Magnetic and magnetocaloric studies of $La_{0.45}Eu_{0.05}Ca_{0.483}Ba_{0.017}MnO_3$ compound

Etude magnétique et magnétocalorique du composé $La_{0,45}Eu_{0,05}Ca_{0,483}Ba_{0,017}MnO_3$

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ABSTRACT. In this work, we have studied the effect of structural disorder on the structural, magnetic and magnetocaloric properties of $La_{0.45}Eu_{0.05}Ca_{0.483}Ba_{0.017}MnO_3$ compound. The magnetization measurements as a function of temperature show a second ordered transition from the paramagnetic to the ferromagnetic state when the temperature decreases at T_C = 85 K. The magnetization isotherms indicate the presence of antiferromagnetic domains through the presence of a metamagnetic transition. The magnetocaloric study reveals the presence of a shoulder peak just above T_C. The origin of this peak can be linked to the field induced conversion of antiferromagnetic domains to the ferromagnetic state. The studied sample is characterized by magnetic phase separation phenomenon at low temperature due to the coexistence of both ferromagnetic and antiferromagnetic domains below T_C.

RÉSUMÉ. Dans ce travail, nous avons étudié l'effet du désordre structural sur les propriétés structurales, magnétiques et magnétocaloriques du composé $La_{0,45}Eu_{0,05}Ca_{0,483}Ba_{0,017}MnO_3$. La mesure de l'aimantation en fonction de la température montre une transition du second ordre de l'état paramagnétique à l'état ferromagnétique lorsque la température diminue à T_C = 85 K. Les isothermes d'aimantation indiquent la présence de domaines antiferromagnétiques à travers l'occurrence d'une transition métamagnétique. L'étude magnétocalorique montre la présence d'un épaulement juste au-dessus de Tc. L'origine de cet épaulement peut être reliée à la conversion des domaines antiferromagnétiques à l'état ferromagnétique sous l'effet du champ magnétique. L'échantillon étudié est caractérisé par le phénomène de séparation des phases magnétiques à basses températures suite à la coexistence de domaines ferromagnétiques et antiferromagnétiques au-dessous de Tc.

KEYWORDS. Manganite, metamagnetic transition, phase separation, magnetocaloric effect.
MOTS-CLÉS. Manganite, transition métamagnétique, séparation de phases, effet magnétocalorique.

1. Introduction

Manganites have been the subject of intense research in recent years, due to the discovery of colossal magnetoresistance in such systems. Lately, a significant magnetocaloric effect (MCE) has been noticed in manganites. In 1918, Weiss and Piccard theoretically expressed this phenomenon and gave it the name of MCE [WEI 21]. This phenomenon is an intrinsic property of magnetic materials when they are close to their magnetic ordering temperature (the Curie temperature T_C, or the Neel temperature T_N). This effect consists in a variation in temperature under an applied magnetic field. The MCE is the key property for magnetic refrigeration. The heat absorbing and releasing process is achieved by adiabatic magnetization/demagnetization of the refrigerant material. The gadolinium represents the reference element for magnetic refrigerants [DAN 98]. This element can be used in magnetic refrigerators at room temperature. However, its high price and limited availability disqualifies this element from being used in large-scale applications of magnetic refrigeration.

Manganites provide an effective option to solve this problem due to their stability and availability as well as the simplicity of the elaboration procedure. In this work, we have tried to investigate the structural, magnetic and magnetocaloric properties of $La_{0.45}Eu_{0.05}Ca_{0.483}Ba_{0.017}MnO_3$.

2. Experimental techniques

The sample was prepared by sol-gel route by using 99.9 % pure precursors. After dissolution in a nitric acid solution at 60°C, citric acid and ethylene glycol were added to achieve the solution homogeneity. After, the solution was heated to 130°C in order to obtain a viscous gel. Subsequently, the temperature was increased to 300°C to transform this gel into ash which have been then ground and calcined at 600°C for 5 hours. Several cycles of grinding, pelleting and sintering (at 600°C, 800°C and 1000°C) were performed to obtain a pure sample. The phase purity was checked out by X-ray powder diffraction. Magnetic measurements were carried out by a vibrating sample magnetometer in the temperature range 5-330 K for magnetic field values up to 7 T.

