Synthesis and sintering of $La_{0.8}Sr_{0.2}Mn0_3$ by rapid microwave heating

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Abstract : We report in this paper the synthesis, the sintering and the properties of $La_{0.8}Sr_{0.2}Mn0_3$ (LSMO) compound. The starting raw material was prepared by solid state reaction. Synthesis and sintering was carried out using both a conventional furnace and a microwave device. The LSMO phase has been successfully synthesized in a microwave cavity in a very short time of few minutes. Scanning electron microscopy (SEM), X-ray diffraction (XRD), magnetic and electrical properties were carried out for both processing conditions. The results and advantages of microwave heating to process manganite oxides are discussed.

Keywords: Powders-solid state reaction**,** Microwave processing, Magnetic properties, Perovskites

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1. Introduction

The discovery of the colossal magnetoresistance (CMR) in the mixed manganese oxides $R_{1-y}A_yMnO_3$ (where R is a trivalent rare-earth element and A the divalent cation) has been a subject of attention in the recent year. The origin of CMR effect is often thought to be based on the double exchange mechanism [1-3]. Potential applications of modern colossal magnetoresistive (CMR) materials, as magnetic sensors or read heads for information storage and actuator maintain intense research of manganate components with different forms [4-9]. Thus large efforts in processing and characterization have been done [10-12]. It is well know

that the microstructure, magnetic and electrical transport properties of the final material are strongly influenced by the precursors as well as the process used. It is generally believed that in spite of the use of advanced chemical processing techniques, the sintering of manganate materials require high temperature during the processing. In the present work, we report the synthesis of $La_{0.8}Sr_{0.2}MnO_3$ (LSMO) rods processed by microwave sintering technique and also by conventional method. The comparison between both heating methods has been investigated.

2. Experimental procedure

The starting chemical pure lanthanum oxide, La_2O_3 (Restapur 99,9%), strontium carbonate $SrCO_3$ (diopma 99.99%) and manganese oxide MnO_2 (cerac 99%) reagents have been mixed according to the stoichiometric proportions using semi-planetary grinder (Fritsch) for 45 minutes in dried condition.

Conventional process: The precursor powder was placed into a Platinum crucible at 1200°C during 12h in air. The resulting powder was subsequently reground manually and the powder was uniaxially pressed under 2800 kg load. The green samples were sintered at 1500°C in air during 24h with 200°C/h slopes.

