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Second Phases in Doped Lanthanum Gallate Perovskites

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Abstract

Synthesis of $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ *with* $0{\cdot}098 \leq x$ *mol%* $\leq 0{\cdot}100$ *and* $0{\cdot}196 \leq y$ *mol%* $\leq 0{\cdot}200$ *was performed in three ways: according to the solid state route either from oxides, or from oxides and carbonates and from powders prepared by ultrasonic spray pyrolysis. The samples were heterogeneous with a 'crust' of a darker color. Impurity phases could be found in this crust and in the nucleus. Their nature and concentration depend on the method of synthesis, the sintering temperature, time and atmosphere and on strontium content.*

La synthèse de $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ *avec* $0{\cdot}098 \leq x$ *%mol* $\leq 0{\cdot}100$ *et* $0{\cdot}196 \leq y$ *%mol* $\leq 0{\cdot}200$ *a été effectuée suivant trois méthodes: par voie solide, la première en partant des oxydes, la deuxième en partant des oxydes et des carbonates et la troisième voie en partant de poudres préparées par pyrolyse d'un aérosol généré par ultrasons. Les échantillons sont en général hétérogènes avec la formation d'une croûte de couleur plus foncée. Des phases secondaires ont été mises en évidence dans la croûte et au coeur du matériau. Leur nature et leur concentration dépendent du mode de synthèse, de la température, du temps et de l'atmosphère de frittage et du taux de strontium.* © *1998 Elsevier Science Limited. All rights reserved*

1 Introduction

Doped lanthanum gallate (LSGM) first synthesized by Ishihara *et al.*[1] and Feng and Goodenough[2] appears highly promising as a new solid oxide electrolyte for use at medium temperature. At 700°C, for instance, its ionic conductivity is around 4 times higher than that of the conventional yttrium stabilized zirconia (YSZ). An additional quality of this perovskite is the width of its electrochemical stability window. According to Ishihara *et al.*,[1] the electromotive force (emf) of an H_2,H_2O/LSGM/air cell is close to the theoretical value. This would definitely put it at advantage with respect to the other potential medium temperature solid electrolytes based on CeO_2 or Bi_2O_3.

However, the synthesis of a pure single phase material is found to be rather difficult.

2 Experimental

2.1 Materials preparation

The synthesis of $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ referred to hereafter as $L_{1-x}S_xG_{1-y}M_y$ with $0{\cdot}098 \leq x$ mol% $\leq 0{\cdot}100$ and $0{\cdot}196 \leq y$ mol% $\leq 0{\cdot}200$ was carried out in three ways: from a mixture of either oxides,[1] or oxides and carbonates[2] and from homogeneous powders prepared by ultrasonic spray pyrolysis. The origins and chemical purity of the raw products are given in Table 1.

2.1.1 Solid state synthesis from oxides (synthesis procedure A)

Calculated amounts of La_2O_3, SrO, Ga_2O_3 and MgO were ground for 3 h in ethanol and, after evaporation, calcined at 1000°C for 6 h.

2.1.2 Solid state synthesis from carbonates and oxides (B)

Calculated amounts of La_2O_3, $SrCO_3$, Ga_2O_3 and $MgCO_3$ were ground in ethanol and then pelletized and fired in a platinum crucible at 1300°C for 24 h.

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Table 1. Supplier and chemical purity of the raw products

Synthesis	*Products*	*% chemical purity*	*Supplier (reference)*
A	La_2O_3	99·995	Prolabo (24960·260)
A	SrO	99·999	Merck (382250)
A	Ga_2O_3	99·99+	Acros (20·110)
A	MgO	99·999	Acros (19343)
B	La_2O_3	99·99	Alfa products (87808)
B	$SrCO_3$	99·99	Alfa products (35793)
B	Ga_2O_3	99·99	Alfa products (32102)
B	$MgCO_3$	99·9	Alfa products (33333)
P	$La(NO_3)_3{\cdot}6H_2O$	99·99	Prolabo (24958·238)
P	$Sr(NO_3)_2$	99	Prolabo (28345·261)
P	$Ga(NO_3)_3$	99·9	Aldrich (28989·2)
P	$Mg(NO_3)_2{\cdot}6H_2O$	97	Prolabo (25134·295)

