

# Characterization of perovskite powders made by different synthesis routes

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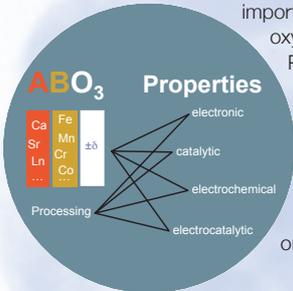
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## Objective

The lanthanide transition-metal oxides are of technological importance for their use in solid oxide fuel cell, catalysis, oxygen membrane reactors and sensors.

Preparation conditions are in many cases responsible for structural differences and thus for the disparity in catalytic and electrocatalytic properties of oxides. In this study, we investigate the influence of different fabrication procedures on the final microstructure and composition of these materials for their use as SOFC cathodes or oxygen membrane materials.



## Powder characterization

ICP analysis		experimental composition					nominal		%	
Label	nominal composition	La	Sr	Mn	Fe	Ca	Pr	sum	sum deviation	
5ULSM73-P	(La <sub>0.7</sub> Sr <sub>0.3</sub> ) <sub>0.95</sub> MnO <sub>3-δ</sub>	0.678	0.288	1	0.03	0	0.02	1.966	1.95	100.8
LSF55-P	La <sub>0.5</sub> Sr <sub>0.5</sub> FeO <sub>3-δ</sub>	0.537	0.507	-	1	-	-	2.044	2	102.2
5ULSF73-P	(La <sub>0.7</sub> Sr <sub>0.3</sub> ) <sub>0.95</sub> FeO <sub>3-δ</sub>	0.733	0.312	0	1	0	0.02	2.045	1.95	104.9
5ULCF73-P	(La <sub>0.7</sub> Ca <sub>0.3</sub> ) <sub>0.95</sub> FeO <sub>3-δ</sub>	0.875	0.01	0.01	1	0.252	0.02	2.127	1.95	109.1
5UPCF73-P	(Pr <sub>0.7</sub> Ca <sub>0.3</sub> ) <sub>0.95</sub> FeO <sub>3-δ</sub>	0.01	0	0	1	0.287	0.828	2.115	1.95	108.5
3ULSM <sup>73</sup> / <sub>1/2</sub> -Ci	(La <sub>0.7</sub> Sr <sub>0.3</sub> ) <sub>0.95</sub> MnO <sub>3-δ</sub>	0.731	0.255	1	-	-	-	1.986	1.97	100.8
5ULSF73-Ci	(La <sub>0.7</sub> Sr <sub>0.3</sub> ) <sub>0.95</sub> FeO <sub>3-δ</sub>	0.685	0.277	0	1	0	0.01	1.962	1.95	100.6
LSF73-Ca	La <sub>0.5</sub> Sr <sub>0.5</sub> FeO <sub>3-δ</sub>	0.3	0.672	-	1	-	-	1.972	2	98.6
LSF55-Ca	La <sub>0.5</sub> Sr <sub>0.5</sub> FeO <sub>3-δ</sub>	0.505	0.494	-	1	-	-	1.999	2	99.95
5ULSF73-Ca	(La <sub>0.7</sub> Sr <sub>0.3</sub> ) <sub>0.95</sub> FeO <sub>3-δ</sub>	0.704	0.283	0	1	0	0.01	1.987	1.95	101.9
LSF73-Ca	La <sub>0.5</sub> Sr <sub>0.5</sub> FeO <sub>3-δ</sub>	0.713	0.295	1	-	-	-	2.008	2	100.4
5OLS73-Ca	(La <sub>0.7</sub> Sr <sub>0.3</sub> ) <sub>0.95</sub> FeO <sub>3-δ</sub>	0.757	0.314	1	-	-	-	2.071	2.05	101.0
5UPSF73-Ca	(Pr <sub>0.7</sub> Sr <sub>0.3</sub> ) <sub>0.95</sub> FeO <sub>3-δ</sub>	-	0.278	1	-	-	0.851	2.129	1.95	109.2

Table 1: Summary of ICP bulk analyses. The powders lay very near to the nominal values.

The prefix and suffix stand for:  
 U: under-stoichiometric  
 O: over-stoichiometric  
 P: «spray pyrolysis»  
 Ci: citrate  
 Ca: carbonate  
 The error on Fe detection is of about 0.03.

## Synthesis related properties

XPS analysis	ratio				TEM distribution				
Powders	Mn/La+Sr	Fe/La+Sr	Fe/La+Ca	Fe/Pr+Ca	La/Sr	La/Ca	Pr/Ca	XPS composition	for Sr or Ca
5ULSM73-P	38/62				71/29			(La <sub>0.71</sub> Sr <sub>0.29</sub> ) <sub>0.62</sub> Mn <sub>0.38</sub>	0.02 ≤ x ≤ 0.44
5ULSF73-P		32/68			70/30			(La <sub>0.70</sub> Sr <sub>0.30</sub> ) <sub>0.68</sub> Fe <sub>0.32</sub>	0.04 ≤ x ≤ 0.24
5ULCF73-P			31/69			71/29		(La <sub>0.69</sub> Ca <sub>0.31</sub> ) <sub>0.71</sub> Fe <sub>0.31</sub>	0.1 ≤ x ≤ 0.3
5UPCF73-P				25/75			74/26	(Pr <sub>0.74</sub> Ca <sub>0.26</sub> ) <sub>0.75</sub> Fe <sub>0.25</sub>	0.04 ≤ x ≤ 0.24
5ULSF73-Ci		45/56			57/44			(La <sub>0.57</sub> Sr <sub>0.43</sub> ) <sub>0.68</sub> Fe <sub>0.32</sub>	0.01 ≤ x ≤ 0.36
5ULSF73-Ca		36/64			63/37			(La <sub>0.63</sub> Sr <sub>0.37</sub> ) <sub>0.64</sub> Fe <sub>0.36</sub>	0.16 ≤ x ≤ 0.34

