



STRUCTURAL, MAGNETIC AND MAGNETOCALORIC PROPERTIES OF $\text{La}_{0.7}\text{Sr}_{0.2}\text{Ba}_{0.1}\text{MnO}_3$ MANGANITE

Mehmet Selim ASLAN^{1,*} , Selda KILIÇ ÇETİN² , Ahmet EKİCİBİL³ 

^{1,2,3} Cukurova University, Faculty of Arts and Sciences, Physics Department, Adana, Türkiye

ABSTRACT

In this present work, the structural, magnetocaloric and magnetic properties of $\text{La}_{0.7}\text{Sr}_{0.2}\text{Ba}_{0.1}\text{MnO}_3$ (LSBM) manganite were investigated. The material was synthesized using the sol-gel method and X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) devices were used to analyze structural properties such as crystal structure and surface morphology. XRD measurement revealed that the crystal structure of LSBM manganite is hexagonal. Based on the magnetic measurements, the T_C value of $\text{La}_{0.7}\text{Sr}_{0.2}\text{Ba}_{0.1}\text{MnO}_3$ manganite compounds was calculated as 362 K. The ΔS_M value of sample is established as 2.79 Jkg⁻¹K⁻¹ in an applied magnetic field of 5T. Arrott curves revealed that the phase transition was second order.

Keywords: Magnetocaloric effect, Perovskite, Magnetic entropy change, Curie temperature.

1. INTRODUCTION

As a result of increasing expectations regarding climate change, population growth and living comfort, energy demands for cooling technologies are increasing worldwide. In addition to the increasing energy demand, it becomes necessary to develop new technologies that can replace the cooling systems that are widely used today. These systems in current use have low energy efficiency and are known for consuming significant amounts of energy. Moreover, the use of high vibration compressors in these systems causes noise pollution and more energy consumption. In addition, the refrigerants used in these systems cause environmental pollution [1, 2].

Magnetic cooling (MC) is an alternative cooling technology that can operate without gas-based coolers. Compared to gas compression systems, they have advantages such as not containing environmentally harmful cooling materials, being more efficient, compactness, and operating without noise and vibration [3, 4]. Although it has been heard by everyone for a long time, magnetic cooling technologies cannot yet be used as a potential cooling method in our daily life and industrial areas. The basis of MC systems is based on the MCE principle [5]. MCE is defined as the change in temperature of a magnetic material under an external magnetic field [6, 7]. MCE covers two fundamental processes: adiabatic temperature change (ΔT_{ad}) and magnetic entropy change (ΔS_M). The important requirement for MC technologies is that these two parameters have high values around room temperature. While various material families are being investigated for this purpose, manganites are promising due to their low costs, high resistivity, reduced eddy-current-loss compared to metallic alloys, simple production methods and second-order phase transition [8]. Additionally, the fact that magnetic phase transition temperatures can be adjusted through doping makes these materials stand out [8, 9]. This work presents the structural, magnetocaloric and magnetic properties of LSBM sample and provides detailed analysis and measurements to reveal the properties of this material.

2. MATERIAL AND METHOD

In the production of magnetic materials with high magnetocaloric effect, doping elements and amounts are also of great importance, as well as the material production method [10, 11]. Among various methods, the sol-gel method was preferred due to its advantages such as obtaining finer and homogeneously dispersed particle sizes.

Firstly, the stoichiometric amounts of the starting compounds were calculated. Then, aqueous solutions of each compound were prepared and mixed with a magnetic stirrer. Ethylene glycol and citric acid are added to the solution in appropriate proportions to obtain the gel structure. The material obtained in gel form was subjected to heat treatment in the oven at 450°C for 1 hour in order to be removed from the beaker properly. The obtained powder sample was calcined at 600°C for 6 hours to remove organic compound residues. Then, the samples were ground in an agate mortar for a total of 60 minutes with 6 grinding sessions of 10 minutes each. The powdered samples were turned into tablets using a hydraulic press. As a final process, the materials were sintered in a cylindrical oven at 1200 °C for 24 hours to crystallize.

* Corresponding author, e-mail: mehmetselimaslan34@gmail.com (M. S. Aslan)

Received: 24.04.2024 Accepted: 30.05.2024

doi: 10.55696/ejset.1417171

STRUCTURAL, MAGNETIC AND MAGNETOCALORIC PROPERTIES OF La_{0.7}Sr_{0.2}Ba_{0.1}MnO₃ MANGANITE

The structural analysis of the produced manganite compound was carried out by XRD and SEM measurements. Diffraction patterns of the manganite compound were analyzed in HighScore Plus programs. Additionally, magnetic properties are evaluated using the PPMS Dynacool 9T instrument to determine key parameters such as Curie temperature, type of magnetic phase transition and ΔS_M values.

