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Determination of Magnetocaloric Effect in $La_{0.67}Ba_{0.33}MnO_3$ from Direct and Indirect Measurements

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Abstract

In this study, we investigated magnetocaloric properties of the perovskite compound $La_{0.67}Ba_{0.33}MnO_3$ synthesized by sol-gel technique. The temperature dependent magnetization measurements at 50Oe applied magnetic field showed that the sample displays a ferromagnetic-paramagnetic transition with increasing temperature. ΔT_{ad} of the sample was measured both on increasing and decreasing fields directly. The results indicate that the magnetocaloric effect is largely reversible due to showing the same ΔT_{ad} for both cases.

Keywords: Magnetic refrigeration, Magnetocaloric effect, Adiabatic temperature change, Manganite

$La_{0.67}Ba_{0.33}MnO_3$' deki Manyetokalorik Etkinin Doğrudan ve Dolaylı Ölçümlerden Belirlenmesi

Öz

Bu çalışmada, sol-jel yöntemi ile üretilen $La_{0.67}Ba_{0.33}MnO_3$ perovskit bileşiğindeki manyetokalorik etki özelliği incelenmiştir. 50 Oe uygulanan manyetik alan altında sıcaklığa bağlı manyetizasyon ölçümlerinden örneğin sıcaklığın artışıyla birlikte ferromanyetik-paramanyetik faz geçişi gösterdiği gözlenmiştir. Örneğin ΔT_{ad} değeri alan artarken ve azalırken doğrudan ölçülmüştür. Sonuçlar ΔT_{ad}'nin her iki durumda da aynı değeri göstermesinden manyetokalorik etkinin tersinir olduğunu göstermektedir.

Anahtar Kelimeler: Manyetik soğutma, Manyetokalorik etki, Adiyabatik sıcaklık değişimi, Manganit

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1. INTRODUCTION

Magnetic refrigeration (MR) based on the magnetocaloric effect (MCE) has potential as a promising alternative to conventional gas compression refrigeration due to its unique advantages such as high energy efficiency, environmentally friendly, low noise, soft vibration and longer usage time [1-3]. Therefore, there is an increasing attention to find materials that show large values of magnetocaloric effect near room temperature. MCE is a magnetothermodynamic phenomenon and induced via coupling of a magnetic sublattice with the magnetic field which alters the magnetic part of the total entropy due to a corresponding change of the magnetic field [4].

The MCE is defined as an isothermal magnetic entropy change (ΔS_M) or an adiabatic temperature change (ΔT_{ad}) when the magnetic material is subjected to a changing magnetic field. The MR technology needs the materials that show large ΔS_M, ΔT_{ad} and refrigerant capacity near room temperature by the application of external magnetic field [5].

The MCE has been studied in a large variety of magnetic materials [6]. The rare-earth perovskite manganites of the general formula $R_{1-x}A_xMnO_3$ (R: rare-earth cation, A: alkali-metal or alkaline-earth cation), due to their adjustable Curie temperature and saturation magnetization by varying the composition, low-cost synthesis, high resistivity and low eddy-current-loss compared to metallic alloys, and large magnetic entropy change are also expected to be promising candidates in magnetic refrigeration technology [4,7-9].

In this work, we have performed a study on magnetic and magnetocaloric properties of $La_{0.67}Ba_{0.33}MnO_3$ manganite. We have investigated the magnetocaloric properties of sample by direct and indirect measurement techniques. We have measured the adiabatic temperature change value of the sample by using an adiabatic magneto-calorimeter system directly.

2. MATERIAL AND METHOD

The $La_{0.67}Ba_{0.33}MnO_3$ sample was synthesized by using the sol-gel technique with high purity powders of La_2O_3, $Ba(NO_3)_2$, $Mn(NO_3)_2.4H_2O$. Monoethylene glycol with 99.9% purity, citric acid monohydrate with 99.9% purity, and nitric acid with 70% purity were used as a chelating substance. Obtained material was mixed and heated by a magnetic stirrer at 300ºC until obtaining gel-like precipitation. This precursor was heated at 500ºC for 1 h to burn. The final material was ground by using an agate mortar to obtain fine powders. Then the material was pressed into pellet form and sintered 1150ºC for 24 h in air.

The crystal structure of the sample was determined by X-ray diffraction (XRD) using Cu Kα radiation. The XRD pattern showed the reflections typical of the perovskite structure with orthorombic symmetry. Magnetization measurements were carried out using a superconducting quantum interface device (SQUID) magnetometer (Quantum Design MPMS XL). The magnetic entropy change values were obtained from isothermal magnetization measurements near the phase transition region and the adiabatic temperature change was measured directly in an adiabatic magneto-calorimeter system.