2.1.3 Ultrasonic spray pyrolysis (P)

This synthesis procedure is derived from that reported elsewhere for thin film elaboration.[3] It is based on the pyrolysis, in a tubular furnace, at 1173 K, of an aerosol produced by ultrahigh-frequency spraying of a precursor solution. The salts used were nitrates (Table 1) which were dissolved in an aqueous solution. The total concentration in nitrates was $5{\times}10^{-2}$ M. A preliminary investigation in a Netzsch STA 409 thermal analyser showed that their total thermal decomposition occured at 650°C. The resulting powder was partially crystallized and was a mixture of several phases (typically $La_4Ga_2O_9$ and La_4SrO_7) indicating an incomplete reaction. A SEM micrograph (Fig. 1) of a powder prepared by this method shows spherical particles with average diameters ranging from 1 to 5 μm. A dilatometric analysis was performed to determine the optimum sintering conditions. Densification was observed around 1500°C.

The samples prepared according to the above synthesis will be identified by the corresponding A, B or P superscripts, as $L_{1\text{-}x}\,S_xG_{1\text{-}y}M_y{}^P$.

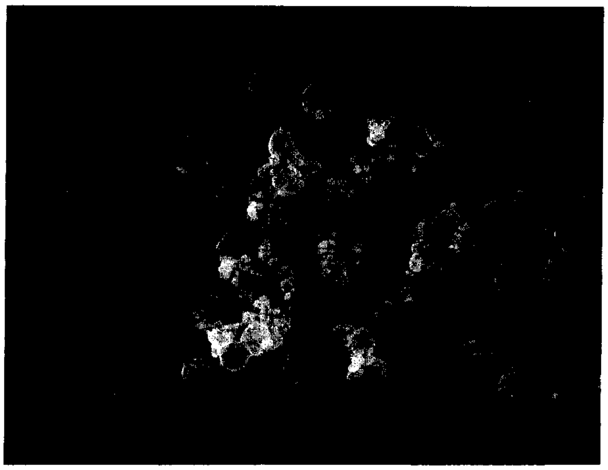

Fig. 1. SEM micrograph of a $L_{1\text{-}x}S_xG_{1\text{-}y}M_y$ powder obtained by spray pyrolysis.

The powders prepared by the three methods were re-ground. The final pressing and sintering conditions for these three series of samples are detailed in Table 2. The isostatic pressing was performed after packing under vacuum.

- Before compaction and sintering, some of the powders of the $L_{.9}S_{.1}G_{.8}M_{.2}{}^{*P}$ series were precalcined under air, for 6 h at 1000, 1250 and 1500°C (G1, G2, G3 samples, Table 3). The corresponding samples were all sintered at 1500°C for 6 h in air (G′1, G′2, G′3 samples, Table 3).
- Numerous samples of the P type were also sintered under different atmospheres to determine the influence of this parameter. The effect of the sintering atmosphere was investigated at 1400°C under air, Ar, Ar/5%H_2 (D3, I2, J1, Tables 3 and 4), at 1450°C under O_2 and Ar (H1 and I1, Table 4) and moist air (K1, Table 4).
- To investigate possible changes in the redox state of the ceramics, $L_{.9}S_{.1}G_{.8}M_{.2}{}^{*P}$ samples were first sintered under various conditions and then annealed under different atmospheres detailed in Table 5.

In the following, the inside of the ceramics will be identified by a prime in the notation (as A′1) in Tables 3 and 4.

The inside of the A1 pellet (A′1, Table 3) which was synthesized at 1500°C for 6 h in air from a mixture of oxides was also annealed in Ar/5%H_2 at 1200°C for 6 h.

- The volatilization of a constituent of the LSGM phases was suspected to explain some of the results. To reduce this possible cause of alteration, some samples were sintered in a crucible filled with a powder of the same composition. These samples will be identified by a VP (volatilization protected) code. To directly characterize the effects of a possible volatilization, we prepared these samples with a cationic non-stoichiometry. They contained either an excess of 2 mol% of Ga on the B-site or an excess of 2 mol% of La on the A-site.