3. RESULTS AND DISCUSSION

XRD method was used to understand the structural properties of the synthesized samples. According to the XRD curve given in Figure 1, the presence of sharp and narrow-based peaks indicates that crystallization has occurred well. The fact that the FWHM value for the $2\theta = 32.576$ peak is 0.25279 supports this. Based on the XRD results, our manganite compound is classified under R-3c space group and exhibits a hexagonal structure. The lattice parameters were obtained using the HighScore Plus program, where $a = 5.5100$, $b = 5.5100$ and $c = 13.3880$ Å, respectively. It was determined that the observed peaks were compatible with the reference code (98-018-7646)[12]. Additionally, the XRD pattern of the compound did not exhibit any peaks associated with undesirable phases. This absence indicates that the synthesis process was successful in obtaining the desired material without significant impurities.

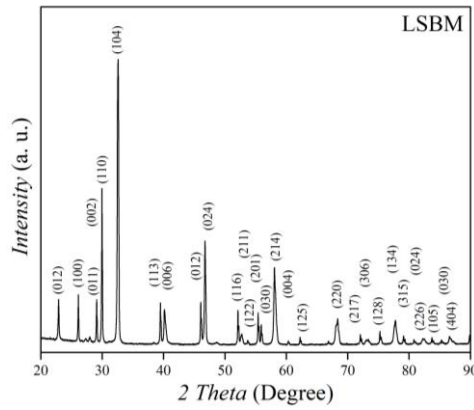


Figure 1. XRD pattern of LSBM manganite.

Scanning Electron Microscope (SEM) technique has been selected to obtain a grain structure image to analyze morphological features of the the sample. SEM images taken at 5, 10, 20 and 40 kX magnifications are given in Figure 2. When the SEM images of the compound are examined, many volumetric particle structures are revealed. These structures exhibit a wide range of different sizes and polygonal shapes, each distinctly separated from each other.

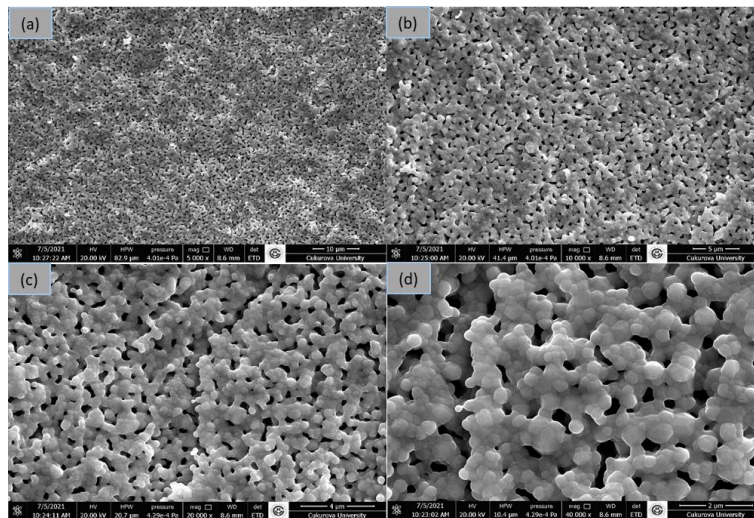


Figure 2. SEM images of LSBM manganite taken at different magnifications; (a) 5 kX, (b) 10 kX, (c) 20 kX and (d) 40 kX

The transition temperature value of the material has been identified using the $M(T)$ curves, and the magnetocaloric features have been examined based on the isothermal magnetization curves obtained in the vicinity of this determined temperature. $M(T)$ measurements have been performed under Field Cooling (FC) and Zero Field Cooling (ZFC) mode. In Figure 3, we observe the temperature-induced magnetization changes in a low magnetic field value of 10mT for both the ZFC and FC processes. While the $M(T)$ curves obtained in the ZFC and FC steps behave similarly at temperatures above T_C , they diverge in the low-temperature range. This distinction between ZFC and FC steps is related to concepts such as spin glass like behavior, long-range or short range magnetic interaction in the material and the magnitude of its magnetic anisotropy [13, 14]. By examining the dM/dT curve, the temperature at which it reaches its minimum point signifies the T_C for this sample. The sample did a transition from ferromagnetic to paramagnetic at $T_C=360$ K.

