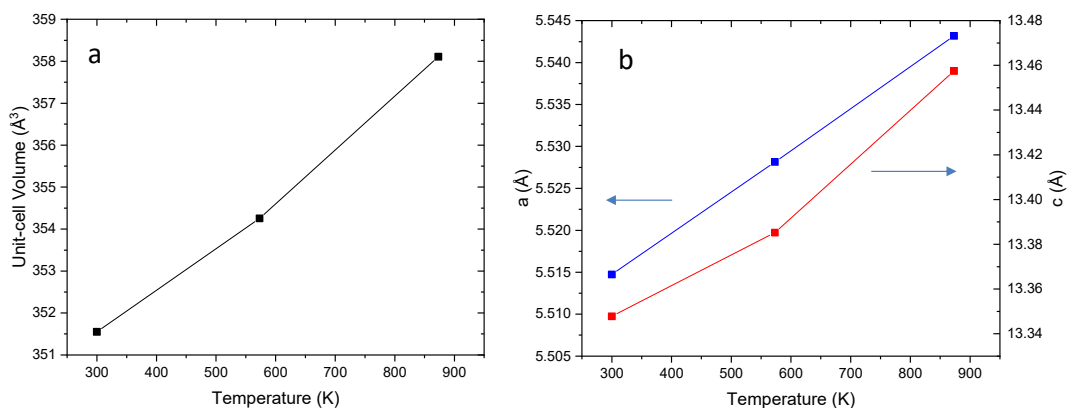
**Table 1 – Crystallographic data for  $\text{La}_2\text{Ge}_{0.55}\text{Cr}_{0.45}\text{MgO}_6$  phase in Rhombohedral R3 space group from NPD at 300 K  $a = 5.5115$  (2) Å,  $c = 13.3485$  (7) Å and  $V = 351.16$  (3) Å<sup>3</sup>.**

	x	y	Z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
La1	0.00000	0.00000	0.2473 (5)	0.0155 (11)*	
La2	0.00000	0.00000	0.7527 (5)	0.0155 (11)*	
Ge	0.00000	0.00000	0.5046 (18)	0.016 (2)*	0.55
Cr	0.00000	0.00000	0.5046 (18)	0.016 (2)*	0.45
Mg	0.00000	0.00000	0.00000	0.007 (2)*	
O1	0.1042 (17)	0.332 (3)	0.0852 (12)	0.017 (3)*	0.925 (2)
O2	0.1252 (14)	0.8022 (15)	0.5998 (6)	0.0013 (10)*	

$R_p = 6.47\%$ ,  $R_{wp} = 8.62\%$ ,  $\chi^2 = 6.52$ ,  $R_{\text{Bragg}} = 6.26\%$   
 Impurities: MgO (0.82%) and  $\text{La}_2\text{O}_3$  (2.48%)



**Fig. 2 – a) Rietveld plot from NPD data. The four series of Bragg reflections (green ticks) correspond to the main R3 perovskite phase, and minor impurities of MgO,  $\text{La}_2\text{O}_3$  and  $\text{La}(\text{OH})_3$ . b) View of the crystal structure of  $\text{La}_2\text{Ge}_{0.55}\text{Cr}_{0.45}\text{MgO}_{6-\delta}$ , illustrating the alternation of  $\text{MgO}_6$  and  $(\text{Ge}/\text{Cr})\text{O}_6$  octahedra. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)**

