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# Effect of trivalent rare earth doping on magnetic and magnetocaloric properties of $\text{La}_{0.47}(\text{Y},\text{Eu})_{0.2}\text{Pb}_{0.33}\text{MnO}_3$ manganites

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## ABSTRACT

The  $\text{La}_{0.47}\text{Ln}_{0.2}\text{Pb}_{0.33}\text{MnO}_3$  (Ln=Eu and Y) polycrystalline has been synthesized using the solid state reaction method at high temperature. The X-ray diffraction shows that the materials crystallized in the orthorhombic structure. Magnetization measurements versus temperature in a magnetic applied field of 0.05 T show that all our samples exhibit a paramagnetic–ferromagnetic transition with decreasing temperature. The value of the Curie temperatures are 275 K and 264 K for Ln=Eu and Y, respectively. The magnetic entropy change reaches a peak ( $-\Delta S_m^{\text{max}}$ ) also decreases from 3.31 J/kg. K for Ln=Eu to 2.97 J/kg. K for Ln=Y, and the corresponding values of relative cooling power (RCP) reach 243.25 and 178.88 J/kg, under a magnetic field of 5 T. The results suggest that those polycrystalline could be useful for magnetic refrigeration in a broad temperature range.

## 1. Introduction

Over many years, the perovskite manganites of the type  $\text{Re}_{1-x}\text{A}_x\text{MnO}_3$  (Re=trivalent rare-earth, A=divalent alkaline earth) have received much attention because of their colossal magnetoresistance (CMR) and magnetocaloric (MC) properties [1–3]. These properties can be tuned by doping of some chemical elements into Re and/or A, Mn sites. These CMR and MCE properties are usually explained by the double exchange (DE) interaction between the trivalent ( $\text{Mn}^{3+}$ ) and tetravalent ( $\text{Mn}^{4+}$ ) ions [4]. It is believed that the magnetic refrigeration is a more energy efficient along with being an environmental, friendly technology when compared with the traditional gas compression refrigeration technology [5]. To find an active magnetic refrigerant (AMR) working at room temperature, most researchers focus on the metal alloys. These refrigerants, e.g. Gd [6],  $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$  [7],  $\text{LaFeSi}$  [8], undergoing the first-order magnetic transition, generally have large magnetic entropy changes ( $\Delta S_m$ ). It should be noticed that although the first-order transition is able to concentrate the MCE in a narrow temperature range producing large ( $\Delta S_m$ ), the relative cooling power (RCP) becomes small. Furthermore, material with a large MCE undergoing first order transition is always in a high magnetic field and has considerable hysteresis. Refrigerants of manganites undergoing second-order magnetic transition with a large MCE take a resurgence of interest given their low hysteresis, affluent meta-magnetic transition and coupling between charge and lattice. Manganites could be one

of the most promising candidates for magnetic refrigeration technology, for the low production cost, ease of Curie temperature ( $T_C$ ) tunability, chemical stability, and a relatively high resistivity. These properties are known for reducing eddy-current heating [9]. The manganite  $\text{La}_{0.67}\text{Pb}_{0.33}\text{MnO}_3$  is one of the extensively studied which undergoes a paramagnetic - ferromagnetic transition around  $T_C=360$  K and it shows a ( $-\Delta S_m^{\text{max}}$ ) of  $4.26 \text{ J kg}^{-1} \cdot \text{K}^{-1}$  under  $\mu_0 H=5 \text{ T}$  [10]. The ferromagnetic transition of the  $\text{La}_{0.67}\text{A}_{0.33}\text{MnO}_3$  can be brought down to room temperature either by the substitution of  $\text{La}^{3+}$  using another isovalent lanthanide ions or by partial replacement of Mn ions by other transition metal ions such as Co, Fe, Al, Ti, etc [11–15]. From this point of view, the main objective of this study is to tune the  $T_C$  from 360 K to near room temperature. We tried to investigate the effect of Eu and Y substitution on the magnetic and magnetocaloric properties of  $\text{La}_{0.47}(\text{Y},\text{Eu})_{0.2}\text{Pb}_{0.33}\text{MnO}_3$  polycrystalline samples with  $\text{Mn}^{3+}/\text{Mn}^{4+}$  constant fraction but within different average ionic radius of the A site  $\langle r_A \rangle$  as well as different values of variance  $\sigma^2$ .

