

CHEMICAL SYNTHESIS OF PURE AND DOPED LaGaO_3 POWDERS OF OXIDE FUEL CELLS BY AMORPHOUS CITRATE/EG-METHOD

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ABSTRACT

Powders of LaGaO_3 , $\text{La}_{0.9}\text{Sr}_{0.1}\text{GaO}_{3.95}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.85}$ were prepared by the amorphous citrate/EG method. The calcination behavior of the precursor powders of the above phases were studied in the temperature range of 200°-1400°C, in an air atmosphere. Characterization of the samples were performed by XRD, TG/DTA, FTIR, SEM, ICP-AES, and carbon and nitrogen analyses.

INTRODUCTION

Sr- and Mg-doped LaGaO_3 ceramics are known [1] to have superior oxygen ion conducting properties as compared, for instance, to yttria-stabilized zirconia electrolytes. In recent years, several researchers have synthesized the Sr- and Mg-doped LaGaO_3 ceramics by mainly using the conventional, 'solid-state reactive firing' method [2-4]. Stevenson, *et al.* [5] have tried the glycine-nitrate combustion synthesis for the preparation of Sr- and Mg-doped LaGaO_3 powders. The route of co-precipitation (w/ NH_4OH addition) from an aqueous mixture of the acetates of La, Sr, and Mg, and of Ga-nitrate have also been attempted by Huang, *et al.*, [6]. In this paper, a chemical preparation route is outlined for the synthesis of pure and doped LaGaO_3 ceramics. The product powders are fully characterized (phase distribution, particle size and morphology, IR behavior, thermogravimetric and chemical analyses).

EXPERIMENT

The powders were synthesized from $\text{La}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck, Germany), $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (Sigma, USA), $\text{Sr}(\text{NO}_3)_2$ (Merck) and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck). A Pechini-type process [7-8] was employed to prepare the polymeric precursors. For each precursor, nitrate salt solutions corresponding to a 5 g yield of LaGaO_3 ceramics were mixed in 50 ml. of boiled, de-ionized water. Citric acid monohydrate (60 wt%-ethylene glycol (40 wt%) mixture was added (mole ratio of citric acid-to-total cations=1.88) to the cations solution. The resulting solution was evaporated until first a yellow gel, then a dark brown resin, formed. The resins were finely ground by using an agate mortar/pestle, and then calcined in air at various temperatures (200°-1400°C). Each calcination batch was heated to the specified temperature at a rate of 5°C/min, annealed at this temperature for 6 h, and furnace cooled to room temperature. The phase distribution in the powders was analyzed as a function of calcination temperature using a Siemens D-5000 X-ray diffractometer and $\text{CuK}\alpha$ radiation (30kV, 20 mA). Pyrolysis and decomposition of 150 mg of the ground, amorphous resin samples were monitored by simultaneous differential thermal and thermogravimetric analysis (STA501, Bahr GmbH) in air at a rate of 5°C/min. FTIR analyses of the samples were performed (IFS 66, Bruker GmbH) by mixing them (1 wt%) with dry KBr to form the pellets. The residual C and N contents of the uncalcined and calcined powders were studied by the combustion-IR absorption method (CS-800, Eltra GmbH). ICP-AES analyses were performed to get the quantitative elemental information (YF-70Plus, Instruments SA). The morphology of the powders was studied by scanning electron microscopy (DSM 982 Gemini, Zeiss GmbH).

RESULTS AND DISCUSSION

The phase evolution and distribution behaviors of pure (i.e., 1G: LaGaO_3) and doped (i.e., 1SG: $\text{La}_{0.9}\text{Sr}_{0.1}\text{GaO}_{3.95}$ and 1SGM: $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.85}$) lanthanum gallate samples are depicted by the XRD spectra of Fig. 1. LGSamples (after calcination in air at 1200°C for 6 h) were found to be orthorhombic with the lattice parameters of $a=5.489$, $b=5.519$, $c=7.751$ Å, which are in close agreement