Table 2: Summary of the XPS surface analyses given in percent and of Sr and Ca content as measured by EDS. Discrepancies are observed between the different synthesis routes.

Powders	PSD (d <sub>50</sub> ) [μm]	BET [m <sup>2</sup> /g]	remark
5ULSM73-P	0.387		bimodal
5ULSF73-P	0.504	15.4	bimodal
5ULCF73-P	0.459		bimodal
5ULSF73-Ci	1-2	3.82	wide range
3ULSM <sup>73</sup> / <sub>1/2</sub> -Ci	1-2	3.73	wide range
5ULSF73-Ca	0.1	8.04	Fig. 4

Table 3: Powder size distribution and BET values.

From TG/DTA analyses on precipitates, the carbonates were found to allow first the perovskite transformation at a temperature of 650°C. The trend was:



From XRD, the oxalate powders were phase pure at temperatures above 1100°C. This was also the case for LCF and LSM obtained from carbonates. For the cyanide, a phase transformation to the perovskite structure is observed at 450°C in which the cyanide ligands in the hexacyano-precipitate are replaced by oxygen (Fig. 1). For the LSF made by carbonates, XRD-phase purity was already reached at 800°C (Fig. 2) in contrast to «spray pyrolysis» where higher thermal treatments were needed (1200°C).

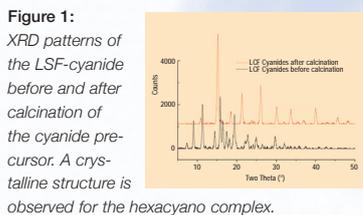
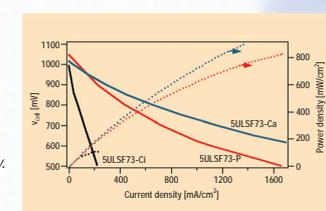
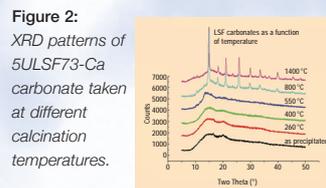


Figure 1: XRD patterns of the LSF-cyanide before and after calcination of the cyanide precursor. A crystalline structure is observed for the hexacyano complex.



Globally, these results indicate the possible implementation of carbonates co-precipitation as an alternative method for the synthesis of ferrites and manganites on a large scale. A preliminary study made on a semi-pilot installation using static mixers and pumps showed the feasibility of this approach (Fig. 5). A few hundreds of grams were produced easily in a few minutes.

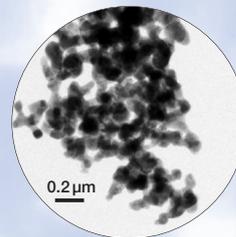


Figure 4: TEM micrograph of 5ULSF73-Ca.

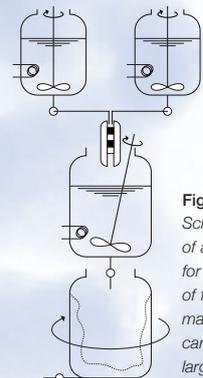


Figure 5: Schematic view of an installation for the production of ferrites and manganites by carbonates on a large scale using static mixers.

## Conclusions

Strontium lanthanum manganite and ferrite were produced by different techniques: «spray pyrolysis», a modified citrate route, oxalate, carbonate and cyanide co-precipitation. The influence of the different fabrication procedures on the final microstructure and composition of these materials were investigated. Powders were characterized by TG/DTA, XRD, ICP, TEM, XPS, PSD and BET.

«Spray pyrolysis» produced mesoporous agglomerates after intensive ball-milling. Powders with a d<sub>50</sub> = 500 nm were thus obtained.

The carbonate route was observed to deliver a finer powder with a more homogeneous composition (100 nm, TEM). These results indicate the possible implementation of carbonate co-precipitation as an alternative route for the synthesis of lanthanide ferrites and manganites. A semi-pilot installation made using static mixers showed the feasibility of this approach.

The co-precipitation of La, Ca and Fe was also possible using the cyanide route giving rise to a crystalline complex. This is to our knowledge the first reported cyanide precipitation relating La, Ca, and Fe using [Fe<sup>II</sup>(CN)<sub>6</sub>]<sup>4-</sup>.

ICP analyses on all samples showed slight fluctuations between the differently sourced powders. However, due to distinct synthesis routes, sintering temperatures and processing steps, morphological major differences were observed by TEM, XPS, BET and PSD techniques.

As expected, the microstructure and surface composition of these powders triggered disparities in their electrochemical response (SOFC cathode tests). The relative importance of each of these properties is not very clear yet.

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