3. RESULTS AND DISCUSSIONS

Figure 1 shows the temperature dependence of low field magnetization for the sample that was measured in a wide range of temperature in 50 Oe applied magnetic field at zero-field cooled (ZFC) and field-cooled (FC) process in order to determine the transition temperature of the material. The paramagnetic to ferromagnetic phase transition temperature which is known as Curie temperature (T_C) is determined as T_C ~245 K from the temperature at which the dM/dT-T curve reaches a minimum.

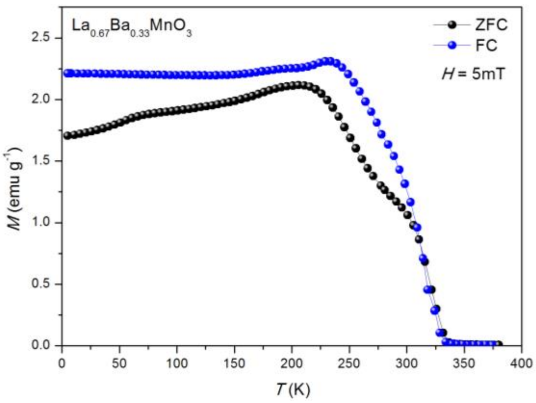

Figure 1. Thermomagnetic curves of the sample in a magnetic field of 5mT at zero-field cooled (ZFC) and field-cooled (FC) process

We have measured *M(H)* isotherms to evaluate the magnetic entropy change around transition region as a function of temperature. Figure 2 shows the *M(H)* curves of the sample which were taken up to 5T at various temperatures near T_C in 4K intervals from 180 K to 304K. While *M(H)* curves at temperatures above T_C show a linear behaviour, as expected in the paramagnetic state, below T_C, they show ferromagnetic behaviour followed by a slow approach to saturation at higher fields. The isothermal magnetic entropy change, induced by the magnetic field change can be calculated using the following relation (Equation 1) [10]:

$$|\Delta S_M| = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H, \qquad (1)$$

where M_i and M_{i+1} are magnetization values measured at temperatures T_i and T_{i+1}, respectively.

We have calculated the ΔS_M *(T)* using the Eq.(1) and showed in Figure 3 at different applied magnetic field. As expected, the sample exhibits a maximum in magnetic entropy change in the vicinity of T_C, where the variation of magnetization with temperature is the fastest and ΔS_M *(T)* increases with the increasing of applied magnetic field. The maximum magnetic-entropy change reaches 0.59, 1.09, 1.51, 1.90 and 2.20 $Jkg^{-1}K^{-1}$ for a field change of 1.0, 2.0, 3.0, 4.0 and 4.8 T, respectively.

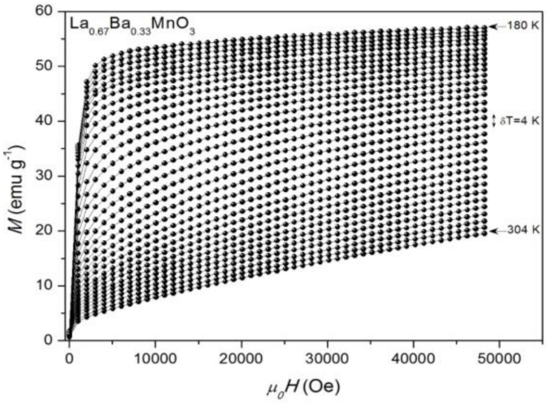

Figure 2. Isothermal magnetization curves around T_C up to 5T

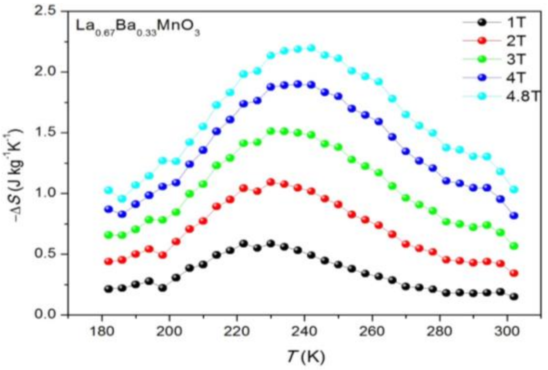

Figure 3. The temperature dependence of ΔS_M at different magnetic fields

Figure 4 shows the Arrott plots which were extracted from the isothermal *M(H)* curves. According to criterion proposed by Banerjee [11], Arrott plots give a positive slope which confirms that the second order ferromagnetic-paramagnetic phase transition occurs.

