Conductivity of strontium- and lithium-doped-lanthanum orthogallate
(La$_{0.9}$Sr$_{0.1}$Ga$_{1-y}$Li$_y$O$_{3-\delta}$; $y=0.05$ and $0.10$) synthesized via
metal nitrate–glycine gel route

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Abstract

Strontium- and magnesium-doped-lanthanum orthogallate have emerged as promising alternative solid electrolytes for solid-oxide fuel cells in the intermediate-temperature regime. In accordance with the theoretical consideration, doping by a monovalent ion at the B-site is envisaged to increase the defect concentration and enhance the oxide ion conductivity. With this aim, strontium- and lithium-doped-lanthanum orthogallate formulations (La$_{0.9}$Sr$_{0.1}$Ga$_{1-y}$Li$_y$O$_{3-\delta}$; $y=0.05$ and $0.10$) were synthesized via soft-chemistry route of metal nitrate–glycine combustion. Systematic phase and microstructural evolution as a function of processing temperature was followed by X-ray diffraction and scanning electron microscopy of the calcined and sintered samples. Electrical characterization on the sintered sample by the 4-point DC and AC impedance measurements in the temperature range of 550–850 °C showed that Li-doping at B-site in LaGaO$_3$ yielded conductivity higher than that of yttria-stabilized zirconia, but somewhat inferior to the Mg-doped analogs.

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1. Introduction

Among several material-related problems encountered by present days’ high temperature (1000 °C) yttria-stabilized zirconia (YSZ) electrolyte-based SOFCs, the interaction and pronounced thermal expansion mismatch among cell components are the most significant [1–5]. An effective way of diminishing the impact of these mitigating factors is to lower the operating temperature to about 800 °C. This calls for the development of new material formulations. It is well known that the solid solution range of a perovskite structure could be extended greatly by balancing the oxygen vacancies corresponding to ionic substitution at the A- and the B-site [6]. It was proposed that a predominant and exclusive oxide ion conductor could be realized by doping LaGaO$_3$ with Mg-ions at the Ga-site [7], thereby providing an alternative oxygen ion membrane for solid-oxide fuel cell (SOFC) application. Based on this it has been shown that LaGaO$_3$ doped with Sr for La (A-site) and Mg for Ga (B-site) exhibits high and exclusive oxide ion conductivity, and studies published during the past decade, have shown that doped-LaGaO$_3$ is indeed a viable alternative to the high temperature yttria-stabilized zirconia (YSZ) electrolyte in the intermediate-temperature ceramic solid-oxide fuel cells (IT-SOFCs) [8–20]. The rare-earth orthogallates (RGAO$_3$, $R$=La to Lu) are known to crystallize in perovskite structures that are either cubic or orthorhombic (pseudocubic). These have been grown as single crystals and their structural aspects studied in detail for almost half a century [21–26]. The conductivity of formulations partially doped with Mg$_{2+}$ ions at the B-site and with Sr$_{2+}$ ions at the A-site were found to be better or comparable to that exhibited by YSZ. Other compositions wherein the B-site cation (Ga$_{3+}$) is partially substituted by Ni$_{2+}$ or Zn$_{2+}$ and Fe$_{3+}$ or Cr$_{3+}$ have also been synthesized and
their microstructural and electrical characterization carried out [27–35]. Advancing the state-of-the-art, composite anode (Ni-LSGX) and cathode (LSM-LSGX) formulations, where X is an aliovalent cation of ionic size comparable to that of Ga$^{3+}$, have been fabricated and tested in button fuel cell formats [36–39].

It has been observed that the synthesis of doped-LaGaO$_3$ invariably leads to the formation of La$_4$Ga$_2$O$_9$ (La$_2$O$_3$ : Ga$_2$O$_3$ = 2:1) as the most prominent impurity phase, irrespective of the method of synthesis. When the A-site is partially substituted by an aliovalent ion such as strontium, other phases such as LaSrGaO$_4$, are also formed. A microstructural evidence of the formation and increasing amount of unwanted phases with systematic increase in the dopant concentration in the La$_{0.9}$Sr$_{0.1}$Ga$_{1-x}$Mg$_x$O$_{3-\delta}$ ($0.2 \leq x \leq 0.5$; $\delta$ = oxygen non-stoichiometry factor) system has been reported by Azad and Er [40], where the formulations were shown to have undergone drastic microstructural changes in the sintered bodies both in terms of the morphological features and abnormal grain growth. These impurity phases which are either semiconducting or insulating in nature, tend to disappear (via reaction) at higher temperatures. However, if their residual concentration is appreciable, it would have a direct and undesirable influence on the conductivity of the electrolyte composition.

