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Materials processed by indirect microwave heating in a single-mode cavity

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Abstract

We report in this paper the synthesis, the sintering and the properties of $La_{0.8}Sr_{0.2}MnO_3$ (LSMO) and $BaZrO_3$ (BZ) compound using microwave heating. The starting raw material was prepared by solid state reaction. Synthesis and sintering were carried out using an indirect microwave heating process. SiC susceptor tube was utilized to produce the indirect heating in a microwave symmetrical single mode cavity TE10p. The LSMO and BZ phases have been successfully sintered in a microwave cavity in a very short time. Scanning electron microscopy (SEM), X-ray diffraction (XRD), magnetic or dielectric and electrical properties were carried out for both processing conditions, i.e., using classical and microwave heating. The results and advantages of this microwave process to synthesize many materials with various physicals properties are discussed.

Keywords: A. Microwave processing; C. Dielectric properties; C. Magnetic properties; D. Perovskites; Magnetoresistance

1. Introduction

Microwave heating is generally used to treat dielectric materials such as alumina [1], silica or perovskites ($Ba(Zn_{1/3}Ta_{2/3})O_3$ [2], $Ba(Mg_{1/3}Ta_{2/3})O_3$ [3]). Heating is hence produced by dielectrics losses consecutively to the interaction between the material and the electric field. The well known Eq. (1) gives the relation between the dissipated power (P_d) and the electrical field (E) (f is the frequency, ε' is the imaginary part of the permittivity and tan (δ) is the dielectric losses [4]). Nevertheless, other works have investigated the contribution of the magnetic field (H) to the heating of materials with non negligible conductivity ($\sigma \approx 10^{-2}\ \Omega^{-1}\ cm^{-1}$). The microwave sintering of various materials such as $LaCrO_3$ [5], $LiFe_5O_8$ [6], $YBa_2Cu_3O_{7-\delta}$ [7,9] highlights this mechanism. In this case, the dissipated power is proportional to the square of the magnetic field (Eq. (2)).

$$P_d \cong 2\pi f \varepsilon' \tan(\delta) E^2 \quad (1)$$

$$P_d \alpha H^2 \quad (2)$$

From a practical point of view, the use of a susceptor can be envisaged when materials are poorly absorbing. This method consists in using an absorbing susceptor which transmits the energy to the sample by infra-red radiation. This 'indirect' microwave heating could reduce the heating anomalies like cut-off, run-away, etc. [4]. Moreover, large range of materials (semi-metallic to insulator) could be easily performed with this process because, using a susceptor, the materials properties have low influence on the heating process. In this article, we report the high temperature sintering of $La_{0.8}Sr_{0.2}MnO_3$ (LSMO) and $BaZrO_3$ (BZ) compounds by indirect microwave process exploiting the contribution of the magnetic field. These materials have different properties (LSMO is magneto-resistive and BZ is insulator). The goal is to demonstrate how microwave heating, owing to an appropriate susceptor, can be successfully used to sinter rapidly a large variety of refractory materials.

2. Experimental procedure

2.1. Microwave process

The starting chemical pure lanthanum hydroxide, $La(OH)_3$ (Rectapur 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

