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Processing and electrical properties of doped-$LaGaO_3$ by gelcasting

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Abstract

Sr- and Mg-doped $LaGaO_3$ ($La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.8}$) powders have been successfully synthesized from carbonate and oxides based on the principle of gelcasting. X-ray diffraction patterns indicate the perovskite structure is formed without any second phases after sintering the powders at 1400°C for 6 h. Compacts of the gelcast powders heated at 1000°C were sintered to densities greater than 97% of theoretical at 1450°C for 6–18 h; then the relative density decreased to 95.5% sintered for 36 h. From the XRD patterns and SEM photographs, some impure phases were observed for long-sintering samples. The total electrical conductivity was greatly depended on the sintering time, whereas peak values were obtained when the pellet was sintered at 1450°C for 24 h. A transitional temperature T^* (at about 675°C) in the plot of $\ln(\sigma T)$ vs $1000/T$ exhibits a somewhat higher activation energy at lower temperatures, due to the trapping of vacancies by the dopant cations for all sintering conditions. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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1. Introduction

Oxygen-ion conductors have received increasing attention in the past decade due to their potential applications in fields such as solid oxide fuel cells (SOFCs), membrane reactors, and oxygen sensors. Yttria-stabilized zirconia with the cubic-fluorite structure has been used as traditional electrolyte for SOFCs, because of its good ionic conductivity at the elevated temperatures (ca. 0.1 S/cm at 1000°C) and its stability in oxidizing and reducing atmospheres. Other fluorite oxides have also been extensively investigated as SOFC electrolyte candidates, particularly aiming to reduce the operation temperature of SOFCs. These materials mainly include doped CeO_2 and doped Bi_2O_3. However, they are prone to electronic conduction under the reduce environments at the anode side. Recently Ishihara et al. [1,2] has reported that doped $LaGaO_3$ of the perovskite system has shown very high oxygen-ion conductivity. $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.8}$, for example, has been reported to have a conductivity of 0.14 S/cm at 800°C [3], which is almost one magnitude higher than with 8%YSZ electrolyte. Doped $LaGaO_3$ exhibits almost pure oxide ion conduction in the range of oxygen partial pressures from 10^5 to 10^{-16} Pa. However, as prepared by conventional ceramic techniques [4], this gallate requires high temperature and long time for sintering; and it often contains some second phases such as $LaSrGaO_4$ and $LaSrGa_3O_7$, which can be detected by powder X-ray diffraction.

In this paper we report the synthesis of the doped lanthanum gallate as a single, homogeneous phase by means of gelcasting process. This process, which has been developed for the production of complex-shaped parts [5], has been introduced to prepare perovskite ceramics from metal oxides and its precursors [6]. The gelcasting process has proven to be an attractive synthetic route for the preparation of multicomponent oxides, since a homogeneous mixture of several components which are fixed by organic monomer to form a polymer network can be easily reached. In addition to the homogeneity and purity of the product, the gelcasting method allows a lower crystallizing temperature than the traditional solid state reaction. Moreover, this process is easily operated and inexpensive. In this work, we report the preparation of $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.8}$, hereinafter referred to LSGM, by the gelcasting method and characterization

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of the ceramic powder as well as the final product of sintered pellets.

2. Experimental

2.1. Sample synthesis

Stoichiometric amounts of La_2O_3 (3N purity), $SrCO_3$ (3N purity), Ga_2O_3 (5N purity) and MgO (2N5 purity) were weighed as the starting materials. Before weighing, MgO and La_2O_3 were fired at 1000°C for 6 h in order to remove the carbonate and hydroxide. $SrCO_3$ and Ga_2O_3 were preheated at 120°C for 24 h for dewatering and deairing. Then the chemicals, mixed in aqueous monomer (20 wt.% acrylamide and 80 wt.% N,N′-methylenebis-acrylamide) solution with a concentration of 10 wt.% in stoichiometric ratio of LSGM, were ball-milled in distilled water with zirconia media for 24 h. The as-prepared slurry, added with the initiator ammonium bisulphate $(NH_4)_2S_2O_8$ (1.5 wt.% of organic monomers) and a few drops of catalyst N,N,N′,N′-tetramethylenediamine, was cast into a corundum crucible and solidified about 30 min later. The solid gelcasts were dried in an oven at 100°C and calcined in air at different temperatures (1000 ~1600°C) for 6 h. The calcined samples were ground into powders in a mortar to carry out X-ray diffraction measurement.