A clear understanding of the reaction pathways leading to the impurity phases would certainly provide a mechanism to suppress their formation to begin with. With this aim the study reported in this communication, using pure lanthanum orthogallate as the model system and that on the A- and B-site substituted formulations was undertaken. In order to avoid the

Fig. 1. Systematic progress (L to R) of gel formation leading to exothermic combustion and ceramic phase formation from the metal nitrate–glycine precursor solution at $\sim$ 200 °C.
use of extreme processing conditions, which generally lead to impure materials, the materials were synthesized by a soft-chemistry route, viz., the metal nitrate–glycine combustion technique. The as-combusted and the processed powders were thoroughly characterized by simultaneous TG-DSC (thermo-gravimetry-differential scanning calorimetry), XRD (X-ray diffraction), laser-Raman spectroscopy and density measurements. The morphological features in the calcined powders and the sintered compacts were ascertained by scanning electron microscopy (SEM), while the technique of ICP-MS was employed for the compositional analyses. Electrical conductivity of the sintered bodies was measured by the 4-point DC and AC impedance techniques.

2. Experimental

Lanthanum nitrate (La(NO$_3$)$_3$·6H$_2$O, purity 99.9%), gallium nitrate (Ga(NO$_3$)$_3$·xH$_2$O; $x=7.7$–9.6, purity 99.999%), strontium nitrate (Sr(NO$_3$)$_2$, purity 99.999%), lithium nitrate (Li(NO$_3$), purity 99.999%), glycine (CH$_2$NH$_2$COOH, purity 98.5+) from
Alfa-Aesar, and ammonium nitrate (NH$_4$NO$_3$, purity 99.3%) from Fischer Scientific, were used as the starting material for the synthesis of pure (x$_{Sr}$=0) and (x$_{Sr}$=0.10 and y$_{Ga}$=0.05 and 0.01) lanthanum orthogallate utilizing the following combustion reactions:

$$9[\text{La(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O}] + 9[\text{Ga(NO}_3\text{)}_3 \cdot 9.6\text{H}_2\text{O}] + 32\text{CH}_2\text{NH}_2\text{COOH} + 9\text{NH}_4\text{NO}_3 \rightarrow 9\text{LaGaO}_3 + 238.4\text{H}_2\text{O} + 64\text{CO}_2 + 52\text{N}_2$$

(1)

$$0.9[\text{La(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O}] + 0.1\text{Sr(NO}_3\text{)}_2 + 0.95[\text{Ga(NO}_3\text{)}_3 \cdot 7.7\text{H}_2\text{O}] + 0.05\text{LiNO}_3 + (13/4)\text{CH}_2\text{NH}_2\text{COOH} + (1/8)\text{NH}_4\text{NO}_3 \rightarrow \text{La}_4\text{O}_6\text{Sr}_2\text{Ga}_9\text{O}_{10.05}\text{O}_2.9 + (67/8)\text{H}_2\text{O} + 12.71\text{H}_2\text{O} + (13/2)\text{CO}_2 + (9.3/2)\text{N}_2$$

(2)

$$0.9[\text{La(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O}] + 0.1\text{Sr(NO}_3\text{)}_2 + 0.9[\text{Ga(NO}_3\text{)}_3 \cdot 7.7\text{H}_2\text{O}] + 0.1\text{LiNO}_3 + (13/4)\text{CH}_2\text{NH}_2\text{COOH} + (3/8)\text{NH}_4\text{NO}_3 \rightarrow \text{La}_4\text{O}_6\text{Sr}_2\text{Ga}_9\text{O}_{10.1}\text{O}_{0.85} + (71/8)\text{H}_2\text{O} + 12.33\text{H}_2\text{O} + (13/2)\text{CO}_2 + (9.7/2)\text{N}_2$$

(3)

As can be seen, the stoichiometry was so chosen that the amount of ammonium nitrate was minimized and that all the byproducts were gaseous water, carbon dioxide and nitrogen. Glycine was used as a fuel for the combustion reaction while ammonium nitrate served as the initiator/igniter.