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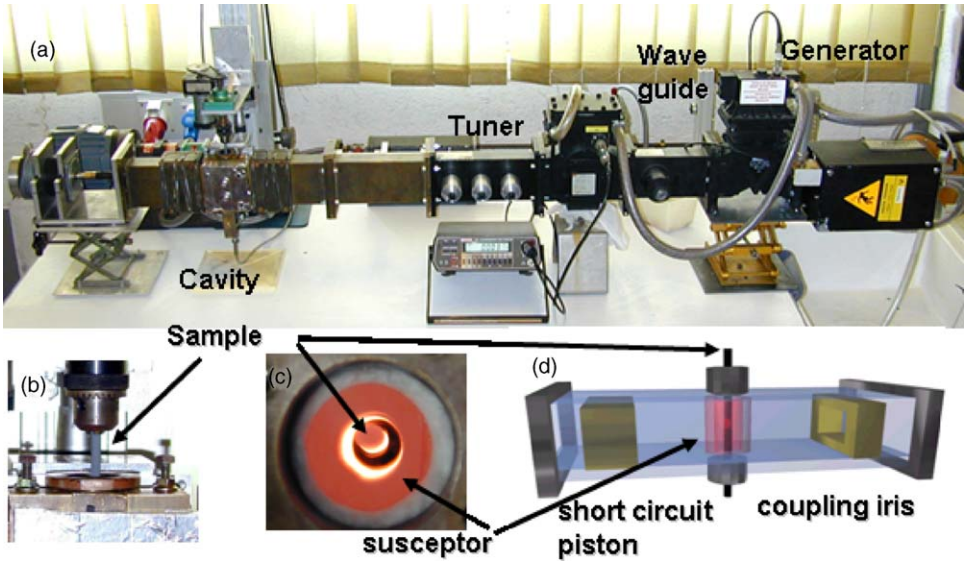

Fig. 1. Pictures of indirect microwave single-mode cavity process.

using semi-planetary grinder (Fritsch) for 45 min in dried condition. In the case of BZ, commercial powder was utilized (Johnson Matthey 99%). Cylindrical samples (5 mm diameter and 120 mm height) were made from precursor powder using cold isostatic pressure of 3000 bar. The cylinder bar was fixed in a rotary support and placed in the center of the microwave cavity where a dense SiC tube is located to act as susceptor (show Fig. 1). The bar as well as the susceptor is positioned perpendicularly to the electrical field. This bar could be translated vertically at various speeds. The equipment constitutes of a microwave generator (2.45 GHz Sairem GMP20KSM) which delivers variable power from 0 to 2000 W. A rectangular waveguide (WR340) allows the transport of the microwave radiation to the rectangular TE10p cavity [8]. This specific symmetrical resonant cavity [8] allows the transfer of the microwave energy to the susceptor.

Optimal transfer is achieved owing to:

(i) the tuner (impedance agreement accord);
(i) the movable distance between the coupling iris and the short circuit piston which is tuned to be at the TE_{102} mode.

During the process, temperatures were measured by bicolour pyrometer (Williamson).

2.2. Materials characterizations

All the materials synthesized 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 by Rigaku apparatus using Cu Kα radiation. Magnetic moment and transport properties were measured using a SQUID and a PPMS set-up from Quantum Design, respectively. In the case of BZ, the dielectric measurements performed at 1 MHz were carried out versus temperature (−60 to 160 °C) using an RLC Bridge (Flucke PM6306) and the resistivity was measured using a SEFELEC DM500A megohmmeter at 1 kV.

3. Results and discussion

3.1. LSMO sintering study

Bar samples of LSMO were positioned into the cavity and no transition was applied. The microwave exposure time was fixed at 10 min. Several microwaves input powers have been selected: 700, 750, 800, 900, 950 and 1000 W. Each sample is named, respectively, MW700, MW750, MW800, MW900, MW950 and MW1000 according to the power used to treat it.

Temperature–time curves (Fig. 2) recording during the microwave process shows two different behaviours and highlight incident power threshold. If the microwave power is higher than or equal to 800 W, sample temperatures achieve values higher than the detection limit (2000 °C). Kinetic heating acceleration (thermal run-away) is observed when temperatures are above 1500 °C. If the microwave power is lower than or equal to 750 W, the achieved temperature is about 1400 °C and no thermal run-away occurs. At the end of the