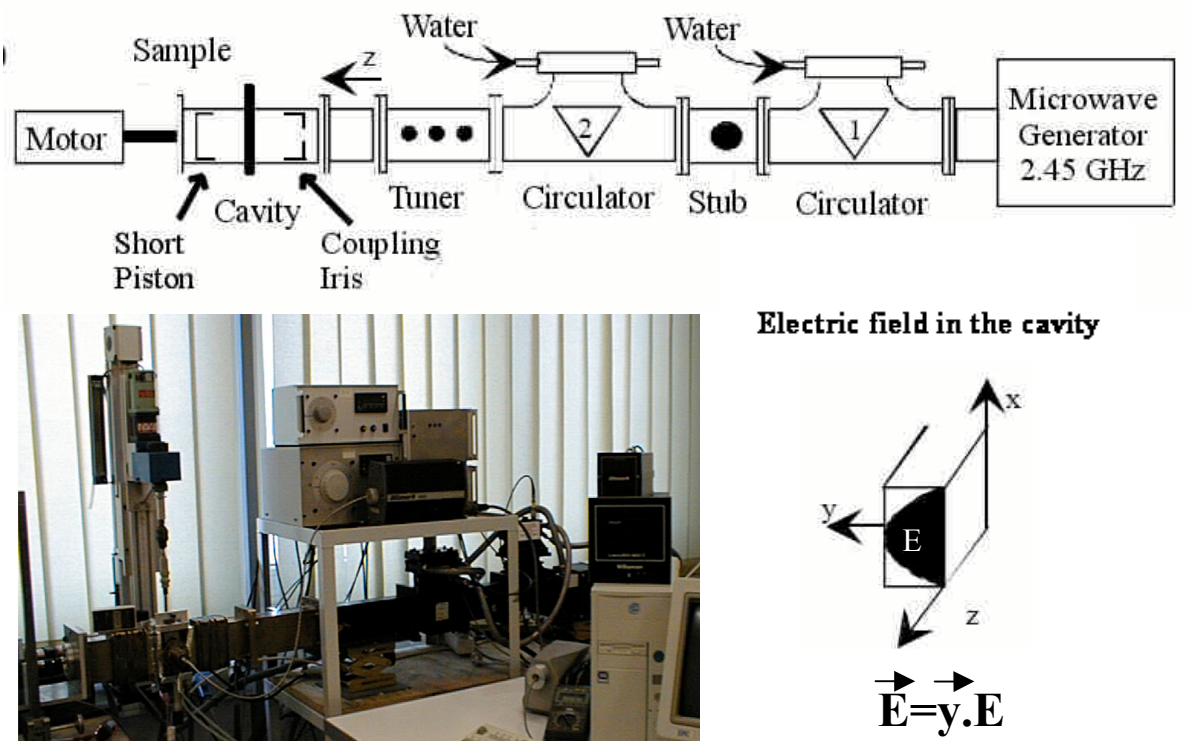

Figure 1: Symmetrical single mode microwave cavity TE10p

Microwave process: Cylindrical samples (5 mm ∅ and 120 mm height) were made from precursor powder using cold isostatic pressure of 3000 bar. The bar was fixed in a rotary support and placed in the center of the microwave cavity where is located a dense SiC tube to act as susceptor. The bar is positioned perpendicularly to the electrical field (figure 1) and is translated vertically at various speeds. The device is constituted by a microwave generator (2.45 GHz sairem GMP20KSM) which delivers a variable power from 0 to 2000 W. A rectangular waveguide (WR340) allows the transport of the microwave radiation to the rectangular TE10p cavity [13]. A specific symmetrical resonant cavity [13] was used to allow the transfer of the microwave energy to the susceptor.

Optimal transfer was achieved owing to:

(i) the tuner (impedance agreement accord)

(ii) The movable distance between the coupling iris and the short circuit piston which is tuned to be at the TE_{102} mode.

The susceptor tube axis was positioned on the center of the cavity and perpendicularly to the electrical field. This susceptor absorbs the microwave energy and the heat is transmitted to the sample by Infra-Red radiation. In our case the microwave input power was fixed at 900W and the heating time was 30 min.

All the materials synthesized either by conventional heating or microwave heating were characterized by scanning electron microscope-SEM (Philips FEG XL'30) couple to EDX (Oxford) . The X-ray powder diffraction pattern was recorded at room temperature using a Rigaku apparatus using the CuK_α radiation. Magnetic and transport properties were measured using SQUID and PPMS set-up from Quantum Design.

3. Results and discussion

a) Microstructure

Figure 2 shows the X-ray diffraction (XRD) patterns for the precursor powder, the conventional and the microwave synthesis powder (previously reground). The patterns show that all the samples are single-phase perovskites without any secondary phase or impurity. All the diffractogramms were successfully indexed with respect to the rhomboedral structure using Rietveld analyze with JANA [14]. The lattice parameters are quite similar for both materials :

Conventional synthesis: Rp%=4.58 Rwp%=6.17 gof=1.02 space groupe ($R\bar{3}c$), the lattice parameters (a=5.5282(1) Å , c= 13.3758(2) Å)

Microwave synthesis: Rp%= 4.79 Rwp%= 6.35 gof=1.05 space groupe ($R\bar{3}c$) the lattice parameters (a= 5.5323(1) Å , c= 13.3776(1)Å).