2.2 Characterization

X-ray characterization at room temperature was carried out on the powders and the ceramics, using a Siemens D500 diffractometer equipped with a

Table 2. Final pressing and sintering conditions

Synthesis	*Cold pressing (MPa)*	*Sintering temperature in air (°C)*	*Sintering time (h)*
A	250 isostatic	1500	6
B	100 uniaxial	1430–1500	24
P	250 isostatic	1200–1550	0·25–48

Table 3. Effects of the sintering temperature and time (in air)

Sample		*I/S*	*Temperature (°C)*	*Time (h)*	*Colour*	*$LaGaO_3$*	*La_2O_3*	*MgO*	*$LaSrGa_3O_7$*	*$Sr_3Ga_2O_6$*	*$La_4Ga_2O_9$*	*$La_3Ga_5O_{12}$*	*$MgGa_2O_4$*	*La_2SrO_x*	*$LaSrGaO_4$*	*Non assigned peaks and additional observations*
$L_{.9}S_{.1}G_{.8}M_{.2}{}^{*A}$	A′1:	I	1500	6	Grey	x	x	ε								
	A1:	S	1500	6	Black	x										Cubic phase isotypic of $Sr_3Ce(PO_4)_3$
$L_{.8}S_{.2}G_{.85}M_{.15}{}^{*B}$	B′1:	I	1430→1500	24	Grey	x			x	ε						
	B1:	S	1430→1500	24	Brown	x										
$L_{.8}S_{.2}G_{.8}M_{.2}{}^{*P}$	C′1:	I	1500	6	Light brown	x				x	ε					38° and 44·2°
	C1:	S	1500	6	Brown	x										
$L_{.9}S_{.1}G_{.8}M_{.2}{}^{*P}$	D1:	S	1400	0·25	Light brown	x				x						
	D2:	S	1400	2	Brown	x				x						
	D3:	S	1400	6	Black	x					x					33·5°,49·5°,55°
	D3′:	I	1400	6	Grey	x	ε				x					
	E′1:	I	1500	48	Light brown	x				x	ε					38° and 44·2°
	E1:	S	1500	48	Dark brown	x					x					38° and 44·2°
	F1:		1550	2	Dark grey											partial fusion
$L_{.9}S_{.1}G_{.8}M_{.2}{}^{*P}$ Powder	G1:		1000	6	White	x					x				x	24°, 49·5, 55°
	G2:		1250	6	Ivory	x				x	x				ε	24°
	G3:		1500	6	Ivory	x				x	ε					41·5°, 54°
$L_{.9}S_{.1}G_{.8}M_{.2}{}^{*P}$ Ceramic	G′1:	I	1500	6	Brown	x				x						38°, 44·2°
	G1:	S	1500	6	Dark brown	x				x	x					> 38°,41·5°,44·2°,54°
	G′2:	I	1500	6	Grey	x	x			x						38° and 44·2°
	G2:	S	1500	6	Black	x	x			x						38° and 44·2°
	G′3:	I	1500	6	Light brown	x				x	x					38°, 41·5°,44·2°,54°
	G3:	S	1500	6	Brown	x				x	ε					38°, 41·5°, 44·2°, 54°

*A: Solid state route from oxides;
*B: solid state route from oxides and carbonates;
*P: pyrolysis method.
I/S: Inside/surface layer

