Sol–gel approach to low-temperature synthesis of single-phase metastable La$_2$Ga$_3$O$_{7.5}$ melilite with enhanced grain-boundary oxide ionic conductivity via a kinetically favorable mechanism

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Abstract: Starting with the stoichiometric and highly homogeneous gel-precursor, single-phase metastable melilite La$_2$Ga$_3$O$_{7.5}$, as the end-member of solid solution La$_{1+x}$Sr$_{1-x}$Ga$_3$O$_{7+x/2}$ (0 ≤ x ≤ 1), has been synthesized by solid-state reaction at 700 ℃ for 2 h via a kinetically favorable mechanism and characterized by X-ray diffraction (XRD), Raman, X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), AC impedance spectroscopy, etc. It has been revealed that the as-synthesized melilite La$_2$Ga$_3$O$_{7.5}$ shows an orthorhombic symmetry with crystal cell parameters $a = 11.4690(1)$ Å, $b = 11.2825(4)$ Å, and $c = 10.3735(4)$ Å, while has more Raman active modes than LaSrGa$_3$O$_7$ with a tetragonal structure, which was also synthesized under the same conditions for comparison, but tends to slowly decompose into perovskite LaGaO$_3$ and Ga$_2$O$_3$ when annealed at 700 ℃ for over 20 h driven by its meta-stability. Moreover, the metastable La$_2$Ga$_3$O$_{7.5}$ shows a higher XPS binding energy for the excess oxide ions in the crystal structure than those at normal lattice sites. Its intrinsic grain oxide ion conductivity can reach as high as 0.04 and 0.51 mS·cm$^{-1}$ at 550 and 700 ℃, respectively, characterized by a simple Arrhenius relationship ln($\sigma T$)–$1/T$ with invariable activation energy, $E_a = 1.22$ eV, over the temperature range from 300 to 700 ℃, along with an apparent grain boundary conductivity that is about double that from the grains thanks to the clean grain boundaries. This paper provides a new strategic approach to the synthesis of complex oxides that may be of high performance but are difficultly achieved by the conventional ceramic method at high temperatures.

Keywords: melilite; La$_2$Ga$_3$O$_{7.5}$; low temperature synthesis; gel-precursor; meta-stability; kinetic mechanism

1 Introduction

Oxide ion conductors are solid electrolyte materials which are widely applied in modern electrochemical devices, including solid oxide fuel cells (SOFCs), oxygen sensors, oxygen pumps, etc. [1–4], and their oxide ion conductivities can decisively define the minimum operating temperatures for the SOFCs built upon them. In recent years, with the further development of medium- and low-temperature solid oxide electrolyte materials, several interstitial oxide ion conductors with tetrahedral structures, such as apatite- [5,6], scheelite- [7–9], and melilite-type oxides [10], have aroused wide research interests. Among them, melilite-type oxides possess a self-adaptable layered tetrahedral network...
structure for the accommodation and transport of interstitial oxide ions. Especially, since the successful synthesis of La$_{1-x}$Sr$_x$Ga$_3$O$_{7+0.5x}$ by Rozumek et al. [11,12] and the finding of the interstitial oxide ion migration mechanism by Kuang et al. [13], more efforts have been devoted to the unfolding researches of the melilite-structured oxides with high oxygen ionic conductivities.

The chemical formula of the melilite structured oxides is ABC$_3$O$_7$, where A/B is divalent or trivalent metal cations (e.g., Ln, Ca, Sr, Ba, etc.), and C is Mg, Ga, Al, Si, Ge, etc. The crystal structure of LaSrGa$_3$O$_7$, as an example, is composed of [GaO$_4$] tetrahedral layers stacked alternately with La/Sr cation layers along the c-axis. In the tetrahedral layers, the [GaO$_4$] tetrahedra are connected by corner-sharing to form a planar network structure featured with five-membered rings. The interstitial oxide ions are located nearly at the centers of some of the five-membered rings and coordinated up and down by two A/B cations and by the centers of some of the five-membered rings and rings. The interstitial oxide ions are located nearly at the centers of some of the five-membered rings and coordinated up and down by two A/B cations and by the Ga$^{2+}$ ions within the tetrahedral layer [14,15]. Such a coordination structure can be stabilized by the distortion of the [GaO$_4$] tetrahedra and the formation of [GaO$_5$] polyhedron [16,17]. The cooperative migration mechanism involving the concerted knock-on motion of the interstitial oxide ions and lattice oxide ions along certain directions in the two-dimensional tetrahedral layers was revealed by molecular dynamics (MD) simulations [18] and supported by density functional theory (DFT) calculation and Kinetic Monte Carlo simulations [19], which leads to the significant anisotropy of oxide ion conductivity in the melilite structured oxides [20].