3. Results and discussions

The obtained X-ray diffraction measurements were refined by Rietveld method and the refined X-ray diffraction pattern is shown in figure 1. The refinement results show that the sample is pure and crystallizes in an orthorhombic structure with *Pnma* space group. The lattice parameters are a = 5.4079 Å, b = 7.6221 Å, and c = 5.4113 Å.

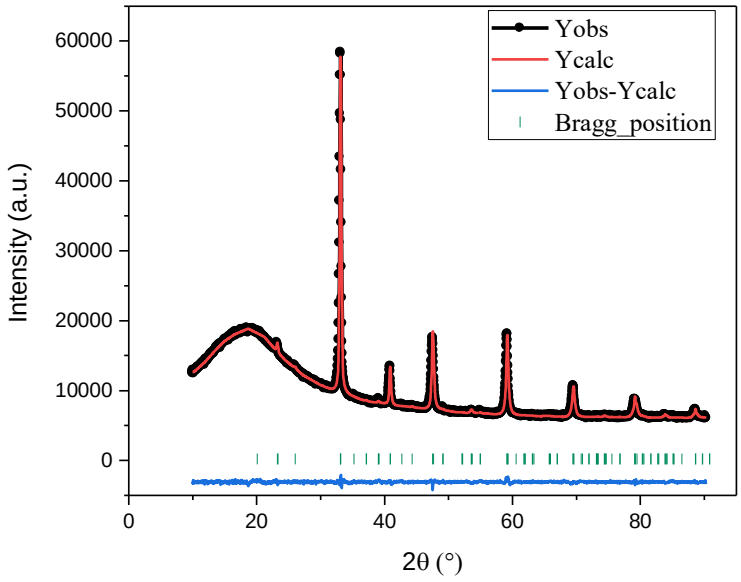

Figure 1. *Experimental X-ray powder diffractogram (red), calculated diffractogram (black), the difference between experimental and calculated diffractogram (blue) and Bragg positions (green) for* $La_{0.45}Eu_{0.05}Ca_{0.483}Ba_{0.017}MnO_3$ *compound*

The magnetization measurements as a function of temperature are presented in figure 2. These data show a second ordered transition from the ferromagnetic to the paramagnetic state at T_C = 85 K. By comparison with previous works performed on $La_{0.5}Ca_{0.5}MnO_3$ compound, it seems that the substitution weakens the ferromagnetic state characterizing the pristine compound [KRI 12, KRI 13, KRI 15, SCH 95]. The Curie temperature T_C shifts from 220 K for $La_{0.5}Ca_{0.5}MnO_3$ to 85 K in our case. Such decrease can be linked to the structural disorder induced by the substitution. Moreover, we cannot detect in figure 1 the ferromagnetic-antiferromagnetic transition at T_{CO} = 150 K, characterizing $La_{0.5}Ca_{0.5}MnO_3$ compound.

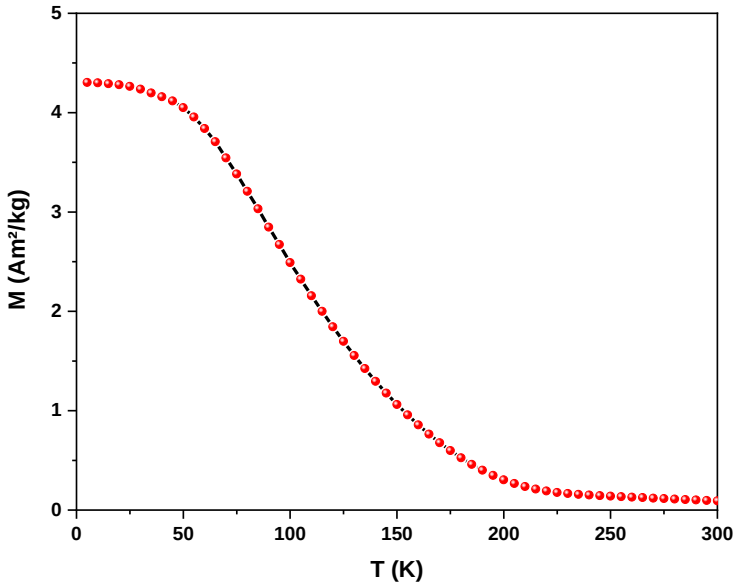

Figure 2. *Temperature dependence of magnetization under an applied magnetic field of 0.05 T for $La_{0.45}Eu_{0.05}Ca_{0.483}Ba_{0.017}MnO_3$ compound*