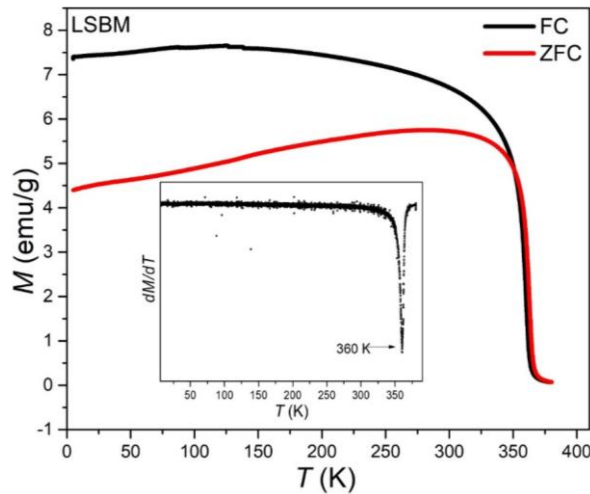


Figure 3. The $M(T)$ curves of the LSBM manganite subjected to a 10 mT magnetic field in both ZFC and FC modes. Inset figures display (dM/dT) - T curves of the sample.

After determining the magnetic phase transition temperature, isothermal magnetization measurements, $M(H)$, were conducted in the vicinity of that temperature region. Measurements were taken from 254 K to 378 K, with a 4 K increment, as illustrated in Figure 4. $M(H)$ curves exhibit transitions from saturated curves in the ferromagnetic region to linear curves in the paramagnetic region as the temperature increases. This observation suggests a shift in magnetic behavior from one dominated by ferromagnetic alignment, where the magnetic moments of atoms align parallel to each other resulting in saturation of magnetization, to one characterized by paramagnetic behavior, where the alignment becomes disordered with increasing temperature, leading to a linear relationship between magnetization and magnetic field.

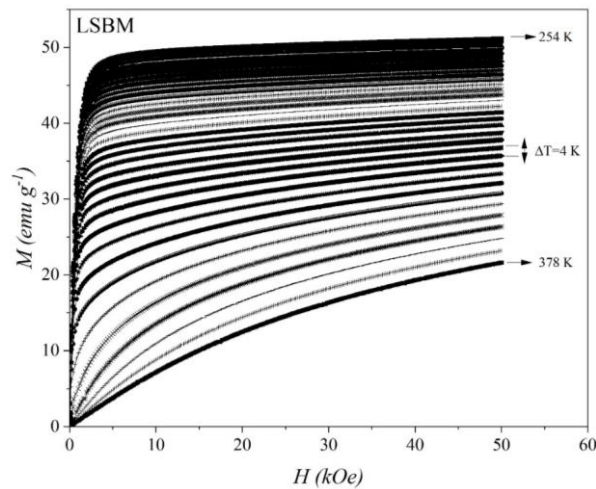


Figure 4. $M(H)$ curves of LSBM at 4K temperature steps around T_C temperature.

STRUCTURAL, MAGNETIC AND MAGNETOCALORIC PROPERTIES OF $La_{0.7}Sr_{0.2}Ba_{0.1}MnO_3$ MANGANITE

Isothermal magnetic entropy change, ΔS_M , serves a crucial parameter for characterizing the magnetocaloric properties of a magnetic material. The values of ΔS_M were determined by performing a series of calculations on the isothermal $M(H)$ curves, which are given in Figure 5. The ΔS_M as a function of temperature curves showed a peak around the Curie temperature region, as expected. Moreover, the ΔS_M values increased with increasing applied field strengths. This observation is consistent with the behavior typically exhibited by magnetic materials undergoing phase transitions, where the ΔS_M tends to peak around the critical temperature and shows dependence on the applied magnetic field strength. The ΔS_M values corresponding to various applied magnetic fields are listed in Table 1.

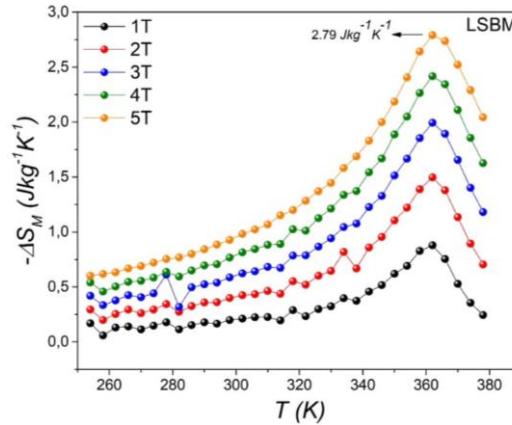


Figure 5. The magnetic entropy change curves of LSBM compound at different field values.

