Available online at www.sciencedirect.com

ScienceDirect

Trans. Nonferrous Met. Soc. China 24(2014) s141−s145

Transactions of Nonferrous Metals Society of China

www.tnmsc.cn

Effect of sintering temperature on structure, magnetic and magnetocaloric properties of $La_{0.6}Ca_{0.4}MnO_3$ manganite

Seung Rok LEE, M. S. ANWAR, Faheem AHMED, Bon Heun KOO

School of Materials Science and Engineering, Changwon National University,
Changwon, Gyeongnam, 641-773, Korea

Received 18 June 2013; accepted 20 March 2014

Abstract: The effect of sintering temperature on the structure, magnetic transition and magnetic entropy of $La_{0.6}Ca_{0.4}MnO_3$ manganite was studied. It was observed that this compound belongs to the orthorhombic structure with the *Pnma* space group without any impurity phase. The effect of sintering temperature on the Curie temperature (T_C) was studied. The small increment in T_C is found with increasing the sintering temperature. The magnetocaloric study exposes a quite large change of the magnetic entropy, which varies with sintering temperature. For an applied magnetic field of 3 T and sintering temperature of 1300 °C, the relative cooling power (RCP) is 89 J/kg. As a result, the studied compound can be considered as potential material for magnetic refrigeration near and below room temperature.

Key words: manganite; magnetocaloric effect; sintering temperature; colossal magnetoresistance

1 Introduction

Magnetic refrigeration has been paid much attention in recent years due to its high energy efficiency and being environment friendly, in contrast to the traditional gas-compression refrigeration technology [1,2]. More recently, an interesting property has been found in the manganites near the Curie temperature, the magnetocaloric effect (MCE) for refrigeration [3]. The phenomenon was firstly observed by WARBURG [4] in 1881. In ferromagnetic manganites, the magnetic spins align with an applied magnetic field, reducing the magnetic entropy of that spin system. If this process is performed adiabatically, this reduction in the spin entropy is accompanied by an increase in the lattice entropy. And then the temperature of the material rises. In contrast, when the field is removed, the spins tend to randomize, increasing the magnetic entropy and lowering the lattice entropy and the temperature. The possible use of the MCE at near room temperature requires the exploration of new kind of magnetic materials [5]. Most important requirements for magnetic refrigeration are large magnetic entropy change, magnetic phase transition, and Curie temperature near room temperature. The giant MCE in the pseudo-binary alloy $Gd_5(Si-Ge)_4$ in the range of 50 to 280 K [6,7] and at about 300 K has been measured in $MnFeP(O_{0.45}As_{0.55})$ [8]. Gd based materials are considered for a large magnetocaloric effect near its Curie temperature (293 K) [9,10]. Although they are good candidates for magnetic refrigeration, they are limited either by the dangerous pnictides used in their fabrication or by expensiveness. In recent years, various types of ferromagnetic manganese oxides have attracted attention as alternative candidates to replace Gd for this purpose [11,12].

In this work, the experiment was carried out on the bulk polycrystalline samples of $La_{0.6}Ca_{0.4}MnO_3$ manganite. the effects of sintering temperature on structure, magnetic and magnetocaloric properties of $La_{0.6}Ca_{0.4}MnO_3$ manganite were investigated. The MCE properties of the samples were analyzed by computing the magnetic entropy change using magnetization data.

2 Experimental

Polycrystalline sample of nominal composition $La_{0.6}Ca_{0.4}MnO_3$ was fabricated by using standard

Foundation item: Project (2012-RIAIB300784) supported by Basic Science Research Program through the NRF of Korea funded by the MEST; Project (2012HIB8A2026212) supported by the MEST and NRF of Korea the Human Training Project for Regional Innovation
Corresponding author: Bon Heun KOO; Tel: +82-55-264-5431; Fax: +82-55-262-6486237; E-mail: bhkoo@changwon.ac.kr
DOI: 10.1016/S1003-6326(14)63301-X

solid-state reaction procedure under ambient condition. Stoichiometric amounts of high-purity analytical grade (99.99%) La_2O_3, CaO and Mn_2O_3 powders were mixed by ball-mill process for 24 h in ethanol medium. The mixed powder was first calcined at 950 °C in air for 10 h and then heated up to 1050 °C for 10 h. After grinding, mixed powder was pressed into pellets and sintered at 1000 °C for 20 h and cooled down to room temperature. This sintering process was repeated at 1100, 1200, 1300 °C for 20 h. The structure and phase purity of the sample were checked at room temperature by means of X-ray diffraction (XRD) using Phillips X'pert (MPD 3040) X-ray diffractometer with Cu K_α radiations (λ=0.15406 nm) operated at voltage of 40 kV and current of 30 mA. The morphologies of grain boundaries and surfaces were investigated by scanning electron microscope (SEM-JSM5610). The magnetic measurements in the temperature range of 100−350 K with a frequency of 40 Hz were performed on a quantum design vibrating sample magnetometer PPMS-6000 VSM.