Appropriate amounts of the chemicals were weighed and dissolved separately in minimum amount of de-ionized water by gentle but constant stirring for 1 h. The clear solutions were combined and further stirred for additional 1 h to ensure thorough and homogenous mixing of all the constituents on an ionic level. The solution (in 40 mL aliquots) was placed in a 1000 mL capacity beaker and heated gradually on a hotplate up to $\sim 200 \degree C$ (2º/min) in a fume hood. Aluminum foil in the form of a snugly fitting long hollow cylinder was fitted at the open end of the beaker in order to avoid/minimize the loss of solid material from getting airborne due to the reactive exothermic combustion. As the water evaporation in the mixture neared completion, the solution turned brownish, became a viscous, and somewhat frothy gel which finally combusted into visible flames, releasing copious amount of gases as per the reactions shown above. After the combustion was complete, the resulting light, dry and fluffy powder was collected and crushed in a mortar and pestle, ball-milled for 1 h followed by sieving through a 325 mesh.

A portion of the as-combusted powder was used for analysis by TG-DSC, XRD and Raman spectroscopy, while the larger portion was calcined in a range of temperatures to examine the systematic evolution of phase structure and their crystallinity.

![Fig. 4. Phase evolution in precursor gel fired at 800 °C for 4 h and 1000 °C for 2 h in air.](image)

Table 1

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<th>b (pm)</th>
<th>c (pm)</th>
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<td>548.40</td>
<td>777.87</td>
<td>234.57</td>
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</table>

Comparison of the lattice parameters of LaGaO$_3$ reported in the literature.
via powder X-ray diffraction. Phase identification was carried out by power X-ray diffraction on a Scintag 2000 machine at room temperature, in the range of 20–60° (2θ) at a scan rate of 1° min⁻¹, using monochromatic CuKα₁ (λ=1.5406 Å) radiations and Ni filter. The X-ray data were used to derive the lattice parameters and unit cell volume. The X-ray data were used to derive the lattice parameters and unit cell volume. The as-combusted gel and the calcined samples were subjected to Raman spectroscopic measurement to discern the presence/absence of any functional groups and the carbon impurities in the ceramic powders. The powder density measurements were carried out on an AccuPyc 1330 Automatic Gas Pycnometer (Micromeritics, Norcross, GA, USA) and the morphological features in the as-combusted and calcined powders as well as those in the sintered bodies were ascertained by scanning electron microscopy (Philips XL30 SEM). The calcined material was crushed, homogenized by thorough mixing, mixed with small amount of aqueous solution of polyvinyl alcohol (PVA) as binder and pressed into pellets by uniaxial pressing with a force of 6000 lb followed by cold isostatic pressing at 25,000 psi. The pellets were sintered in air at 1450 °C for 2 h. The density of the sintered

Fig. 5. Systematic variation of crystallographic density of REGaO₃ for La to Lu (○) [26]; ♦ is the density value computed from X-ray data and ▲ is the pycnometric powder density of LaGaO₃ measured experimentally in this work.

Fig. 6. Room temperature Raman spectra of the as-combusted gel and the samples fired at 800 °C/4 h and 1000 °C/2 h.
bodies was measured by Archimedes principle using a Mettler kit. The 4-point DC conductivity measurements were carried out on rectangular bars cut from sintered discs using an Agilent 34401A digital multimeter, while the AC impedance data were collected on the sintered pellets using a Solartron 1260 impedance analyzer in the frequency range of $10^{-3}$ Hz to $10^6$ Hz.

3. Results and discussion

3.1. Pure lanthanum orthogallate (LaGaO$_3$)

The chronological progress of the organometallic nitrate–glycine complex through the stages of solution, gelation and combustion is shown in Fig. 1.

![Figure 7](image1.png)

**Fig. 7.** Morphological features in the as-combusted gel of the glycine–nitrate precursor (top) and the gel fired at 800 °C/4 h (bottom left) and 1000 °C/2 h (bottom right).

