

# Performance of $\text{La}_{1-x}\text{Sr}_x\text{Al}_{1-y-y'}\text{Fe}_y\text{Mg}_{y'}\text{O}_{3-\delta}$ perovskites in methane combustion: effect of aluminum and magnesium content

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## Abstract

Perovskites of different  $\text{La}_{1-x}\text{Sr}_x\text{Al}_{1-y-y'}\text{Fe}_y\text{Mg}_{y'}\text{O}_{3-\delta}$  compositions ( $x = 0, 0.1, 0.15, 0.2$  and  $y = 0.1, 0.3, 0.5, 0.8$ ) were prepared from a reactive precursor slurry of hydrated oxides. Each sample was aged between 16 and 26 h up to 1473 K. Activity in methane combustion (1%/air) was determined in a plug-flow reactor, with 1 g catalyst and 24 l/h flowrate. Gradual decrease in activity due to thermal aging was observed, the degree of activity loss being composition dependent. Nevertheless, activity of samples aged at 1370 K was nearly independent of composition. The best thermal stability showed  $\text{LaAl}_{0.65}\text{Fe}_{0.15}\text{Mg}_{0.2}\text{O}_3$  perovskite. None of the magnesium substituted perovskites performed better than a  $\text{La}_{0.85}\text{Sr}_{0.15}\text{Al}_{0.87}\text{Fe}_{0.13}\text{O}_3$  reference sample.

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## 1. Introduction

Fossil fuels continue to be an economic source of energy. Catalytic combustion, a part from fuel cells, is recognized as one of the most environmentally acceptable means for their direct exploitation [1–3]. In spite of successful development of different technologies, including gas turbines [4,5], to put the catalytic combustion technologies into wider practical use, low cost highly reliable catalysts are still needed. Especially demanding is the development of systems and devices for high energy outputs necessitating exceptionally robust catalytic materials. For such applications the catalysts should resist temperatures above 1270 K and

high gas throughputs in a relatively corrosive atmosphere of combustion products [1–3]. Only restricted number of materials can actually meet the stringent criteria for high temperature operation: reasonable activity, excellent thermal stability, low volatility, and good resistance to thermal shock [6–8]. Over the last years, two types of very good candidates have been developed: manganese substituted hexaaluminates [9,10], the  $\text{Sr}_{0.8}\text{La}_{0.2}\text{MnAl}_{11}\text{O}_{19}$  (SLMA) representing the optimum composition [8,9], and more recently base-metal substituted refractory perovskites [8,11]. Hexaaluminates (SLMA) can be prepared with reasonably large and relatively stable specific surface area (SSA) and exhibit good activity even after being exposed for extended time to high temperatures. Nevertheless, their resistance to thermal shock, when in form of monoliths is poor, mainly due to their two dimensional thermal expansion. On the other hand, since

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perovskites exhibit an isosteric thermal expansion, they can be expected to be more resistant to thermal shock. In addition, the intrinsic (areal) catalytic activity of a number of base-metal doped, refractory perovskites, for instance  $\text{La}_{0.85}\text{Sr}_{0.15}\text{Al}_{0.87}\text{Fe}_{0.13}\text{O}_{3-\delta}$ , is comparable or even higher than that of SLMA. In fact, even specific activity (per gram) of optimized compositions can become nearly comparable to that of SLMA, in spite of inherently low SSA of perovskites. This is, in part, due to relatively high oxygen conductivity in perovskites with some oxygen nonstoichiometry ( $\delta$ ), because at high temperatures, the catalytic combustion tends to be controlled by oxygen bulk mobility. The oxygen nonstoichiometry is typically adjusted by an A-site substitution with strontium, which is well known to enhance the catalytic activity, but it may also be varied by selection of a suitable B-site cation. However, it is not easy to predict the individual effects of such substitutions, because several factors, undoubtedly correlated, play a role in the overall performance. For example, substitution of chromium or manganese by magnesium in  $\text{LaCrO}_3$  and  $\text{LaMnO}_3$ , respectively seems to improve not only the activity, but also the thermal stability [12,13], although it is at the expense of increased susceptibility to poisoning by sulfur oxides [14]. Conversely, in samples calcined at 1073 K (5 h) substitution by magnesium in  $\text{LaFe}_{1-y}\text{Mg}_y\text{O}_3$  caused a decrease in activity [15].

