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# Variation of surface properties and textural features of spinel ZnAl<sub>2</sub>O<sub>4</sub> and perovskite LaMnO<sub>3</sub> nanoparticles prepared via CTAB–butanol–octane–nitrate salt microemulsions in the reverse and bicontinuous states

A.E. Giannakas,<sup>a</sup> T.C. Vaimakis,<sup>a</sup> A.K. Ladavos,<sup>a</sup> P.N. Trikalitis,<sup>b</sup> and P.J. Pomonis<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, University of Ioannina, Ioannina 45110, Greece <sup>b</sup> Department of Chemistry, Michigan State University, East Lansing, MI 48824, USA

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#### Abstract

Two binary oxides, a spinel, ZnAl<sub>2</sub>O<sub>4</sub>, and a typical perovskite, LaMnO<sub>3</sub>, have been prepared via CTAB–1-butanol–*n*-octane–nitrate salt microemulsion in the reverse and bicontinuous states. The exact point of the reverse and bicontinuous states of the microemulsion used in the synthesis was determined by conductivity experiments. The materials obtained after heating at 800 °C were characterized by XRD analysis for their crystal structure, N<sub>2</sub> porosimetry for their surface area and porosity, and SEM and TEM photography for their texture. The ZnAl<sub>2</sub>O<sub>4</sub> spinel obtained via the reverse microemulsion appears in SEM in a more fragmented form and with a higher specific surface area (143.7 m<sup>2</sup> g<sup>-1</sup>), compared to the corresponding solid prepared via the bicontinuous microemulsion, which appears more robust with lower surface area (126.7 m<sup>2</sup> g<sup>-1</sup>). Nevertheless both materials reveal in TEM a sponge-like structure. The perovskite materials LaMnO<sub>3</sub> prepared via the reverse microemulsion showed in SEM a peculiar doughnut-like texture, each doughnut-like secondary particle having a diameter of 2 µm. The corresponding sample developed via the bicontinuous microemulsion showed in SEM uniform secondary particles of size ~0.2 µm. Both perovskite samples LaMnO<sub>3</sub> appear well crystallized with relative low surface areas, 23.7 m<sup>2</sup> g<sup>-1</sup> for the reverse sample and 10.9 m<sup>2</sup> g<sup>-1</sup> for the bicontinuous one. The TEM photographs reveal that both of them, of reversed and bicontinuous origin, are made up of primary nanoparticles in the size range 40–100 nm. In SEM those materials showed a different secondary structure.

Keywords: Microemulsion; Reverse microemulsion; Bicontinuous microemulsion; Spinel ZnAl<sub>2</sub>O<sub>4</sub>; Perovskite LaMnO<sub>3</sub>

# 1. Introduction

The reverse micelle method [1], utilizing aquatic solution nanodrops surrounded and stabilized by surfactant molecules, has been used extensively for the synthesis of inorganic nanocrystallites in the past 10–15 years. The types of clusters and nanoparticles studied include cadmium sulfides CdS [2], cadmium selenides CdSe [3] for electronic applications, titanium oxides TiO<sub>2</sub> [4], zircon oxides ZrO<sub>2</sub> [5], tin oxides SnO<sub>2</sub> [6], metallic nickel Ni<sup>0</sup> particles [7], cobalt– molybdenum Co–Mo clusters [8], silver bromide AgBr for photographic films [9], superconductor nanoparticles, notably Y–Ba–Cu–O [10], and calcium phosphates Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> for biomedical applications [11]. Another large group of nanomaterials prepared via emulsion and/or microemulsion techniques includes ferrites BaFe<sub>12</sub>O<sub>4</sub> [12] and other magnetic particles containing iron [13]. But materials such as spinels  $AB_2O_4$  and perovskites  $ABO_3$  have attracted rather little attention. For the spinel class of solids, some relevant work is that of the Saar group [14] on  $MAl_2O_4$  (M = Mg, Co, Ni, Cu) binary oxides. Such materials show significant potential for diverse applications such as catalysis and catalyst support, pigments, and infrared windows [15]. There is also some work on Fe-containing simple CoFe<sub>2</sub>O<sub>4</sub> or substituted Mn<sub>0.45</sub>Rn<sub>0.55</sub>Fe<sub>2</sub>O<sub>4</sub> spinels for possible magnetic applications [16]. In relation to perovskites the relevant literature includes mainly zirconates such as PbZrO<sub>3</sub> [17], BaZrO<sub>3</sub>, SrZrO<sub>3</sub>, and titanates such as BaTiO<sub>3</sub> and SrSiO<sub>3</sub> [18] for piezoelectric applications.