In order to investigate the observed transition, the magnetic isotherms M(H) were plotted in figure 3. One can see a strong increase of the magnetization for lower field values ($\mu_0 H \leq 0.5$ T) for temperature values lower than T_C, which confirms that the ground state of our sample is ferromagnetic. Both isotherms recorded at 25 K and 65 k show unsaturated behavior with a clear metamagnetic transition observed at 65 K, which confirms the presence of the antiferromagnetic behavior at low temperature. Thus, our compound is characterized by magnetic phase separation phenomenon due to simultaneous coexistence of both ferromagnetic and antiferromagnetic domains at low temperature.

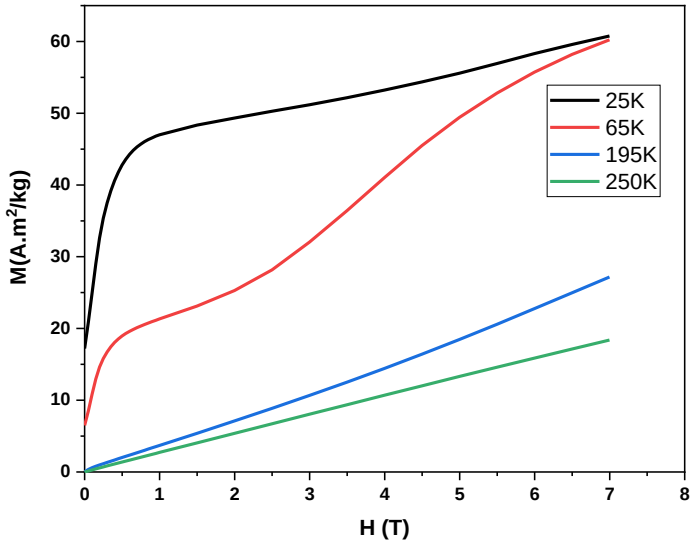

Figure 3. *Magnetic field dependence of magnetization for $La_{0.45}Eu_{0.05}Ca_{0.483}Ba_{0.017}MnO_3$ compound*

The Arrott plots giving the evolution of M^2 as a function of $\mu_0 H$ are shown in figure 4. The isothermal curve at 195 K shows a negative slope, indicating the existence of a first-ordered transition from the antiferromagnetic state to the ferromagnetic state above T_C. A similar behavior has also been observed when studying the $La_{0.4}Re_{0.1}Ca_{0.5}MnO_3$ compounds. With Re = Gd, Eu and Dy [KRI 13, KRI 18]. This fact indicates that substitution did not collapse the antiferromagnetic

state characterizing the parent compound at low temperature. The metamagnetic transition is typically accompanied by a discontinuous fluctuation in magnetization, which is generally caused by the anisotropy of the crystal lattice. In order to overcome the anisotropy's energy and achieve such transition, either a magnetic field or a temperature variation must be applied.

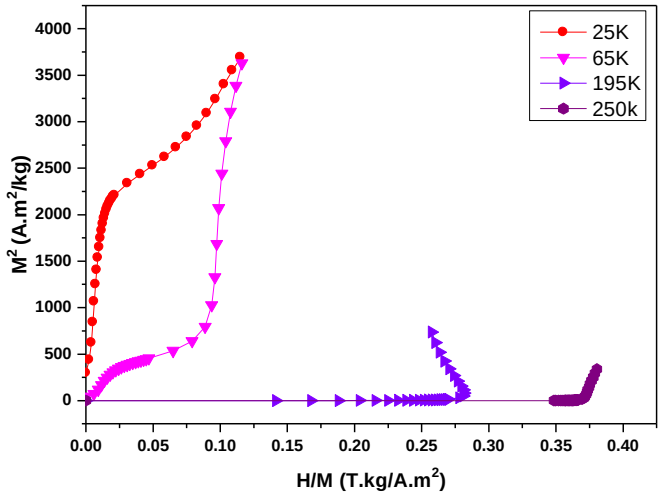

Figure 4. *Arrott plots for $La_{0.45}Eu_{0.05}Ca_{0.483}Ba_{0.017}MnO_3$ compound*

