



Preparation of dense $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ ceramics by plasma activated sintering and hot-pressing

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ABSTRACT

Highly dense $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (LCMO) ceramics were prepared by plasma activated sintering (PAS) and hot-pressing (HP). The comparison of structural, magnetic, and electrical transport properties of the LCMO ceramics after PAS and HP were investigated. XRD and SEM analyses confirmed that both samples exhibited orthorhombic phase with highly dense microstructure. The differences of magnetic and electrical transport properties in PAS and HP LCMO ceramics could be attributed to the different grain sizes, which have an effect on grain boundaries, domain states, Mn–O–Mn bond angles and Mn–O bond lengths. On analyzing the fitting data with several empirical equations, the conduction mechanism of the samples was found to be electron-magnon scattering in the ferromagnetic low-temperature region and variable range hopping (VRH) in the paramagnetic high-temperature region.

1. Introduction

In the past few decades, rare-earth doped perovskite manganites in the formula of $\text{La}_{1-x}\text{B}_x\text{MnO}_3$ (where B is the divalent alkaline-earth metal) have attracted much interest because of their unique electromagnetic properties, such as the interplay between spins, charges, and orbitals. Among them, the discovery of the colossal magnetoresistive (CMR) effect in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (LCMO) [1] has been drawing considerable attention for potential application as magnetic field sensors, memory devices, and so on [2–4]. The CMR effect is usually accompanied by other interesting behaviors such as paramagnetic-ferromagnetic (PM-FM) transition and metal-insulator (M-I) transition. The CMR phenomenon could be explained by the double exchange (DE) effect between Mn^{3+} and Mn^{4+} , deriving from the motion of an e_g electron between two partially filled d shells with strong on-site Hund's coupling [5]. The doping level or grain size could adjust the Mn–O bond length or Mn–O–Mn bond angle [4], which would affect the magnetic and magnetoresistance properties of LCMO by altering electron hopping and carrier localization.

LCMO ceramics are usually prepared by traditional pressureless sintering, where a rather high sintering temperature (1200–1600 °C) and a long sintering period (20–100 h) are necessary. However, high density is still difficult to obtain (68–90% relative density) [6–10] due to the poor sinterability of LCMO. Plasma activated sintering (PAS) and hot-pressing (HP) are two specific techniques for yielding compact

structures and superior performances that have been widely applied to various ceramics and metals [11–14]. As compared with traditional sintering methods, those techniques require a lower sintering temperature and a shorter sintering period because of the coupling of temperature and stress during the sintering process. Unfortunately, little work has been reported on LCMO ceramics prepared by PAS or HP.

In the present study, we prepared dense LCMO ceramics by using PAS and HP techniques, with the goal of obtaining high relative density at a low sintering temperature. The structural, magnetic, and electrical transport properties of the LCMO ceramics after PAS and HP were investigated.

2. Methods

$\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (LCMO) powders were synthesized by conventional solid-state reaction. High-purity raw powders of La_2O_3 , CaCO_3 , and MnCO_3 were weighed according to the stoichiometric composition and mixed homogeneously in ethanol by ball-milling for 24 h. The mixed powders were first calcined at 1300 °C for 15 h and then at 1350 °C for 25 h, to synthesize the single-phased LCMO powders. The calcined powders were further ball-milled for 20 h prior to sintering by PAS and HP, which was about 0.5 μm in particle size.

For the PAS process, the LCMO powders were placed in a graphite die and heated in a vacuum using a plasma activated sintering

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apparatus (ED-PAS-111, ELENIX). The sintering temperature was kept at 975 °C with a heating rate of 80 °C/min, and the holding time was 10 min under a pressure of 80 MPa. The LCMO ceramic prepared by PAS was referred to LCMO-PAS. For the HP process, the LCMO powders were placed in a graphite die and hot pressed (ZRY-40, Jinzhou Star) at 925 °C for 2 h in a vacuum and under a load of 100 MPa. The LCMO ceramic prepared by HP was referred to LCMO-HP. Both samples, ~ 1.5 μm in thickness and 20 mm in diameter, were finally annealed at 900 °C for 10 h in air, to remove oxygen vacancies.

The crystalline structure of the samples was characterized by X-ray diffraction using a Rigaku diffractometer with Cu K α radiation (Rigaku, Ultima III) followed by Rietveld refinement. Volume density was measured by Archimedes' method. The microstructure was observed by scanning electron microscopy (SEM, Quanta, FEG250). The magnetic properties were measured using a superconducting quantum interference magnetometer (SQUID, Quantum Design). Resistivity and magnetoresistance were measured by a physical property measurement system (PPMS, Quantum Design).

3. Results and discussion

3.1. Structure

Fig. 1 shows the Rietveld fitted X-ray diffraction patterns of the LCMO-PAS and LCMO-HP ceramics as performed by the GSAS and EXPGUI programs. The refined structural parameters are summarized in Table 1. Both samples are single-phased without any trace of impurity and crystallized in orthorhombic symmetry with a space group of Pbnm. Compared with the LCMO-PAS ceramic, the unit cell volume and Mn–O bond length of LCMO-HP ceramics are bigger, while the Mn–O–Mn bond angle is smaller. From the SEM images of fracture surface (insets of Fig. 1), the two samples are nearly pore-free, and their

Table 1

The refined structural parameters of LCMO-PAS and LCMO-HP ceramics.