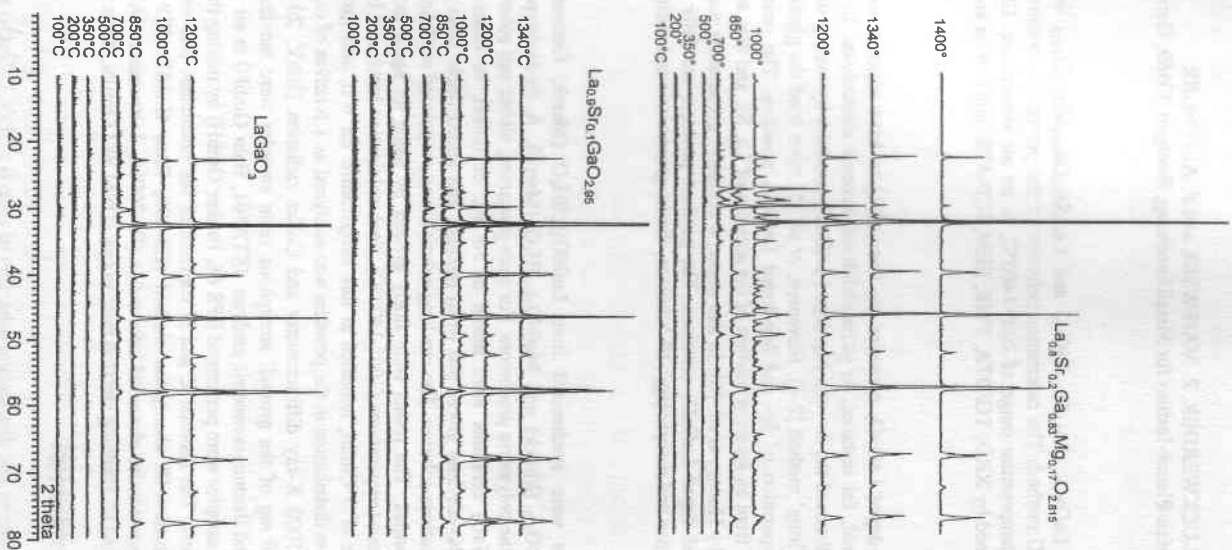


Fig. 1 XRD spectra of precursor powders of LG, LSG and LSGM samples

with the previously reported values [3]. LSG samples (after calcination at 1340°C for 6 h) were also orthorhombic with the lattice parameters of $a=5.491$, $b=5.523$, $c=7.764$ Å. Although the single-phase LG was formed from the starting X-ray amorphous resins at about 850°C, single-phase LSG could only be produced after calcination at 1340°C for 6 h. The resins of the LSG stoichiometry, after calcination at 1200°C, still contained the secondary phases of $\text{La}_2\text{Ga}_2\text{O}_9$ and $\text{SrLaGa}_3\text{O}_{10}$. The resins of the LSGM stoichiometry, on the other hand, contained about 3–4 wt% of the above-mentioned secondary phases even after calcination at 1400°C for 8 h. The crystal structure of the LSGM samples of this study were found to be non-cubic (i.e., orthorhombic), in sharp contrast to many earlier reports [2–4, 6], and this finding about the crystal structure of LSGM is in accordance with the recent study of fishihara, *et al.* [9].

The results of the simultaneous TG/DTA analyses are given in Fig. 2. The DTA traces of LSG and LSGM resins showed exotherms at -400° , 490° , and 605°C . The first exotherm was associated with charring of the polymer, the second with the pyrolysis of the organics, and the last one resulted from char burnout. TG analysis showed that most of the weight loss occurred at temperatures between 250° and 500°C . This corresponded to the range where polymer burnout occurred. The results of residual carbon analyses (as a function of calcination temperature) are shown in Table 1. The nitrogen content of the 100°C-calcined precursor samples were found to be in the range of 1.05 to 1.2 wt%, but with increasing calcination temperatures (starting from 200°C) it decreased to levels below the reliable detection level (i.e., 100 ppm) of the equipment used.

ICP-AES analysis results (in terms of mole ratios) of the 1340°C-calcined samples of LSG (i.e., $\text{La}/\text{Sr}=8.984$, $\text{La}/\text{Ga}=0.912$) and LSGM ($\text{La}/\text{Sr}=3.990$, $\text{La}/\text{Ga}=0.958$, $\text{La}/\text{Mg}=4.693$) compositions confirmed the theoretical mole ratios of elements present. Amorphous citrate/EG method, therefore, is shown to be able to yield LSG and LSGM ceramics of high elemental uniformity.