Table 4. Effects of the sintering atmospheres

Sample		I/S	Atmosphere	Temperature (°C)	Time (h)	Colour	$LaGaO_3$	La_2O_3	MgO	$LaSrGa_3O_7$	$Sr_3Ga_2O_6$	$La_4Ga_2O_9$	$La_3Ga_5O_{12}$	$MgGa_2O_4$	La_2SrO_x	$LaSrGaO_4$	Non assigned peaks and additional observations
$L_{.9}S_{.1}G_{.8}M_{.2}{}^{*P}$	H′1:	I	O_2	1450	12	Light brown	x				x						38° and 44·2°
	H1:	S	O_2	1450	12	Dark brown	x										38° and 44·2°
	I1:	S	Ar	1450	12	Light pink	x				ε	x	x				
	I2:	S	Ar	1400	2	Light pink	x				ε	x	x				38 and 44·2°
	J1:	S	$Ar/5\%/H_2$	1400	6	Ivory						ε			x	x	53,5° and 56°; decomposition in air as powder
	J1 annealed:	S	Air	1450	12	Black		x				x		ε	x	x	24°, 44·2°, 47°, 53.5°
	first I2 annealed:	S	Air	1400	6	Black	x										38° and 44·2°, 19.5°, 24·5°, 30·5°, 47·5°, 50·5°, 53·5°
	second I2 annealed:	I	Air	1500	6	Light Brown	x				x						28·8°, 41·5°, 53·5°
	second I2 annealed:	S	Air	1500	6	Black	x										38°
$L_{.9}S_{.1}G_{.8}M_{.2}{}^{*A}$																	
	A1 annealed:	I	$Ar/5\%/H_2$	1200	6	Grey		x						ε	x	x	24°, 43·5°, 47°, 53·5°
	A1 annealed:	S	$Ar/5\%H_2$	1200	6	Dark grey	x					x					27°, 31°, 32° + cubic phase isotypic of $Sr_3Ce(PO_4)_3$
$L_{.9}S_{.1}G_{.8}M_{.2}{}^{*P''}$																	
	D3 annealed:	S	Ar	1350	6	Dark brown	x				x						
	K′1:	1	Moist air	1500	6	Light brown	x				x						28·8°, 41·5°, 53·5°
	K1:	S	Moist air	1500	6	Black	x				ε						28·8°
	K′2:	I	Dry air	1500	6	Light brown	x				x						28·8°, 41·5°, 54°
	K2:	S	Dry air	1500	6	Black	x				ε						28°8°, 41·5°, 54°
	L′1:	I	VP	1450	6	Light brown	x				x						38°, 44·2°, ε28·8°
$L_{.882}S_{.098}G_{.8}M_{.2}{}^{*P}$	L1:	S	VP	1450	6	Light brown	x				x						28·8°
	L′2:	I	Air	1450	6	Brown	x				x						38° and 44·2°
	L2:	S	Air	1450	6	Black	x										28·8°, ε31°, 47°, 53·5°
	L′3:	I	Air	1500	6	Grey	x				x						28·8°, 41·5°, 53·8°
	L3:	S	Air	1500	6	Black	x										
	M′1:	I	VP	1450	6	Light brown	x				x						38°, 41·5°, 44·2°, 54
$L_{.9}S_{.1}G_{.784}M_{.196}{}^{*P}$	M1:	S	VP	1450	6	Light brown	x				x						28·8°, 41·5°, 48°, 54°
	M′2:	I	Air	1450	6	Light brown	x				x						38°, 41·5°, 44·2°, 54°
	M2:	S	Air	1450	6	Black	x										48°, 53·5°
	M′3:	I	Air	1500	6	Grey	x				x						28·8°, 41·5°, 54°
	M3:	S	Air	1500	6	Black	x										28·8°

*A: solid state route from oxides;
*B: solid state route from oxides and carbonates;
*P: pyrolysis method
VP: Volatilization protected. x′: Twinned LG phase.
I/S: Inside/surface layer

Table 5. Sintering and annealing conditions of $L_{.9}S_{.1}G_{.8}M_{.2}{}^{*P}$ samples

Sintering conditions	*References in Table 4*	*Annealing conditions*	*References in Table 4*
1400°C, 6 h, air	D3	1350°C, 6 h, Ar	Annealed D3
1400°C, 2 h, Ar	I2	1400°C, 6 h, air	I2 (1st anneal)
		1500°C, 6 h, air	I2 (2nd anneal)
1400°C, 6 h, Ar/5%H_2	J1	1450°C, 12 h, air	Annealed J1

linear detector (Cu $K_\alpha 1$ radiation, $\lambda = 1{\cdot}5406$ Å). The nature of the phases was determined using the Diffrac-AT software (Socabim, Paris). The grain size and the morphology of the powders were characterized by scanning electron microscopy (SEM Jeol JSM-35).

3 Results and Discussion

3.1 Impurity phases

In a first investigation, the $L_{1-x}\,S_xG_{1-y}M_y$ powders and ceramics with $x = 0{\cdot}10$ and $0{\cdot}20$ and $y = 0{\cdot}15$ and $0{\cdot}20$ were studied as functions of the sintering temperature and time (Table 3).

Phases with the orthorhombic $LaGaO_3$ structure (JCPDS 24-1102) will be called LG phases.

B and P synthesis methods give the pure LG phase at the surface of the ceramics while the inside is multiphased. The analysis of the results on the pellets prepared from pyrolysed powders shows that the pure LG phase is obtained in surface at 1500°C for 6 h in air with 20% strontium (C1, Table 3). The strontium content is a favorable parameter. The $La_4Ga_2O_9$ impurity phase is present in $L_{.9}S_{.1}G_{.8}M_{.2}{}^{*P}$ prepared at 1400°C for 6 h in air (D3, Table 3). The main impurity phase is $LaSrGa_3O_7$ for the B method (B′1, Table 3) and $Sr_3Ga_2O_6$ for the P method (C1, Table 3) (Fig. 2). In contrast, the A method yields the purer LG phase inside the pellet ($A_1{}'$, Table 3).