The powder calcined at 1000°C was chosen to be pressed unaxially under 250 MPa into cyclindrical of 13 mm diameter and 1–2 mm thick. Buried in LSGM powder (calcined at 1500°C for 6 h) to prevent being contaminated, the pellets were sintered at 1450°C for 6–36 h, with a heating and cooling rate of 2°C/min. After sintering, the pellets all turned into the brownish red. The bulk densities of the pellets are measured by the Archimedes method.

2.2. Powder formation

The decomposition of the dried gelcasts was monitored with a Netzsch STA429 thermal analyzer in an oxidizing atmosphere ($N_2+21\%O_2$, flow rate 100 ml/min). Simultaneous differential thermal analysis (DTA) and thermogravimetry (TG) were carried out from room temperature to 1000°C at a rate of 10°C/min. An Al_2O_3 standard was used for the DTA measurement.

Phase development of the calcined gelcast powders was determined by X-ray diffraction (XRD) analysis using Cu K_α radiation (Kigaqu D/Maz-γ_A) at room temperature. This procedure was also performed to reveal the phase constitution of the pellets sintered in the different periods.

2.3. Microstructure

The microstructures of well-polished pellets, sintered at 1450°C, were observed with a Hitachi X-650 scanning electron microscope (SEM). The pellets were sanded, polished, and then thermally etched for 1 h at 1400°C. The surfaces and fracture surfaces were conducted by an Au coating to prevent charging of the sample before observation and photo-taken.

2.4. Electrical conductivity

The ac conductivity of sintered pellets was obtained from two-probe impedance spectroscopy. The two electrodes were formed by applying platinum paste to the two ends of the pellet and firing at 850°C for 15 min. Measurements were made with an impedance analyzer (GenRad 1689 Precision RLC Digibridge) over a frequency of 12–10 kHz in the temperature range 450–900°C (total of 90 experimental points) at an ac voltage amplitude of 50 mV. The furnace was monitored by a precision temperature controller (ÜGU, Al-708) with an accuracy of 1°C. The lead resistance, as obtained by measuring the impedance of a blank cell, was subtracted out from all of the impedance measurements.

3. Results and discussion

3.1. Thermal analysis

The DTA/TGA curves of the gelcasting-derived precursor are presented in Fig. 1. At $T<335°C$, there is approximately 7% mass loss, which may be caused by endothermic removal of occluded water of polymer network in gelcast specimens. In the temperature range (around 335–390°C), there is a rapid mass loss for the specimen, accompanied by a large exothermic DTA peak. This attributes to the burnout of the cross-linked polymer network. At approximately 700°C, another mass loss starts, which is complete at approximately 890°C. This may be ascribed to the thermal decomposition of $SrCO_3$ due to solid state reaction among carbonate and oxides

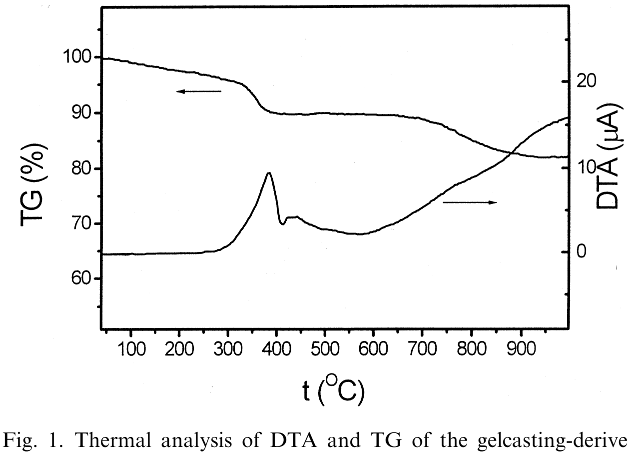


Fig. 1. Thermal analysis of DTA and TG of the gelcasting-derived precursor.

and the formation of a $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.8}$ perovskite phase, as evidenced by XRD.