With respect to its lowest volatility among the transition metal oxides, iron oxide can be considered as the most suitable catalytic component for high temperature applications [6,7]. Similarly, being refractory and nonvolatile, magnesium oxide appears as an excellent complementary constituent of thermally stable combustion catalysts [7]. However, due to its ionic size ( $\leq 72$  pm)  $\text{Mg}^{2+}$  is not acceptable as an A-site substituent. Furthermore, in order to respect the electroneutrality, its degree of B-site substitution is limited to less than about 30 at.%. These are the reasons why magnesium was not included in our previous work. Nevertheless, in view of some of the reported effects, we have considered worthwhile to examine its potential as a component of iron doped lanthanum aluminum based perovskite combustion catalysts, selecting  $\text{La}_{0.85}\text{Sr}_{0.15}\text{Al}_{0.87}\text{Fe}_{0.13}\text{O}_3$  (LSAF) perovskite as a reference.

To assess objectively the actual effect of Mg substitution on the overall catalyst performance, several

$\text{La}_{1-x}\text{Sr}_x\text{Al}_{1-y-y'}\text{Fe}_y\text{Mg}_{y'}\text{O}_{3-\delta}$  perovskites of different compositions were prepared and their activity as a function of aging was evaluated.

## 2. Experimental

### 2.1. Catalyst preparation and physical characterization

All samples evaluated in this study were prepared by a method involving aqueous precursor slurry of reactive, in situ hydrated metal oxides or hydroxides, processed by freeze drying and subsequent controlled calcination [16]. The reactive precursor slurry is typically prepared by first hydrating lanthanum oxide in water or a solution of strontium nitrate and then adding, under a vigorous mixing using a high speed mixer, the resulting suspension into the solution of metal nitrates of remaining components. Part of the components may have been suspended in the solution of metal nitrates in form of highly reactive solids. Boehmite or precipitated aluminum hydroxide was used as the precursor of aluminum oxide, whereas basic magnesium carbonate partially dissolved in a slightly acidified ferric nitrate solution was the source of magnesium. To form the perovskite phase, the freeze-dried stoichiometric precursor mixture was first calcined 12 h at 863 K, 5 h at 923 K and 7 h at 1100 K followed by further heat treatment. To assess the effect of aluminum and magnesium content on the thermal stability, all samples were aged 24 h at 1370 and 1470 K prior to catalytic activity evaluation. The formation of perovskite phase was monitored by powder X-ray diffractometry. Before use, the slightly agglomerated powder was dry-milled in a polyethylene bottle using zirconia cylinders to a particle size of less than 5  $\mu\text{m}$ . SSA of each sample was determined by a single point BET method with 30% nitrogen in helium as an adsorbate, on a Micromeritics FlowSorb 2300 apparatus. Nominal composition and SSA of the studied perovskites are presented in Table 1.

### 2.2. Catalytic performance

A steady-state activity in methane combustion of each sample was determined in an integral plug-flow reactor made of an alumina ceramic tube placed

Table 1

Activity of catalyst powders in the system of  $\text{La}_{1-x}\text{Sr}_x\text{Al}_{1-y-y'}\text{Fe}_y\text{Mg}_{y'}\text{O}_3$  perovskites