Therefore, the pure LG phase is not always located inside the pellet, as usually assumed. The distribution of the impurity phases depends on the method of synthesis. Other secondary phases detected as traces are listed in Table 3. Some of the observed rays could not be assigned; they are listed in the last column of Table 3.

3.2 Color

The inside of the samples is always clearer than the surface. This is a common observation. According to the results of the phase purity analysis reported above, the color should not be viewed as an indication of the phase purity.

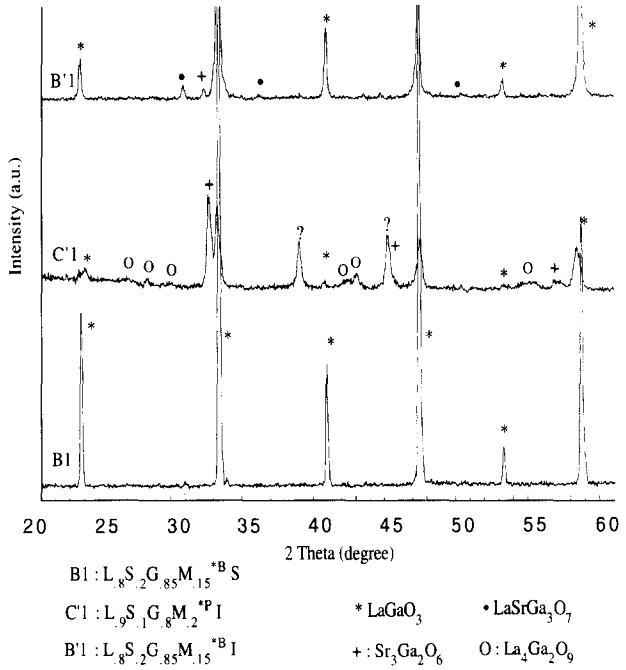

Fig. 2. Inside and surface layer XRD of $L_{1-x}S_xG_{1-y}M_y{}^{*B,P}$.

3.3 Sintering temperature

The temperature dependence of the phase purity of the $L_{.9}S_{.1}G_{.8}M_{.2}{}^{*P}$ ceramics (Fig. 3) was studied in air under the following conditions:

- 1400 and 1500°C, 6 h (D3 and C1, Table 3).
- 1550°C, 2 h (F1, Table 3).

At 1400°C, neither the surface nor the inside is a pure LG phase.

When the sintering temperature reached 1500°C, the reaction was 'completed' and led to pure LG at

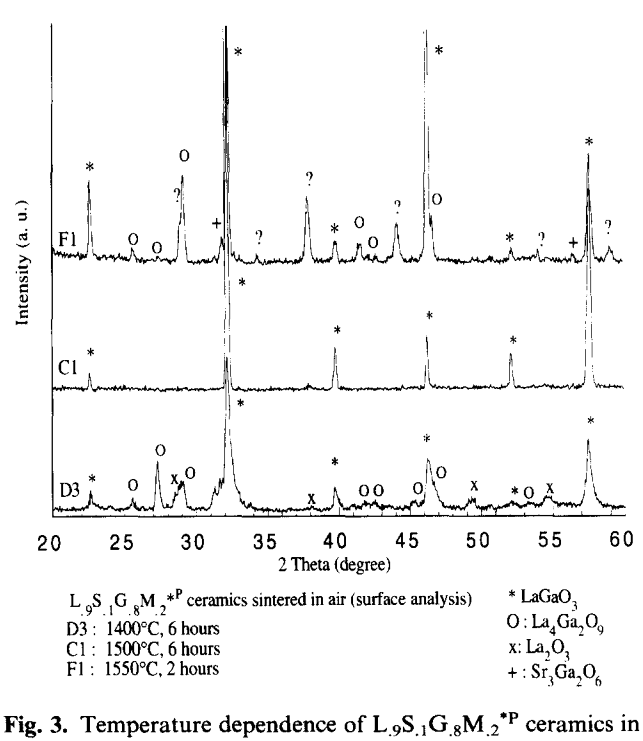

Fig. 3. Temperature dependence of $L_{.9}S_{.1}G_{.8}M_{.2}{}^{*P}$ ceramics in air for two different times (2 and 6 h).

the surface. A partial fusion was observed at 1550°C for 2 h in air. Then, the XRD pattern became more complicated.