<sup>\*</sup> Corresponding author. *E-mail address:* ppomonis@cc.uoi.gr (P.J. Pomonis).



Bicontinuous phase of microemulsion

Microemulsion (o/w)



Fig. 1. The transformation of reverse microemulsion (w/o) first to a bicontinuous phase and next to a microemulsion (o/w) with the addition of the aquatic phase.

The emphasis in almost all the above studies was given to the preparation of nanoparticles with uniform size controlled by the size L = 2R (R =radius) of nanodroplets of reverse water-in-oil (w/o) microemulsions. It is well established that R and L are practically controlled by the ratio  $w = (H_2O)/(s)$  where the brackets mean concentration and s-surfactant [1,19]. As the concentration of water increases, the nanodroplets of the microemulsion increase in size and eventually form a cluster, which is considered infinite [20]. At this stage the microemulsion possesses a bicontinuous structure. Further addition of the aquatic phase transforms the bicontinuous system into an oil-in-water (o/w) microemulsion, where the nanodrops of the organic phase are surrounded by the water bath and the interface is made up of surfactant species. The kind of transformation is depicted in Fig. 1.

The development of those totally different kinds of dispersion can be followed very conveniently by conductivity experiments [21]. Before the formation of the infinite cluster and the achievement of the percolation threshold [21], the conductivity  $\sigma$  is low. Then, at the threshold,  $\sigma$  increases, more or less suddenly, and obtains a relative high value which does not change appreciably when the o/w state is achieved. This kind of conductivity behavior allows the observer to distinguish relatively easily the noncontinuous w/o microemulsion and the bicontinuous range of the system.

Now a relevant question is: what might be the difference in the external geometrical features of a ceramic material, let us say spinel or perovskite particles, formed in the two different microreactor systems-the first represented by the isolated spherical aquatic drops and the second by the elongated bicontinuous aquatic cluster? Will the geometry of the "microreactor" also be somehow transferred and become apparent in the final solid? A relevant question is the following: Will the surface composition of such an otherwise similar solid, i.e., a spinel AB<sub>2</sub>O<sub>4</sub> or a perovskite ABO<sub>3</sub>, be affected by the variation of shape and/or size of the "microreactor"? The answer to this question might not be trivial since the various cations, i.e.,  $Al^{3+}$ ,  $Mg^{2+}$ ,  $La^{3+}$ , etc., in the spherical or bicontinuous microreactor phase might show differentiated concentration and accumulation at the interface compared to the bulk.

This work deals with the differentiated surface properties, such as surface area and pore volume, as well as the differentiated textural features, such as particle size and shape, of one typical spinel, ZnAl<sub>2</sub>O<sub>4</sub> and one typical perovskite, LaMnO<sub>3</sub>, both prepared in two different states of microemulsions, the reverse phase and the bicontinuous phase. The different microemulsion states were pinpointed via conductivity experiments.

Table 1

The composition of microemulsions	employed for the	preparation of spine	l ZnAl <sub>2</sub> O <sub>4</sub> and perovskite	e LaMnO <sub>3</sub>
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	СТАВ	1-butanol	<i>N</i> -octane	Zn(NO <sub>3</sub> ) <sub>2</sub> 0.4 M Al(NO <sub>3</sub> ) <sub>3</sub> 0.8 M	NH <sub>3</sub> 8 N
		Reverse micelle for spin	els ZnAl <sub>2</sub> O <sub>4</sub>		
Reverse microemulsion A	0.52 M	1.73 M	4.6 M	0.037 M 0.073 M	_
Reverse microemulsion B	0.51 M	1.67 M	4.51 M	_	0.92 M
	Bie	continuous micelle for s	pinels ZnAl <sub>2</sub> O <sub>4</sub>		
Bicontinuous microemulsion A	0.47 M	1.58 M	4.2 M	0.067 M 0.135 M	_
Bicontinuous microemulsion B	0.48 M	1.48 M	6.2 M	-	1.64 M
	CTAB	1-butanol	N-octane	La(NO <sub>3</sub> ) <sub>3</sub> 0.8 M Mn(NO <sub>3</sub> ) <sub>2</sub> 0.8 M	NH <sub>3</sub> 8 N
	Re	eversed micelle for perov	vskite LaMnO <sub>3</sub>		
Reverse microemulsion A	0.63 M	2.1 M	4.2 M	0.048 M 0.096 M	_
Reverse microemulsion B	0.61 M	2.0 M	4.1 M	-	1.23M
	Bicc	ontinuous micelle for per	ovskite LaMnO <sub>3</sub>		
Bicontinuous microemulsion A	0.51 M	3.4 M	3.4 M	0.12 M 0.24 M	_
Bicontinuous microemulsion B	0.44 M	1.5 M	3.1 M	_	2.82 M