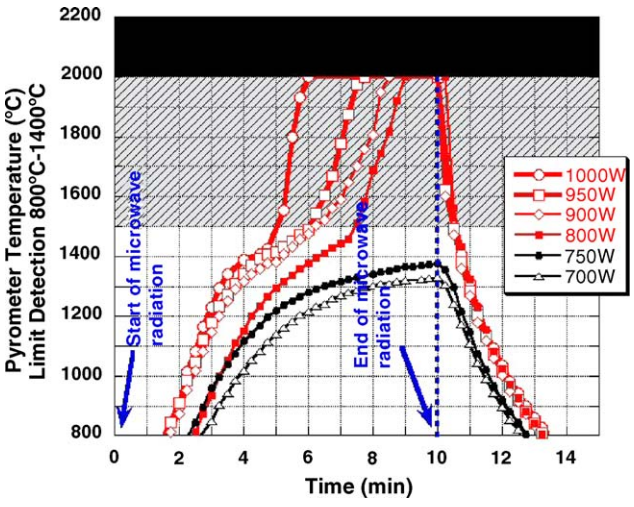

Fig. 2. Temperature vs. time during LSMO sintering.

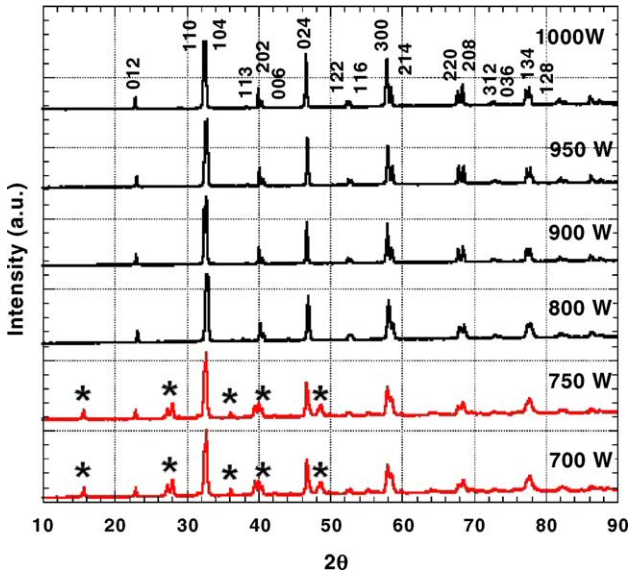

Fig. 3. X-ray diffraction varying as a function of incident microwave power ((★) impurity).

heating, a selected area (1 cm of height) was cut from the middle of each sample, and characterizations were done on this selected part.

X-ray analyses were performed on all samples (Fig. 3). LSMO phase and traces of precursor were observed for samples MW700 and MW750. In these cases incident microwave powers were too low for full LSMO synthesis, temperature and/or process time may be too low. In contrast, the X-ray diagrams of MW800, MW900, MW950, MW1000 samples show that a unique LSMO phase was obtained. Crystallographic parameters were refined by JANA2000 software and these data are in good agreement with usual parameters [10,11] (for MW900 Rp% = 4.79, Rwp% = 6.35, space group: R-3c, a = 5.5323 Å, c = 13.3776 Å).

Samples were sintered in a conventional furnace (ConV) at 1500 °C during 24 h. Raw surface microstructure of conventional sample (ConV) and MW samples (MW800, MW900, MW950 and MW1000) are shown in Fig. 4. ConV sample microstructure shows grains poorly connected revealing an initial stage of the sintering (grains consolidation). In contrast, MW samples microstructures reveals a dense microstructure showing that the sintering process is completed.

Grain size statistic analyses (Fig. 5) were performed from image Fig. 4. Grains sizes distributions are really different between ConV sample and MW samples except for MW800. On MW samples, increasing grain size is observed when microwave incident power increase from 800 to 950 W.

Ferromagnetic-paramagnetic transition on LSMO samples is shown in Fig. 6. Sharp transition and high magnetic moment in ferromagnetic state are researched. Temperature transition is close to 320 K for all MW samples. In the case of MW700, MW750 and MW800, samples transitions (150 K) are larger than those samples MW900, MW950 and MW1000 (40 K). The largest transition in the case of MW700 and MW750 are explained by the crystallized impurity phase (see Fig. 3). In the case of MW800, observed magnetic behaviour could not be explained so easily, because crystallized impurity phase is not observed for this sample (Fig. 3). The observed magnetic behaviour may be explained by the presence of an amorphous

