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The Investigation of Structural, Magnetic and Magnetocaloric Properties of $(La_{0.9}Er_{0.1})_{0.85}K_{0.15}MnO_3$ Manganite Compound

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Abstract

In this study, the structural, magnetic and magnetocaloric properties of the polycrystalline $(La_{0.9}Er_{0.1})_{0.85}K_{0.15}MnO_3$ manganite compound synthesized by sol-gel method have been studied. X-ray diffraction measurement at room temperature shows that the sample crystallizes in rhombohedral structure. The temperature dependence of magnetization measurement reveals that the sample undergoes ferromagnetic-paramagnetic phase transition with increasing temperature. Maximum magnetic entropy change (ΔS_M^{max}) of the sample has been calculated as 2.30 $Jkg^{-1}K^{-1}$ for magnetic field change of 5 T from isothermal magnetization curves.

Keywords: Manganite, Magnetocaloric effect, Magnetic refrigeration, Curie temperature

$(La_{0.9}Er_{0.1})_{0.85}K_{0.15}MnO_3$ Manganit Bileşiğinin Yapısal, Manyetik ve Manyetokalorik Özelliklerinin Araştırılması

Öz

Bu çalışmada, sol-jel yöntemi ile sentezlenen polikristal $(La_{0.9}Er_{0.1})_{0.85}K_{0.15}MnO_3$ manganit bileşiğinin yapısal, manyetik ve manyetokalorik özellikleri çalışılmıştır. Oda sıcaklığında x-ışını kırınımı ölçümü, numunenin rhombohedral yapıda kristalleştiğini göstermektedir. Sıcaklığa bağlı manyetizasyon ölçümleri, artan sıcaklıkla numunenin ferromanyetik-paramanyetik faz geçişi sergilediğini göstermektedir. Numunenin maksimum manyetik entropi değişimi ($\Delta S_M^{mak.}$) izotermal mıknatıslanma eğrilerinden 5 T manyetik alan değişimi için 2.30 $Jkg^{-1}K^{-1}$ olarak hesaplanmıştır.

Keywords: Manganit, Manyetokalorik etki, Manyetik soğutma, Curie sıcaklığı

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1. INTRODUCTION

Modern world needs cooling technologies for almost all living areas such as food safety, comfort and medical [1-3]. Most of the cooling systems used at present time are based on vapor compression/expansion refrigeration cycle which uses strong greenhouse or ozone depleting refrigerating gases [4]. In addition, the energy consumption of these systems is very high and the energy efficiency has reached its limits [5]. Therefore, researchers and engineers have been working to find alternative systems for long years.

Magnetic refrigeration (MR) technology foreseen alternative to vapor compression/expansion systems is a kind of cooling technology that uses a magnetic material as a working material [6]. The basic working principle of these system is magnetocaloric effect (MCE) expressed as the observed change in the temperature and entropy of the magnetic material when magnetic field is applied to a material in the adiabatic or isothermal conditions [7].

Perovskite manganites with general formula $RE_{1-x}A_xMnO_3$ (RE = La, Pr, Nd, Sm; A = alkali-metal or alkaline-cation) have been studied extensively respect to their advantages in magnetic refrigeration technology, such as tunable T_C, ease of handling and low cost [3]. The physical and magnetocaloric properties of these manganites strongly depend on doping the ratio of Mn^{3+}/Mn^{4+} ions, the average ionic radius size, $\langle r_A \rangle$, and the degree of disorder at the A-cation site [8]. In this study, we have worked out the effect of substitution of Er ion into La-site on structural, magnetic and magnetocaloric properties in $(La_{0.9}Er_{0.1})_{0.85}K_{0.15}MnO_3$ perovskite manganite compound.

2. EXPERIMENTAL PROCEDURE

The polycrystalline $(La_{0.9}Er_{0.1})_{0.85}K_{0.15}MnO_3$ (LEKM) perovskite compound has been synthesized by the sol-gel method. Stoichiometric amounts of La_2O_3, MnO_2, $Er(NO_3)_3$ and KNO_3 compounds were dissolved in convenient solvent. Solutions were mixed and heated to 300 ˚C by using a magnetic stirrer. Then, appropriate amount of citric acid and ethylene glycol were added to solution and the stirring and heating processes were continued until dry gel form was obtained. Afterwards, the dry-gel was heated to 550 ºC for 5 h to eliminate organic substances from structure. The final powder pressed and sintered at 1150˚C for 24 h. Identification phase and the crystal structure of the sample was checked out by using an x-ray diffractometer (XRD) with CuK_α radiation at room temperature. The temperature and magnetic field dependence of magnetization of the sample was measured by a physical property measurement system (PPMS). The temperature dependence of magnetization measurement was performed in the temperature interval 5-300 K. To calculate magnetic entropy change, isothermal magnetization measurements were performed up to 6 T at various temperature around T_C.