![Figure 8](image2.png)

**Fig. 8.** Comparative XRD patterns of the 5 mol% Li-doped-lanthanum orthogallate powders calcined at different temperature; as prep: as-combusted gel, 8004: calcined at 800 °C/4 h, 9002: calcined at 900 °C/2 h, and 9008: calcined at 900 °C/8 h.
A simultaneous TG-DSC scan on the as-combusted gel collected on a simultaneous thermal analyzer (TA Instruments, Model SDT Q600) in air at a heating rate of 10°/min is shown in Fig. 2. Though the sample continued to lose weight up to about \( \sim 1200 \) °C, the overall weight loss in the entire temperature range is only about \( \sim 3\% \). Moreover, the DSC profile shows very small heat changes. Therefore, the observed weight changes are mostly the loss of moisture or that of adsorbed gases from the combustion reaction Eq. (1) in the lower temperature regime and are not accompanied by any significant decomposition, compound formation or phase transformation. This indicates that the combustion reaction at \( \sim 200 \) °C was complete and did lead to the formation of the lanthanum orthogallate as a dominant phase with no discernable remnant of the undecomposed glycine complex in the combusted gel.

This conclusion is strengthened by the XRD patterns collected on the as-combusted gel as well as on the powders fired at 700 °C for 4 h, shown in Fig. 3. For the ready identification, peaks belonging to the target phase have been indexed. It can be seen that LaGaO\(_3\) is formed as a majority phase even in the as-combusted powder. The un-indexed peaks were identified as those belonging to lanthanum oxide and gallium oxide which are noticeably present even in the powder calcined at 700 °C for 4 h.

Based on these results and in order to discern the heat treatment that would lead to phase-pure LaGaO\(_3\), small portions of the powder from combusted gel were fired for 4 h at 800 and 900 °C and for 2 h at 1000 °C. The XRD patterns of the powders calcined at 800 and 1000 °C are shown in Fig. 4.

It is evident that lanthanum orthogallate of extremely high phase purity could be derived by firing the as-combusted...
precursor to as low a temperature as 800 °C for 4 h. There was no change in the XRD signature of the powders fired at temperatures higher than 800 °C, as seen from Fig. 4. This is in an obvious and advantageous contrast to the traditional ceramic processing route of ‘heat-and-beat’, where the powder mixtures are required to be heated several times at much higher temperatures with multiple intermittent grinding and homogenization. Even the precursors derived via co-precipitation, such as mixed oxalate, ought to be calcined at relatively much higher temperatures than reported here in order to obtain the target compound with such a high purity. Similar solution–combustion-synthesis scheme has been employed by several groups in the past for the preparation of perovskite-based systems [41–44].

The XRD data on the powders calcined at 800 °C and above were used to determine the lattice parameters of the unit cell of the LaGaO₃ synthesized in this work and are given as:

\[
a = 549.881(2) \times 10^{-12} \text{ m}, \quad b = 548.400(0) \times 10^{-12} \text{ m} \quad \text{and} \quad c = 777.872(0) \times 10^{-12} \text{ m}
\]

From these, the unit cell volume was computed as 234.571 × 10⁻³⁰ m³ [45]. These values are shown in Table 1 along with those reported by other investigators, for ready comparison.

As can be seen from Table 1, there is a total consensus about the crystal structure and lattice parameters of lanthanum orthogallate, though there are some reported disagreements regarding those of the doped-LaGaO₃ phase.

Surprisingly, there is no data reported in the literature on the density of LaGaO₃ powder. Geller [21] has listed a value of 7.21 g cm⁻³ for the X-ray density of LaGaO₃, presumably for the single crystal sample. Based on the reported crystallographic data on rare-earth orthogallates (REGaO₃, where RE = La to Lu) [22], their theoretical densities were calculated by using the relationship:

\[
\rho (\text{g/cm}^3) = \frac{Z \times \text{MW(g/mol)}}{N_A \times (\text{mol}) \times V_C (\text{cm}^3)}
\]

(5)

where Z = coordination number (= 4) for perovskite belonging to the space group Pbnm, \(N_A\) = Avagadro’s number (= 6.023 × 10²³/mol), and \(V_C\) = unit cell volume.

A plot of X-ray density thus calculated vs. atomic number of the rare-earth element in the orthogallate is found to be linear and is shown in Fig. 5.