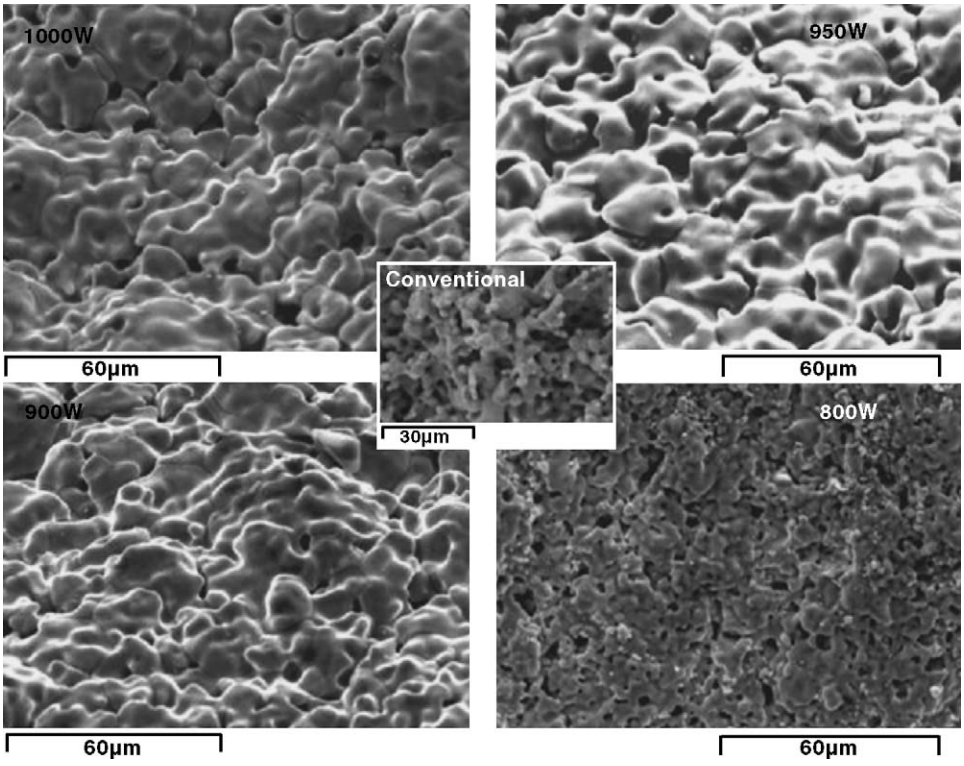

Fig. 4. SEM of LSMO samples.

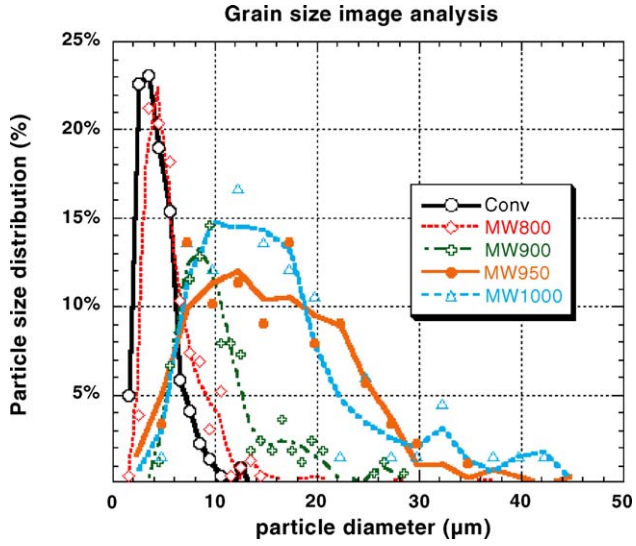

Fig. 5. Grain size image analysis.