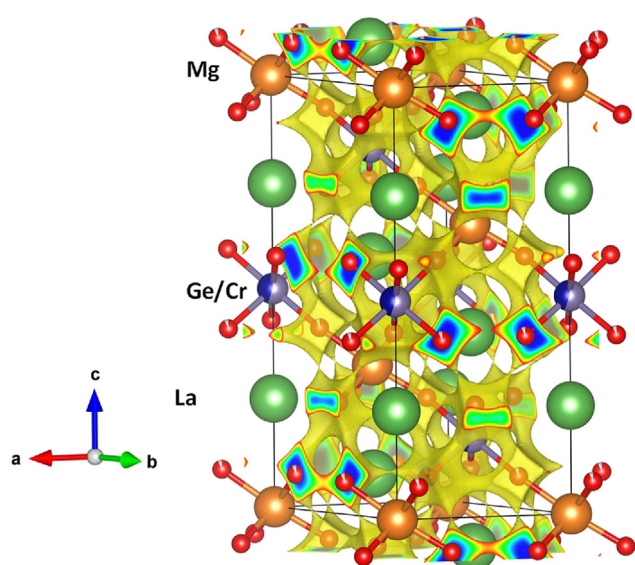


**Fig. 3 – a) Unit-cell volume and b) unit-cell parameters thermal variation for  $\text{La}_2\text{Ge}_{0.55}\text{Cr}_{0.45}\text{MgO}_6$ .**

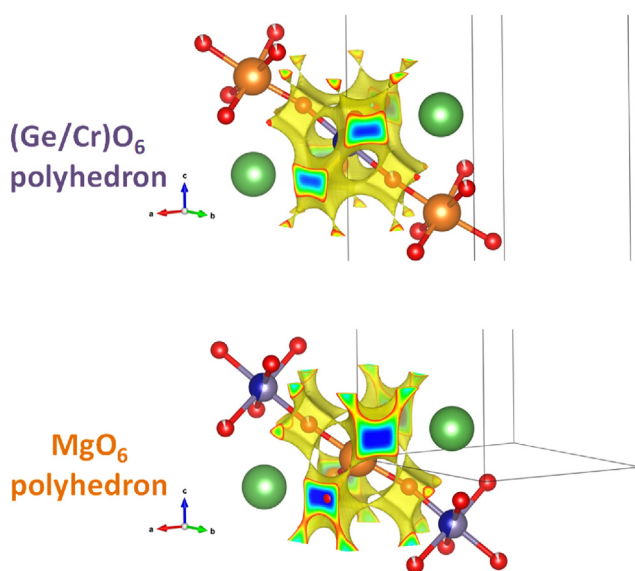
compositions are shown in Fig. 6(a–b). An additional plot of the conductivity measured in different atmospheres is shown in Fig S3. Almost the same oxide-ion conductivity was observed for the  $\text{La}_2\text{Ge}_{0.5}\text{Cr}_{0.5}\text{MgO}_{6-\delta}$  sample in all environments, which indicates the presence of a minimal electronic conductivity in the sample. The conductivity measurement

was done by cooling the sample from 800 °C to 25 °C, which also rules out the presence of protons in the sample for any protonic conductivity. The conductivities ( $\sigma_0$ ) are thus assumed to be oxide-ion only; the values determined at different temperatures and the activation energies for the different compositions of  $\text{La}_2\text{Ge}_{1-x}\text{Cr}_x\text{MgO}_{6-\delta}$  are given in Table





**Fig. 4 – Oxygen diffusion pathways across the  $\text{La}_2\text{Ge}_{0.55}\text{Cr}_{0.45}\text{MgO}_6$  structure at 873 K.**



**Fig. 5 – Percolation pathways for O diffusion around the  $(\text{Ge}/\text{Cr})\text{O}_6$  and  $\text{MgO}_6$  octahedra.**

S5 (Supporting Information). The Arrhenius plot is almost linear in the temperature range of 25–900 °C, which indicates a low activation energy (Table S5) of the mobile species (~0.25 eV) and the apparent absence of condensation of mobile oxide-ion vacancies above 200 °C. The oxidation of some  $\text{Cr}^{3+}$  to  $\text{Cr}^{4+}$  introduces a polaronic conduction that contributes little to the low-temperature conductivity. The oxide-ion conductivity increases with increasing amount of  $\text{Cr}^{3+}$  substitution for  $\text{Ge}^{4+}$  ( $x$ ), which increments the oxide-ion vacancy concentration. The maximum oxide-ion conductivity of  $1.37 \times 10^{-2} \text{ Scm}^{-1}$  at  $T_{\text{op}} = 300 \text{ }^\circ\text{C}$  was observed for  $x = 0.5$ ,  $\text{La}_2\text{Ge}_{0.5}\text{Cr}_{0.5}\text{MgO}_{6-\delta}$  (Table S5). A similar conductivity was observed for other well-known oxide-ion conductors only at much higher temperatures, i. e. for YSZ ( $\text{Zr}_{1-x}\text{Y}_x\text{O}_{2-0.5x}$  ( $x = 0.08$ )