3.2. Phase development

The LSGM gelcasts were calcined between 1000 and 1600°C, at 100°C intervals, for 6 h, and the products were identified by XRD after grounded. As shown in Fig. 2, the crystallinity is already started at 1000°C. At 1300°C, most of the carbonate and oxides has transferred into perovskite phase, with the formation of a pure single phase [7] after sintering at 1400°C for 6 h. Compared with the traditional solid reaction method, by which the perovskite formation temperature is above 1500°C and often exists impure phases such as $LaSrGaO_4$ and $LaSrGa_3O_7$, the gelcasting procedure can lower the formation temperature by more than 100°C and maintains a single cubic-phase perovskite above 1400°C. This is because in the gelcasting procedure, homogeneous submicrometer-sized particles are immobilized by cross-linked polymer network in the dried gelcast body. The immobilized particles are ideal for consequent solid state reaction. Thus, perovskite phase of LSGM could be formed at a reduced temperature.

3.3. Sintering and microstructure

Sintered densities of LSGM pellets calcined at 1450°C for different times from 6 to 36 h are listed in Table 1. Relative density was determined by dividing the bulk density of the specimens by the theoretical density (6.45 g/cm^3). The theoretical density was obtained using the lattice parameter obtained from the XRD analysis: $a=$ 3.9206 Å. Although the gelcast powder converts thoroughly into the pervoskite phase at 1400°C, the higher calcined temperature of 1450°C was still chosen for the reason of densification. All samples have more than 95.5% relative density, while as the firing time increased, the relative density grows to a peak of 98.3% for 18 h, then it decreases to 95.5% for 36 h.

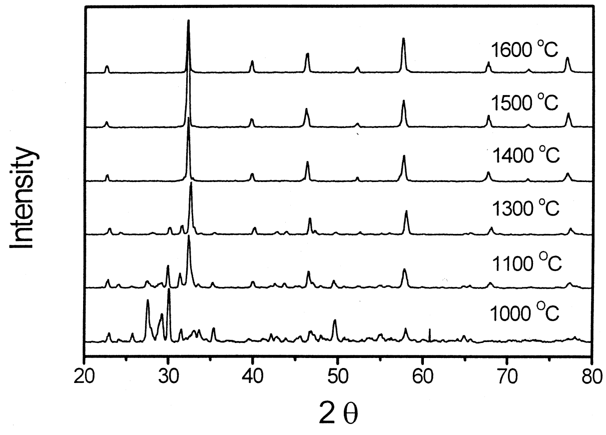


Fig. 2. Thermal evolution of the powder X-ray diffraction patterns of the LSGM gelcast powders calcined for 6 h.