## 2. Experimental procedures

Polycrystalline samples of nominal compositions  $\text{La}_{0.47}\text{Ln}_{0.2}\text{Pb}_{0.33}\text{Mn}_{0.67}\text{Mn}_{0.33}\text{O}_3$  (Ln=Y and Eu) were synthesized by a conventional solid-state reaction method. Raw materials of  $\text{Ln}_2\text{O}_3$ ,  $\text{PbCO}_3$  and  $\text{Mn}_2\text{O}_3$ , of purities higher than 99% were weighed in stoichiometric amounts. The detailed preparation of the samples is

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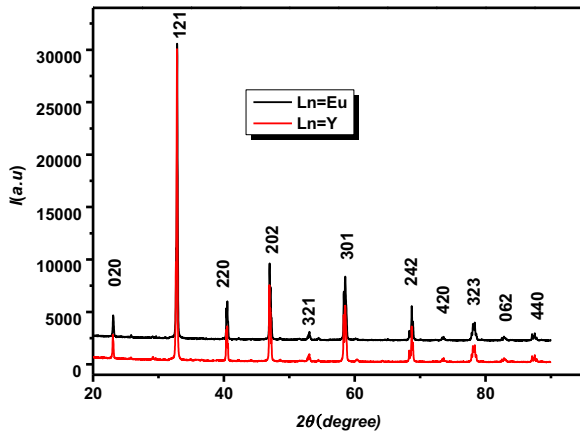


Fig. 1. X-ray diffraction pattern obtained of  $\text{La}_{0.47}\text{Ln}_{0.2}\text{Pb}_{0.33}\text{MnO}_3$  samples.

reported in the work [16]. The phase purity and structure of polycrystalline samples were identified by X-ray diffraction (XRD) technique at room temperature using a Panalatical X'pert PRO diffractometer with  $\text{CuK}\alpha_1$  radiation ( $\lambda=1.54056 \text{ \AA}$ ) in the  $2\theta$  range  $20\text{--}90^\circ$  with step size of  $0.017^\circ$  and counting time of 16 s per step. The temperature dependence and the magnetic-field-dependence of the magnetization,  $M(T)$  and  $M(\mu_0H)$ , were measured using magnetometer developed in Louis Néel Laboratory of Grenoble France.

### 3. Results and discussions

#### 3.1. X-ray diffraction

The X-ray powder diffraction (XRD) patterns for  $\text{La}_{0.47}(\text{Y}, \text{Eu})_{0.2}\text{Pb}_{0.33}\text{MnO}_3$  samples is illustrated in Fig. 1. This figure presents sharp and intense peaks corresponding to the manganite phase without any detectable secondary phases within the sensitivity limits of the experiment. In order to determine the crystalline structure of our samples, we now calculated the ( $t_G$ ) Goldschmidt tolerance factor [17] defined by:

$$t_G = \frac{\langle r_A \rangle + r_O}{\sqrt{2} (\langle r_B \rangle + r_O)} \quad (1)$$

(see Table 1) also confirms the structure to be orthorhombic (as it falls within the specified limits ( $0.89 < t_G < 1.02$  [18,19])). Here  $\langle r_A \rangle$ ,  $\langle r_B \rangle$  and  $r_O$  are respectively the average ionic radii of A and B perovskite sites and oxygen anion (the data of ionic radii are obtained from Ref. [20]). To confirm this, we analyzed the XRD patterns (as shown in Fig. 1) obtained from our samples using the “X’Pert HighScore Plus” software. The analysis revealed that all samples crystallize in an orthorhombic structure with  $Pnma$  space group (no.62). In the Table 1 the average size of A site cations ( $\langle r_A \rangle$ ) and the mismatch size ( $\sigma^2$ ) are also listed. In addition, the parent compound  $\text{La}_{0.67}\text{Pb}_{0.33}\text{MnO}_3$  [10], crystallize in the rhombohedra structure. The structural transition can be explained by the fact that radii of  $\text{Y}^{3+}$  ion ( $1.075 \text{ \AA}$ ) and  $\text{Eu}^{3+}$  ion ( $1.120 \text{ \AA}$ ) are smaller than that of  $\text{La}^{3+}$  ion ( $1.216 \text{ \AA}$ ) which causes a decrease of the tolerance factor.

Table 1

Some physical parameters of  $\text{La}_{0.47}\text{Ln}_{0.2}\text{Pb}_{0.33}\text{MnO}_3$  (Ln=Eu and Y) compounds.