### 2. Experimental and results

#### 2.1. Microemulsion used and preparation of samples

The microemulsion A used for the preparation of the solids was based on CTAB/1-butanol/*n*-octane/M<sub>1</sub>(NO<sub>3</sub>)<sub>*x*</sub> + M<sub>2</sub>(NO<sub>3</sub>)<sub>*y*</sub>, where M<sub>1</sub>(NO<sub>3</sub>)<sub>*x*</sub> and M<sub>2</sub>(NO<sub>3</sub>)<sub>*y*</sub> are the corresponding metal nitrates.

In this microemulsion A a second microemulsion B based on CTAB/1-butanol/*n*-octane/NH<sub>3</sub> was added under stirring at room temperature. After several conductivity tests (see below) we reached the conclusion that the compositions of the microemulsion shown in Table 1 were worthwhile for the synthesis of the corresponding spinels and perovskites and their subsequent comparison.

Those compositions shown in Table 1 were selected according to the conductivity experiments reported below; a full report on them will be the subject of a future paper.

The precipitation took place by adding the microemulsion A to B, in which B has an excess of  $NH_3$  equal to 100% for the precipitation of the corresponding hydroxides. The rest of the emulsion agents were steady for all the cases described in Table 1.

The prepared precursor phases were then filtered, dried at room temperature, heated at 800 °C for 4 h under atmospheric conditions, and ground in an agate mortar.

#### 2.2. Conductivity experiments

As mentioned above, prior to the synthesis step, extended conductivity experiments were carried out in order to decide about the exact synthesis conditions/concentrations. Those experiments were carried out using an Inolab Terminal Level 3 conductivity meter. A mixture of  $C_{19}H_{42}NBr(CTAB)$  (Merck), *n*-octane (Fluka), and 1-butanol 99.4% (Aldrich) in the ratios shown in Table 1 was put into a double-walled glass beaker, kept at  $\Theta = 25$  °C using circulating water of controlled temperature from a Bioline Scientific temperature stabilizer. Typical results are shown in Fig. 2.

This figure summarizes the conductivity results in the form  $\sigma = f(V)$ , i.e., conductivity  $\sigma = f(\text{added ml} \text{ of} aquatic solution of metals nitrates) and <math>d\sigma/dV = f(V)$ , as well as the points chosen for the synthesis of the samples  $\text{ZnAl}_2\text{O}_4$  and  $\text{LaMnO}_3$  in the reverse and the bicontinuous phases. The initial concentrations of CTAB, 1-butanol, and *n*-octane are shown in each case. In this mixture, an aquatic solution of the corresponding nitrates  $\text{Zn}(\text{NO}_3)_2$ , 0.4 M, plus Al(NO<sub>3</sub>)<sub>3</sub>, 0.8 M, in the case of spinels, and La(NO<sub>3</sub>)<sub>3</sub>, 0.8 M, plus Mn(NO<sub>3</sub>)<sub>2</sub>, 0.8 M, in the case of perovskites, was added dropwise under stirring. After the experiment was finished the choices for the corresponding reverse microemulsion and the bicontinuous microemulsion are shown in the same figure. Those chosen points are shown in Fig. 3 in the form of triangular phase diagrams.

#### 2.3. Thermogravimetric studies

The precursor phases obtained, after drying at room temperature, were checked for their thermogravimetric behavior in a NETZSCH STA 449C thermobalance. The TG and the DTA signals were recorded from RT up to 1000 °C and are shown in Fig. 4.