Table 1
Relative densities of the pellets sintered at 1450°C

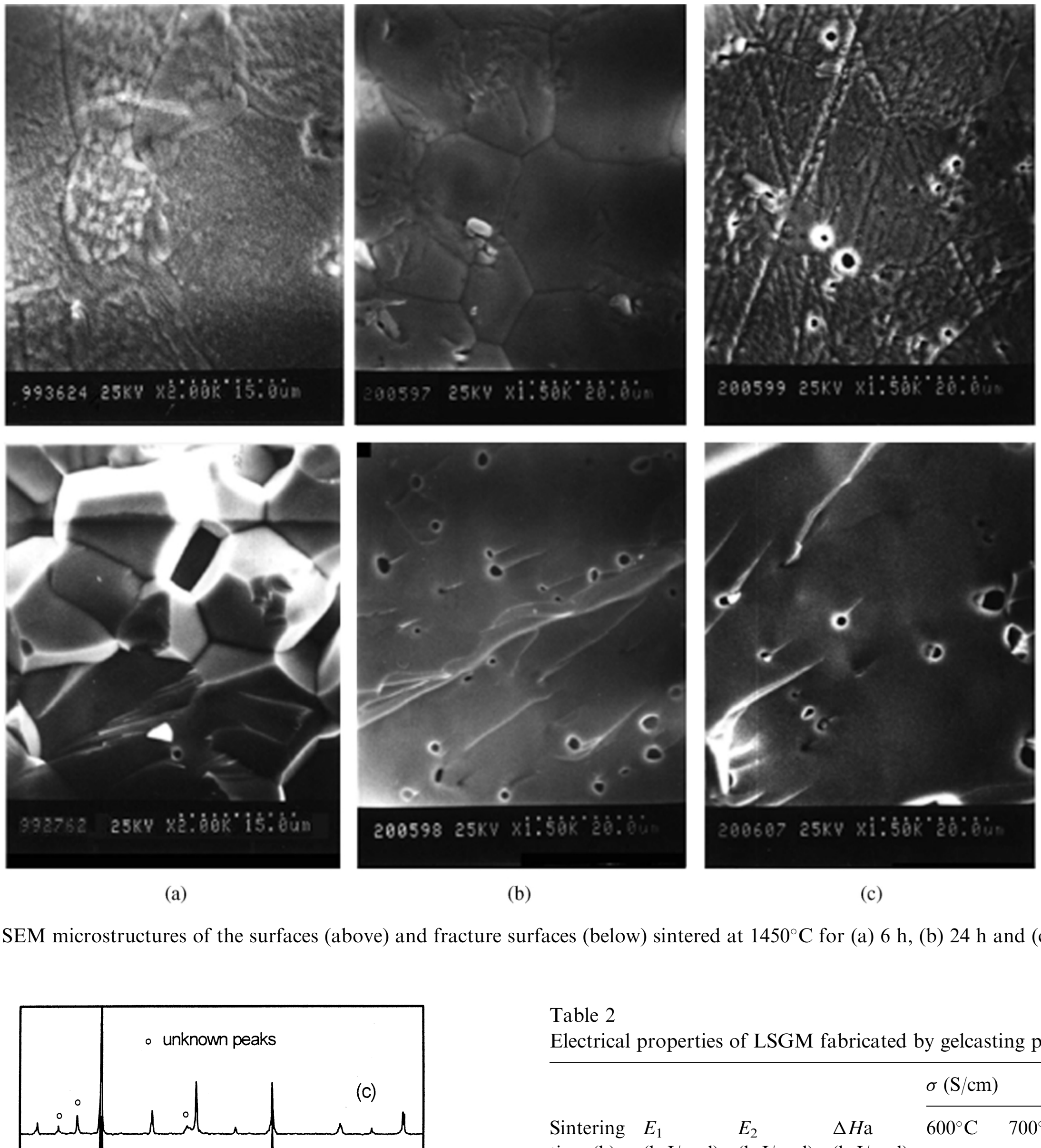
The sintering time (h)	6	12	18	24	36
Relative densities (%)	97.4	97.7	98.3	95.8	95.5

SEM photographs of the surfaces and fracture surfaces of the sintered samples for 6, 24 and 36 h are shown in Fig. 3. From this figure, it can be seen that with calcining time increasing the grain particles become more indistinguishable and the size and quantity of holes among the triple boundaries grow larger, which is in accordance to the density-changing pattern. Moreover, as shown in Fig. 3(c), some tiny particles are formed in the triple boundaries where the impurity phases are prone to accumulate at an ordinary occasion. Further research is needed to identify the materials and phase constitutions of them. However, a small proportion of unidentified phases indeed exist in the long-period calcining specimens (24 and 36 h), which can be seen in Fig. 4 of XRD patterns.