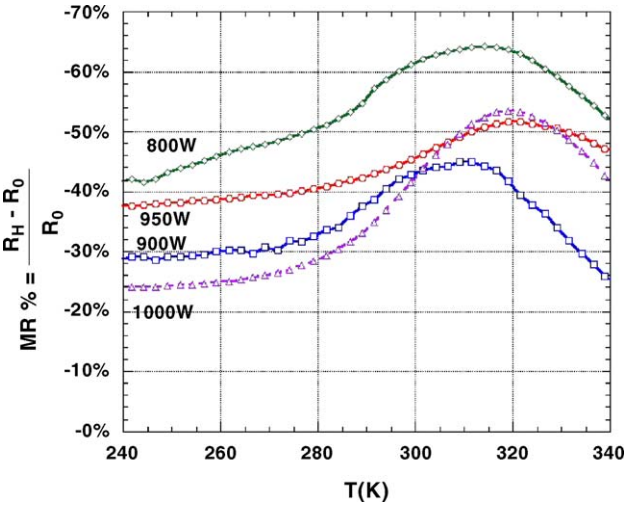

Fig. 7. Magnetoresistance of MW samples.

impurity, a variation of the oxygen content or by grain boundary effects [11]. Further investigations are needed to clarify this point. In the cases of MW900, MW950 and MW1000, expected curves of magnetic moment are obtained [11].

Magnetoresistance can be calculated by formula (3) from resistance at 0 T (R_0) and 7 T (R_H).

$$\mathrm{MR}\% = \frac{R_H - R_0}{R_0} \times 100 \quad (3)$$

Fig. 7 shows the MR% curves versus temperature for MW samples. Samples MW800 and MW900 show temperature transition close to 310 K and samples MW950 and MW1000 show temperature transition near 320 K. This shift of temperature transition may be explained by grain size difference [12]. The highest magnetoresistance values are measured for sample MW800, but the magnetic moment versus temperature of this sample is redhibitory (too large transition see Fig. 6). Magnetoresistance values of samples MW900, MW950 and MW1000 are in good agreement with values usually observed [11]. The sample processed at 900W has satisfying properties.

A last experiment was done to evaluate the possibility to have a continuous process. Power was fixed to 900 W and samples were translated at 4 cm h^{-1}. Physical properties variation along the bar was studied in order to control the homogeneity of the properties (Fig. 8). One could underline that properties were not function of the position except for the end of the bar where properties were degraded. Average values of temperature Insulator-Metal transition ($T_{I–M}$) at 0 and 7 T were close to 326 and 384 K, respectively. Magnetoresistance peak intensity (MR) was close to 60% at 307 K (T_{Max}(MR)). Samples were hence successfully obtained and properties were comparable to those measured on static samples. Acceptable microwave radiation leakages

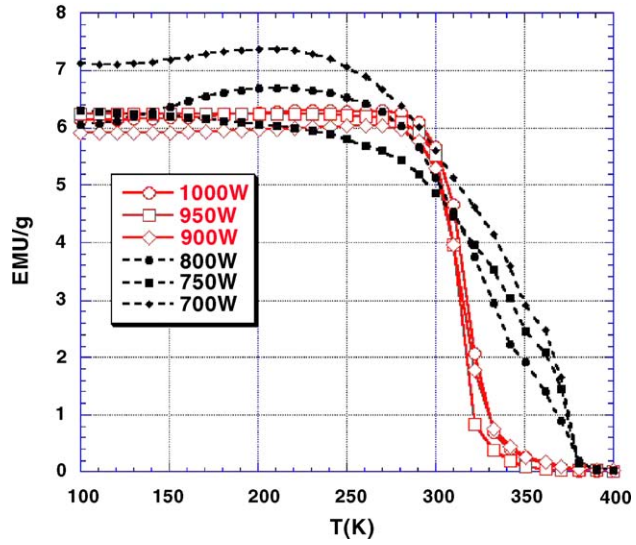

Fig. 6. Magnetic moment vs. temperatures.