The experiments employed 100 mg of the sample. The heating rate was  $5^{\circ}$ /min under a N<sub>2</sub> flow of 30 ml/min.



Fig. 2. Conductivity experiments for the choice of microemulsion A (aquatic phase consists of nitrate salts) and B (aquatic phase consists of ammonium) shown in Table 1. Dash–dot line shows the points chosen for the synthesis of bicontinuous phases of spinel (left) and perovskite (right), dotted line shows the points chosen for the reverse phases of the spinel (left) and perovskite (right).

#### 2.4. XRD analysis

The samples, after heating at 800 °C, were examined for their structure in a Brüker Advance D8 system employing Cu*Ka* radiation ( $\lambda = 1.5418$  Å) in the range 10° < 2 $\theta$  < 80° with a resolution of 0.02°/2 $\theta$ . The results are shown in Fig. 5.

The identification of the crystal phases took place using the data library JCPDS of the Brüker Advance D8 system. The only phases detected were spinel  $ZnAl_2C_4$  in the first case and perovskite LaMnO<sub>3</sub> in the second case. The striking difference between the two cases was the poor crystallization of the spinel  $ZnAl_2O_4$  and in contrast the good crystallization of the perovskite LaMnO<sub>3</sub> (see Fig. 5).

## 2.5. Surface area and porosity

The specific surface area  $S_p$  (m<sup>2</sup> g<sup>-1</sup>), as well as the specific pore volume  $V_p$  (cm<sup>3</sup> g<sup>-1</sup>), was detected by N<sub>2</sub> adsorption-desorption porosimetry at 77 K via the BET method. The instrument employed was a Fisons 1900 Sorptomatic system. Prior to the measurement, the sample (~250 mg) was degassed overnight (12 h) at 200 °C under pressure *P* of 10<sup>-2</sup> bar. In the case of spinels, those measurements showed a hysteresis loop and considerable internal porosity. The surface area was determined to be  $S_p = 143.7 \text{ m}^2 \text{ g}^{-1}$  for the reverse sample and  $S_p = 126.7 \text{ m}^2 \text{ g}^{-1}$  for the bicontinuous, while for corresponding pore volumes were  $V_p = 0.23 \text{ cm}^3 \text{ g}^{-1}$  and  $V_p = 0.21 \text{ cm}^3 \text{ g}^{-1}$ , respectively. The maxima of pore size distribution was found to be at  $D_p = 4.74 \text{ nm}$  for the reverse sample and  $D_p = 4.26 \text{ nm}$  for the bicontinuous one. In the case of the perovskite LaMnO<sub>3</sub> the N<sub>2</sub> adsorption was very limited, without a hysteresis loop. The corresponding specific surface areas were found to be  $S_p = 23.7 \text{ m}^2 \text{ g}^{-1}$  for the reverse perovskite and  $S_p = 10.9 \text{ m}^2 \text{ g}^{-1}$  for the bicontinuous solid. No attempt to determine the pore size distribution is possible in such cases, since the only porosity is external between the solid particles, which do not possess any internal surface area due to pores.

# 2.6. SEM photographs

The prepared samples  $ZnAl_2O_4$ -reverse,  $ZnAl_2O_4$ -bicontinuous,  $LaMnO_3$ -reverse, and  $LaMnO_3$ -bibicontinuous were observed and photographed by SEM using a JEOL JSM 5600 instrument. The results are shown in Fig. 6.



Fig. 3. Phase diagrams for the systems *n*-octane–CTAB/1-butanol 1.5% w/w–Zn(NO<sub>3</sub>)<sub>2</sub> 0.4 M + Al(NO<sub>3</sub>)<sub>3</sub> 0.8 M (upper left); *n*-octane–CTAB/1-butanol 1.5% w/w–La(NO<sub>3</sub>)<sub>3</sub> 0.8 M + Mn(NO<sub>3</sub>)<sub>2</sub> 0.8 M (upper right); and *n*-octane–NH<sub>3</sub>–CTAB/1-butanol 1.5% w/w (lower). The points A<sub>1</sub>, A<sub>2</sub> correspond to the chemical composition employed (also in Table 1) for the synthesis of the spinel ZnAl<sub>2</sub>O<sub>4</sub> and the points A'<sub>1</sub>, A'<sub>2</sub> correspond to the chemical composition for the perovskite LaMnO<sub>3</sub> using reverse and bicontinuous microemulsion correspondingly. The points L<sub>1</sub>, L<sub>2</sub> correspond to the area for reverse and bicontinuous microemulsion as determined by conductivity experiments, similar to the ones in Fig. 2, which are depicted by the dashed lines. The L area in the NH<sub>3</sub>-containing system (lower part) corresponds to the microemulsion.