Powder <sup>a</sup>	SSA (m <sup>2</sup> /g)	$T_{10}$ <sup>b</sup> (°C)	$T_{50}$ <sup>b</sup> (°C)	$E_{\text{app}}$ (kJ/mol)	ln A (μmol/g s bar)	$k_{1000}$ (μmol/g s bar)
Samples calcined for 16 h at 980 °C						
$\text{LaAl}_{0.52}\text{Fe}_{0.15}\text{Mg}_{0.33}\text{O}_3$ -980	13.2	523	629	111	20.09	945
$\text{La}_{0.85}\text{Sr}_{0.15}\text{Al}_{0.52}\text{Fe}_{0.3}\text{Mg}_{0.18}\text{O}_3$ -980	7.5	541	642	118	20.83	880
$\text{La}_{0.85}\text{Sr}_{0.15}\text{Al}_{0.3}\text{Fe}_{0.5}\text{Mg}_{0.2}\text{O}_3$ -980	4.4	499	609	98	18.67	750
Samples calcined for 26 h at 1096 or 1100 °C						
$\text{LaAl}_{0.65}\text{Fe}_{0.15}\text{Mg}_{0.2}\text{O}_3$ -1096	7.6	564	665	124	21.24	534
$\text{LaAl}_{0.52}\text{Fe}_{0.15}\text{Mg}_{0.33}\text{O}_3$ -1096	7.0	559	661	120	20.70	534
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Al}_{0.72}\text{Fe}_{0.15}\text{Mg}_{0.13}\text{O}_3$ -1100	3.2	548	660	118	20.55	567
$\text{La}_{0.85}\text{Sr}_{0.15}\text{Al}_{0.72}\text{Fe}_{0.1}\text{Mg}_{0.18}\text{O}_3$ -1096	4.9	567	671	120	20.53	455
$\text{La}_{0.85}\text{Sr}_{0.15}\text{Al}_{0.67}\text{Fe}_{0.15}\text{Mg}_{0.18}\text{O}_3$ -1096	4.2	560	666	119	20.54	508
$\text{La}_{0.85}\text{Sr}_{0.15}\text{Al}_{0.52}\text{Fe}_{0.3}\text{Mg}_{0.18}\text{O}_3$ -1096	3.9	560	668	117	20.29	493
$\text{La}_{0.85}\text{Sr}_{0.15}\text{Al}_{0.3}\text{Fe}_{0.5}\text{Mg}_{0.2}\text{O}_3$ -1100fd <sup>b</sup>	2.7	538	654	102	18.51	508
$\text{La}_{0.85}\text{Sr}_{0.15}\text{Al}_{0.3}\text{Fe}_{0.5}\text{Mg}_{0.2}\text{O}_3$ -1080ad <sup>c</sup>	2.5	545	656	107	19.12	513
$\text{La}_{0.85}\text{Sr}_{0.15}\text{Al}_{0.8}\text{Fe}_{0.15}\text{Mg}_{0.05}\text{O}_3$ -1100	4.8	555	665	98	17.94	467
$\text{LaAl}_{0.68}\text{Fe}_{0.14}\text{Mg}_{0.18}\text{O}_3$ -1100	8.0	542	650	120	20.84	607
Samples calcined for 16 h at 1200 °C						
$\text{LaAl}_{0.65}\text{Fe}_{0.15}\text{Mg}_{0.2}\text{O}_3$ -1200	2.05	563	676	110	19.21	380
$\text{LaAl}_{0.52}\text{Fe}_{0.15}\text{Mg}_{0.33}\text{O}_3$ -1200	1.80	588	708	96	16.94	240
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Al}_{0.72}\text{Fe}_{0.15}\text{Mg}_{0.13}\text{O}_3$ -1200	1.76	560	680	104	18.34	350
$\text{La}_{0.85}\text{Sr}_{0.15}\text{Al}_{0.72}\text{Fe}_{0.1}\text{Mg}_{0.18}\text{O}_3$ -1200	1.51	591	711	111	18.79	230
$\text{La}_{0.85}\text{Sr}_{0.15}\text{Al}_{0.67}\text{Fe}_{0.15}\text{Mg}_{0.18}\text{O}_3$ -1200	1.52	586	697	118	19.85	290
$\text{La}_{0.85}\text{Sr}_{0.15}\text{Al}_{0.52}\text{Fe}_{0.3}\text{Mg}_{0.18}\text{O}_3$ -1200	1.86	576	696	107	18.56	281
$\text{La}_{0.85}\text{Sr}_{0.15}\text{Al}_{0.3}\text{Fe}_{0.5}\text{Mg}_{0.2}\text{O}_3$ -1200	1.75	562	745	80	14.84	190
$\text{La}_{0.85}\text{Sr}_{0.15}\text{Al}_{0.8}\text{Fe}_{0.15}\text{Mg}_{0.05}\text{O}_3$ -1200	1.71	568	680	108	18.92	376
$\text{LaAl}_{0.68}\text{Fe}_{0.14}\text{Mg}_{0.18}\text{O}_3$ -1200fd	2.10	555	665	110	19.29	428
Reference sample						
$\text{La}_{0.85}\text{Sr}_{0.15}\text{Al}_{0.87}\text{Fe}_{0.13}\text{O}_3$ -1080 <sup>c</sup>	4.3	525	620	106	19.42	812
$\text{La}_{0.85}\text{Sr}_{0.15}\text{Al}_{0.87}\text{Fe}_{0.13}\text{O}_3$ -1250 <sup>d</sup>	1.95	537	650	106	18.96	500