at  $T \geq 700 \text{ }^\circ\text{C}$ , LSGM ( $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{3-\delta}$ ) at  $T \geq 600 \text{ }^\circ\text{C}$ , for GDC ( $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ ) at  $T \geq 500 \text{ }^\circ\text{C}$  and SNS ( $\text{Sr}_{0.55}\text{Na}_{0.45}\text{SiO}_{2.775}$ ) at  $T \geq 500 \text{ }^\circ\text{C}$ ) [29].

Fig. S4 shows the thermogravimetric analysis (TGA) of nominal  $\text{La}_2\text{Ge}_{0.5}\text{Cr}_{0.5}\text{MgO}_{6-\delta}$  obtained in air and 5% $\text{H}_2/\text{N}_2$  flow. The curves display the loss of adsorbed  $\text{H}_2\text{O}/\text{CO}_2$  between 225 and 400 °C in oxidizing atmosphere, and also oxygen between 300 and 800 °C in reducing atmosphere. In oxidizing conditions, we observed an oxidation step of the sample above 620 °C that is due to the oxidation of  $\text{Cr}^{3+}$  to  $\text{Cr}^{4+}$ . The difference in the weight loss between the TGA runs in air and in 5%  $\text{H}_2/\text{N}_2$  clearly shows the presence of  $\text{Cr}^{4+}$  in a sample prepared at 1350 °C and slow-cooled in air, as well as the possibility of eliminating the oxidation of the  $\text{Cr}^{3+}$  by reducing the electrolyte at or above 800 °C and retaining the reducing atmosphere to below 620 °C. Upon cooling, there is little change in the weight from the high-temperature value in either atmosphere. A  $T_{\text{op}} < 600 \text{ }^\circ\text{C}$  would prevent oxidation of  $\text{Cr}^{3+}$  in an operating SOFC. However, the red color of our sample indicates the 3d electrons on the  $\text{Cr}^{4+}/\text{Cr}^{3+}$  couples are localized; the polaronic contribution to the conductivity is, therefore expected to be small. In order to show the performance of the electrolyte containing a small  $\text{Cr}^{4+}$  concentration, we have used the electrolyte disk/pellets as-sintered at 1400 °C. We also characterized the samples after TGA up to 900 °C in air and 5% $\text{H}_2/\text{N}_2$  by XRD. Rietveld refined powder XRD profiles of the samples after TGA are shown in Fig. S5 at the Supporting Information. The compound remained in the perovskite R3 structure and no impurity phases were detected, which confirms the stability of the material in a reducing as well as an oxidizing environment.

#### Thermal expansion (dilatometry)

In order to determine the applicability of the electrolyte in a SOFC, the mechanical compatibility of the electrolyte with other SOFC components was determined: a dilatometric analysis was performed between 35 and 900 °C for several cycles; the data were only recorded during the heating runs. Fig. 7 shows no abrupt changes in the thermal expansion of  $\text{La}_2\text{Ge}_{0.5}\text{Cr}_{0.5}\text{MgO}_{6-\delta}$  in all the temperature range under measurement. The thermal expansion coefficient (TEC) measured under air and 5%  $\text{H}_2/\text{N}_2$  atmospheres between 100 and 900 °C are  $11.3 \times 10^{-6} \text{ K}^{-1}$  and  $11.1 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ , respectively. Similar values for both electrolyte and electrode components are critical to avoid cracking problems during the start-up/shut-down cycles and the SOFC operation. These values match well with the values usually displayed by SOFC electrodes and other electrolytes (e.g. for LSGM,  $\text{TEC} = 11.6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ) [52,53]. The chemical compatibility of  $\text{La}_2\text{Ge}_{0.5}\text{Cr}_{0.5}\text{MgO}_{6-\delta}$  with a  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  cathode was checked by firing (1:1) mixtures of the powdered materials at 600 °C in air for 24 h; the inset of Fig. 7 shows a Rietveld analysis of the products consisting of a mixture of the unaltered phases.