#### 2.7. TEM photographs

TEM photographs were recorded in a JEOL 120CX equipped with a CeB6 filament. The results are shown in Fig. 7.

#### 3. Discussion

Following the well-known proverb that one picture is better than one thousand words, let us start this discussion with the SEM photographs in Fig. 6. The four photos in the upper part concern the spinel ZnAl<sub>2</sub>O<sub>4</sub>, while the four in the lower part concern the perovskite LaMnO<sub>3</sub>. The lefthand photographs depict the spinel and perovskite materials prepared via the reverse microemulsion, while the right-hand photos depict the materials obtained via the bicontinuous microemulsion.

# 3.1. The spinel $ZnAl_2O_4$

We observe that the spinels prepared by reverse microemulsion possess a much more fragmented structure, which somehow reflects the isolated nanodrops/nanoreactors where, theoretically, the reaction took place. In contrast, the spinel  $ZnAl_2O_4$  prepared in the bicontinuous phase appears much more robust and its structure recalls a semicontinuous folded surface.

The difference in the structure is also reflected in the specific surface area  $S_p$ , which is 143.7 m<sup>2</sup> g<sup>-1</sup> for the



Fig. 4. Thermogravimetric experiments TG-DTA for the precursor phases of the spinel  $ZnAl_2O_4$  and the perovskite  $LaMnO_3$  obtained via reverse and bicontinuous microemulsions.



Fig. 5. XRD of the ZnAl<sub>2</sub>O<sub>4</sub> and LaMnO<sub>3</sub> prepared by reverse and bicontinuous microemulsions after heating at 800 °C.

reverse spinel and 126.7 m<sup>2</sup> g<sup>-1</sup> for the bicontinuous spinel. At the same time, the specific pore volume is 0.23 cm<sup>3</sup> g<sup>-1</sup> for the reverse and 0.20 cm<sup>3</sup> g<sup>-1</sup> for the bicontinuous samples. Finally, the pores in the reverse spinel appear larger, with  $R_{\text{max}} = 23.7$  Å compared to  $R_{\text{max}} = 21.3$  Å for the bicontinuous phase.

Another difference between the two kinds of solids is that the bicontinuous solid is better crystallized, as seen from the X-ray diffractograms in Fig. 5. Using the well-known Scherrer relationship,

$$d = 0.9\lambda/b\cos\theta,$$



ZnAl<sub>2</sub>O<sub>4</sub> revers e 800°C



ZnAl<sub>2</sub>O<sub>4</sub> reverse 800°C



LaMnO3 reverse 800°C



LaMnO3 reverse 800°C



ZnAl<sub>2</sub>O<sub>4</sub> bicontinuous 800°C



ZnAl<sub>2</sub>O<sub>4</sub> bicontinuous 800°C



LaMnO3 bicontinuous 800°C



LaMnO<sub>3</sub> bicontinuous 800°C

Fig. 6. SEM photographs for the spinel  $ZnAl_2O_4$  (upper quartet) and  $LaMnO_3$  (lower quartet) obtained by reverse (left hand) and bicontinuous (right hand) microemulsions.

where *d* is diameter of crystallites in Å,  $\lambda$  is wavelength in Å,  $\theta$  is the Bragg angle in degrees, and *b* is the observed peak width at half maximum peak height in rads, we estimated the diameter of the crystallites to be  $d_{\text{cryst}} = 73.86$  nm for the reverse ZnAl<sub>2</sub>O<sub>4</sub> and  $d_{\text{cryst}} = 58.39$  nm for the bicontinuous

 $ZnAl_2O_4$ . All these data reflect the differences in the texture of the two final products  $ZnAl_2O_4$  obtained by the two different microemulsions.