<sup>a</sup> Precursor slurry was freeze dried (fd) and air dried (ad).<sup>b</sup> For 1 g catalyst, 2% methane/air and 24 l/h.<sup>c</sup> Aged 26 h at 1353 K.<sup>d</sup> Aged 26 h at 1353 K + 16 h at 1423 K + 5.5 h at 1523 K.

horizontally in a programmable furnace [8], using 1 g catalyst powder dispersed in 10 ml of precalcined (10 h at 1150 K) pumice, 1 vol.%  $\text{CH}_4$ /air flowing at 24 l/h. The temperature of the catalytic bed was monitored by a thermocouple, protected by an alumina sheath, inserted in the center of the catalytic bed. The SSA of the calcined pumice was 1 m<sup>2</sup>/g, particle size between 247 and 450 μm. The catalyst activity was monitored as methane conversion to carbon dioxide at several steady temperatures between 650 and 1000 K. Analysis of the reaction mixture stripped of water by passing it over a desiccant was made by gas chromatography using Porapak Q column for separating methane and carbon dioxide; molecular sieve 5 Å was used for

determining the presence of carbon monoxide, which however was below the detection limit in most cases.

### 3. Results and discussion

#### 3.1. Selecting catalyst composition

To limit the number of evaluated samples to the most representative, selection was made on the basis of literature information and our own experience. Several aspects were considered. First of all, on the grounds of the percolation effect, the estimated maximum magnesium substitution was 33% and corresponding oxygen

deficiency  $\delta \leq 0.17$ . In  $\text{LaFeO}_3$ , the maximum reported solubility of magnesium is 30% [15]. To satisfy the latter requirement, the sum of the strontium and magnesium substitution ( $x + y'$ ) was kept at 0.34 or lower. Thus, for the highest magnesium substitution,  $y' = 0.33$ , strontium was eliminated as a component. For lower magnesium substitutions, strontium was introduced to a level which would keep the nominal oxygen nonstoichiometry below 0.17. The minimum value of nominal  $\delta$  is not really known, but judging from data on oxygen ion conductivities [17], it may be assumed as about 0.05. Iron content was in most cases kept at 15 at.%, apparently an optimum level [8], but to confirm the effect of higher iron concentrations, compositions with 30 and 50 at.% were included in the study. In addition, samples of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.8}\text{Mg}_{0.2}\text{O}_3$  were used for comparison. Although strontium oxide is relatively volatile (in comparison with refractory oxides) and as such is not the best candidate as a component of catalysts for high temperature applications, its stabilization in the perovskite structure may possibly be sufficient for some practical use.