3 Results and discussion

The results of the X-ray diffraction (Fig. 1) of $La_{0.6}Ca_{0.4}MnO_3$ sample sintered at various temperatures indicate that all the samples have single phase without a detectable secondary phase. The absence of any kind of impurity phase suggests the complete reaction among the reactants during the sintering process. As the sintering temperature increases, the increase in the crystallinity is

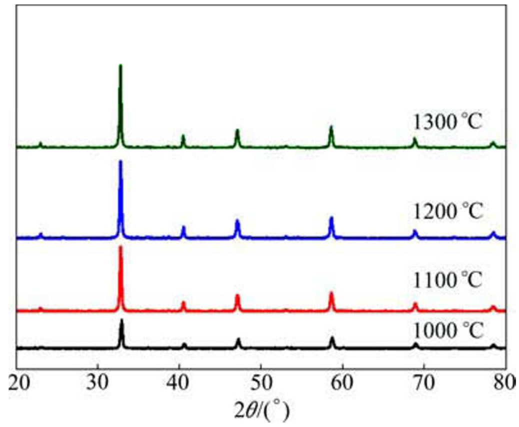

Fig. 1 XRD patterns of $La_{0.6}Ca_{0.4}MnO_3$ samples sintered at various temperatures

found, as shown in the XRD patterns.

All the observed XRD peaks were indexed to the orthorhombic structure with *Pnma* space group using powder-X software, which matches very well with the PDF card No. 89-8080. The SEM image (Fig. 2) reflects a smooth polycrystalline structure with inhomogeneous grain size distribution. By increasing the sintering temperature, the average grain size increases.

The temperature dependence of magnetization for the samples was measured at the constant field of 0.5 T, as shown in Fig. 3. The Curie temperature (T_C), defined by the maximum in the "absolute value" of dM/dT, has been determined from the magnetization versus

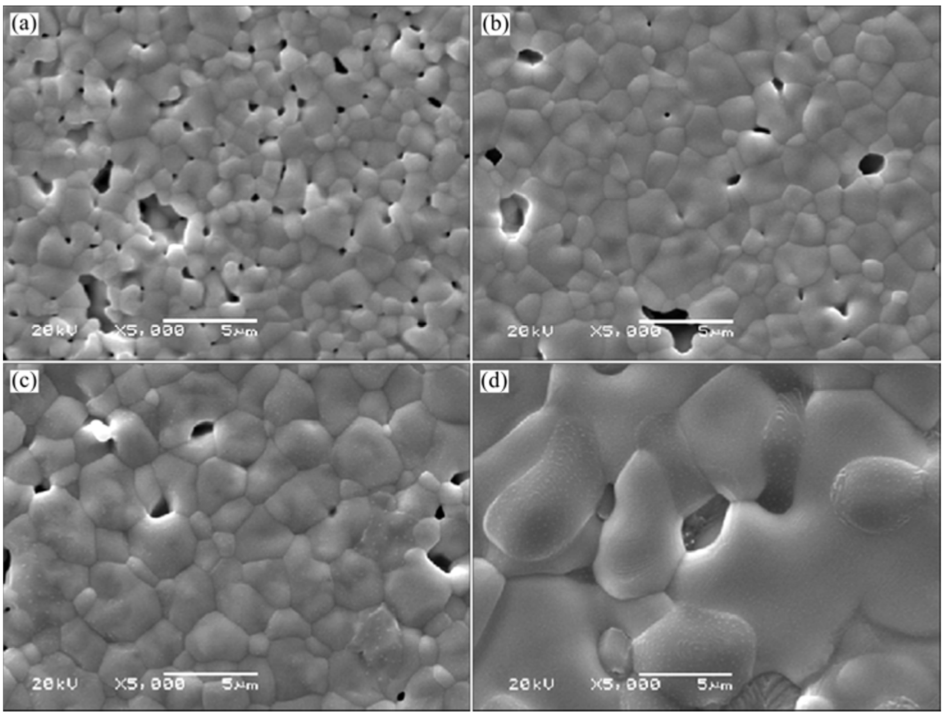

Fig. 2 SEM images of $La_{0.6}Ca_{0.4}MnO_3$ samples sintered at various temperatures: (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, and (d) 1300 °C