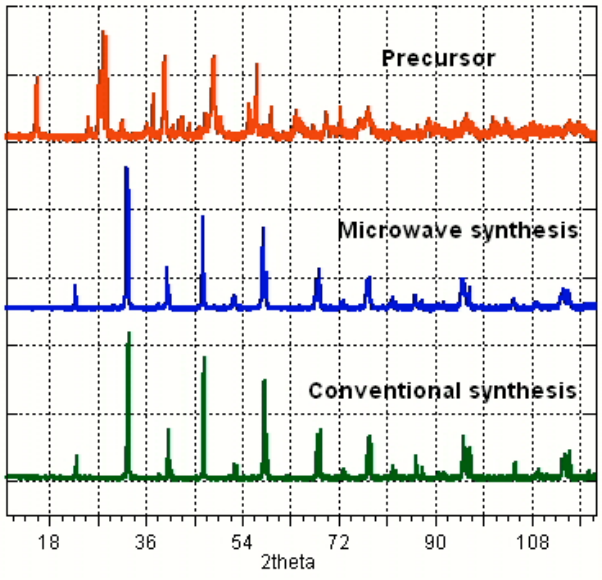

Figure 2: XRD patterns of Precursor and LSMO powder after microwave synthesis and conventional synthesis.

The SEM pictures of the microstructures samples sintered using microwave heating and conventional heating are presented in figure 3. Although the temperature is not known in the case of the microwave process, the most important result is that the phase $La_{0.8}Sr_{0.2}MnO3$ has been successfully synthesized in only 30 minutes. Moreover, the microstructure of the sample (figure 3a) shows without any ambiguity that the sample is well sintered. According to the literature [15], this material can be sintered at a very high temperature (T>> 1500°C) that could give us an indication of the temperature into the susceptor. The grains size has a large distribution with size < 30 µm. In the conventional process we can clearly observe the morphology smaller grain size (5µm) and it is also evidenced a very porous microstructure revealing that 1500°C, is not enough to sinter our ceramic.

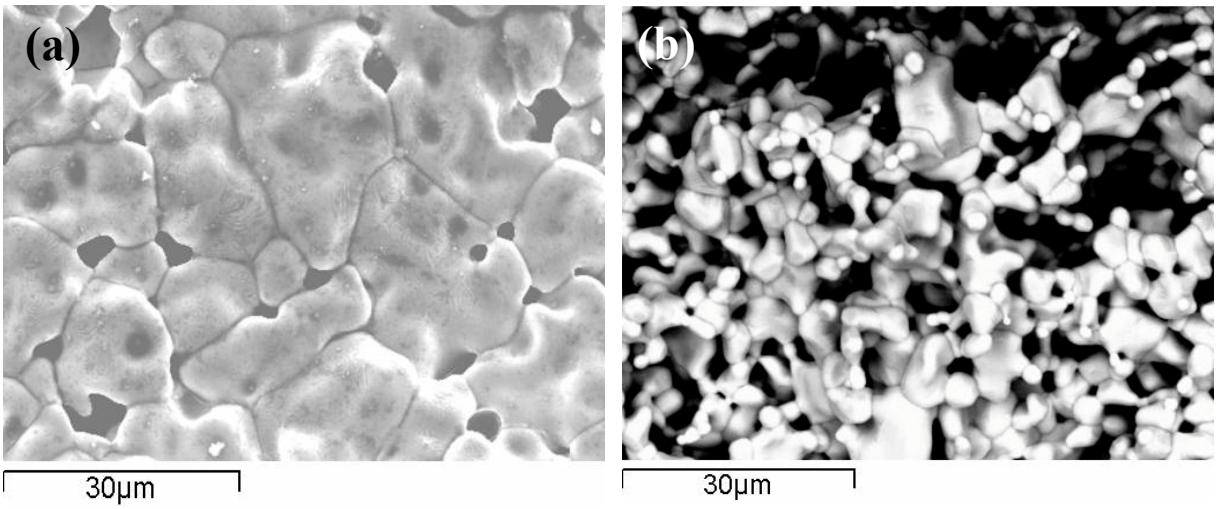

Figure 3: SEM Pictures of (a) microwave and (b) conventional sintered LSMO samples microstructure

b) Physical properties

The temperature dependence of the magnetization at 0.01T for processed sample using both method is shown in figure 4. The field cooled magnetization shows that all samples undergo a sharp paramagnetic to ferromagnetic transition revealing that the Curie temperature (inflection point on the M(T) curve) is above the room temperature at about 325 K for both samples.