The thermographs in Fig. 4 show that the two solid phases develop in a seemingly similar mode, but with some



ZnAl<sub>2</sub>O<sub>4</sub> reverse



ZnAl<sub>2</sub>O<sub>4</sub> reverse



LaMnO3 reverse



LaMnO3 reverse



ZnAl<sub>2</sub>O<sub>4</sub> bicontinuous



ZnAl<sub>2</sub>O<sub>4</sub> reverse



LaMnO3 bicontinuous



LaMnO<sub>3</sub> bicontinuous

Fig. 7. TEM photographs for the spinel  $ZnAl_2O_4$  (A, B, and C) and the perovskite LaMnO<sub>3</sub> (D, E, F, and G). Left: materials obtained via reversed micelles. Right: materials obtained via bicontinuous micelles. The selected area electron diffraction (SAED) pattern is referred to sample C.

quantitative differences. Both samples lose weight between RT <  $\Theta$  < 500 °C, which accounts for 65% for the reverse and 72% for the bicontinuous precursor. Then from 500 up to 1000 °C they lose ~12% for the reverse and ~10% for the bicontinuous phase. The total weight loss for the reverse

precursor totals  $\sim$ 77% while for the bicontinuous one it is higher,  $\sim$ 82%. This difference, although small, may be due to the fact that the bicontinuous dried precursor entraps a larger amount of organic molecules in various internal cavities, channels, etc. In contrast, the reverse precursor possess a more open and fragmented structure and the organic species, especially the nonvolatile CTAB, are not trapped in the structure but exist in the outer surface of the micelles and remove partly but easily during drying and filtration.

No important thermal effects are apparent in either case and the burning/removal of organic matter remaining is rather gradual and smooth, a fact due certainly to the middle catalytic action of  $Al^{3+}$  ( $d^0$ ) and  $Zn^{2+}$  ( $d^{10}$ ) cations [20]. It is worth mentioning that the bicontinuous precursor, which withholds larger amounts of organics, shows somewhat stronger thermal effects. This is in contrast to the strongly exothermic weight loss observed in the LaMnO<sub>3</sub> precursors, where the well-known catalytic activity of Mn<sup>3+</sup> ( $d^4$ ) results in fast burning of organics and stabilization of the weight already at 500 °C.

# 3.2. The perovskite $LaMnO_3$

The perovskite LaMnO<sub>3</sub> is developed in two totally different kinds of particles, as seen in Fig. 6. The material originated from the reverse perovskite shows some impressive forms of "doughnuts." Their external diameter is  $\sim 2 \,\mu\text{m}$  and the cavity in the middle is  $0.5-1 \,\mu\text{m}$ . Such structures, called "catenoids" in mathematics [21], are not very probable to be developed in microemulsions [19]. The reason is that such a configuration does not lead to minimization of the total external area of the structure. It would certainly be worthwhile to scrutinize further the precise conditions leading to the development of such structures.

The material originated from the bicontinuous spinel is made up of spherical particles of uniform size with a diameter  $d \cong 0.2 \,\mu\text{m}$ . According to the N<sub>2</sub> porosimetry discussed previously, these particles have no internal porosity, as testified by the absence of any hysteresis loop, and all their surface area, which is low,  $S_p = 10.9 \,\text{m}^2 \,\text{g}^{-1}$ , should be external. Indeed for such systems [21]

$$S_{\rm p} = 6/\rho d$$
,

where  $\rho$  is density. For  $\rho = 3 \text{ g cm}^{-3}$ , which is a typical value for such systems,  $S_p = 10 \text{ m}^2 \text{ g}^{-1}$ , in perfect correspondence with the experimental results.

The specific surface area of the particles originated from the reverse microemulsion, the "doughnuts," is almost double,  $S_p = 23.7 \text{ m}^2 \text{ g}^{-1}$ . This system, too, does not show any hysteresis loop in N<sub>2</sub> porosimetry, so the surface area should be somehow external and is developed in the interparticle voidages.

