Effect of Low Doped Calcium on the Magnetic Properties of La$_{0.7}$Ba$_{0.297}$Ca$_{0.003}$MnO$_3$ for Magnetocaloric Application

B Kurniawan*, S Winarsih, and T Komala
Department of Physics, Faculty of Mathematics and Natural Sciences (FMIPA)
Universitas Indonesia, Depok 16424, Indonesia

E-mail: bkuru@fisika.ui.ac.id or bkuru07@gmail.com

Abstract. Effect of low doped calcium concentration to the magnetic properties of La$_{0.7}$Ba$_{0.3}$MnO$_3$ material has been reported in this paper. This compound was chosen because it has high potential to be applied in electronic devices. The most intensive research in the last decade is about magnetocaloric effect (MCE). Magnetic refrigeration will replace Freon R12 that is used in conventional refrigeration with magnetic material which has MCE properties. It is due to conventional refrigeration produce chlorofluorocarbons (CFC) and hydrochlorofluorocarbons (HCFCs) gases which causes ozone depletion. The magnetic measurement was performed by using Vibrating Sample Magnetometer in the range of temperature between 300-400 K under external magnetic field until 20 kOe. By using derivative of magnetization as a function of temperature of the material’s result, Curie temperature ($T_c$) of the material is 332.7 K. By using equation (5) for calculating magnetic field dependence of magnetization at various temperature result, magnetic entropy change value ($\Delta S_M$) of the material can be obtained. The $\Delta S_M$ of the material is -2.928 Jkg$^{-1}$K$^{-1}$. The material has highest magnetic entropy change value around its $T_c$. It is due to there is strong lattice spin coupling around its $T_c$ and would be weak at below and above its $T_c$.

1. Introduction
Lanthanum manganites La$_{1-x}$A$_x$MnO$_3$ with A is divalent ions doped have been intensively explored in the last two decades. It is because they have multi physical properties such as magnetoresistance, magnetocaloric effect (MCE), and microwave absorbance so that these materials can be applied to various electronic devices [1–4]. One of those electronic devices is magnetic refrigeration which use MCE principal [5,6]. Increment of conventional refrigeration usage causes ozone depletion on our earth because this refrigeration produces chlorofluorocarbons (CFC) and hydrochlorofluorocarbons (HCFCs) gases [7]. Magnetic refrigeration is expected to decrease that effect. In magnetic refrigeration, magnetic material which has MCE properties will be used to replace Freon R12 that is used in conventional refrigeration [7]. MCE properties value and external magnetic field strength play an important role to the magnetic refrigeration system.

There are two conditions in MCE, adiabatic and isothermal. In adiabatic condition, when external magnetic field is applied to the system, its magnetic entropy will be reduced. In the same time, lattice entropy and electronic entropy of the system will be increased because of spin lattice connections and vibrations. It is happened to compensate the loss energy of the system. Thus, there is a decrement of system temperature which depends on the magnetic field strength [7]. The magnetic entropy will back to be normal by capturing energy from the lattice when external magnetic field is removed from system. The consequence system temperature returns to its initial temperature [7]. Meanwhile, in isothermal condition, the magnetic spins of the material tend to polarize in the same direction with an
external magnetic field. It is caused magnetic entropy of the system reduce so that the system temperature also decrease [7]. When external magnetic field is removed from the material, magnetic spin back to randomly oriented. Hence the system temperature will be increase [7].

Technically, isothermal condition is easier to measure MCE properties of the material than adiabatic condition [5,6]. The $\Delta S_M$ as a function of external magnetic field from 0 to $H_0$ is given by Eq. (1) and Eq. (2).

$$\Delta S_M(T, H_0) = S_M(T, H_0) - S_M(T, 0)$$  \hspace{1cm} (1)

$$\Delta S_M(T, H_0) = \int_0^{H_0} \left( \frac{\partial S(T, H)}{\partial H} \right)_T \, dH$$  \hspace{1cm} (2)

Thermodynamics Maxwell relation is used to relate the magnetization data and magnetic entropy change as described in Eq. (3) [5,8]:

$$\left( \frac{\partial S}{\partial H} \right)_T = \left( \frac{\partial M}{\partial T} \right)_H$$  \hspace{1cm} (3)

Then, we can calculate the isothermal magnetic entropy:

$$\Delta S_M(T, H) = S_M(T, H) - S_M(T, 0) = \int_0^H \left( \frac{\partial M}{\partial T} \right)_H \, dH$$  \hspace{1cm} (4)

At a discrete field and different temperature, the magnetic entropy change can be approximated as described in Eq. (5):

$$|\Delta S_M| = \sum_{n=1}^{N_{\text{field}}} \left( \frac{M_n - M_{n+1}}{T_{n+1} - T_n} \right) \Delta H_0$$  \hspace{1cm} (5)

Where $T$ is temperature, $H_0$ is variation of external magnetic field, $S_M$ is magnetic entropy, $M$ is magnetization, $M_n$ and $M_{n+1}$ are the magnetization values when measured at temperature $T_n$ and $T_{n+1}$ [5,8].