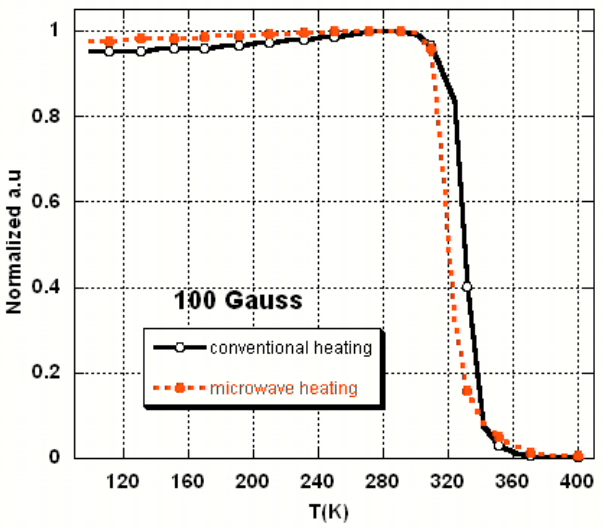

Figure 4: Temperature dependence of the normalized magnetization

Figure 5 presents the resistance measurements versus temperature under various field up to 7 T. The both samples show a metal-insulator transition at about room temperature. At zero field, $La_{0.8}Sr_{0.2.}Mn0_3$ shows an insulator-to-metal (IM) transition temperature T_{IM} = 340 K, and the transition temperature shifts to higher temperatures as the applied magnetic field increases. A positive magnetoresistance (MR) is still as large as 50% at 320K, 7T. In the literature similar behavior has been observed on samples [10-12] conventionally sintered at very high sintering temperature (T>>1500°C) but with T_{IM} = 305 K. The difference T_{IM} observed can be interpreted by the oxygen rate or to the connectivity between grains. Furthermore more investigations will be done shortly to clarify this point.

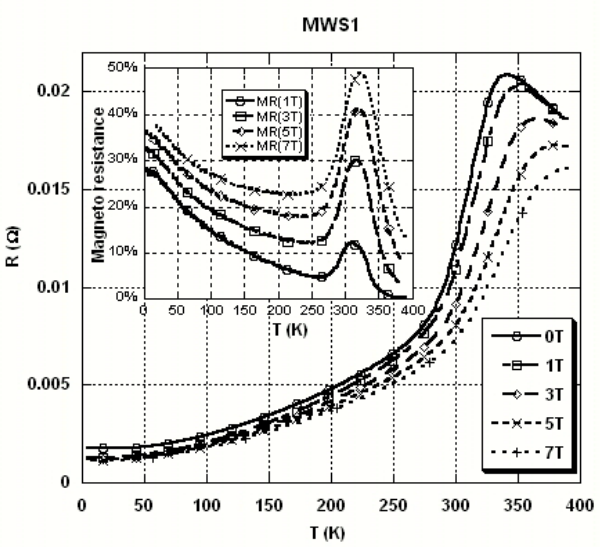

Figure 5: Temperature dependence of MR (inset) and resistance at various applied field for microwave sintered sample.

4. Conclusion

Bulk ceramic samples were prepared using the conventional solid-state reaction and microwave heating respectively. From the present studies it could be concluded that, a microwave assisted synthesis and sintering of $La_{0.8}Sr_{0.2}MnO_3$ could be successfully accomplished in a very short time of 30 minutes with silicon carbide as a susceptor. The properties of the fast heating microwave materials are comparable to those measured on

sintered conventionally samples. More experience will be done in order to optimize the microwave sintering schedule and to determine at least approximately the temperature inside the susceptor. Concerning the material's properties, there are still some questions: for example why the T_{IM} is different, this point will be further investigated because it is well know that the grain size plays a crucial role in the magnetotransport property

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