The TEM images of the spinel materials (Fig. 7) clearly show the formation of highly disordered, sponge-like, porous solids. There are no differences between them. They show exactly the same morphology and structural features. One could say that these solids are wormhole mesoporous solids. This is in full agreement with the N<sub>2</sub> absorption experiments. The XRD patterns show the formation of a crystalline ZnAl<sub>2</sub>O<sub>4</sub> spinel-type structure. The fact that the Bragg reflections are broad is not actually due to the poor crystallization of these materials. The reason for the broadening is the small size of crystallites in the walls of sponge solids, as clearly observed by TEM, which is < 10 nm. We have recorded the corresponding selected area electron diffraction pattern (SAED) (Fig. 7), which shows well-defined diffraction rings, indicating a polycrystalline material, and can be fully indexed to the spinel structure of ZnAl<sub>2</sub>O<sub>4</sub>. The electron diffraction pattern serves also as proof that the particles under observation are representative of the bulk material. In other words, the mesoporous particles are entirely composed of the spinel ZnAl<sub>2</sub>O<sub>4</sub> crystallites.

For the perovskite materials the TEM images show the formation of cubic nanocrystals with size in the range 20–100 nm. Both samples, inverse and bicontinuous, are almost identical, including quality, shape, and size of the nanocrystals.

Both systems, LaMnO<sub>3</sub>-reverse and LaMnO<sub>3</sub>-bicontinuous, according to the XRD spectra appear very well crystallized after heating at 800 °C (Fig. 5). The broadening of the XRD lines in the case of spinels (same Fig. 5) is not actually due to worse crystallization but rather to the size of the crystallites which made up the walls of the sponge, as mentioned above. Those walls are less than 10 nm thick and result in slightly diffused and out-of-focus X-ray diffracted beam.

The above discussion, and especially the combination of information taken from the SEM and TEM images, shows that there is a primary structure revealed by TEM which is almost similar or even identical for the spinels ZnAl<sub>2</sub>C<sub>4</sub> (sponge-like structure with nanowalls) and for the perovskites LaMnO<sub>3</sub> (nanoparticles of similar shape and size 20–100 nm). Nevertheless it seems in SEM that those primary particles form/sinter/coagulate to different secondary particles or structures. Thus for spinels ZnAl<sub>2</sub>O<sub>4</sub> the reverse secondary structure is more fragmented than the bicontinuous one. For the perovskites this differentiation leads to uniform spherical secondary particles with  $d \approx 0.2 \ \mu m$  for the bicontinuous sample and some peculiar doughnut-like structures for the reverse samples. Those fine differences in the development of the final solids might reflect some intrinsic differences in the coagulation of nanodrops and eventually of nanoparticles during drying. Indeed it is difficult to estimate whether such a gradual secondary development is a sole result of the kind of microemulsion (reverse or bicontinuous) or/and the effect of different load with surfactant, which might lead to collision and coagulation of nanodrops during drying and of the resulting nanoparticles during firing. For the moment we cannot express a definite opinion about the reason of this result, while the exact pathways followed during the development of the final product remain elusive. Some very powerful techniques will be needed to

trace answers to such questions referring to the mechanism of initial crystallization.

#### 4. Conclusions

Two kinds of microemulsions, one in the reverse and the second in the bicontinuous state, have been employed for the preparation of two kinds of binary oxides, one spinel, ZnAl<sub>2</sub>O<sub>4</sub>, and one perovskite, LaMnO<sub>3</sub>. The exact composition of the microemulsion employed in each synthesis route was chosen after relevant conductivity experiments. The ZnAl<sub>2</sub>O<sub>4</sub> synthesized via the reverse microemulsion appears more fragmented in SEM than the sample obtained via the bicontinuous state. The latter appears more robust, with lower surface area, and is better crystallized than the former. Nevertheless, both samples show similar sponge-like structures in TEM. The LaMnO<sub>3</sub> sample from the reverse phase according to SEM photographs is developed in secondary particles of peculiar doughnut-like forms with a diameter of  $\sim 2 \mu m$ . The sample from the bicontinuous phase is developed in secondary uniform-sized spherical particles of similar size with a diameter of  $\sim 0.2 \,\mu\text{m}$ . Nevertheless, according to TEM photographs, both kind of perovskite are made up of similar nanoparticles of size 20-100 nm. The most promising aspect of this work is the perovskite LaMnO<sub>3</sub> solid particles, developed in uniform shapes and possessing relatively high specific surface areas ( $\sim 20 \text{ m}^2 \text{ g}^{-1}$ ) compared to similar solids prepared with different techniques. Such materials are promising catalysts on de-NO<sub>x</sub> applications as substitutes for noble metals.

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