Table 1. ΔS_M values obtained under different applied magnetic fields.

Sample	ΔS_M (Jkg ⁻¹ K ⁻¹)					T_C (K)
	1 T	2 T	3 T	4 T	5 T	
LSBM	0.89	1.52	2.01	2.24	2.79	360

Figure 6 displays Arrott measurements conducted to determine the type of magnetic phase transition of our manganite compound. Curves can exhibit positive or negative slope. In the case where the Arrott curve exhibits a positive slope, as observed in our material, it indicates a second-order magnetic phase transition [15]. The positive slope of the Arrott curve suggests that the material undergoes a gradual transition from one magnetic phase to another, without the formation of domain walls or the release of latent heat, which are characteristic of first-order phase transitions [16].

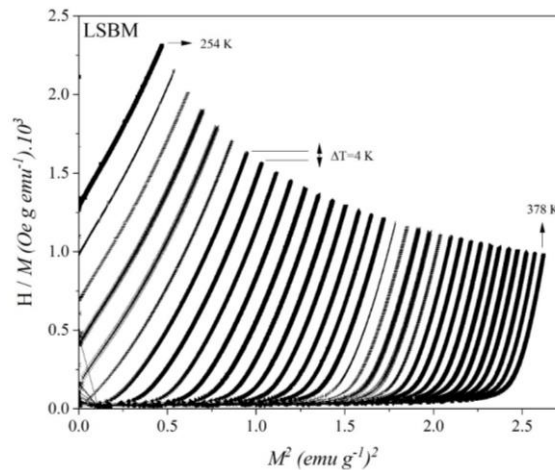


Figure 6. Arrott curves of LSBM manganite.

4. CONCLUSION

In the present study, $\text{La}_{0.7}\text{Sr}_{0.2}\text{Ba}_{0.1}\text{MnO}_3$ manganite was synthesized using the Sol-Gel method. The structural, magnetocaloric and magnetic properties of the synthesized this compound were examined in detail. XRD analysis revealed that the compound crystallized in the R-3c space group, exhibiting a hexagonal structure. SEM images taken at magnifications of 5, 10, 20 and 40 kX revealed volumetric particle structures of various sizes and polygonal shapes. Measurements of magnetization as a function of temperature indicated that as the temperature decreased, the sample transitioned from a ferromagnetic state to a paramagnetic state. To determine ΔS_M values, isothermal magnetization measurements were made around the transition temperature of the sample, where the magnetization change is maximum. As a result of magnetic studies, it was determined that the T_c temperature of our manganite was 360 K and the ΔS_M value under a 5T changing magnetic field was $2.79 \text{ Jkg}^{-1}\text{K}^{-1}$. Furthermore, it is understood from the Arrott curves that the sample has a second-order magnetic phase transition.

SIMILARITY RATE: 16%

AUTHOR CONTRIBUTION

Mehmet Selim ASLAN: Conceptualization, methodology, data curation, writing, editing etc.
Selda KILIÇ ÇETİN: Conceptualization, methodology, data curation, writing, editing etc.
Ahmet EKİCİBİL: Characterization, editing.

CONFLICT of INTEREST

The authors declared that they have no known conflict of interest.

ACKNOWLEDGEMENT

We are grateful that present study is supported by the Çukurova University Scientific Research Projects under grant agreement no: FDK-2021-13983.