The evolution of the magnetic entropy change was determined by using isothermal magnetization measurements based on the following relation:

$$\Delta S(T,H) = \sum_i \frac{M_{i+1}(T_{i+1},H_i) - M_i(T_i,H_i)}{T_{i+1} - T_i} \Delta H_i \qquad [1]$$

where M_i and M_{i+1} are the experimental values of magnetization measured at temperatures T_i and T_{i+1}, respectively, under magnetic applied field H_i. We have depicted in figure 5 the magnetic entropy changes for our sample.

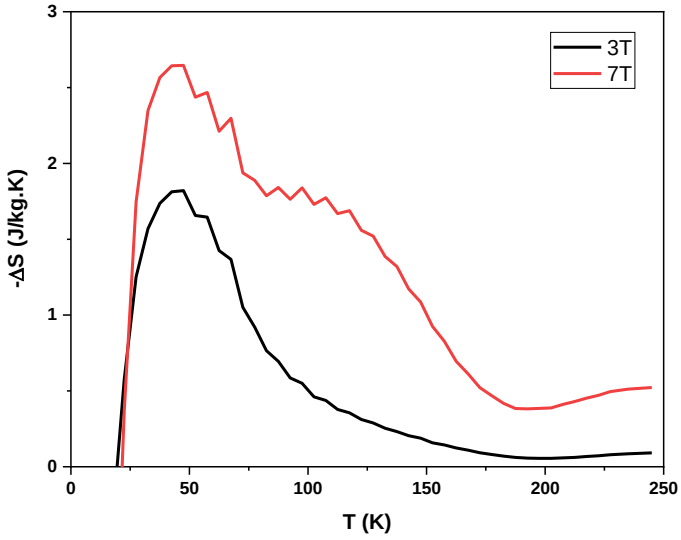

Figure 5. *Temperature dependence of magnetic entropy change for $La_{0.45}Eu_{0.05}Ca_{0.483}Ba_{0.017}MnO_3$ compound under 3T and 7T applied magnetic fields*

The curves show that the $La_{0.45}Eu_{0.05}Ca_{0.483}Ba_{0.017}MnO_3$ compound only exhibits negative values of magnetic entropy change. The important magnetic the entropy change in perovskite manganites was already related to the double exchange interactions between Mn^{3+} and Mn^{4+} ions [GSC 99]. An interesting phenomenon is noticed in our case, which is the occurrence of a shoulder peak near 100 K, which is clearly developed under high magnetic field (not detected under 3T field). Hence, the magnetic entropy peak is broadened, making it a useful feature for Ericsson cycle magnetic refrigeration [GSC 99, TAK 94]. The shoulder peak may imply that the microscopic magnetic structure above the Curie temperature T_C is not just paramagnetic. The occurrence of the shoulder peak at high magnetic field values can be ascribed to the metamagnetic transition. In fact, the high field values convert the antiferromagnetic domains to the ferromagnetic state, and by increasing the temperature, these domains shift to the paramagnetic state, leading to an enhancement of the MCE for high magnetic field values.

4. Conclusion

In this work, the structural, magnetic and magnetocaloric properties of $La_{0.45}Eu_{0.05}Ca_{0.483}Ba_{0.017}MnO_3$ compound were studied. We have observed a transition from the paramagnetic state to the ferromagnetic state at T_C = 85K. Isothermal magnetization curves testify the presence of antiferromagnetic state at low temperature through the presence of a metamagnetic transition. At 7T field, a shoulder peak is observed near 100K, leading to the enhancement of MCE. The appearance of such peak was linked to first-ordered transition from the antiferromagnetic to the paramagnetic state.

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