### 3.2. Catalyst preparation and characteristics

In view of the anticipated aging, no special effort was made to select a preparation procedure assuring the perovskite formation at the lowest possible temperatures. Instead, emphasis was given to the sim-

plicity and a low cost of precursor materials, similarly as in the previous work [8]. For this reason we have opted for using the precursors very fine powders of reactive oxides of some of the components, at least in part. Although in this way, the initial homogeneity is somehow penalized and higher reaction temperatures and/or time are needed to obtain the perovskite phase than when the B-site components are precipitated in situ [16], good results can be obtained with careful control and when very fine powders are used. Most of the compositions required several hours of heat treatment at above 1150 K to give principally perovskite (less than 10% minor phases) with SSA ranging between 4.4 and 13.2 m<sup>2</sup>/g. After thermal aging in air (26 h) at 1370 K only peaks corresponding to perovskite were observed in most cases and SSA dropped to between 2.5 and 7.6 m<sup>2</sup>/g. Largest SSA retained the compositions without strontium, while lowest exhibited those with 50 at.% iron. Additional aging of 16 h at 1470 K resulted in low SSA of  $1.8 \pm 0.3$  m<sup>2</sup>/g, nearly independent of composition. Interestingly, the order of SSA of samples aged at 1473 K did not follow that of samples aged at 1370 K (Table 1). Nevertheless, the obtained values of SSA agree well with those typically reported for different perovskite compositions aged at similar temperatures. In fact, they are somehow higher than for perovskites based only on transition metal oxides, (for example those in Table 2) but lower than SSA of the reference LSAF

Table 2

Activity in methane combustion of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.8}\text{Mg}_{0.2}\text{O}_3$  (LSFMg) perovskite compared with samples of  $\text{La}_{0.66}\text{Sr}_{0.34}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  (LSCF) perovskite prepared from different precursors both calcined at different temperatures

Powder <sup>a</sup>	Calcination (°C/h)	SSA (m <sup>2</sup> /g)	$T_{10}^b$ (°C)	$T_{50}^b$ (°C)	$E_{\text{app}}$ (kJ/mol)	ln A (μmol/g s bar)	$k_{1000}$ (μmol/g s bar)
LSFMg-980	866/9 + 980/16	3.4	495	598	102	19.41	1200
LSFMg-1080	866/9 + 1080/26	2.1	550	665	114	19.93	498
LSCF-fo.b-980	855/12 + 980/21	2.5	475	572	105	20.18	1940
LSCF-fo.b-1070	855/12 + 1070/26	1.5	495	595	103	19.55	1287
LSCF-g-1000	750/10 + 980/21 + 1000/4	3.9	476	579	102	19.69	1670
LSCF-g-1070	750/10 + 1070/26	1.3	510	629	100	18.53	743
LSCF-g-1078	750/10 + 1078/26	1.0	553	675	102	19.69	369
LSCF-fo.r-980	855/12 + 980/21	3.4	—	—	92 <sup>c</sup>	18.43 <sup>c</sup>	1530
LSNF-fo.r-980 <sup>d</sup>	855/12 + 980/21	3.7	—	—	92 <sup>c</sup>	18.48 <sup>c</sup>	1640

<sup>a</sup> Samples identified as fo.b and fo.r were prepared from  $\text{Fe}_2\text{O}_3$  brown and red respectively, samples identified as 'g' were prepared from  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  via gel precipitation.

<sup>b</sup> For 1 g catalyst, 2%  $\text{CH}_4$ /air and 241/h.

<sup>c</sup> Kinetic parameters determined under programmed continuous heating 2 K/min (0.1 g, 1%  $\text{CH}_4$ /air and 4.51/h).