Parameters	LCMO-PAS	LCMO-HP
	Pbnm	
a (Å)	5.4755	5.5062
b (Å)	5.4701	5.4783
c (Å)	7.7388	7.74113
V (Å ³)	231.78	233.51
χ^2	0.3884	0.4437
Mn-O ₁ (Å)	1.961	1.976 (9)
Mn-O ₂ (Å)	1.936	1.958 (7)
Mn-O ₂ (Å)	1.979	2.008 (7)
< Mn-O ₁ -Mn > (°)	161.21	156.65
< Mn-O ₂ -Mn > (°)	162.55	156.58

relative density are 97.4% and 95.8% for LCMO-PAS and LCMO-HP, respectively.

Fig. 2 shows the SEM images of surface morphology (polished and thermally etched) and corresponding energy dispersive spectrometer (EDS) analyses for LCMO-PAS and LCMO-HP ceramics. Both samples show well-shaped grains with clear grain boundaries without visible pores. The grain size, measured by Nano Measurer 1.2 software, of LCMO-PAS and LCMO-HP ceramics are estimated to be 1.27 μm and 2.48 μm, respectively. The larger grain size of LCMO-HP ceramics can be attributed to the much longer holding time (2 h) compared to that of rapid PAS process (10 min). The corresponding surface EDS analyses (Fig. 2) indicate little difference in oxygen content observed in the two samples.

The LCMO ceramics prepared by PAS and HP techniques are denser than most of those obtained by a traditional sintering method, and the sintering temperature or holding time can be greatly reduced. This should be attributed to the specific characteristics of PAS and HP and the coupling of temperature and stress during the sintering process.

3.2. Magnetic properties

Fig. 3(a) shows the temperature-dependent magnetizations under a magnetic field of 0.1 T for LCMO-PAS and LCMO-HP ceramics that were measured from 5 to 350 K. The M-T curves indicate that both samples undergo a paramagnetic (PM) to ferromagnetic (FM) transition at the Curie temperature (T_C), which is defined as the temperature corresponding to the peak of dM/dT . As listed in Table 2, the T_C of LCMO-PAS and LCMO-HP ceramics are 183 K and 177 K, respectively. Both samples were annealed in air at 900 °C for 10 h. As confirmed by the EDS in Fig. 2, little difference in oxygen content was observed in those samples, so the larger T_C values of LCMO-PAS ceramic may be ascribed to the smaller grain size as compared to that of LCMO-HP ceramic. A similar phenomenon has also been reported in previous studies [15,16]. According to the DE theory [15], T_C is closely related to the magnitude of the oxygen 2p-like bandwidth which strongly depends on the Mn–O–Mn bond angle and Mn–O bond length. As proved by XRD structural refinement analysis, the LCMO-PAS ceramic with smaller grain size shows larger Mn–O–Mn bond angle and smaller Mn–O bond length, which results in an enhanced T_C due to the weaker exchange interaction between the Mn ions.

Fig. 3(b) shows the magnetic hysteresis (M-H) loops of LCMO-PAS and LCMO-HP ceramics measured at 10 K; the inset shows the partially enlarged loops. The magnetization of those two samples increases sharply at low fields and gradually tends to be saturated above 0.5 T. Compared with LCMO-PAS ceramic, the LCMO-HP ceramic shows larger saturation magnetization (M_S) and smaller coercive field (H_C). The larger M_S may be a result of the random canting of the grain surface spins due to the competition between ferromagnetic and anti-ferromagnetic exchange interactions near the surface [17], while the smaller H_C could be attributed to the change from single domain to

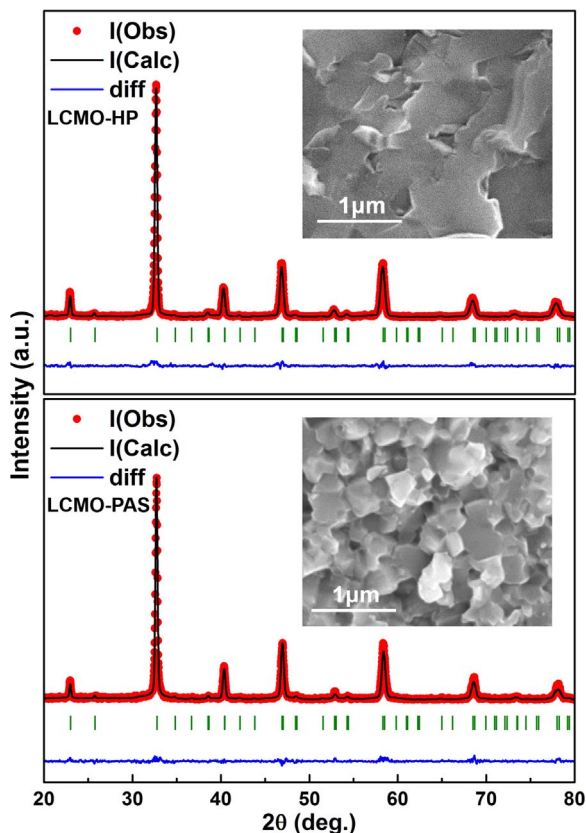


Fig. 1. Rietveld fitted X-ray diffraction patterns and fracture surfaces of LCMO-PAS and LCMO-HP ceramics.

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