Previous research proved that La$_{0.7}$Ba$_{0.3}$MnO$_3$ has Curie temperature ($T_c$) of 336 K with magnetic entropy change ($\Delta S_M$) of -1.67 KJ kg$^{-1}$ K$^{-1}$ while La$_{0.5}$Ca$_{0.0}$MnO$_3$ has $T_c = 267$ K with $\Delta S_M = -6.40$ KJ kg$^{-1}$ K$^{-1}$ [5,6,8]. Curie temperature is transition temperature from metallic-ferromagnetic state to the insulator-paramagnetic state. At this temperature, the material has highest magnetic entropy change value [5,6,8]. Hence, doped calcium (Ca) to the La$_{0.7}$Ba$_{0.3}$MnO$_3$ is aimed to decrease its $T_c$ near room temperature and increase its magnetic entropy change.

In this work, we reported magnetic properties of La$_{0.7}$Ba$_{0.3}$MnO$_3$ polycrystalline material to observe effect of low doped calcium on the doped La$_{0.7}$Ba$_{0.3}$MnO$_3$. This work will be completed our study about low doping calcium concentration to the physical properties of La$_{0.7}$Ba$_{0.3}$MnO$_3$ where our previous publication explained about structure, resistivity, and magnetoresistance properties of this material [9]. Low doped concentration study is important to be observe in order to understand the characteristic change gradually due to calcium concentration. Sol-gel method was chosen to obtain the material because by using this method, homogenization of particle distribution of the material will be achieved [10]. So, it will influence its physical properties.

2. Experiment Method

The bulk sample material of La$_{0.7}$Ba$_{0.3}$MnO$_3$ was obtained by using a sol-gel method. La$_2$O$_3$, BaCO$_3$, CaCO$_3$, and Mn(NO$_3$)$_2$$ \cdot $4H$_2$O with high purity from Merck were used as starting precursors. Firstly, stoichiometric amounts of all precursors were weighed. Each of carbonate and oxide precursors were mixed with nitric acid until transparent solution were formed. Meanwhile, nitrate precursor was mixed with aquabidestilnte solution. After that, all of those precursors were mixed become one solution. Secondly, citric acid was added to the solution with citric acid/total metal ions ratio 4:1. Then, the mixture was stirred for 2 hours at room temperature. Homogenization of particle distribution of the precursor was achieved by sonication for 30 minutes. The precursor was dried at 100°C for 24 hours, and then calcined at 800°C for 3 hours to get the polycrystalline material. The magnetic properties of the material was measured using a magnetic field of 0 to 100 kOe at room temperature.
molar ratio is 1:1. Thirdly, ammonia solution was used for making its pH’s solution become 7. Forthly, stirred that solution at 353-363 K until gel was formed and then heated at 393 K for 3-4 hours to evaporate the excess solvent. After dried gel was obtained by that process, it was heated at 873 K for 8 hours for decomposing the organic precursors. Finally, it was heated at 1123 K for 10 hours until powder was formed. The obtained powder was compacted and sintered at 1573 K for 30 hours to crystal growth process.

Vibrating Sample Magnetometer (VSM) was used to measure magnetic properties of the material in the range of temperature 300-400 K under external magnetic field until 20 kOe. By using derivative of magnetization as a function of temperature of the material’s result, we can analyze the $T_c$ (Curie temperature) of the material. After that, magnetic field dependence of magnetization at various temperature around its $T_c$ was measured. These data were used for calculating magnetic entropy change ($\Delta S_m$) as described in Equation 5 [5,6].

3. Results and Discussion
The bulk polycrystalline La$_{0.7}$Ba$_{0.297}$Ca$_{0.003}$MnO$_3$ was successfully obtained by sol-gel method. Our previous publication showed that the material is single phased with rhombohedral structure and R-$\overline{3}$c space group, it also does not has additional elements or in the other words, compositional purity of the material already confirmed in here [11].

Temperature dependence of magnetization at 100 Oe under Zero Field Cooling (ZFC) is depicted in Figure 1. The $T_c$ of the material is determined by minimum value of derivative of this graph (see inset Figure 1). From this measurement, it is obtained that $T_c$ of the material is 332.7 K. This result proved that Ca substitution to the La$_{0.7}$Ba$_{0.3}$MnO$_3$ material has lowered its $T_c$ although only in low doped concentration.

Figure 2 demonstrate the magnetization dependent magnetic field at various temperature of the material. There is a saturation condition by increasing magnetic field strength at $T = 297$ K which is this temperature is below Curie temperature. It is inferred that the material has ferromagnetic behaviour which has ordered spin at below Curie temperature. On the other hand, it has linear graph with raising external magnetic field strength at above Curie temperature. Hence, the material is in paramagnetic condition which has disordered spin. It is clearly seen that there is magnetic transition from ferromagnetic become paramagnetic with increasing temperature more than $T_c$. This kind of behaviour plays an important role to the MCE properties as shown in Eq. (5).