Among the melilite oxide electrolytes [13,15,17,21–25], La$_{1+x}$M$_{1-x}$Ga$_3$O$_{7+0.5x}$ (M = Ca, Sr, and Ba) [13,21,22] are the most representative ones. The La$_{1+x}$Ca$_{1-x}$Ga$_3$O$_{7+0.5x}$ system has a tetragonal symmetric structure when $0 \leq x \leq 0.54$, and shows an orthorhombic symmetry when $0.55 < x \leq 0.64$. In La$_{1+x}$Sr$_{1-x}$Ga$_3$O$_{7+0.5x}$, the tetragonal structure is stable in the range of $0 \leq x \leq 0.60$, while the orthorhombic structure occurs at $0.60 < x \leq 0.65$. The La$_{1+x}$Ba$_{1-x}$Ga$_3$O$_{7+0.5x}$ system has a stable tetragonal structure with $0 \leq x \leq 0.35$. Apart from the above La-containing melilite oxides, unfortunately, few melilite phases with the other lanthanides than La were synthesized so far by the conventional solid-state reactions, except for Pr$_{1.3}$Sr$_{0.7}$Ga$_3$O$_{7+0.5}$ and Ln$_{1.3}$Sr$_{0.7}$Ga$_3$O$_{7+0.5}$ (Ln = Pr, Nd, and Sm) [23]. However, Boyer et al. [26] recently reported the successful synthesis of melilite Ln$_{1.3}$Sr$_{1.2}$Ga$_3$O$_{7+0.5}$ (Ln = Gd, Eu, and Tb) with $x$ up to 0.6 by the aerodynamic levitation (ADL) laser heating method through direct crystallization of the under-cooled melt. Afterwards, Xu et al. [27] synthesized melilite La$_{1+x}$Ca$_{1-x}$Al$_3$O$_{7+0.5}$ ($0 \leq x \leq 0.6$) by the same method, which has not been obtained so far for $x > 0$ by the conventional solid-state reaction method. More interestingly, Fan et al. [28] successfully obtained metastable melilite La$_2$Ga$_{1.5}$O$_{7.5}$ by a similar method, in which the maximum solid solution limit ($x_{\text{max}}$) is extended to 1 from $\sim 0.64$, and the nominal interstitial oxide ion content is as high as 0.5 per unit formula in the crystal structure. Moreover, such a metastable melilite La$_2$Ga$_{1.5}$O$_{7.5}$ has been found to possess a greatly suppressed oxide ionic conductivity due to the long-range ordering of the interstitial oxide ions in the crystal structure [29].

Nevertheless, the crystallization of under-cooled melt appears not to be a flawless approach to the synthesis of complex oxides that are difficultly obtained by the conventional methods. The compositional deviation of the melt for different volatilities of raw oxides at high temperatures and incomplete crystallization would yield impurity phases at the grain boundaries, which may significantly deteriorate the grain boundary conductivity. As reported in the literature [28], although Ga-excess recipe can be used empirically to compensate for the loss of Ga during the high temperature melting process of the starting oxides, it is still too difficult to achieve an accurate chemical composition for the desired melilite phase. As a result, the nonconductive impurity phases inevitably remain at the grain boundaries in the crystallization products.

In this paper, the highly homogeneous gel-precursors with precisely controlled chemical compositions, instead of the under-cooled melt or glassy materials, were adopted to synthesize the single-phase melilite La$_2$Ga$_3$O$_{7.5}$ and LaSrGa$_3$O$_7$ by the solid-state reactions at low temperatures. After a full characterization by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Raman, AC impedance spectroscopy, etc., we found that the single-phase melilite La$_2$Ga$_3$O$_{7.5}$ and LaSrGa$_3$O$_7$ can be easily synthesized from their gel-precursors at 700 °C for 2 h, and the as-synthesized La$_2$Ga$_3$O$_{7.5}$ shows an orthorhombic symmetry, but can spontaneously decompose into the perovskite LaGaO$_3$ and Ga$_2$O$_3$ when annealed at 700 °C for a prolonged time due to its meta-stability. More interestingly, its
total oxide ion conductivity exhibits a simple Arrhenius relationship \(\ln(\sigma T) = 1/T\) with invariable activation energy over the temperature range in this study without the bending reported previously in the literature [28]. In addition, based on the analysis of the relevant experimental results, a kinetically favorable mechanism is proposed, which provides a way to better understand how the precursors or reactants with different spatial inhomogeneity of chemical species would likely give rise to the formation of different products.

2 Experimental

2.1 Reagents

Lanthanum oxide (La\(_2\)O\(_3\), 99.99%), strontium carbonate (SrCO\(_3\), 99.95%), and gallium oxide (Ga\(_2\)O\(_3\), 99.99%) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Ethylenediaminetetraacetic acid (EDTA, analytical reagent (AR)), citric acid (CA·H\(_2\)O, AR), ammonia (NH\(_3\)·H\(_2\)O, 25%–28%), and polyvinyl alcohol (PVA, 99%) were from the Sinopharm Chemical Reagent Co., Ltd. Concentrated nitric acid (HNO\(_3\), 65%) came from Shanghai Lingfeng Chemical Reagent Co., Ltd. Deionized water was provided by Nanjing Wanqing Chemical Glassware Instrument Co., Ltd. All chemicals were used directly without further purification.

2.2 Preparation of samples

Using analytic grade La\(_2\)O\(_3\), SrCO\(_3\), and Ga\(_2\)O\(_3\) as raw materials and EDTA–CA as co-complexant, the single-phase La\(_2\)Ga\(_3\)O\(_{7.5}\) and LaSrGa\(_3\)O\(_7\) samples were synthesized and prepared through the EDTA–CA co-complex sol–gel process, solid-state reaction, and sintering at elevated temperatures. Specifically, the calculated amounts of La\(_2\)O\(_3\), SrCO\(_3\), and Ga\(_2\)O\(_3\) according to the targeted melilite phases were dissolved in an appropriate volume of concentrated nitric acid to obtain a clear and transparent nitrate solution. Then, EDTA ammonia buffer solution and CA·H\(_2\)O were added to the nitrate solution in the molar ratio 1 : 1.5 : 1 of total metal ions M to CA to EDTA. Ammonia was subsequently introduced dropwise to adjust the pH to 7, and then the solvent was evaporated under continuous stirring in a water bath at 80 °C to obtain a viscous transparent gel. The gels were dried at an oven at 120 °C and calcined in a muffle furnace at 700 °C for 2 h to synthesize the La\(_2\)Ga\(_3\)O\(_{7.5}\) and LaSrGa\(_3\)O\(_7\) powders. These powders were ball-milled with ethanol as a dispersant for 12 h, and dried before uniaxially pressed into pellets of 12 mm in diameter and 1 mm in thickness at 300 MPa with PVA as the binder. The binder was removed by calcining the pellets in the air at 300 °C for 1 h, and then the sintering was carried out at 700 °C for 2 h to obtain the sintered La\(_2\)Ga\(_3\)O\(_{7.5}\) and LaSrGa\(_3\)O\(_7\) samples.