#### Test SOFC

The performance of  $\text{La}_2\text{Ge}_{0.5}\text{Cr}_{0.5}\text{MgO}_{6-\delta}$  as an electrolyte was tested in single cells in a 300- $\mu\text{m}$ -thick electrolyte-supported configuration. Fig. 8 illustrates the cell voltage

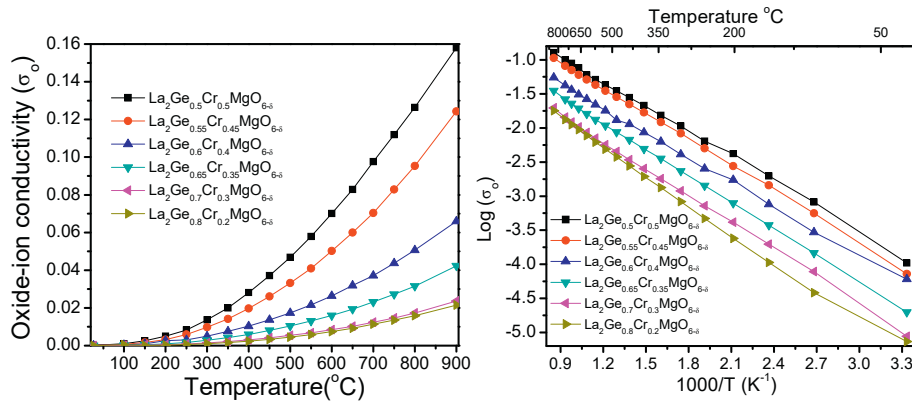


Fig. 6 – (a) Oxide-ion plus polaronic conductivity ( $\sigma_0$  vs temperature ( $^{\circ}\text{C}$ )); (b) Arrhenius ( $\text{Log } \sigma_0$  vs  $1000/T(\text{K})$ ) plot for  $\text{La}_2\text{Ge}_{1-x}\text{Cr}_x\text{MgO}_{6-\delta}$ .

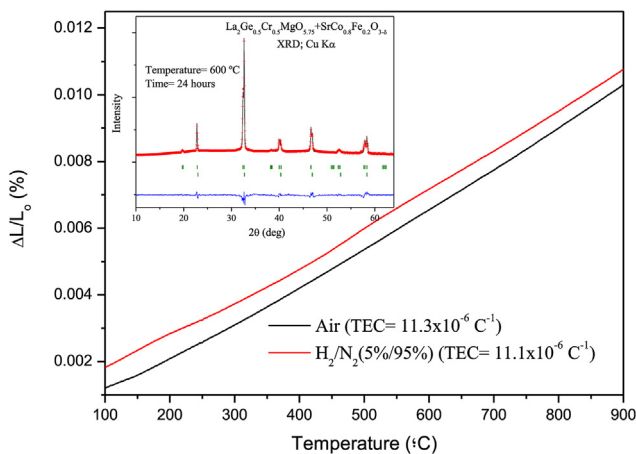


Fig. 7 – Thermal expansion determined by dilatometry of the  $\text{La}_2\text{Ge}_{0.5}\text{Cr}_{0.5}\text{MgO}_{6-\delta}$ . The inset shows the Rietveld-refined XRD profiles of a mixture of unaltered  $\text{La}_2\text{Ge}_{0.5}\text{Cr}_{0.5}\text{MgO}_{6-\delta}$  and  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  after a thermal treatment at  $600^{\circ}\text{C}$  in air, showing no reaction products.