3.4 Sintering time

At 1400°C in air, the synthesis of the LG phase is not completed even after 6 h. For a sintering time of 0·25 h at this temperature (D1, Table 3), the main impurity is $Sr_3Ga_2O_6$. After 6 h, it is $La_4Ga_2O_9$.

At 1500°C, the phase purity of $L_{.9}S_{.1}G_{.8}M_{.2}{}^{*P}$ ceramic is deteriorated at the surface with the appearance of $La_4Ga_2O_9$ when the sintering time is extended from 6 to 48 h in air (D3, and E1, Table 3) (Fig. 4), while the inside shows no evidence of any changes in the composition.

3.5 Powder versus dense materials

After calcination at 1000°C (G1, Table 3) for 6 h in air, the $L_{.9}S_{.1}G_{.8}M_{.2}{}^{*P}$ powder is white and contains secondary phases. It becomes ivory after calcinations at 1250°C (G2) and 1500°C (G3) for 6 h in air. As the calcination temperature increases, the concentration of $La_4Ga_2O_9$ and $LaSrGaO_4$ decreases and that of $Sr_3Ga_2O_6$ increases to become the main impurity after calcination at 1500°C. Ceramics were sintered at 1500°C for 6 h in air from these three powders. The measured densities of the pellets (determined from the size and the weight of the samples) are, respectively, 96, 94 and 77% of the theoretical density after a calcination of the powders, respectively, at 1000°C (G1), 1250°C (G2) and 1500°C (G3). The main secondary phases at the surface of these ceramics are:

- $Sr_3Ga_2O_6$ and $La_4Ga_2O_9$ (G1)
- $Sr_3Ga_2O_6$ and La_2O_3 (G2)
- $Sr_3Ga_2O_6$ and traces of $La_4Ga_2O_9$ (G3).

A comparison to the results obtained on ceramics directly sintered from pyrolised $L_{.9}S_{.1}G_{.8}M_{.2}{}^{*P}$ powders (C1, Table 3) shows that the pre-calcination is not favorable. We noted that the thermal treatments of $L_{.9}S_{.1}G_{.8}M_{.2}{}^{*P}$ powders lead to an homogeneous mixture of the impurity phases in the entire samples. The main impurity phase was $La_4Ga_2O_9$. This impurity phase already exists in the pyrolysed $L_{.9}S_{.1}G_{.8}M_{.2}{}^{*P}$ powders. Therefore, the pressing and sintering steps that we used are not sufficient to obtain a complete solid state reaction. In fact, with respect to the other samples, the impurity phases ($Sr_3Ga_2O_6$, $La_4Ga_2O_9$, La_2O_3) are simply homogeneously distributed over the inside and the surface. An increase of the pre-calcination temperature of the powders yields an increase in the amount of these secondary phases. Furthermore, it lowers the density of the ceramics.

3.6 Sintering atmospheres

The amount of second phases in the $L_{.9}S_{.1}G_{.8}M_{.2}{}^{*P}$ samples was much larger when the sintering was carried out at 1400°C, in inert and reducing atmospheres (I2 and J1,Table 4) as shown in Fig. 5. At 1450°C, the conclusion is the same (I1,Table 4).

No differences in the XRD pattern were detected upon exposure of the pellet to a moist atmosphere during sintering (K1, Table 4).