In addition to the indirect measurement of the magnetic entropy change, the adiabatic temperature change, ΔT_{ad}, of the sample was estimated directly using an adiabatic magneto-calorimeter system. In the direct measurement, the initial temperarature of sample, $T_i(H_i)$ and the final one $T_f(H_f)$ at the end of the applying of magnetic field were measured. And the ΔT_{ad} at T_i has been determined from (Equation 2) [12],

$$\Delta T_{ad} = T_f(H_f) - T_i(H_i). \qquad (2)$$

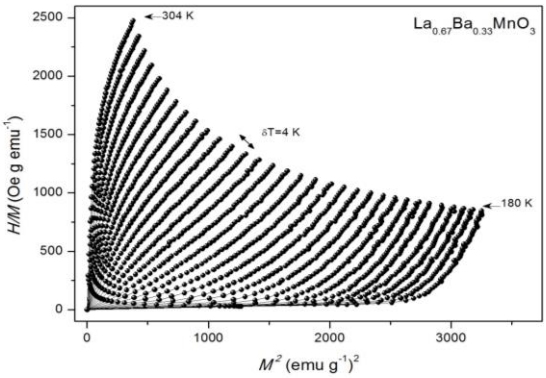

Figure 4. Arrott plots, H/M vs. M^2 around phase transition region at different temperatures

We have placed a chromel-constantan thermocouple into the sample to detect the temperature as the same like in our previous work [5-14]. Figure 5 shows the directly measured ΔT_{ad} obtained both on increasing and decreasing fields near the magnetic phase transition region at 5K intervals. It is clear from the Figure 5 that the ΔT_{ad} is nearly the same for both cases indicating that the MCE is largely reversible. The maximum adiabatic temperature change is measured about 0.78 K around 240 K. We have also measured the cyclic adiabatic temperature-change of the sample at 234K.

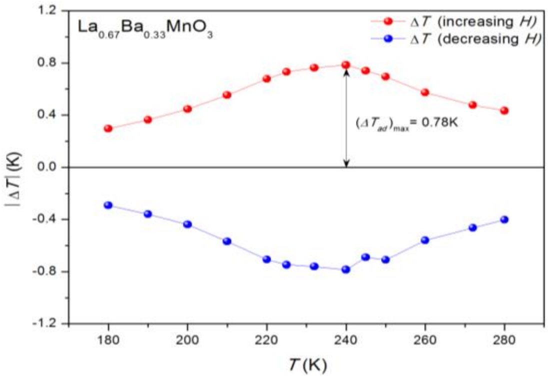

Figure 5. Directly measured adiabatic temperature-change of the sample induced by a magnetic field change of 3T. Red and blue curves represent ΔT measured in increasing and decreasing fields, respectively

Figure 6 shows the cyclic adiabatic temperature change that the magnetic field is applied and removed five times up to 3T. Each step on the time-dependent temperature curve is associated with a magnetizing and a subsequent demagnetizing sequence.

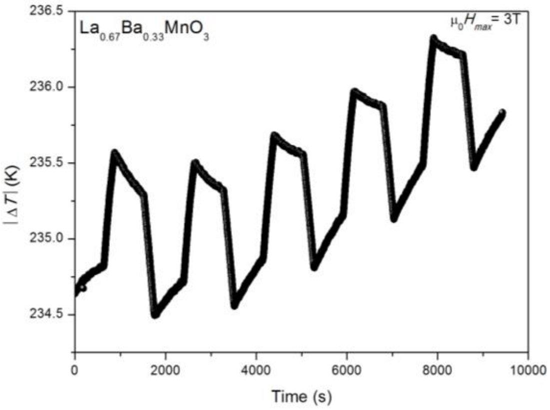

Figure 6. Direct measurement of cyclic adiabatic temperature change of the sample at 235K

From Figure 6, we conclude that the sample shows reversible magnetocaloric effect and no hysteresis loss because each step gives nearly the same value of adiabatic temperature change.

3. CONCLUSION

In summary, we have investigated the magnetic and magnetocaloric properties of $La_{0.67}Ba_{0.33}MnO_3$ perovskite manganite synthesized by sol-gel technique. The thermomagnetic measurements showed that the sample shows ferromagnetic to paramagnetic phase transition with increasing temperature. The Curie temperature of the sample was determined as T_C ~245 K. We have performed the isothermal magnetization measurements near the phase transition region to determine the magnetic entropy change. The maximum magnetic entropy change was determined as 0.59, 1.09, 1.51, 1.90 and 2.20 $Jkg^{-1}K^{-1}$ for a field change of 1.0, 2.0, 3.0, 4.0 and 4.8 T, respectively. We have also measured the adiabatic temperature change using an adiabatic magneto-calorimeter system directly under a magnetic field change of 3T. The maximum adiabatic temperature change is determined as 0.78 K at 240 K. The cyclic adiabatic temperature change measurements indicated that the sample shows a reversible magnetocaloric effect due to showing the same ΔT_{ad} for each step. And this means that the sample shows no magnetic hysteresis loss which is essential for the magnetic refrigeration systems.

4. ACKNOWLEDGEMENTS

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