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Influence of synthesis conditions on magneto caloric effect in lanthanum manganites.

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Introduction

The manganites are ceramic compounds with great interest due to the colossal magnetoresistance effect and also they present a rich set of physical phenomena, such as spin, charge, and orbital orderings, which impart them interest for applications as well as theoretical studies. In recent years, the research on the magnetocaloric properties of lanthanum manganites have attracted considerable attention due to the considerable advantages in magnetic refrigeration system, such as high efficiency, good chemical stability, tunable ordering temperature, and low working magnetic field [1-4]. According to the Negaev prediction, metamagnetism is also possible in magnetic systems, which include perovskite manganites, as a result of both spin-phonon interaction and the influence on spin exchange due to Jahn-Teller ordering of the electron orbits [5]. In the lanthanum manganites, the magnetic properties are very sensitive to the synthesis conditions [6]. In this study, we present the magneto caloric effect tuned by sintering conditions of La$_{0.7}$Ca$_{0.3}$Mn$_{0.995}$Fe$_{0.01}$O$_3$, prepared by sol-gel method.

Experiments

La$_{0.7}$Ca$_{0.3}$Mn$_{0.995}$Fe$_{0.01}$O$_3$ compounds were prepared by a sol-gel method. Stoichiometric amounts of high purity La(NO$_3$)$_3$.6H$_2$O, Ca(NO$_3$)$_2$.4H$_2$O, (C$_2$H$_3$CO$_2$)$_2$Mn.4H$_2$O, and Fe isotope were dissolved in ethanol and distilled water. For the Mössbauer measurement, we have doped $^{57}$Fe by dissolving iron isotope in a diluted HNO$_3$ and adding the proper amount of $^{57}$Fe into the solution. The solution was refluxed at 80 °C for 24 h and dried at 120 °C for 48 h in oven. The obtained powder was calcined at 400 °C and sintered at 1000 °C for 4 h. To investigate the effect of sintering conditions on LCMO, the samples were sintered in air and evacuated sealed quartz tube. These were designated as SA and ST, respectively. The crystal structure of the samples was examined using a x-ray diffractometer with Cu-$K\alpha$ radiation and analyzed by Rietveld refinement. Magnetic properties were measured by vibrating samples magnetometer (VSM) in the temperature range of 50-300 K with magnetic field up to 1.5 T. Mössbauer spectra were recorded using a constant acceleration Mössbauer spectrometer with a $^{57}$Co source in Rh matrix.

Results and discussion

X-ray diffraction pattern for La$_{0.7}$Ca$_{0.3}$Mn$_{0.995}$Fe$_{0.01}$O$_3$ which sintered different atmosphere show single phase. The crystal structure of the samples at room temperature are determined to be an orthorhombic $Pnma$ structure. The x-ray diffraction pattern of the samples was refined by Rietveld profile analysis using the FULLPROF program, with the peak shapes approximated by a Pseudo-Voigt function. Considering the analyzed results of both samples, there are significant changes in oxygen contents, Mn-O-Mn bond angles, and O-Mn bond distance. The Mn-O-Mn bond angles of SA and ST are calculated to be 156° and 169°, respectively, and O-Mn bond distance of SA and ST are calculated to be 1.97 Å and 1.94 Å, respectively. These changes in bond angles and distance are affected to the lattice constant $c_0$.

Temperature dependence of magnetization show different shape which affected by sintering conditions is shown in Fig. 1. Temperature dependence of magnetization of ST shows a sharp drop at Curie temperature which was higher than that of SA. The evaluated magnetic entropy changes are presented in Fig. 2. The magneto caloric effect (-$\Delta S_m$) of SA and ST are observed 1.6 and 3.2 J/kg K in the temperature of 242 K and 262 K, respectively. We suggest that the control of magneto caloric effect on LCMO was accomplished by evacuated sealed annealing process.

Fig. 1. Temperature dependence of magnetization for La$_{0.7}$Ca$_{0.3}$Mn$_{0.995}$Fe$_{0.01}$O$_3$ with 100 Oe external fields.

Fig. 2. Magnetic entropy change of La$_{0.7}$Ca$_{0.3}$Mn$_{0.995}$Fe$_{0.01}$O$_3$.