![Figure 1. Temperature dependence of magnetization at 100 Oe of polycrystalline La$_{0.7}$Ba$_{0.297}$Ca$_{0.003}$MnO$_3$. In set figure is derivative of magnetization vs temperature data.](image-url)
The data from figure 2 was used to calculate the magnetic entropy change of the material using Equation (5). Magnetic entropy change as a function of temperature is shown in Figure 3. From this measurement, it is obtained that polycrystalline La$_{0.7}$Ba$_{0.297}$Ca$_{0.003}$MnO$_3$ material has $\Delta S_M = -2.928$ Jkg$^{-1}$K$^{-1}$. This value is proved that magnetic entropy value of La$_{0.7}$Ba$_{0.3}$MnO$_3$ has been increased by calcium low doped in La-site. It might occur because double exchange (DE) and super exchange (SE) interactions is influenced by divalent ions (in this case the divalent ions are barium and calcium) substitution in La site [12,13]. DE interaction is simultaneous hopping electron from Mn$^{3+}$ ion to Mn$^{4+}$ ion via O$^{2-}$ ion which leads metallic ferromagnetic state in lanthanum manganites materials [14]. On the other hand, SE interaction is coulomb interaction between Mn$^{4+}$ ion and Mn$^{4+}$ ion. SE interaction causes electron could not travel easily so that causes the material has insulator-paramagnetic behaviour [13,14]. These interactions can artificially control by tuning doping concentration and doping ion in La and Mn sites [12,13].

Around Curie temperature of La$_{0.7}$Ba$_{0.297}$Ca$_{0.003}$MnO$_3$, magnetic entropy change of the material reaches maximum value. It is due to there is an additional of magnetic entropy value of the material around its transition temperature [3,8]. Strong spin lattice coupling at that point is the main factor of this phenomenon and it would be weak at below and above Curie temperature of material [3,8].

4. Summary
The effect of low doped calcium on the magnetic properties of La$_{0.7}$Ba$_{0.297}$Ca$_{0.003}$MnO$_3$ for magnetocaloric application has been successfully studied. The material has Curie temperature ($T_c$) = 332.7 K with magnetic entropy change ( $\Delta S_M$) = -2.928 Jkg$^{-1}$K$^{-1}$. This value is proved that magnetic entropy value of La$_{0.7}$Ba$_{0.3}$MnO$_3$ has been increased by calcium low doped in La-site. It might occur because double exchange (DE) and super exchange (SE) interactions is influenced by divalent ions (in this case the divalent ions are barium and calcium) substitution in La site. The material has highest magnetic entropy change value around its $T_c$ due to spin lattice coupling at this point.

5. Acknowledgment
This work is financially supported by Universitas Indonesia under research grant “Hibah PITTA (Hibah Publikasi Internasional Terindeks untuk Tugas Akhir Mahasiswa Universitas Indonesia” with grant contract number is 634/UN2.R3.1/HKP.05.00/2017. The authors are also grateful to Department of Physics, Universitas Indonesia for research facilities.
6. References

[1] Manjunatha S O, Rao A, Lin T-Y, Chang C-M and Kuo Y-K 2015 *J. Alloys Compd.* **619** 303–10.

[2] Manjunatha S O, Rao A, Subhashini and Okram G S 2015 *J. Alloys Compd.* **640** 154–61.

[3] Ayadi F, Reguieg Y, Cheikhrouhou-koubaa W, Koubaa M and Cheikhrouhou A 2015 *J. Magn. Magn. Mater.* **381** 215–9.

[4] Islam M S, Hanh D T, Khan F A, Hakim M A, Minh D L, Hoang N N, Hai N H and Chau N 2009 *Phys. B* **404** 2495–8.

[5] Phan M, Tian S, Yu S and Ulyanov A N 2003 *J. Magn. Magn. Mater.* **256** 306–10.

[6] Phan M and Yu S 2007 *J. Magn. Magn. Mater.* **308** 325–40.

[7] Gomez J R, Garcia R F, Catoira A D M and Gomez M R 2013 *Renew. Sustain. Energy Rev.* **17** 74–82.

[8] Phan M, Yu S, Hur N H and Jeong Y 2004 *J. Appl. Phys.* **96** 1154–8.

[9] Winarsih S, Kurniawan B, Imaduddin A and Manaf A 2017 *AIP Conf. Proc.* **1862** 1–5.

[10] Gaur A and Varma G . D 2006 *J. Phys. Condens. Matter* **18** 8837–46.

[11] Winarsih S, Kurniawan B, Manaf A, Saptari S A and Nanto D 2016 *J. Phys. Conf. Ser.* **776** 1–5.

[12] Coey J M D and Molnar S Von 1999 *Adv. Phys.* **48** 167–293.

[13] Salamon M B and Jaime M 2001 *Rev. Mod. Phys.* **73** 583–628.

[14] Viret M, Ranno L and Coey J M D 1997 *Phys. Rev. B* **55** 8067–70.