Table 1. Results of residual carbon analyses (wt%)

Temp. (°C)	LaGaO_3	$\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.815}$	$\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.815}$
100	31.7 (3)	33.3 (2)	32.7 (6)
350	10.3 (3)	10.4 (1)	13.8 (2)
700	0.530 (3)	0.550 (5)	0.280 (4)
850	0.059 (1)	0.143 (9)	0.168 (3)
1000	0.042 (2)	0.050 (3)	0.060 (2)
1340	0.010	0.0124 (2)	0.0143 (4)

FTIR plots (as a function of calcination temperature) of the LG, LSG, and LSGM samples are given in Fig. 3. The broad band at $3500\text{--}2500\text{ cm}^{-1}$ is due to O-H stretching. The presence of the citrate ion was detected by the band at $2990\text{--}2874\text{ cm}^{-1}$ at low calcination temperatures. Dissolved or atmospheric CO_2 was indicated by the band at 2350 cm^{-1} . The carboxylate anion (COO) stretching was seen by two bands in the range of $1740\text{--}1380\text{ cm}^{-1}$, and the structural CO_3^{2-} was observed by the broad band at $1500\text{--}1300$, also at $1080\text{--}1030$, and 800 cm^{-1} . The existence of a covalent carbonyl bond (C=O stretching vibration) was found by the bands at $1730\text{--}1700$ and $1190\text{--}1075\text{ cm}^{-1}$, and the bands at $1440\text{--}1300$ and $1070\text{--}1030\text{ cm}^{-1}$ indicated the trace presence of nitrate ions in the low temperature (100°C) samples. Because of the appearance of bands due to CO_2 adsorbed on the metal cations, the decrease in the intensity of the bands due to citrate/carboxylate groups and the lower intensity of the water stretching band, one may conclude that the metal-carbonyl links begin to break after heating to $>350^\circ\text{C}$. Samples calcined at 700°C basically show the CO_3^{2-} and OH^- ions in their IR spectra. After calcination at 1200°C , all IR bands attributed to anion vibrations disappeared in all samples.