3.4. Electrical conductivity

The results of electrical conductivity measurements of LSGM sintered at 1450°C for different times (6, 12, 24 and 36 h) are shown in Fig. 5(a) as a plot of ln (σT) vs $1/T$. For clarity, since the data on the logarithmic plot tend to overlap, the specific values of conductivity are shown in Fig. 5(b). It can be seen that the sintering time has much effect on the electrical conductivity of LSGM synthesized by the gelcasting method. The electrical conductivity of LSGM increases with sintering time up to 24 h. Then it drops down as the sintering time is as long as 36 h. The first rising tendency is ascribed to the grain boundary effect which is believed that the conduction of grain boundary increases along with the increase of its size scale when the grain size is larger than 3 μm [8]. The SEM photographs can confirm this. On the other hand, just as discussed at the above section, the following decreasing trend indicates that too long sintering time induces some possible low-conductive phases and thus reduces the total bulk conduction. Another influential factor on the conduction decrease may be partly due to the lower relative density of the long sintering sample for 36 h [9,10]. The above results ascertain that appropriate selection of sintering time is definitely important considering the function of final materials and the consumption of energy.

The theory of electrical conduction has been described by Kilner and Steele [11]. In the perovskite structure of doped $LaGaO_3$, ionic conductivity resulted from the migration of oxygen vacancies due to doping effect both on A (La^{3+}) and B (Ga^{3+}) sites. The temperature dependence of the electrical conductivity σ of such a



(a) (b) (c)

Fig. 3. SEM microstructures of the surfaces (above) and fracture surfaces (below) sintered at 1450°C for (a) 6 h, (b) 24 h and (c) 36 h.

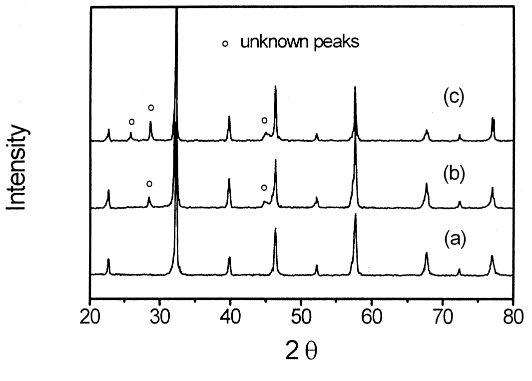


Fig. 4. Thermal evolution of the XRD patterns of the LSGM pellets sintered at 1450°C for (a) 6 h, (b) 24 h and (c) 36 h.

bulk conduction process is given by the theory of random walk, which can be empirically written as the following equation:

$$\sigma T = A\exp(-E_a/RT) \qquad (1)$$

where A is a pre-exponential factor and E_a is the activation energy of electrical conduction (or the enthalpy of vacancy migration). Thus, in the case of constant carrier concentration and constant activation energy, a plot of ln (σT) vs $1/T$ should give a straight line of slope -E_a/R.

Table 2
Electrical properties of LSGM fabricated by gelcasting powder

				σ (S/cm)		
Sintering time (h)	E_1 (k J/mol)	E_2 (k J/mol)	ΔHa (k J/mol)	600°C	700°C	800°C
6	94.3	51.4	42.9	0.014	0.041	0.073
12	92.2	51.2	41.0	0.017	0.047	0.081
24	93.3	50.2	43.1	0.018	0.053	0.096
36	87.6	57.4	30.2	0.015	0.042	0.076
Ref. [4][a]	86.0	67.1	18.9	0.021 (595°C)	0.065 (702°C)	0.140

[a] See Ref. [4]. $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.8}$ made by solid state reaction method was sintered at 1470°C for 24 h.

In fact, the plots in Fig. 5(a) exhibit differing slopes in the low- and high-temperature regions with the transitional temperature (T*) at about 675°C; the calculated activation energies in the two regions are summarized in Table 2, where E_1 is the low temperature activation