<sup>d</sup> LSNF stands for  $\text{La}_{0.66}\text{Sr}_{0.34}\text{Ni}_{0.2}\text{Fe}_{0.8}\text{O}_3$ .

composition. Since the procedure for the preparation of the present magnesium containing samples was not necessarily optimized, we cannot say whether the observed characteristics are reflecting mainly the composition. Yet, comparison of SSA data in Table 1 with those in Table 2 suggests that the sintering of the new aluminum comprising compositions is slower than sintering of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.8}\text{Mg}_{0.2}\text{O}_3$  perovskite. The effect of aluminum to slow the sintering is perhaps the strongest in the case of  $\text{LaAl}_{0.65}\text{Fe}_{0.15}\text{Mg}_{0.2}\text{O}_3$ . This perovskite exhibited the highest SSA ( $13.2 \text{ m}^2/\text{g}$ ) after aging of 16 h at 1250 K and retained SSA of  $2.05 \text{ m}^2/\text{g}$  after additional aging of 16 h at 1470 K. In comparison, the published SSA for  $\text{LaFe}_{1-y}\text{Mg}_y\text{O}_3$  perovskites ( $x = 0, 0.1, 0.2, 0.3$ ) prepared by the citrate method and calcined only for 5 h at 1073 K, rising continuously from 2.9 to  $9.3 \text{ m}^2/\text{g}$  with increasing magnesium substitution  $y$  [15], are relatively low and would most likely fall on further aging. Low values of SSA, only about  $1 \text{ m}^2/\text{g}$ , were also reported for  $\text{LaMn}_{1-y}\text{Mg}_y\text{O}_3$  calcined for 4 h at 1473 K. In contrast, significantly higher SSA values ( $\sim 5 \text{ m}^2/\text{g}$ ), even after calcination for 5 days at 1373 K, were reported for  $\text{LaCr}_{1-y}\text{Mg}_y\text{O}_3$  prepared also by the citrate method [12]. Fast sintering at temperatures above 1300 K is indeed fairly typical for most transition metal, but especially for iron-based oxides, including perovskites. (see also Table 2). This is due to the high diffusivity of their cations.

### 3.3. Catalytic activity in methane combustion

Under the experimental conditions used in this work, all samples showed some activity starting at about 700 K, while over pumice without catalyst no methane conversion was detected up to 1000 K. For all samples the methane conversion increased with temperature following a typical, smooth S-shape light-off curve. At temperatures between 950 and 1060 K, conversions higher than 90% were obtained. Assuming an integral (plug-flow) reactor, a simple pseudo-first order kinetic model provided an excellent fit to these experimental conversion data over the whole range of temperatures, as usual. The derived apparent activation energies  $E_{\text{app}}$ , and corresponding preexponential factors  $A$  are collected in Table 1. To facilitate comparison of activities of individual samples, Table 1 includes specific kinetic constants at

1000 K ( $k_{1000}$ ) as well as temperatures of 10 and 50% conversion ( $T_{10}$ ,  $T_{50}$ ).

Only three compositions, indicated in Table 1, were selected for activity evaluation after aging at relatively low temperature, 1253 K. As expected, these three samples were the most active, the specific activity (per gram) decreases with decreasing SSA, in parallel with the increasing iron content. Nevertheless, when compared with other perovskite compositions calcined at similar conditions, activities of these magnesium substituted perovskites are somewhat inferior, in spite of larger SSA. For example, the most active composition of the three was about 30% less active than  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.8}\text{Mg}_{0.2}\text{O}_3$ -980 (Table 2) and about as active as  $\text{La}_{0.85}\text{Sr}_{0.15}\text{Al}_{0.87}\text{Fe}_{0.13}\text{O}_3$ -980. It can also be mentioned that these partially substituted refractory perovskites when calcined below 1270 K are nearly 50% less active than iron-based perovskite substituted by cobalt or nickel, ( $\text{La}_{0.66}\text{Sr}_{0.34}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ ,  $\text{La}_{0.66}\text{Sr}_{0.34}\text{Ni}_{0.2}\text{Fe}_{0.8}\text{O}_3$ ), for which, however, the temperature limit of operation is below 1373 K (Table 2).