Table 2
<table>
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<th>Parameter</th>
<th>LG</th>
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<td>a</td>
<td>5.524</td>
<td>5.543</td>
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<tr>
<td>b</td>
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<td>5.516</td>
<td>5.516</td>
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<tr>
<td>c</td>
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<tr>
<td>Volume</td>
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<tr>
<td>(\rho \text{ (g/cm}^3)</td>
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<td>6.853</td>
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that in the lower wavenumber regime (< 1000 cm\(^{-1}\) and not shown here) the Raman excitations typical of lanthanum oxide [50,51] or gallium oxide [52–54], were totally absent in the fired samples. These experimental findings corroborate the observation made in the light of X-ray diffraction results discussed above.

The morphological features of lanthanum orthogallate in the as-combusted gel are shown in Fig. 7 (top) and those of the fired samples in Fig. 7 (bottom). Submicron particles with uniform and narrow particle size distribution can be clearly seen in the agglomerates.

3.2. Li-doped-lanthanum orthogallate (La\(_{0.9}\)Sr\(_{0.1}\)Ga\(_{1−y}\)Li\(_y\)O\(_{3−δ}\))

The XRD patterns of La\(_{0.9}\)Sr\(_{0.1}\)Ga\(_{0.95}\)Li\(_{0.05}\)O\(_{2.90}\) (LSGL1) and La\(_{0.9}\)Sr\(_{0.1}\)Ga\(_{0.90}\)Li\(_{0.10}\)O\(_{2.85}\) (LSGL2) powders calcined at 800 and 900 °C for different duration are compared with those of the as-combusted gels in Figs. 8 and 9, respectively.

A careful analysis of the diffraction pattern collected on the as-combusted gel revealed the formation of the targeted phase along with La\(_4\)Ga\(_2\)O\(_9\). Thus, it appears that the formation of this phase is inevitable when working with doped-lanthanum gallate system as reported by others [54–56]. Furthermore, Li\(_2\)CO\(_3\) was also detected (in addition to La\(_4\)Ga\(_2\)O\(_9\)) in the calcined powders whose concentration (in terms of peak intensity) increased monotonically as lithium doping increased. The analysis of the diffractograms shown in Figs. 8 and 9 further suggests that the amount of the target phase in calcined samples increased progressively, compared to that in the as-prepared samples.

The SEM images shown in Fig. 10 compare the morphological features of the as-combusted LSGL1 gel with those in calcined powder. These micrographs show that the particle size in the material derived via soft-chemistry route is much smaller compared to that generally seen in the solid-state reaction-derived samples. Also, the particle size distribution is narrow (varying between 200 to 500 nm). Hence, the nitrate–glycine gel route offers a clear advantage over the solid-state reaction which requires calcination at much higher temperatures than employed hitherto. The morphological features of the calcined LSGL2 powders are shown in Fig. 11.

The XRD signatures of the sintered bodies are shown in Fig. 12.

A comparison of the diffractograms shown in Fig. 12, with those for the calcined samples shown earlier, reveals that the expected phase purity in the sintered samples was achieved with a small amount of the impurity phase (La\(_4\)Ga\(_2\)O\(_9\)). The diffraction data was used to determine the cell constants and the unit cell volume of the doped formulations, which are given in Table 2 along with those of pure lanthanum orthogallate.

The calculations show that the cell parameters remain unaltered up to a Li-doping of 10 mol%; however, the density

<table>
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<th>Treatment</th>
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<th>Ga</th>
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Table 3

ICP-MS results (in ppm) on the LSGL compositions
showed a monotonic decrease. These observations should be substantiated in the light of other characterizations, such as microstructural, chemical and electrical measurements.

The electron micrographs collected on the sintered samples show the material possessing rather small (≤ 1 μm) grains, as seen from Fig. 13. In order to assess the uniformity of densification in the bulk of the samples, images were also collected on the fractured (but unpolished) surfaces as well.

Solid electrolytes for use as oxide ion membranes in SOFCs are required to have a fully dense microstructure. The presence of pores in the structure and the impurity phase, if present, will reflect on the conductivity of these formulations. Fig. 14 shows the conductivity of the two doped compositions, measured by using 4-point as well as the impedance technique.