2.3 Structural characterization

A Fourier infrared spectrometer (FTIR, iN10, Nicolet) with the wavenumber range from 400 to 4000 cm\(^{-1}\) was used to determine the complexation state of the gels. The reaction process of the gels was tracked by a thermogravimetry-differential scanning calorimeter (TG–DSC, STA 449 F1, NETZSCH) in a temperature range from room temperature to 900 °C at a ramping rate of 5 °C/min in the air. An X-ray diffractometer (40 kV/30 mA, \(\lambda = 1.5418 \text{ Å/Cu K}_\alpha\), SmartLabTM 3KW, Rigaku) was used for phase identification and structural characterization of the samples in the 2\(\theta\) range from 10° to 80°. The morphology of the samples was characterized by a field emission scanning electron microscope (FESEM, SU8200, Hitachi). A high-resolution transmission electron microscope (HRTEM, Tecnai G2 F30, FEI) was used to observe the grain microstructure and crystal structure of the samples. The relative densities of the sintered samples were determined by the Archimedes drainage method. To determine the constituent elements and their chemical states, the XPS spectra of the samples were recorded by an X-ray photoelectron spectrometer (K-Alpha, Thermo Fisher Scientific) and analyzed by XPSPEAK 4.1 software after the calibration of binding energy by C 1s (284.8 eV) of carbon. The Raman spectra of the synthesized samples were measured by a Raman spectrometer (LabRAM HR Evolution, HORIBA) with a laser excitation wavelength of 514 nm to deeply investigate the structural characteristics.

2.4 Electrical property measurements

The sintered bulk samples were ground, polished, and ultrasonically cleaned, and then coated with Ag paste on both sides to form thin film electrodes for measuring the oxide ion conductivities. The samples were measured by an electrochemical workstation (SI-1260, Solartron Metrology) with a constant amplitude AC signal of 5 mV in the frequency range of 0.1 Hz to 1 MHz at temperatures ranging from 300 to 700 °C. Based on the appropriate equivalent circuit, the measured impedance
spectra were numerically analyzed by ZSimpWin software, and then the oxide ion conductivities of the La$_2$Ga$_3$O$_{7.5}$ and LaSrGa$_3$O$_7$ bulk samples at different conditions were obtained.

3 Results and discussion

3.1 Synthesis and structures of La$_2$Ga$_3$O$_{7.5}$ and LaSrGa$_3$O$_7$

To track the formation and change of the gels, the FTIR spectra of EDTA, CA·H$_2$O, complexed dry gel, and La$_2$Ga$_3$O$_{7.5}$ samples obtained by calcining the dry gel at 700 °C were recorded, and the results are shown in Fig. S1 in the Electronic Supplementary Material (ESM). It can be noted that, the metal ions can be complexed well with both EDTA and CA molecules, which allows the well-complexed metal ions to be uniformly distributed in the gel network and leads to the formation of a highly homogeneous gel-precursor by esterification cross-linking. The typical TG–DSC curves of the gel-precursor for La$_2$Ga$_3$O$_{7.5}$ are shown in Fig. 1. It can be seen that the gel decomposition process mainly goes through four stages. The small DSC endothermic peaks at 168 and 212 °C, accompanied by a weight loss of about 10% in the TG diagram, should be attributed to the volatilization of free water and crystallized water. The sharp DSC exothermic peak at 267 °C, corresponding to a weight loss of about 35%, may result from the violent oxidation of complexing agents with the nitrate oxidant, which is tailored in quantity so as not to initiate a sustainable auto-combustion but provoke the pyrolysis of complexing agents. A broad exothermic peak at 359 °C corresponds to a weight loss of about 25% and can be attributed to the oxidative decomposition of the metal carboxylate in the initial pyrolytic products and the release of large amounts of CO$_2$ and H$_2$O. Similarly, the broad exothermic peak at 444 °C, corresponding to a weight loss of about 10%, is attributable to the oxidation of pyrolytic product N(CH$_2$)$_3$ with oxygen in the air [30]. After that, the sample gradually tends to keep a constant weight as the temperature is increased over 500 °C, suggesting that the gel’s thermal decomposition is going to be close to the end, and the subsequent weight loss of about 6% should come from slow oxidation of the residual carbon. Finally, the sample retains about 14% of the initial weight for the dry gel.

The XRD patterns of LaSrGa$_3$O$_7$ and La$_2$Ga$_3$O$_{7.5}$ obtained by calcining the gel from EDTA–CA co-complexation at 700 °C for 2 h are shown in Fig. 2, where the inset photo is the FESEM image of the as-prepared La$_2$Ga$_3$O$_{7.5}$. It is clear to note that, the diffraction peaks of LaSrGa$_3$O$_7$ are all consistent with that of tetragonal LaSrGa$_3$O$_7$ (JCPDS Card No. 45-0637), while all the diffraction peaks of La$_2$Ga$_3$O$_{7.5}$ coincide with that of orthorhombic La$_{1.64}$Ca$_{0.36}$Ga$_3$O$_{7.32}$ (JCPDS Card No. 04-017-7922). This result manifests that La$_2$Ga$_3$O$_{7.5}$ is of orthorhombic symmetry. With the help of MDI Jade 6.5 software using a Pseudo–Voigt peak function, both XRD patterns were numerically analyzed by whole pattern fitting to determine the lattice parameters. In the meanwhile, the crystal structure relations between