As the temperature of aging was increased, all the catalysts became less and less active. This was of course expected. However, the extent of this activity loss for individual samples and its correlation with composition and SSA could not have been well envisaged. For instance, taking into account the experimental uncertainty of about 7%, the specific activity of samples aged at 1370 K varies but little with composition. Furthermore, activity of these samples compares fairly well with the activity of LSAF calcined (aged) at similar conditions. It is tempting to consider this temperature as an upper limit of their thermal stability. Still, careful analysis of the data reveals some subtle effects of composition, which are better discernible among the samples aged at 1473 K. For example, among the samples aged at 1370 K, the composition with the lowest substitution by magnesium ( $\text{La}_{0.8}\text{Sr}_{0.2}\text{Al}_{0.72}\text{Fe}_{0.15}\text{Mg}_{0.13}\text{O}_3$ -1100) is the most active and this composition remains the second most active when aged at 1473 K. On the other hand, composition with only 10% iron was the least active among samples aged at 1370 K and second least active from samples aged at 1473 K. Overall, the data suggest that B-site substitution with magnesium could at some level, depending on the overall composition, be actually detrimental, in part confirming the observations



made for samples in an  $\text{LaFe}_{1-y}\text{Mg}_y\text{O}_3$  system calcined 5 h at 1073 K [15]. To some extent this could be related to the basic character of magnesium. Although the  $\text{LaAl}_{0.65}\text{Fe}_{0.15}\text{Mg}_{0.2}\text{O}_3$  composition showed the highest thermal stability and could therefore be considered as the best performing of this system, it is less active than LSAF. We may thus surmise that strontium is the substituent that is more effective to control activity than magnesium. This however, would need to be confirmed by longer term tests, preferably under conditions simulating the practical operation. Such evaluation should also include assessment of the resistance to sulfur oxide poisoning. In view of its inherently low volatility, in a long run,  $\text{LaAl}_{1-y-y'}\text{Fe}_y\text{Mg}_{y'}\text{O}_3$  might prove as superior to LSAF. Certainly, it seems clear that several factors, most likely strongly correlated, operate in determining the actual catalytic activity of perovskites. Even if there is a relatively small range of possibilities for designing an efficient perovskite-type catalyst for high temperature combustion, there still exists some room for improvement. For instance, in view of the results, we have prepared two additional compositions targeted for an optimum content of iron or magnesium:  $\text{La}_{0.85}\text{Sr}_{0.15}\text{Al}_{0.8}\text{Fe}_{0.15}\text{Mg}_{0.05}\text{O}_3$  and  $\text{LaAl}_{0.68}\text{Fe}_{0.14}\text{Mg}_{0.18}\text{O}_3$ . Data for these two perovskites are also included in Table 1. Interestingly, this attempt was more or less successful, but only within the system of compositions containing magnesium. Overall, 15% iron substitution appears slightly too high. Similar may possibly be said about the content of magnesium.

#### 4. Summary and conclusions

For its highly refractory character, magnesium oxide would appear to be an attractive complementary component to consider when designing an efficient perovskite-type catalyst for high temperature combustion. However, the ionic size of  $\text{Mg}^{2+}$  ( $\leq 72$  pm) is too small for an A-site lanthanum substitution. Furthermore, to respect the electroneutrality, the degree of substitution is restricted to about 30 at.%, which in the case of  $\text{LaFe}_{1-y}\text{Mg}_y\text{O}_3$  is apparently also a limit of the solubility.

The results of the present work on samples aged 26 h at 1473 K indicate that in aluminum–iron-based perovskite, B-site magnesium substituted perovskites are less active than similar A-site strontium substituted compositions.

To assure a high thermal stability and reasonable activity the optimum iron concentration is about 13 to 14 at.%, while that of magnesium seems to be below 18 at.%.

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