Samples	$\text{La}_{0.67}\text{Pb}_{0.33}\text{MnO}_3$ [10]	$\text{La}_{0.47}\text{Eu}_{0.2}\text{Pb}_{0.33}\text{MnO}_3$	$\text{La}_{0.47}\text{Y}_{0.2}\text{Pb}_{0.33}\text{MnO}_3$
$\langle r_A \rangle$ (Å)	1.260	1.241	1.232
$t_G$	0.935	0.928	0.925
$T_C$ (K)	360	275	264
$\sigma^2$ (Å <sup>2</sup> ×10 <sup>-3</sup> )	4.52	7.18	9.68

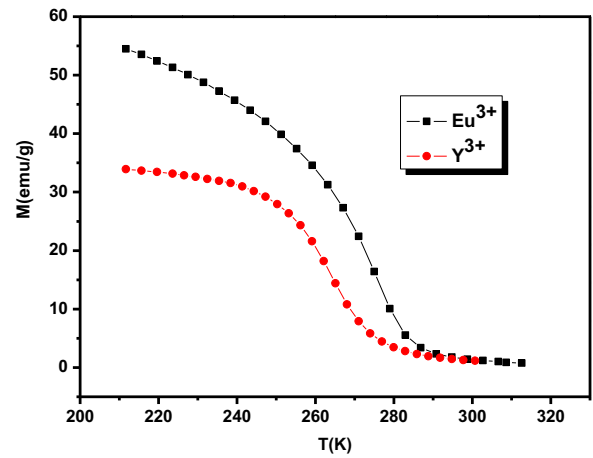


Fig. 2. Magnetization vs. Temperature for  $\text{La}_{0.47}\text{Ln}_{0.2}\text{Pb}_{0.33}\text{MnO}_3$  sample under 0.05 T.

#### 3.2. Magnetic properties

Fig. 2 shows  $M(T)$  curves measured under magnetic field 0.05 T for  $\text{La}_{0.47}(\text{Y}, \text{Eu})_{0.2}\text{Pb}_{0.33}\text{MnO}_3$  samples. The curve  $M(T)$  does not reveal any secondary magnetic phases, which confirms the good crystallization of the  $\text{La}_{0.47}(\text{Y}, \text{Eu})_{0.2}\text{Pb}_{0.33}\text{MnO}_3$  samples. All the samples exhibit a transition from paramagnetic (PM) to ferromagnetic (FM) with decreasing temperature. As estimation of the Curie temperature ( $T_C$ ) can be obtained from the maximum value of  $|dM/dT|$  vs  $T$ ,  $T_C$  values are found to be 275 K and 264 K for Ln=Eu and Y, respectively. For the parent compound  $\text{La}_{0.67}\text{Pb}_{0.33}\text{MnO}_3$ , we have found that  $T_C=360 \text{ K}$  [10]. It is clear from Table 1 that  $T_C$  decreases with decreasing average of A-site cation size  $\langle r_A \rangle$  and the tolerance factor  $t_G$ , as a consequence of substituting some rare earth ( $\text{Ln}^{3+}=\text{Eu}^{3+}$  and  $\text{Y}^{3+}$ ) partially for  $\text{La}^{3+}$  which has a smaller radius than  $\text{La}^{3+}$ . The decrease of  $\langle r_A \rangle$  and  $t_G$  will cause a tilt and rotation of the  $\text{MnO}_6$  octahedra which surrounds the A-site ions, adjusting thereby the Mn-O-Mn bond angle and the Mn-O bond length. This will cause a weakening of the double exchange interaction between neighboring  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  [21]. To determine the nature of the magnetic phase transition (first or second order) for  $\text{La}_{0.47}\text{Ln}_{0.2}\text{Pb}_{0.33}\text{MnO}_3$  (Ln=Y and Eu) samples, we illustrated the inset in Fig. 3, the Arrott’s plots ( $\mu_0H/M$  versus  $M^2$ ) [22]. The  $\mu_0H/M$  versus  $M^2$  curves exhibit in the vicinity of  $T_C$  a positive slope indicating that the phase transition is of second-order [23].

#### 3.3. Magnetocaloric effect and universal magnetic entropy curve

A giant field-induced entropy change is one of the important criteria for magnetocaloric materials like manganites. In fact, the isothermal  $M(\mu_0H, T)$  measurements are carried out at different temperatures around their phase transitions. The obtained isothermal magnetization curves for  $\text{La}_{0.47}\text{Ln}_{0.2}\text{Pb}_{0.33}\text{MnO}_3$  (Ln=Y and Eu) are displayed in Fig. 3. On the basis of the isothermal magnetization we can calculate the isothermal entropy change of our samples under an applied magnetic field using the Maxwell equation:

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