![Fig. 1](image1.png)

**Fig. 1** TG–DSC curves of EDTA–CA complexed gel-precursor for La$_2$Ga$_3$O$_{7.5}$.

![Fig. 2](image2.png)

**Fig. 2** XRD patterns of LaSrGa$_3$O$_7$ and La$_2$Ga$_3$O$_{7.5}$ synthesized at 700 °C in the air, along with an inset FESEM image of La$_2$Ga$_3$O$_{7.5}$ powder sample.
the tetragonal LaSrGa$_3$O$_7$ and the orthorhombic La$_2$Ga$_3$O$_{7.5}$ were considered: $a_{\text{orth}} \approx b_{\text{orth}} = \sqrt{2} a_{\text{tetra}}$ and $c_{\text{orth}} \approx 2c_{\text{tetra}}$ [28], as shown in Fig. 3. Thus, upon the best-fits with the residual fitting errors $R_{wp} = 5.24\%$ and 7.31\%, the cell parameters were derived for LaSrGa$_3$O$_7$ and La$_2$Ga$_3$O$_{7.5}$: $a_{\text{tetra}} = 8.0474(2)$ Å, $c_{\text{tetra}} = 5.3283(3)$ Å, and $a_{\text{orth}} = 11.4690(1)$ Å, $b_{\text{orth}} = 11.2825(4)$ Å, $c_{\text{orth}} = 10.3735(4)$ Å, which are very close to the data reported in the literature [28,31].

To further characterize the crystal structures of La$_2$Ga$_3$O$_{7.5}$ and LaSrGa$_3$O$_7$, the as-synthesized samples were studied by HRTEM and selected area electron diffraction (SAED). Figures 4(a), 4(b) and Figs. 4(d), 4(e) show the HRTEM images of the LaSrGa$_3$O$_7$ and La$_2$Ga$_3$O$_{7.5}$ samples, respectively, in which the insets are their respective TEM images. Figures 4(c) and 4(f) show the SAED images of LaSrGa$_3$O$_7$ and La$_2$Ga$_3$O$_{7.5}$ samples, respectively. As shown in the HRTEM images, both of them exhibit neat lattice stripes. The lattice fringe spacing of LaSrGa$_3$O$_7$ sample is estimated at 0.533 nm, corresponding to the lattice spacing of the (001) plane in its tetragonal structure. For the La$_2$Ga$_3$O$_{7.5}$ sample, a lattice fringe width of 1.085 nm can be determined, which corresponds to the lattice spacing of the (001) plane in its orthorhombic structure. In the SAED image of La$_2$Ga$_3$O$_{7.5}$ sample, the (002) and (004) spots should be from the Ga atomic planes in the [Ga$_3$O$_{7.5}$] polyhedral layers and the La atomic planes between the adjacent [Ga$_3$O$_{7.5}$] polyhedral layers, respectively. More interestingly, additional faint diffraction spots can be seen between the diffraction spots corresponding to the (002) and (004) planes, which may be related to the long-range ordering chain-like arrangement of the interstitial oxide ions. The chain-like arrangement of the interstitial oxide ions is staggered in the adjacent [Ga$_3$O$_{7.5}$] polyhedral layers, resulting in a periodic deviation of the La ions from the (004) crystal plane in the c-axis direction and thus producing the extraordinary diffraction spots.

In addition, the structural differences between La$_2$Ga$_3$O$_{7.5}$ and LaSrGa$_3$O$_7$ are also clearly demonstrated by their Raman spectra, as shown in Fig. 5. According to the symmetry group analysis, LaSrGa$_3$O$_7$ with a tetragonal structure should have 45 Raman active vibrational modes, but the experimental Raman spectrum of the LaSrGa$_3$O$_7$ sample gives less than half of its theoretical vibrational bands, which should be due to the degeneration or low intensity of some vibrational modes [32]. Compared with LaSrGa$_3$O$_7$, the Raman spectrum of La$_2$Ga$_3$O$_{7.5}$ with the orthorhombic structure exhibits more vibrational modes, evidently revealing the lower structural symmetry of La$_2$Ga$_3$O$_{7.5}$. The characteristic peaks of La$_2$Ga$_3$O$_{7.5}$ at 531 cm$^{-1}$ and LaSrGa$_3$O$_7$ at 528 cm$^{-1}$ correspond to the symmetric
stretches of the Ga–O₉–Ga bonds [32], where O₉ is the bridge oxygen at the [GaO₄] tetrahedral co-vertex. In comparison with LaSrGa₃O₇, the apparent shoulder peaks at 482 and 570 cm⁻¹ near the characteristic peak of the Ga–O₉–Ga bonds for La₂Ga₃O₇.₅ can be attributed to the tetrahedral vibrations [33], suggesting that the coordination environment of O₉ is more complex, and may be related to the position and coordination details of O in La₂Ga₃O₇.₅. The characteristic peaks at 640 cm⁻¹ for La₂Ga₃O₇.₅ and 677 cm⁻¹ for LaSrGa₃O₇ correspond to the symmetric stretching vibrations of the Ga–O₉ bonds [34], where O₉ is the non-bridging oxygen without being shared in [GaO₄] tetrahedrons. Compared to LaSrGa₃O₇, the characteristic peak of Ga–O₉ bonds for La₂Ga₃O₇.₅ is significantly shifted toward the lower wavenumber, and an obvious shoulder peak is also observed nearby, indicating that the presence of O₉ has a greater influence on O₉ because it may cause the coordination of the [GaO₄] tetrahedrons to change. It also laterally demonstrates that the realistic presence of O₉ in La₂Ga₃O₇.₅ is the result of the deformation and modulation of the [GaO₄] tetrahedral. The extra vibrational peaks for La₂Ga₃O₇.₅, in comparison with the Raman spectrum of LaSrGa₃O₇, may be related to the M–O₉ bonds consisting of metal cation M and O₉, and therefore the small and sharp vibrational peak at 737 cm⁻¹ in the Raman spectrum of La₂Ga₃O₇.₅ can be attributed to the characteristic stretching vibration of the Ga–O bonds.