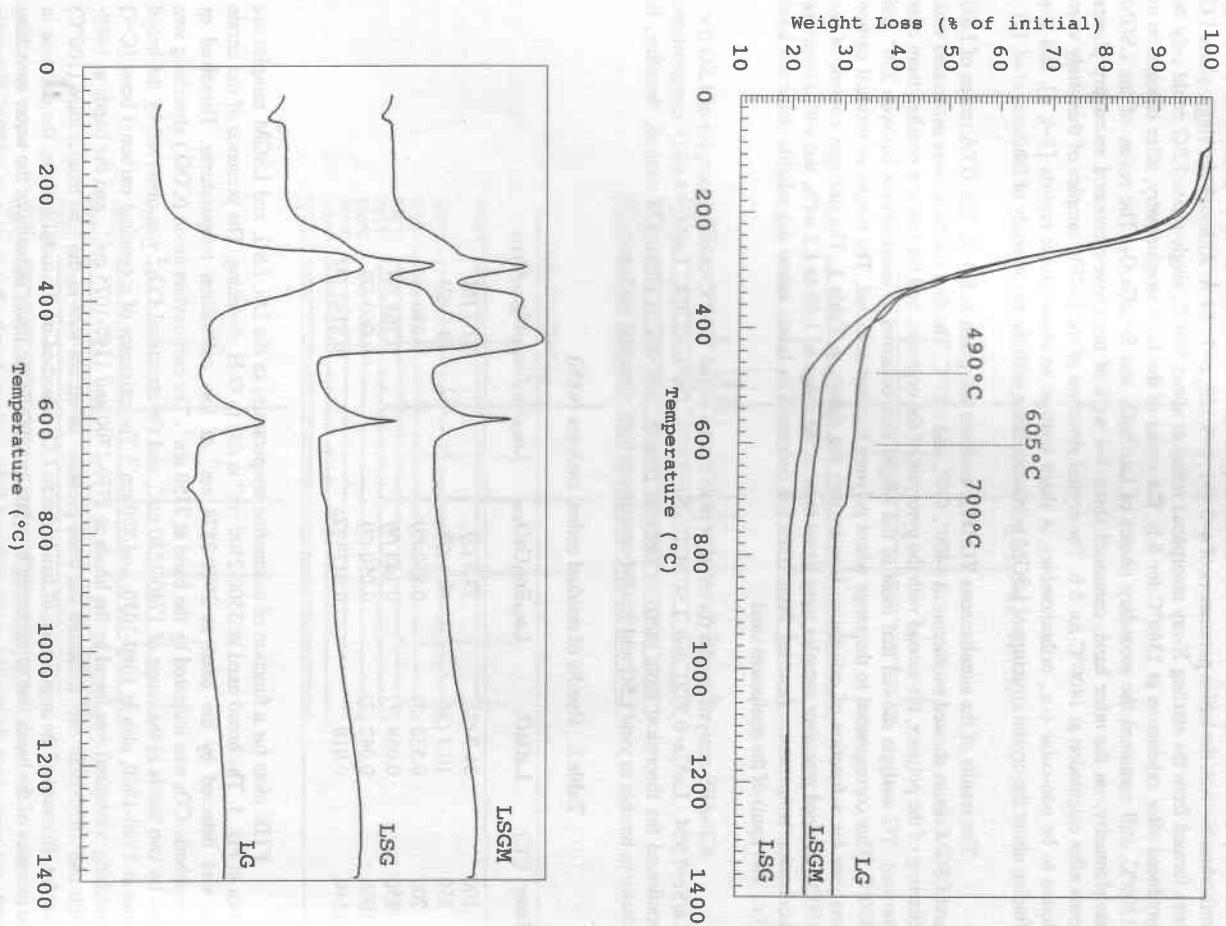


Fig. 2 TG (top) and DTA (bottom) spectra of precursors of LG, LSG and LSGM samples