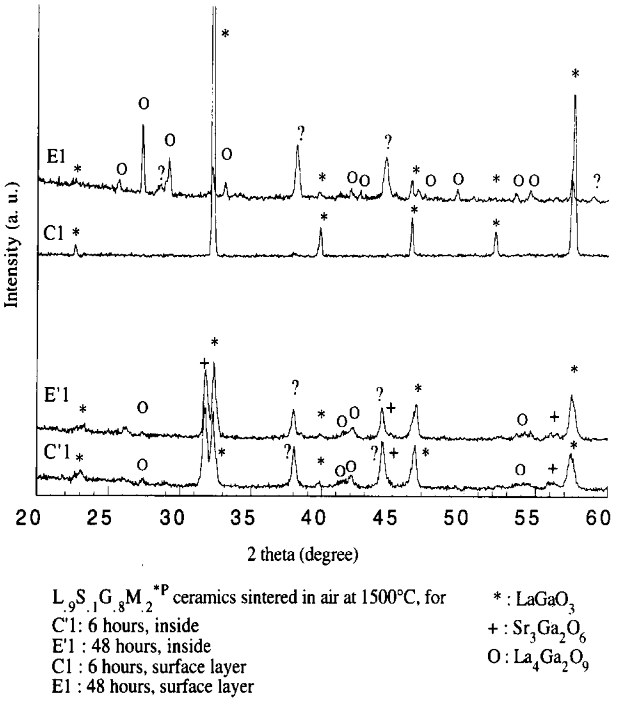

Fig. 4. Time dependence of $L_{.9}S_{.1}G_{.8}M_{.2}{}^{*P}$ ceramics in air at 1500°C.

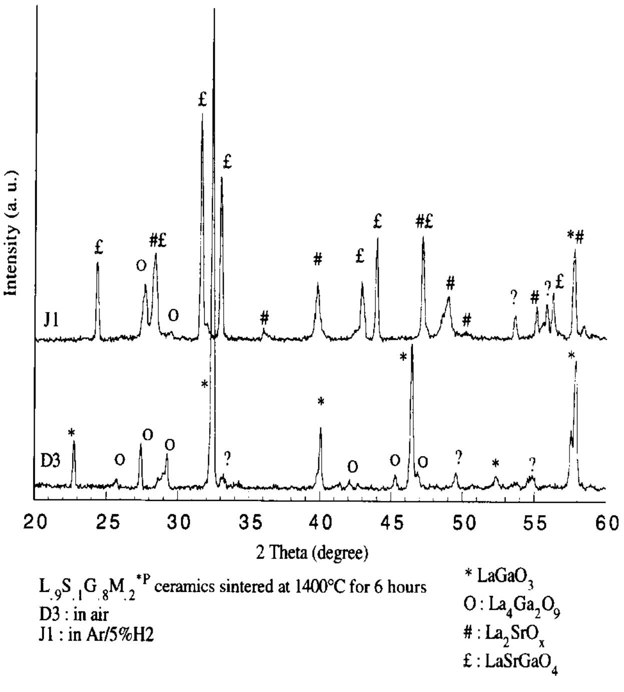

Fig. 5. Atmosphere dependence of $L_{.9}S_{.1}G_{.8}M_{.2}{}^{*P}$ ceramics at 1400°C for 6 h.

3.7 Annealing atmospheres

3.7.1 *Oxidizing annealing*

- The J1 sample (Ar/5%H_2, 1400°C, 6 h) was annealed in air (1450°C, 12 h). Its color went from ivory to black. Moreover, the pellet decomposed into powder.
- The light pink exterior face of I2 (Ar, 1400°C, 2 h) became black after a first annealing in air at 1400°C for 6 h. And after a second curing in air at 1500°C for 6 h, a large diminution of the impurities was observed.

3.7.2 *Reducing annealing*

- The pure gallate prepared by a mixture of oxides in air at 1500°C for 6 h (A1) which was virtually black, became grey after an annealing in Ar/5%H_2 at 1200°C for 6 h with the appearance of numerous extra lines not assigned.
- When the D3 sample (1400°C, 6 h, in air) is annealed in Ar (1350°C, 6 h), the surface layer goes from black to dark brown.

As conclusions, the color of the material is clearer when the annealing is carried out in a reducing atmosphere after an oxidizing sintering and darker in the opposite conditions (oxidizing annealing after a reducing sintering). The concentration in secondary phases appears larger after annealing under reducing conditions.