To explore the chemical states of the constituent elements, especially of the oxide ions, the full-scale survey spectra of the sintered La₂Ga₃O₇.₅ and LaSrGa₃O₇ and local sub-spectra for individual elements were registered by XPS. All XPS spectra, calibrated in terms of the carbon’s binding energy at 284.8 eV for C 1s to eliminate charging effects, are demonstrated in Fig. 6. From Fig. 6(a), it can be seen that the characteristic peaks of La, Ga, and O elements appear in the spectra of both samples, with the peaks of Sr 3d and Sr 3s showing up only in the spectrum of LaSrGa₃O₇. In Fig. 6(c), the two peaks at binding energies of 134.9 and 133.1 eV for the LaSrGa₃O₇ sample are corresponding to Sr 3d₃/2 and Sr 3d₅/2, respectively, while no peaks for the Sr element can be seen in the sub-spectrum of La₂Ga₃O₇.₅. The La 3d sub-spectra for the LaSrGa₃O₇ and La₂Ga₃O₇.₅ samples are presented in Fig. 6(b), where the two samples exhibit the highly parallel characteristic peaks of La 3d₅/2 and La 3d₃/2 at 835.0, 838.6 and 851.8, 855.4 eV for LaSrGa₃O₇ and at 835.2, 838.9 and 852.0, 855.7 eV for La₂Ga₃O₇.₅, respectively. Similar results can be noticed in Fig. 6(d), where two characteristic peaks of Ga 2p₃/2 and Ga 2p₁/2 are located at 1117.8 and 1144.6 eV for LaSrGa₃O₇ and at 1118.2 and 1145.0 eV for La₂Ga₃O₇.₅, respectively. By comparison, it is easy to find that the characteristic peaks of La and

![Fig. 6](https://www.springer.com/journal/40145)
Ga in La$_2$Ga$_3$O$_{7.5}$ have higher binding energies than that in LaSrGa$_3$O$_7$. This result strongly suggests that the densities of the outer electron cloud of La and Ga in La$_2$Ga$_3$O$_{7.5}$ should be lower than those in LaSrGa$_3$O$_7$, since the lower density of the outer electron cloud implies a stronger binding of the nucleus to the inner electrons, namely a higher energy is required to excite the inner electrons into photoelectrons [35].

The O 1s sub-spectra for the two samples are shown in Fig. 6(e). It can be seen that, the O 1s sub-spectrum of LaSrGa$_3$O$_7$ comprises two characteristic peaks at 530.4 and 532.0 eV, with the former being attributed to $O_B$ and the latter to $O_{NB}$. Also, the O 1s sub-spectrum of La$_2$Ga$_3$O$_{7.5}$ contains the peak at 530.7 eV from $O_B$ and the one at 532.3 eV from $O_{NB}$. However, more interestingly, an additional peak at 533.6 eV can be seen in the sub-spectrum of La$_2$Ga$_3$O$_{7.5}$, which may originate from the $O_i$ in the crystal structure [36–39]. Therefore, for the La$_2$Ga$_3$O$_{7.5}$ sample, a sequence of the binding energies for $O_B$, $O_{NB}$, and $O_i$ can be written as $O_B < O_{NB} < O_i$. This means that the density of the outer electron cloud of $O_i$ is lower than those of $O_B$ and $O_{NB}$, i.e., the interstitial $O_i$ ions possess fewer electrons from La and Ga atoms due to the longer distances of $O_i$ from La and Ga. The higher binding energy of the oxide ions indicates a weaker bonding force between the metal ion and the oxide ion [40,41], suggesting that $O_i$ has a higher migration activity compared to $O_B$ and $O_{NB}$.

To quantitatively evaluate the atomic concentrations of different oxide ions $O_B$, $O_{NB}$, and $O_i$, the O 1s sub-spectra of the LaSrGa$_3$O$_7$ and La$_2$Ga$_3$O$_{7.5}$ samples were deconvolved by the software XPSPEAK 4.1, and the results are listed in Table 1. For the LaSrGa$_3$O$_7$ sample, the areal percentages of $O_B$ and $O_{NB}$ peaks are 70.62% and 29.38%, and for the La$_2$Ga$_3$O$_{7.5}$ sample, the areal fractions of $O_B$, $O_{NB}$, and $O_i$ peaks are 65.88%, 27.65%, and 6.47%, respectively, which are in good agreement with the theoretical values according to the chemical formula, with the acceptable relative deviations presented in Table 1.

### Table 1 XPS parameters of various oxide ion species in LaSrGa$_3$O$_7$ and La$_2$Ga$_3$O$_{7.5}$

| Oxide ion species | LaSrGa$_3$O$_7$ | La$_2$Ga$_3$O$_{7.5}$ |
|-------------------|----------------|---------------------|
| Binding energy (eV) | Peak area (%) | Relative deviation (%) | Binding energy (eV) | Peak area (%) | Relative deviation (%) |
| $O_B$ | 530.4 | 70.62 | −1.13 | 530.7 | 65.88 | −1.18 |
| $O_{NB}$ | 532.0 | 29.38 | +2.83 | 532.3 | 27.65 | +3.69 |
| $O_i$ | — | — | — | 533.6 | 6.47 | −2.95 |

3.2 Oxide ionic conductivities of La$_2$Ga$_3$O$_{7.5}$ and LaSrGa$_3$O$_7$

The La$_2$Ga$_3$O$_{7.5}$ and LaSrGa$_3$O$_7$ samples for the measurements of the oxide ion conductivity were those sintered at 700 °C for 2 h to reach a relative density of 50%, as indicated by the Archimedean test. The typical cross sectional FESEM image of the La$_2$Ga$_3$O$_{7.5}$ pellet coated with silver films as electrodes on its both sides is shown in Fig. 7. It can be seen that the sample’s microstructure is highly homogeneous, and the electrodes are well attached on the sample’s side surfaces.