The activation energy calculated from the Arrhenius plots ($\sigma = A\exp(\frac{Q}{kT})$) are 1.11, 0.74, 0.76, and 0.86 eV, for YSZ, La$_{0.9}$Sr$_{0.1}$Ga$_{0.95}$Li$_{0.05}$O$_{2.9}$ (LSGL1) La$_{0.9}$Sr$_{0.1}$Ga$_{0.90}$Li$_{0.10}$O$_{2.85}$ (LSGL2) and La$_{0.9}$Sr$_{0.05}$Ga$_{0.8}$Li$_{0.01}$O$_{3}$−δ, respectively. The conductivity of the LSGL1 and LSGL2 is seen to decrease with increasing Li concentration. This is contrary to the expected trend, since the conductivity should ideally increase with the level of B-site substitution by an aliovalent ion by virtue of increase in the oxygen ion vacancies. The comparative Arrhenius plots also show that both the compositions (LSGL1 and LSGL2) have better conductivity than YSZ up to 650 °C. However, when compared with the much studied Mg-doped-lanthanum gallate compositions, the conductivity of even LSGL1 is about an order of magnitude lower [57]. This is in fundamental contradiction with the theoretical predictions of the defect equilibria that monovalently doped-lanthanum gallate would have superior conductivity than the divalent doped analog due to the higher concentration of oxygen ion vacancies in the former. Among all, the conductivity reported by Jena et al. [49] on La$_{1-x}$Sr$_{x}$Ga$_{5-y}$O$_{3-4x}$ is the most inferior. As such, it is rather difficult to justify the stoichiometry of this sample, since the material balance at both A- and B-sites cannot be justified unless the composition is cation-deficient at both A- and B-sites. The authors [49], however, do not shed any light on this aspect. Furthermore, as stated above, the sample was sintered at 1350 °C and achieved a density of ~ 89% theoretical. Thus, the inferior conductivity observed by Jena et al. [49] could be an artifact of significant porosity in conjunction with rather low level of lithium dopant concentration.

In order to understand the observed anomaly in the measured conductivity data, a thorough and systematic compositional analysis of the powder and the sintered samples is warranted. For that purpose, the as-prepared, calcined and sintered samples were analyzed using inductively coupled plasma-mass spectrometry (ICP-MS) and the results are presented in Table 3.

The compositional analysis of the as-prepared and the calcined powder samples show that the composition of all the metallic constituents are in the expected range within the limits of experimental errors except for Li. The amount of Li decreased from that in the as-prepared to the calcined powders and further in the sintered bodies. It is reasonable to speculate that as far as lithium is concerned, the good agreement among the expected values and those in the as-prepared and calcined powders is due to the fact that lithium was present in the latter samples albeit as Li$_2$CO$_3$. It may be recalled that this was evidenced in the XRD signatures of all the calcined samples. Giving the cognizance to the fact that Li$_2$CO$_3$ melts at 723 °C and boils at 1310 °C, it is likely to have escaped during sintering before in lieu of being incorporated completely into the structure of lanthanum gallate. This theory is corroborated by the lower than expected density values in the calcined powders and sintered bodies. As seen from Table 4, the low density values of the as-prepared and the calcined powders are due to the presence of the impurity phases such as La$_6$Ga$_2$O$_9$ and Li$_2$CO$_3$. The effect of the presence of Li$_2$CO$_3$ is more pronounced in the as-combusted and calcined powders because of its lower density (2.11 g/cm$^3$). The density of the sintered bodies is significantly lower than the theoretical values (shown within parentheses, derived from XRD data) and could be explained due to the aforementioned loss of lithium at high temperatures leading to the presence of pores seen in the electron micrographs shown above.

These density values together with the microstructural artifacts and compositional analyses corroborate the unexpectedly somewhat inferior conductivity of the Li-doped-LaGaO$_3$.

4. Conclusions

High phase purity undoped and Li-doped-lanthanum orthogallate have been prepared by a soft-chemistry route employing the nitrate–glycine combustion of the precursor solution at ~ 200 °C. The formation of the target compound was evident even in the as-combusted gel. Systematic heat treatment of the gel in the temperature range of 700–1000 °C followed by XRD and Raman spectroscopy on the fired samples revealed that single-step calcination at 800–900 °C for 4 h is adequate to yield the desired perovskite. The 4-point DC and AC impedance measurements in the temperature range of 550–850 °C showed that the conductivity of the Li-doped-LaGaO$_3$ was higher than that of ytrria-stabilized zirconia up to 650 °C, but lower than that of the Mg-doped analogs. Corroboration based on the XRD, SEM and ICP-MS analyses suggests that loss of lithium in the sintered samples is the likely cause of this anomaly.

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References