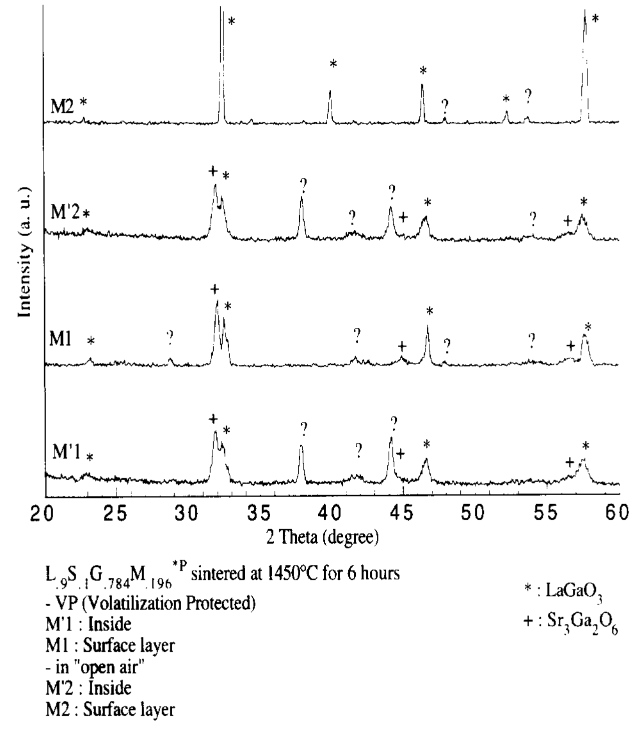

Fig. 6. Inside and surface layer XRD of $L_{.9}S_{.1}G_{.784}M_{.196}{}^{*P}$ sintered in air and in the powder (VP) at 1450°C for 6 h.

3.8 Cation non-stoichiometry

Measurements were carried out on samples containing an excess of either Ga (2 mol%) or La (2 mol%) (L1,L2,L3,M1,M2,M3, Table 4). The powders were prepared by spray pyrolysis. For both compositions, one sample was sintered (1450°C, 6 h) (L2 and M2, Table 4) in 'open-air' and another in a crucible filled with powder of the same composition and covered by a lid (VP) (L1 and M1, Table 4).

The main observations were:

- There are no significant differences between the samples with an excess of Ga or La.
- The color of the VP samples is homogeneous (light brown) and clearer than that of the 'open-air' samples which are black on the surfaces and brown inside.
- In terms of secondary phases, $Sr_3Ga_2O_6$ is detected everywhere in the VP samples and only inside the 'open-air' samples (Fig. 6).
- The other detected impurity phases were homogeneously distributed in the VP samples.

4 Conclusion

La_2O_3, MgO, $LaSrGa_3O_7$, $Sr_3Ga_2O_6$, $La_4Ga_2O_9$, $La_3Ga_5O_{12}$, $MgGa_2O_4$, La_2SrO_x and $LaSrGaO_4$ were characterized by XRD as impurity phases in the powders prepared by ultrasonic spray pyrolysis and in the sintered ceramics. Reactivity of LG pure phase and secondary phases are really dependent on different raw products. Furthermore, intermediate reactions which are taking place in carbonates favor a complete solid state reaction inside the pellet prepared by the A method. In the A, B and P methods, the 1500°C sintering temperature for 6 h plays a key role in the synthesis of LG pure phase. Moreover, the strontium content seems to be an essential parameter. It is actually necessary to have 20 mol% of SrO in the synthesis from oxides and carbonates or from spray pyrolysed powders (B or P methods) in order to obtain the pure LG phase in the surface of the pellet prepared in an oxidizing atmosphere at 1500° for 6 h (respectively, C1 and B1 samples, Table 3). In the case of the solid state route starting from oxides (A method), only 10 mol% of SrO are enough to produce the pure LG phase in the nucleus of the pellet synthesized at 1500°C for 6 h (A1 sample, Table 3).

The causes for the existence of different regions within the reacted samples could not he elucidated here. The best conditions for obtaining a fairly pure doped $LaGaO_3$ phase are 1500°C, 6 h in air.

However, when the sintering time is extended from 6 to 48 h in air at 1500°C, a deterioration of the purity of the material is observed.

Under reducing conditions, no adequate sintering temperature and time could be found. Furthermore, the amounts of secondary phases formed in a reducing, atmosphere are much larger than in an oxidizing atmosphere.

These two observations shed some doubt on the long term stability of the phase. A comparison of the results obtained on ceramics prepared from spray pyrolysed $L_{.9}S_{.1}G_{.8}M_{.2}$ powders which were pre-calcined shows that pre-calcination does not play a favorable role in order to obtain the pure LG phase. Pellets were obtained with secondary phases homogeneously distributed and with lower density. A partial fusion is observed at 1550°C after 2 h in air. The compound from spray pyrolysed synthesis is not sensitive to a moist atmosphere.

Cation non-stoichiometry does not appear to be a key parameter for an optimization of the synthesis.

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