3. RESULTS AND DISCUSSION

The x-ray diffraction pattern of the sample is given in Figure 1. The structural parameters were determined by using the standard Rietveld technique. The results indicate that the sample is crystallized in rhombohedral structure. The lattice parameters *a*, *b* and *c* of the sample are $a = b =$ 5.5228 (Å) and c = 13.3546 (Å), respectively. The unit cell volume of the sample is 352.7580 ($Å^3$). Compared to undoped $La_{0.85}K_{0.15}MnO_3$ (LKM) sample mentioned at our previous work [9], the unit cell volume and the lattice parameters of the LEKM sample are smaller than those of LKM sample. This difference is arisen from having the smaller ionic radius of the Er ion than La ion.

Tolerance factor (*t*) which controls deviation from perovskite structure [10] is calculated with the relation given by;

$$t=(r_A+r_O)/\sqrt{2}(r_{Mn}+r_O) \quad (1)$$

where r_A, r_{Mn} and r_O values are the average ionic radii of A-site, Mn ions and oxygen ions, respectively. For ideal cubic structure system, *t* value is equal to 1. If *t* value changes between 0.96 and 1, rhombohedral distortions occur. If *t* value is smaller than 0.96 [11] occurred distortions are orthorhombic. According to the calculated *t* (0.9946) value for the LEKM sample, the crystal

structure is rhombohedral and this is consistent with the XRD result.

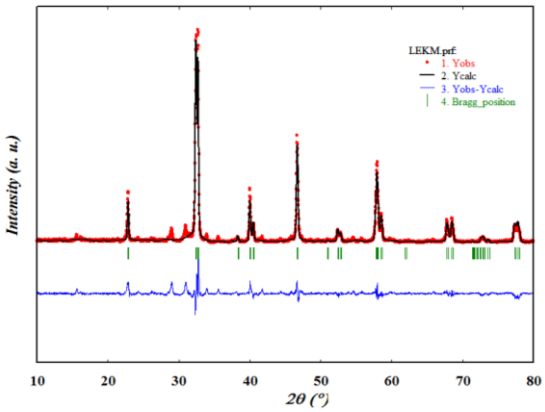

Figure 1. The x-ray diffraction of the LEKM sample at room temperature. Solid circle and solid line are the observed and calculated data, respectively. The vertical bars indicate Bragg positions

Figure 2 exhibits that the temperature dependence of the zero-field cooled (ZFC) magnetization of LEKM sample performed under 250 Oe in 5-300 K temperature range. It is seen from the temperature dependence of magnetizaiton curve that the sample displays ferromagnetic-paramagnetic phase transition with increasing temperature. The magnetic phase transition temperature (Curie temperature, T_C) can be determined from the minimum value of dM/dT vs. T graph [12] as presented in the inset of Fig.2. The graph has only one minimum point confirmed that the sample has single magnetic phase [13]. T_C is found as 171 K for LEKM sample. In our previous study [9], T_C value is 238 K for undoped LKM manganite sample. The results represent that the T_C value of the Er doped sample is lower than that of the undoped sample. This difference can be arisen from smaller ionic radius of Er ion than that of La. The T_C value of the manganite compounds is also controlled by the average ionic radius of A-site [14]. The discrepancy occurred in the average ionic radius of the A-site changes the Mn-O-Mn bond angle and Mn-O bond length originating MnO_6 [7]. As a result of the variation taken place in these parameters, double exchange (DE) mechanism weakens and T_C value decreases.

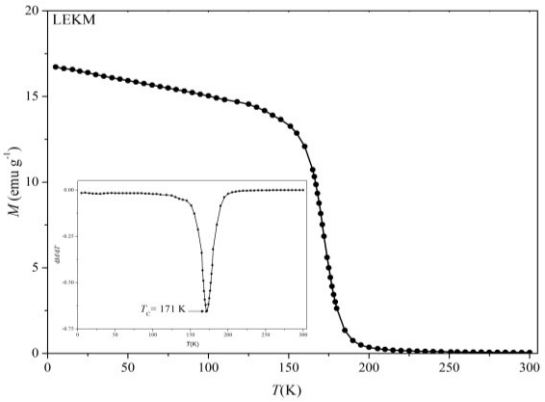

Figure 2. The temperature dependence of the LEKM sample in a magnetic field of 250 Oe at zero-field cooled process. Inset: dM/dT-T graph of LEKM sample

In order to analyze the magnetic behavior of the sample at low temperature and calculate the magnetic entropy change (ΔS_M) value of the sample, $M(H)$ measurements were performed at different temperatures taken at ~ 4K intervals below and above the T_C. The $M(H)$ isotherms of the sample taken up to 6 T is given in Fig. 3. Below T_C, magnetization increases rapidly with increasing magnetic field for $\mu_0 H$ = 0.5 T and saturates above 1 T. This is an expected behavior for ferromagnetic materials [15].