Figure 8 shows the typical AC-impedance spectra of the sintered La$_2$Ga$_3$O$_{7.5}$ sample at 300, 400, 500, and 700 °C, while other impedance spectra at 350, 450, 550, 600, and 650 °C are demonstrated in Fig. S2 in the ESM, and those for LaSrGa$_3$O$_7$ at different temperatures are presented in Fig. S3 in the ESM. For La$_2$Ga$_3$O$_{7.5}$, its impedance spectrum at 300 °C shows two complete semicircular arcs corresponding to the grain and grain boundary processes. With the increase of the measurement temperature, the semicircular arc corresponding to the grain process gradually disappears, and at the temperature of 700 °C, only a partial arc corresponding to the grain boundary process can be observed. This is because the response frequency of the grain process usually increases with the temperature, and...
its impedance arc cannot be fully obtained when it exceeds the working frequency of the AC impedance spectrometer. Therefore, only the impedance arc corresponding to the grain boundary with a lower response frequency can be observed at higher temperatures. In addition, AC-impedance measurements were performed on the La$_2$Ga$_3$O$_{7.5}$ sample in humid air by bubbling water and dry air at a flow rate of 50 mL/min. The typical AC-impedance spectra at 400 °C and the conductivities at temperatures from 400 to 700 °C in humid and dry airs are presented in Figs. S4 and S5 in the ESM. It can be seen that, the AC-impedance spectra and the conductivities derived from them show no differences in the two cases of humid and dry airs, strongly suggesting that no electrical conductivity for the La$_2$Ga$_3$O$_{7.5}$ sample may come from OH groups or protons.

To perform a quantitative analysis of the AC-impedance spectra of the sintered La$_2$Ga$_3$O$_{7.5}$ and LaSrGa$_3$O$_7$, the appropriate equivalent circuits for polycrystalline ceramic electrolytes were utilized, as shown in Fig. 8, where $R_g$ and $R_{gb}$ represent the grain resistance and the grain boundary resistance, respectively, and CPE$_g$ and CPE$_{gb}$ are the constant phase elements for the corresponding processes. All the parameters of the equivalent circuits were evaluated after a nonlinear fitting analysis of the AC-impedance spectra measured at different temperatures by ZSimpWin software, wherein the results for La$_2$Ga$_3$O$_{7.5}$ and LaSrGa$_3$O$_7$ are listed in Tables S1 and S2 in the ESM, respectively. The grain conductivity ($\sigma_g$), grain boundary conductivity ($\sigma_{gb}$), and total conductivity ($\sigma_t$) of the samples were then calculated by the formulae: $\sigma_g = L/(R_g A)$, $\sigma_{gb} = L/(R_{gb} A)$, and $\sigma_t = L/(R_t A)$, where $L$ and $A$ are the thickness and the electrode area of the samples, respectively, and the total resistance $R_t = R_g + R_{gb}$.

Figure 9 shows the Arrhenius plots ln($\sigma T$)$^{-1}/T$ of various conductivities of the LaSrGa$_3$O$_7$ and La$_2$Ga$_3$O$_{7.5}$ samples, including their total conductivities, grain and grain boundary conductivities of La$_2$Ga$_3$O$_{7.5}$, as well as the grain conductivity of La$_2$Ga$_3$O$_{7.5}$ from the literature [28], while the inset shows the plots of these conductivities versus the temperature. It can be noted that, the sintered La$_2$Ga$_3$O$_{7.5}$ distinctly shows a linear Arrhenius relationship (ln($\sigma T$)$^{-1}/T$) with invariable activation energies of 1.22, 1.18, and 1.24 eV for the grain, apparent grain boundary, and total conductivities over the entire temperature range from 300 to 700 °C, respectively. In addition, the total conductivity of La$_2$Ga$_3$O$_{7.5}$ is about 2
Fig. 9 Arrhenius plots of total conductivity, grain and apparent grain boundary conductivities for La$_2$Ga$_3$O$_{7.5}$, total conductivity for LaSrGa$_3$O$_7$, and grain conductivity for La$_2$Ga$_3$O$_{7.5}$ from Ref. [28], as well as the inset showing the diagrams for the conductivities versus temperature.

orders of magnitude that of LaSrGa$_3$O$_7$ at the temperatures in this study. It takes a value of 0.36 mS·cm$^{-1}$ at 700 °C, alongside an apparent grain boundary conductivity of 1.17 mS·cm$^{-1}$, about twice as high as the grain conductivity at the same temperature.