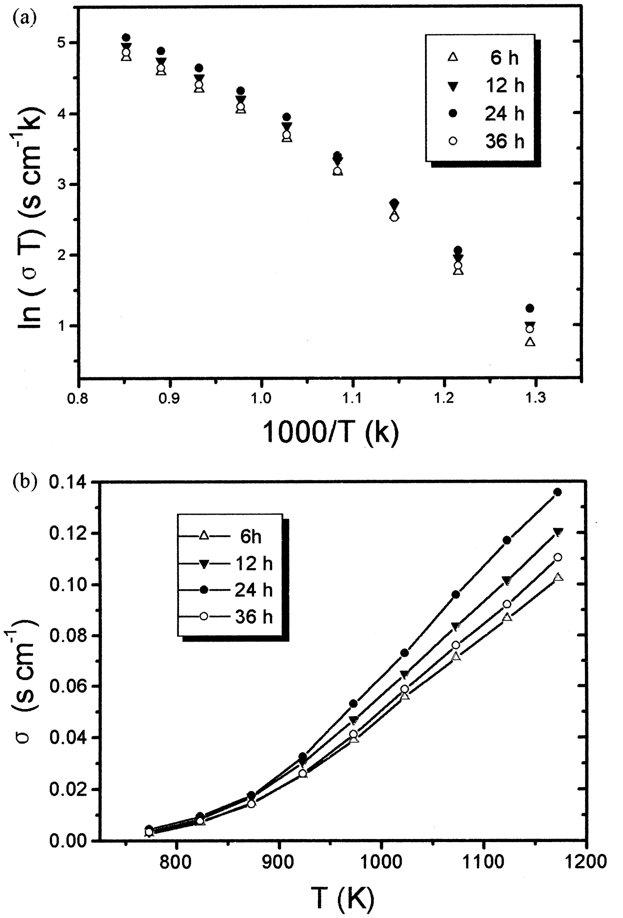


Fig. 5. Electrical conductivity of LSGM: (a) Arrhenius plot $1/T$, and (b) specific values vs T.

energy, E_2 is the high temperature activation energy and the specific values of conductivity at some typical temperatures are also listed. As Huang et al. [4] have stated, the dopant ions such as $\mathrm{Sr}'_{\mathrm{La}}$ and $\mathrm{Mg}'_{\mathrm{Ga}}$ may act not just as traps for isolated oxygen vacancies, but as nucleating centers for the formation of ordered-vacancy clusters. When the temperature is below T^*, the oxygen vacancies are progressively trapped out into the clusters as $\{\mathrm{M}'_{\mathrm{X}}\mathrm{V\ddot{o}}\}$ (here M stands for Sr or Mg, X stands for La or Ga) with decreasing temperature. At higher temperature above T^*, the vacancies are dissolved into the matrix of oxygen sites. The difference of the slopes between the two ranges is the association enthalpy (ΔHa) of $\{\mathrm{M}'_{\mathrm{X}}\mathrm{V\ddot{o}}\}$. As can be concluded from Table 2, the association enthalpy has small difference among 6, 12 and 24 h species. But to the one of 36 h sintering time, the association enthalpy sharply reduces to 30.2 k J/mol. This result also backs up the previous discussion of other newly formed phases other than the perovskite in the 36 h sample.

In this work, the electrical conductivity of the 24 h sample at 800°C is 0.096 S/cm, which is lower compared to the reported result by Huang et al. [4] where the calcination condition was at 1470°C for 24 h (Table 2). However, at the reduced temperatures, for example, σ values at 600 and 700°C are 0.018 and 0.053 S/cm, respectively, which are nearly the same as Huang's results of 0.021 and 0.065 S/cm at 575 and 702°C. In addition, the association enthalpies are much higher than Ref. [4] for all sintering conditions. Further work should be conducted on how to improve the electrical conductivity of LSGM at the elevated temperatures fabricated on the principle of gelcasting.

4. Conclusions

Perovskite $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.8}$ powders have been synthesized from carbonate and oxides based on the principle of gelcasting. A pure cubic phase is formed by sintering at 1400°C for 6 h without formation of any impurity that often existed in the product of traditional ceramic synthesis method. The samples heated at 1450°C have relative densities higher than 95%. The relative density reaches 98.3% for the LSGM pellet heated at 1450°C for 18 h. The electrical conductivity of the obtained LSGM depends on the sintering temperature and time. For the sample sintered at 1450°C for 24 h, the electrical conductivity reaches its highest values in the investigated temperature range. The plots of ln (σT) vs $1/T$ exhibit differing slopes in the low- and high-temperature regions with the transitional temperature T^* at about 675°C, due to the formation of ordered-vacancy clusters at low temperature. Consequently, it can be concluded that gelcasting is a simple and effective method for preparing practical multicomponent perovskite powders of LSGM electrolyte.

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