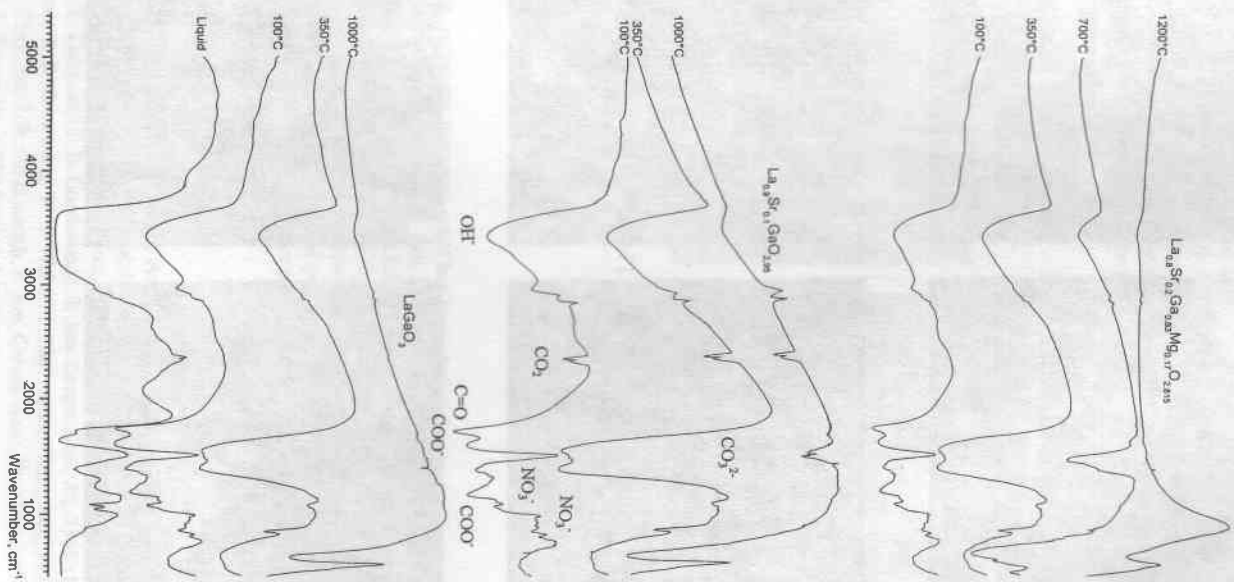


Fig. 3 FTIR spectra of the precursors of LG, LSG and LSGM samples

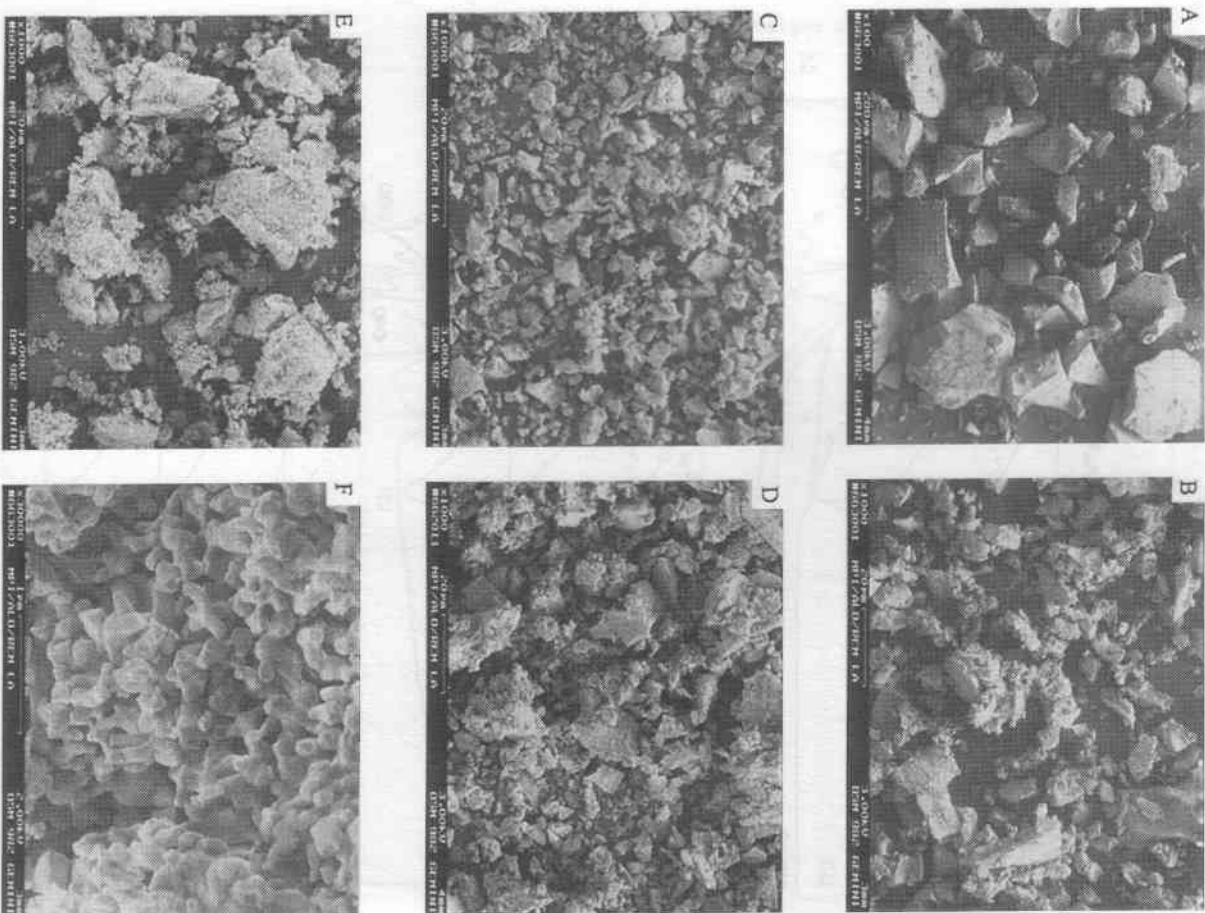


Fig. 4 SEM micrographs of LSGM samples (a) 100°, (b) 350°, (c) 500°, (d) 700°, (e) & (f) 1000°C

The powder morphology of LSGM powders, as a function of calcination temperature, was given by the SEM pictures of Fig. 4. The initially X-ray amorphous particles (of irregular morphology) began decomposing above 500°C (Figs. 4(c) and 4(d)), and after calcination at 1000°C, the bigger chunks consisted of smaller particles (~0.2 µm), fused together (Figs. 4(e) and 4(f)). The fracture surface of a pellet of LSGM powders (CIPped at 650 Mpa and then calcined at 1400°C for 8 h) indicates (Figs. 4(g) and (h)) that after sintering, the final grain size was still ≤ 2 µm.

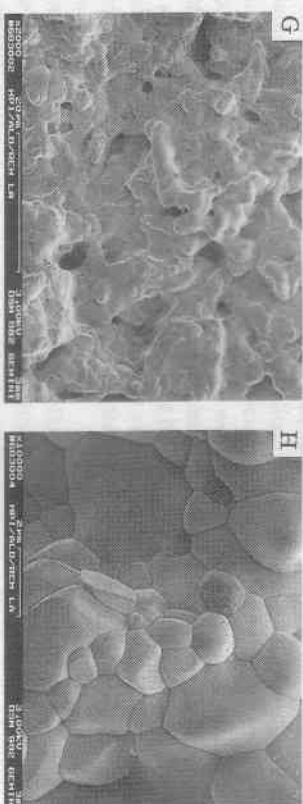


Fig. 4 (cont.) SEM micrographs of LSGM pellets: (g) and (h) 1400°C, 8 h

CONCLUSIONS

A Pechini-type, polymeric precursor route has been studied for the synthesis of powders of LG, LSG and LSGM. Although single-phase LG and LSG powders were successfully synthesized after calcination at 800° and 1340°C, respectively, the LSGM powders still contained 3-4 wt% of secondary phases in them after calcination at 1400°C for 8 h. According to the results of FTIR analysis, LSG samples have shown, at all temperatures, an increased affinity for the atmospheric CO₂, as compared to LG powders. Calculation of LG, LSG and LSGM precursors at temperatures in excess of 1000°C was found to be necessary to reduce the C-content to the ppm levels.

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