However, it should be more interesting to compare the above results with the data reported in the literature [28]. First of all, the grain conductivity of La$_2$Ga$_3$O$_{7.5}$ prepared in this study is very close to that reported in the above literature in the temperature range from 300 to 550 °C, verifying that the La$_2$Ga$_3$O$_{7.5}$ phases achieved by two different methods have almost the same intrinsic properties. However, in the literature [28], the apparent grain boundary conductivity is remarkably smaller than the grain conductivity because of the longer chord made from the intercepts by the impedance response arc of the grain boundary on the real axis $Z' (\Omega \cdot$cm) than that by the grain’s arc for the AC impedance spectrum of La$_2$Ga$_3$O$_{7.5}$ at 400 °C. This is evidently different from our above result. Firstly, it is reasonable to believe that the larger apparent grain boundary conductivity in our La$_2$Ga$_3$O$_{7.5}$ should arise from its clean grain boundaries. Secondly, in contrast to the present study, where the invariable activation energy of 1.22 eV for the grain conductivity of La$_2$Ga$_3$O$_{7.5}$ is clearly shown over the whole temperature range from 300 to 700 °C, whereas an abrupt change in the activation energy of grain conductivity from 1.21 to 1.62 eV around 550 °C can be noticed in the literature [28]. This should be an anomaly. It is well known that a change in the activation energy for the transport of charge carriers usually results from the change of carrier migration mechanism with the temperature mostly because of structural changes like phase transitions. Although the authors simply attributed this anomalous change of the activation energy to the thermally induced disordering of interstitial oxide ions [28], it seems still difficult to understand because thermally induced carrier disordering is normally related to an order parameter that is an asymptotic function of the temperature rather than an abrupt change. Moreover, the increase of the temperature should cause the disordering of carriers and often lead to a decrease rather than an increase in the activation energy. Therefore, it is speculated that this anomalous change, if true, would be closely related to the presence of a peculiar microstructure that might be mediated by the impurity phases formed during the crystallization of the under-cooled melt.

3.3 Meta-stability and synthetic mechanism of La$_2$Ga$_3$O$_{7.5}$

To explore the meta-stability of La$_2$Ga$_3$O$_{7.5}$, the as-synthesized La$_2$Ga$_3$O$_{7.5}$ samples were annealed at 700, 750, 800, and 850 °C for 2 h and then characterized by XRD, with the resulting diffraction patterns shown in Fig. 10(a). It can be noted that some bud-like diffraction peaks attributable to the LaGaO$_3$ phase may be identified clearly with the samples after calcination at 750 °C for 2 h. With the increase of the temperature, the diffraction peaks of LaGaO$_3$ intensify rapidly, and the La$_2$Ga$_3$O$_{7.5}$ sample is completely decomposed into the LaGaO$_3$ and Ga$_2$O$_3$ phases after calcination at 850 °C for 2 h. Figure 11(a) gives a distinct diagram to describe how fast the La$_2$Ga$_3$O$_{7.5}$ decomposes with increasing temperature, wherein the diffraction intensity fraction of LaGaO$_3$ with respect to the total diffraction intensity integrated over the whole 2θ range is used as an index. Evidently, the decomposition of La$_2$Ga$_3$O$_{7.5}$ should be initiated at some temperatures slightly below 750 °C and then accelerated over 775 °C at a blasting rate until the end.
To further investigate the meta-stability of La$_2$Ga$_3$O$_{7.5}$, another attempt was also made to calcine the as-synthesized La$_2$Ga$_3$O$_{7.5}$ again at 700 °C for different time before the characterization by XRD. As shown in Fig. 10(b), no diffraction peaks of LaGaO$_3$ can be observed for the sample after the calcination at 700 °C for 20 h, implying that no noticeable change with the La$_2$Ga$_3$O$_{7.5}$ sample has taken place at this condition. When the annealing time was extended to 40 h, some slight diffraction peaks for LaGaO$_3$ can be observed, suggesting that the La$_2$Ga$_3$O$_{7.5}$ sample has undergone a tiny decomposition. In the same way as the above, a diagram of describing how fast the La$_2$Ga$_3$O$_{7.5}$ decomposes with increasing the calcination time at 700 °C was determined, as shown in Fig. 11(b). It can be seen that, the decomposition of La$_2$Ga$_3$O$_{7.5}$ heated at 700 °C appears to show linear kinetics with a constant but small rate. Obviously, this result unveils the nature of metastable La$_2$Ga$_3$O$_{7.5}$: It can be synthesized from a highly homogeneous gel-precursor at 700 °C for 2 h and can also start to decompose due to heating at the same temperature for over 20 h. It is easy to understand that, increasing the annealing time or temperature will induce La$_2$Ga$_3$O$_{7.5}$ more effectively to lose its meta-stability, given a high kinetic barrier between the metastable La$_2$Ga$_3$O$_{7.5}$ and the thermodynamically stable La$_2$O$_3$ + 1.5Ga$_2$O$_3$.

Although the crystallization of the under-cooled melt was regarded as an appropriate non-equilibrium approach to the synthesis of the metastable La$_2$Ga$_3$O$_{7.5}$ melilite [28], the single-phase metastable La$_2$Ga$_3$O$_{7.5}$ melilite without impurity phases has been obtained indeed from its gel-precursor through a solid phase reaction at as low a temperature as 700 °C. To better understand the synthetic mechanism of the metastable La$_2$Ga$_3$O$_{7.5}$, a kinetically favorable mechanism is proposed here. It means that whether La$_2$Ga$_3$O$_{7.5}$ can be synthesized at a temperature high enough to thermodynamically drive the synthetic reactions is mainly controlled by the microscopic inhomogeneity of chemical species of reactants concerned in the reaction system. The smaller the micro-inhomogeneity is, the more favorable the reaction is to take place kinetically.

Fig. 10 XRD patterns of single-phase La$_2$Ga$_3$O$_{7.5}$ calcined (a) at different temperatures for 2 h and (b) at 700 °C for different time.