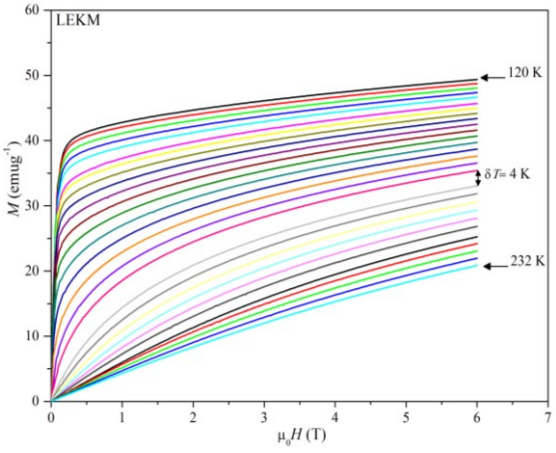

Figure 3. Isothermal magnetization curves for LEKM sample measured at different temperatures near phase transition temperature

The ΔS_M value of a magnetic material is related to the variation of the material magnetization M as a function of temperature and magnetic field [16] and its numerical value can be calculated from the $M(H)$ measurements using the following equation;

$$-\Delta S_M(H,T) = \sum \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H_i \qquad (2)$$

where M_i and M_{i+1} are the magnetization values measured at temperatures T_i and T_{i+1} in a field H, respectively. We have calculated the magnetic entropy change of the samples using by Eq.(1) and isothermal $M(H)$ measurement data. The temperature dependence of ΔS_M curves at different magnetic fields for the sample can be seen from Fig. 4. The ΔS_M curves show a maximum peak which is described as maximum magnetic entropy change (ΔS_M^{max}) in the vicinity T_C. The ΔS_M^{max} values of the sample are 0.71, 1.19, 1.60, 1.84 and 2.30 $Jkg^{-1}K^{-1}$ at 1, 2, 3, 4 and 5 T magnetic fields, respectively. It is observed that ΔS_M^{max} values increase with increasing magnetic field because the number of the oriented magnetic moments increases with increasing applied magnetic field [17].

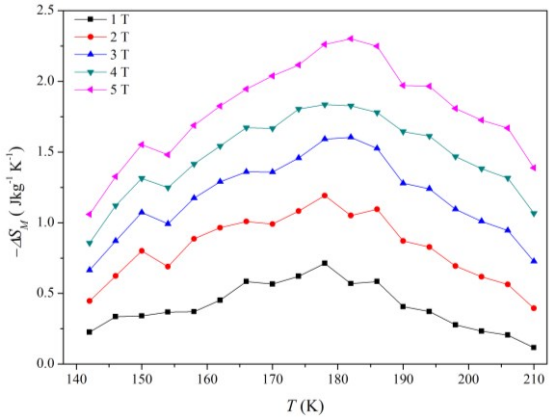

Figure 4. The ΔS_M curves as a function of temperature for the sample at different magnetic fields

For MR systems, the type of magnetic phase transition of the sample is also one of the important factors. For the samples exhibiting the second order magnetic phase transition, the magnetic and isothermal hysteresis are very small [3]. Negligible magnetic and isothermal hysteresis properties are desirable features for the MR technology. To identify the type of magnetic phase transition, we have constructed the M^2 dependence of the H/M curves known as Arrott plots by using isothermal magnetization curves. Banerjee criterion [18] express that if the slope of Arrott plots is positive near T_C, the magnetic phase transition is second order. Figure 5 shows that the type of magnetic phase transition for the sample is second order due to having positive slope of the Arrott plots in the vicinity T_C.

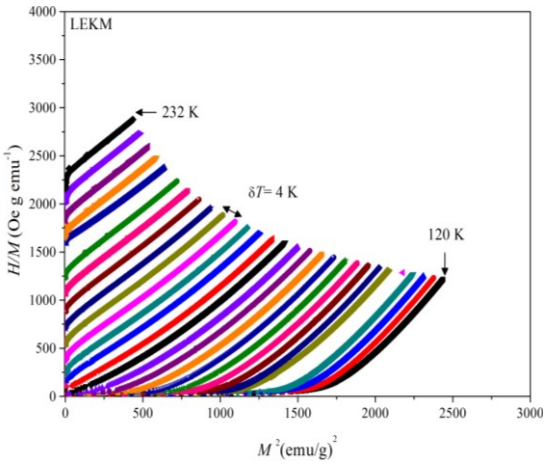

Figure 5. Arrott plots of the sample around T_C

4. CONCLUSIONS

We have investigated the structural, magnetic and magnetocaloric properties of the LEKM sample prepared by sol-gel method. The XRD results exhibit that the crystal symmetry of the sample is rhombohedral. The temperature dependence of magnetization measurement reveals ferromagnetic-paramagnetic phase transition with increasing temperature, around T_C = 171 K. The magnetic entropy change described as a component of magnetocaloric effect was calculated from isothermal magnetization measurements. The maximum magnetic entropy change value for the sample is calculated as 2.30 $Jkg^{-1}K^{-1}$ at 5 T magnetic field. The nature of the magnetic phase transition for the sample is determined from Arrott

plots. Arrott plots have a positive slope confirmed the second order magnetic phase transition.

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