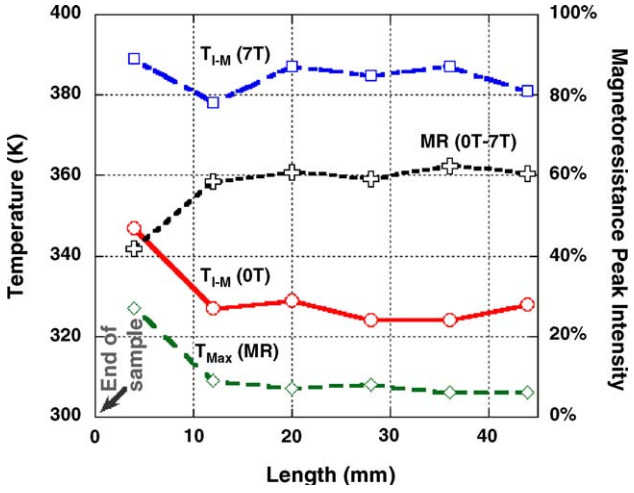

Fig. 8. Temperature transition insulator–metal ($T_{I–M}$) at 0 and 7 T, temperature (T_{Max}(MR)) and intensity (MR) of magnetoresistance peak vs. length.

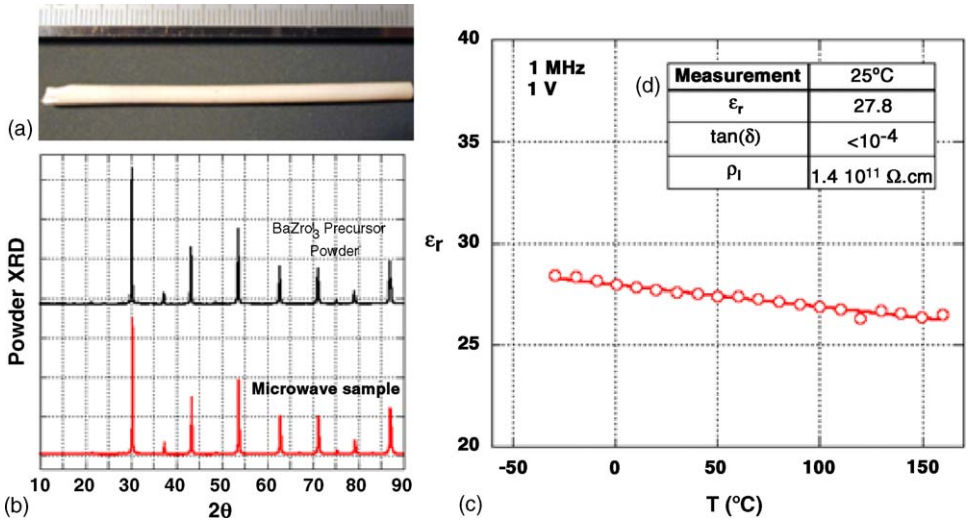

Fig. 9. $BaZrO_3$ dielectric measurement and picture of BZ sample.

were measured when samples were exiting the device (lower than 10 mW cm^{-2} at 5 cm).

3.2. BZ sintering study

BZ samples were sintered by the same process, at 900 W and 4 cm h^{-1}. Relative density of BZ samples (Fig. 9) is measured by Helium pycnometer is near 96.4% of theoretical density. X-ray diffraction and refinement exhibit the $BaZrO_3$ phase (SG: Pm-3m, $a = 4.1932(1)$ Å, Rp: 6.12%, Rw: 8.35%). Dielectric properties at 25 °C (Fig. 9) of BZ sintered in our experimental condition exhibit satisfying values [13]: relative permittivity, $\varepsilon_r = 27.8$; dielectric losses, $\tan(\delta) < 10^{-4}$ and insulator resistivity, $\rho_i = 1.4 \times 10^{11}\ \Omega$ cm.

4. Conclusion

This work reports the synthesis and the sintering of LSMO phase using a microwave TE10p cavity. The use of a susceptor in SiC appropriatively positioned into the cavity, has demonstrated that it is possible to synthesize by solid state LSMO phase and to sinter at the same time. The properties found of the ceramic are as good as the properties obtained classically. It is also shown the possibility to have a continuous process. The described process has also permitted the sintering of BZ, a dielectric material. These results highlight again the efficiency of the process.

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