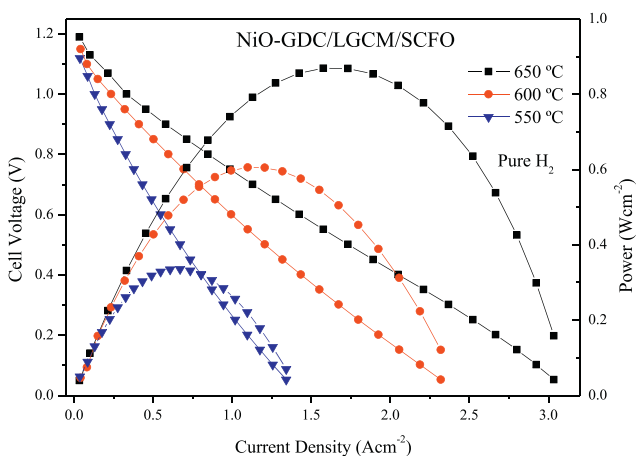


Fig. 8 – Cell voltage (left axis) and power density (right axis) as a function of the current density for the test cell with the configuration Ni-GDC/ $\text{La}_2\text{Ge}_{0.5}\text{Cr}_{0.5}\text{MgO}_{6-\delta}$  (LGCM)/SCFO in pure  $\text{H}_2$  measured at  $T_{\text{op}} = 550, 600$  and  $650^{\circ}\text{C}$ .

and power density as a function of current density at 550, 600 and 650  $^{\circ}\text{C}$  for single cells fed with pure  $\text{H}_2$  with a NiO-GDC anode. The maximum power densities generated by the cell are 336, 606 and 869  $\text{mW cm}^{-2}$ , respectively. The peak power density of 606  $\text{mW cm}^{-2}$  obtained at 600  $^{\circ}\text{C}$  with  $\text{La}_2\text{Ge}_{0.5}\text{Cr}_{0.5}\text{MgO}_{6-\delta}$  is impressive; it overcomes the best peak power densities of 431  $\text{mW cm}^{-2}$  at 600  $^{\circ}\text{C}$  for a 294- $\mu\text{m}$ -thick  $\text{Sr}_{0.55}\text{Na}_{0.45}\text{SiO}_{2.775}$  electrolyte [28,38] and for a 200- $\mu\text{m}$ -thick LSGM-based SOFC, viz. 200  $\text{mW cm}^{-2}$  at 600  $^{\circ}\text{C}$  [54]. This performance represents a more than 3-fold power enhancement. The performance test at 600  $^{\circ}\text{C}$  shows the potential of achieving a low-temperature ( $300^{\circ}\text{C} < T_{\text{op}} < 600^{\circ}\text{C}$ ) SOFC with several important technical application if, in particular, an efficient catalytic cathode for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) at  $T_{\text{op}} < 500^{\circ}\text{C}$  can be developed.

## Conclusions

The double-perovskite  $\text{La}_2\text{MgGe}_{0.55}\text{Cr}_{0.45}\text{O}_{6-\delta}$ , studied from NPD data, illustrates the structural behavior of the  $\text{La}_2\text{Ge}_{1-x}\text{Cr}_x\text{MgO}_{6-\delta}$  series. The presence of Cr distributed at random with Ge ions accounts for the presence of a conspicuous oxygen deficiency, responsible for the transport properties. BVEL maps show that the ionic transport is enabled around the smaller (Ge/Cr)O6 octahedra, probably by a steric effect. The member with  $x = 0.5$  shows a high oxide-ion conductivity  $\sigma_0 > 10^{-2} \text{ Scm}^{-1}$  below 350  $^{\circ}\text{C}$ . The high oxide-ion mobility confirms the strategy of designing a perovskite containing cations stable in both octahedral and tetrahedral oxygen coordination, and the introduction of a cation with a strong octahedral-site preference to frustrate oxygen-vacancy ordering as in a brownmillerite phase. The superior performance of  $\text{La}_2\text{MgGe}_{0.5}\text{Cr}_{0.5}\text{O}_{6-\delta}$  as the electrolyte of a SOFC operating at 600  $^{\circ}\text{C}$  appears to be limited by the catalytic electrodes; the perovskite cathode used may cation-exchange with the electrolyte above 600  $^{\circ}\text{C}$ . The threefold increase in power density output in the SOFC performance test at 600  $^{\circ}\text{C}$  shows the potential of achieving a low-temperature ( $T_{\text{op}} \geq 300^{\circ}\text{C}$ )  $\text{La}_2\text{MgGe}_{0.5}\text{Cr}_{0.5}\text{O}_{6-\delta}$ -based SOFC with important technical applications.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2022.12.193>.

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