REFERENCES

- [1] M. Mazaheri, M. Akhavan, "Electrical behavior of nano-polycrystalline $(\text{La}_{1-y}\text{Ky})_{0.7}\text{Ba}_{0.3}\text{MnO}_3$ manganites", *Journal of Magnetism and Magnetic Materials*, 322 (2010) 3255-3261.
- [2] X. Zhao, X. Zheng, X. Luo, F. Gao, H. Zeng, G. Yu, S.U. Rehman, C. Chen, S. Ma, W. Ren, Z. Zhong, "Large magnetocaloric effect and magnetoresistance in ErNi single crystal", *Journal of Materials Science & Technology*, 86 (2021) 56-63.
- [3] A. Elghoul, A. Krichene, N. Chniba Boudjada, W. Boujelben, "Rare earth effect on structural, magnetic and magnetocaloric properties of $\text{La}_{0.75}\text{Ln}_{0.05}\text{Sr}_{0.2}\text{MnO}_3$ manganites", *Ceramics International*, 44 (2018) 12723-12730.
- [4] S.M. Gombi, D. Sahu, "A Review on Magneto-Caloric Materials for Room Temperature Refrigeration", *International Journal of Automotive and Mechanical Engineering*, 17 (2020) 7805-7815.
- [5] X. Tang, H. Sepehri-Amin, N. Terada, A. Martin-Cid, I. Kurniawan, S. Kobayashi, Y. Kotani, H. Takeya, J. Lai, Y. Matsushita, T. Ohkubo, Y. Miura, T. Nakamura, K. Hono, "Magnetic refrigeration material operating at a full temperature range required for hydrogen liquefaction", *Nat Commun*, 13 (2022) 1817.
- [6] A.M. Gomes, F. Garcia, A.P. Guimarães, M.S. Reis, V.S. Amaral, P.B. Tavares, "Magnetocaloric effect of the $(\text{Pr,Ca})\text{MnO}_3$ manganite at low temperatures", *Journal of Magnetism and Magnetic Materials*, 290-291 (2005) 694-696.
- [7] M. Quintero, J. Sacanell, L. Ghivelder, A.M. Gomes, A.G. Leyva, F. Parisi, "Magnetocaloric effect in manganites: Metamagnetic transitions for magnetic refrigeration", *Applied Physics Letters*, 97 (2010).
- [8] S.K. Çetin, "Reversible Magnetocaloric Effect of $(\text{La}_{0.8}\text{Pr}_{0.2})(\text{Ba}_{0.67})\text{Ba}_{0.33}\text{MnO}_3$ from Direct Measurements", *Journal Of Superconductivity And Novel Magnetism*, 33 (2020) 683-691.
- [9] M.-H. Phan, H.-X. Peng, S.-C. Yu, N. Duc Tho, N. Chau, "Large magnetic entropy change in Cu-doped manganites", *Journal of Magnetism and Magnetic Materials*, 285 (2005) 199-203.

STRUCTURAL, MAGNETIC AND MAGNETOCALORIC PROPERTIES OF $La_{0.7}Sr_{0.2}Ba_{0.1}MnO_3$ MANGANITE

- [10] F. Ayadi, F. Saadaoui, W. Cheikhrouhou-Koubaa, M. Koubaa, A. Cheikhrouhou, L. Sicard, S. Ammar, "Effect of monovalent doping on the physical properties of $La_{0.7}Sr_{0.3}MnO_3$ compound synthesized using sol-gel technique", *IOP Conference Series: Materials Science and Engineering*, 28 (2012).
- [11] S. Choura Maatar, R. M'nassri, W. Cheikhrouhou Koubaa, M. Koubaa, A. Cheikhrouhou, "Structural, magnetic and magnetocaloric properties of $La_{0.8}Ca_{0.2-x}Na_xMnO_3$ manganites ($0 \leq x \leq 0.2$)", *Journal of Solid State Chemistry*, 225 (2015) 83-88.
- [12] A.C.B. Cheikhrouhou, N.;Cheikhrouhou-Koubaa, W.;M'nassri, R., *Journal of Solid State Chemistry*, 119 (1995) 191-196.
- [13] B. Kumar, J.K. Tiwari, H.C. Chauhan, S. Ghosh, "Multiple magnetic phase transitions with different universality classes in bilayer $La_{1.4}Sr_{1.6}Mn_2O_7$ manganite", *Scientific Reports*, 11 (2021) 21184.
- [14] A. Coşkun, E. Taşarkuyu, A.E. Irmak, S. Aktürk, "High magnetic entropy change in $La_{0.70}Ca_{0.21}Ag_{0.09}MnO_3$ compound", *Journal of Alloys and Compounds*, 669 (2016) 217-223.
- [15] M. Balli, P. Fournier, S. Jandl, M.M. Gospodinov, "A study of the phase transition and magnetocaloric effect in multiferroic La_2MnNiO_6 single crystals", *Journal of Applied Physics*, 115 (2014).
- [16] J.Y. Law, V. Franco, L.M. Moreno-Ramírez, A. Conde, D.Y. Karpenkov, I. Radulov, K.P. Skokov, O. Gutfleisch, "A quantitative criterion for determining the order of magnetic phase transitions using the magnetocaloric effect", *Nat Commun*, 9 (2018) 2680.