Fig. 11 X-ray diffraction intensity fraction of LaGaO$_3$ with respect to the total diffraction intensity integrated over the whole 2θ range in this study as an index of decomposition of La$_2$Ga$_3$O$_{7.5}$ calcined at (a) different temperatures for 2 h and (b) at 700 °C for different time.
Assuming that the spatial inhomogeneity of the chemical species concerned in the reaction system can be defined as a characteristic size \( \xi \), and their average diffusion coefficient is \( D \). Then, the minimum time \( \tau \) required to accomplish an elementary solid-state reaction controlled by the diffusion should be expressed as Eq. (1):

\[
\tau \propto \frac{\xi^2}{D}
\]

It is easy to perceive that here the minimum reaction time is also the time required for the system to change from one state to another by jumping over an energy barrier. Thus, it is a measure of the energy barrier to characterize the kinetics of the reaction. A shorter minimum reaction time means a lower energy barrier. Therefore, a larger probability with which the reaction is accomplished based on Eqs. (2) and (3):

\[
\Delta E_r = kT = k \xi^2 / D
\]

\[
p \propto \exp \left( \frac{-\Delta E_r}{k_B T} \right) = \exp \left( \frac{-k \xi^2}{D k_B T} \right)
\]

where \( \Delta E_r \) is the kinetic potential barrier of the reaction, and \( k \) is the proportional factor, \( p \) is the probability with which the reaction is accomplished , \( k_B \) is the Boltzmann constant, and \( T \) is the absolute temperature.

Obviously, the under-cooled oxide melt or glassy precursor obtained at high temperatures usually has an extremely small spatial inhomogeneity size, say a few atoms across. Also, according to the above exponential dependence of reaction probability on the inhomogeneity size, the formation reaction of \( \text{La}_2\text{Ga}_3\text{O}_{7.5} \) can favorably happen at a great probability almost just through a local structural adjustment at a temperature that can satisfy the kinetic requirement. Naturally, it is also true for the formation of \( \text{La}_2\text{Ga}_3\text{O}_{7.5} \) starting with a highly homogeneous gel-precursor, and the kinetic process should be very similar to the above because of the small spatial inhomogeneity size. However, when the mixture of component oxide particles of micros in average diameter is used as a precursor, the formation of \( \text{La}_2\text{Ga}_3\text{O}_{7.5} \) would become kinetically unfavorable and even too difficult to happen because of the large spatial inhomogeneity size of the mixture, which greatly reduces the probability of the elementary reaction, compared to the use of glass or gel-precursor. In this case, to increase the probability of the elementary reaction, the reaction temperature should be increased, but this is seriously detrimental to metastable \( \text{La}_2\text{Ga}_3\text{O}_{7.5} \) and results in the formation of thermodynamically stable phases \( \text{LaGaO}_3 \) and \( \text{Ga}_2\text{O}_3 \).

As to the specific solid-state reactions involved in this paper, the highly homogeneous gel-precursor with a nominal chemical composition of \( \text{La}_2\text{O}_3 + 1.5\text{Ga}_2\text{O}_3 \) strongly tends to form a single-phase \( \text{La}_2\text{Ga}_3\text{O}_{7.5} \) rather than a two-phase product of \( 2\text{LaGaO}_3 + 0.5\text{Ga}_2\text{O}_3 \). This is because the formation of the two-phase product would destroy the original homogeneity and greatly increase the system’s spatial inhomogeneity size, which leads to a much higher potential barrier for the formation of \( 2\text{LaGaO}_3 + 0.5\text{Ga}_2\text{O}_3 \) than for the formation of \( \text{La}_2\text{Ga}_3\text{O}_{7.5} \), and the probability for the former reaction is then greatly reduced. Besides, the presence of residual \( \text{Ga}_2\text{O}_3 \) can hinder the growth of \( \text{LaGaO}_3 \) in space. In other words, if the reaction needs to proceed, additional energy is required to overcome the potential barrier created by the spatial hindrance of the residual \( \text{Ga}_2\text{O}_3 \) to the growth of \( \text{LaGaO}_3 \), which is not favorable for the reaction to proceed at low temperatures. Therefore, the synthesis of the single-phase metastable \( \text{La}_2\text{Ga}_3\text{O}_{7.5} \) from highly homogeneous gel-precursor at low temperatures is a competing result of multiple kinetic processes of different potential barriers.

## 4 Conclusions

In summary, the single-phase metastable melilitic \( \text{La}_2\text{Ga}_3\text{O}_{7.5} \) with the orthorhombic symmetric structure has been successfully synthesized at 700 °C from a highly homogeneous gel-precursor from the EDTA-CA combined complexion sol–gel process, and a kinetically favorable mechanism is proposed to better understand the formation of the single-phase \( \text{La}_2\text{Ga}_3\text{O}_{7.5} \) rather than \( \text{LaGaO}_3 + \text{Ga}_2\text{O}_3 \). The FTIR spectra and TG–DSC results manifest that the EDTA–CA combined complexion sol–gel process can lead to highly homogeneous gel-precursor. Moreover, the as-synthesized \( \text{La}_2\text{Ga}_3\text{O}_{7.5} \) with the orthorhombic structure shows more Raman active vibrational modes and an additional XPS peak at higher binding energy for the interstitial oxide ions than the tetrahedral \( \text{LaSrGa}_3\text{O}_7 \), but tends to slowly decompose into the perovskite \( \text{LaGaO}_3 \) and \( \text{Ga}_2\text{O}_3 \) when annealed at 700 °C for over 20 h or at higher temperatures driven by its meta-stability. Also, different from the anomalous phenomena reported in the literature [28], the sintered \( \text{La}_2\text{Ga}_3\text{O}_{7.5} \) exhibits linear Arrhenius plots \( \ln(\sigma) = -\frac{1}{T} \) with invariable activation energies for its oxide ion conductivities over the
temperature range from 300 to 700 °C and a significantly higher apparent grain boundary conductivity than the grain conductivity because of clean grain boundaries without any impurity phases. This paper provides a new strategic approach to the synthesis of complex oxides that may be of high performance but difficultly achieved by the conventional ceramic method at high temperatures.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

Electronic Supplementary Material

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