

## Sol-Gel syntheses and phase purity of

### $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$ solid electrolytes

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Lanthanum gallate resins (pure or Sr- and Mg-doped) were synthesized from nitrates to prepare  $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$  (LSGM) ceramic materials with  $0 \leq x, y \leq 0.20$  and by using two different chemical syntheses, namely Pechini (1) or citrate (2) sol-gel method.

The obtained resins (after overnight drying in oven at  $110^\circ\text{C}$ ) were calcined isothermally in the temperature range of  $800\text{--}1500^\circ\text{C}$  ( $5^\circ\text{C}/\text{min}$  heating rate).

Table 1 summarizes the ceramic powders obtained by both sol-gel methods. LG refers to pure lanthanum gallate;  $\text{LS}_x\text{GM}_y$  labels refer to doped  $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$  materials.

	Powder	Calcination treatment
Pechini	LG/P	6 h in the $800\text{--}1200^\circ\text{C}$ range
	$\text{LS}_{0.2}\text{GM}_{0.15}/\text{P}$	9 h in the $900\text{--}1400^\circ\text{C}$ range
	$\text{LS}_{0.15}\text{GM}_{0.15}/\text{P}$	$1400^\circ\text{C}$ , 9 h
	$\text{LS}_{0.1}\text{GM}_{0.15}/\text{P}$	$1400^\circ\text{C}$ , 9 h
	$\text{LS}_{0.1}\text{GM}_{0.1}/\text{P}$	$1400^\circ\text{C}$ , 15 h + $1500^\circ\text{C}$ , 10 h
	$\text{LS}_{0.1}\text{GM}_{0.1}/\text{P}$	$1400^\circ\text{C}$ , 9 h
Citrate	$\text{LS}_{0.1}\text{GM}_{0.1}/\text{C}$	$1400^\circ\text{C}$ , 15 h + $1500^\circ\text{C}$ , 10h
	$\text{LS}_{0.1}\text{GM}_{0.1}/\text{C}$	$1400^\circ\text{C}$ , 9 h
	$\text{LS}_{0.1}\text{GM}_{0.2}/\text{C}$	$1400^\circ\text{C}$ , 9 h
	$\text{LS}_{0.15}\text{GM}_{0.2}/\text{C}$	$1400^\circ\text{C}$ , 9 h
	$\text{LS}_{0.2}\text{GM}_{0.15}/\text{C}$	$1400^\circ\text{C}$ , 9 h

Table 1. Lanthanum gallate ( $\text{LaGaO}_3$ , LG) and  $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$  ( $\text{LS}_x\text{GM}_y$ ) powders prepared by Pechini (P) or citrate (C) sol-gel synthesis.

The calcined powders were characterized by X-Ray Diffraction (XRD) scanning electron microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS).

After calcination of the  $\text{LS}_{0.2}\text{GM}_{0.15}$  resin at  $900^\circ\text{C}$ , only low intensity perovskite peaks could be detected in the XRD spectrum and the powder consisted of a mixture of a number of phases. Even after 9 h calcination at  $1400^\circ\text{C}$ , the precursor powder was not single-phase. In fact, the most intense diffraction peaks of  $\text{SrLaGaO}_4$  and  $\text{SrLaGa}_3\text{O}_7$  were still detectable in the XRD pattern. The relative amounts of these two secondary phases decreased with the increase of calcination temperature and, therefore, it was decided to heat at temperatures not lower than  $1400^\circ\text{C}$  all LSGM precursor powders prepared by both sol-gel methods. Fig. 1 shows the full width at half maximum (FWHM) of the (121) peak of  $\text{LaGaO}_3$  (LG) and  $\text{LS}_{0.2}\text{GM}_{0.15}$  perovskites synthesized by Pechini process as a function of the calcination temperature. For each phase, the data indicated a reduction of FWHM with the increase of calcination temperature.

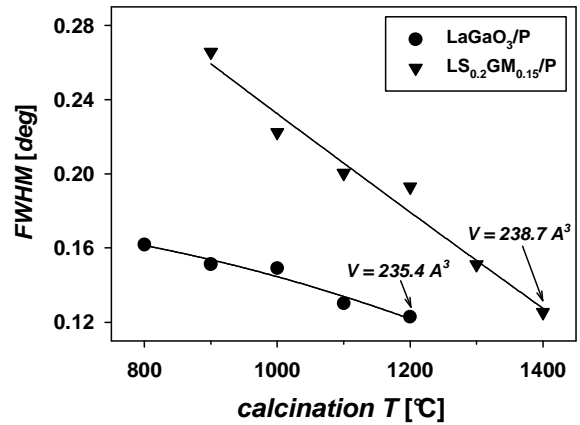


Fig. 1 FWHM of the (121) XRD peak of  $\text{LaGaO}_3$  (circles) and  $\text{LS}_{0.2}\text{GM}_{0.15}$  (triangles) perovskite phases as a function of calcination temperature. LG and LSGM calcination times were 6 h and 9 h, respectively.

However, XRD peaks of  $\text{LS}_{0.2}\text{GM}_{0.15}$  phase were systematically larger than diffraction peaks of LG phase calcined at the same temperature and for a shorter time. The broader XRD peaks of  $\text{LS}_{0.2}\text{GM}_{0.15}$  powder calcined at a given temperature could not be attributed to crystallite size effects, but to the presence of vacancies in the doped phase, which reduce the long range order of the perovskite phase. To study the role of both dopant levels and synthetic route on the presence of secondary phases in calcined powders, the relative amounts of  $\text{SrLaGaO}_4$  and  $\text{SrLaGa}_3\text{O}_7$  were estimated by measuring the ratio,  $A_s/A_p$ , of the total integrated intensities of the most intense XRD peaks of these phases over the integrated intensity of the (121) peak of the perovskite. The data showed that: 1) at a given Sr content, the relative amounts of  $\text{SrLaGaO}_4$  and  $\text{SrLaGa}_3\text{O}_7$  decreased with the increase of Mg, *i.e.* with the decrease of gallium content in the doped perovskite; 2) at a given Mg content, the amount of Sr-containing secondary phases increased with  $x$ , *i.e.* with the strontium content; 3) the performance of a longer calcination run at  $1400^\circ\text{C}$  followed by a further 10 h calcination at  $1500^\circ\text{C}$  did not allow to significantly reduce the amount of  $\text{SrLaGa}_3\text{O}_7$  in the powder; 4) the citrate method did allow to obtain LSGM materials with a slightly larger phase purity.

## REFERENCES

- (1) M. Pechini, U. S. Patent No. 3 330 697 (11 July 1967).
- (2) P. Ciambelli, S. Cimino, L. Lisi, M. Faticanti, G. Minelli, I. Pettiti, P. Porta, *Appl. Catal. B* **33**, 193-203 (2001) and references therein.