

DEVELOPMENT OF MANGANITE MATERIALS FOR ROOM-TEMPERATURE MAGNETOCALORIC APPLICATIONS

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ABSTRACT

Manganites of general formula $ABMnO_3$ (where A is a trivalent rare-earth ion and B is a divalent dopant) have interesting properties, namely colossal magnetoresistance and their applicability as materials for active magnetic regenerators. $La_{0.70}Sr_{0.30}MnO_3$ (LSMO) is a ferromagnet presenting considerable magnetocaloric effect, with operating temperature $T_C \sim 90^\circ C$ and magnetic entropy variation comparable to pure Gadolinium. We studied the LSMO system where Lanthanum ions are substituted by Erbium or Europium, effectively lowering the T_C to near-room temperature and below. This substitution also increases the relative cooling power (RCP) of the materials, an effect associated to the increased magnetoelastic contribution to the magnetic free energy. These results permit the creation of composites or thermal cascades of chemically similar compounds to produce an active magnetic element with a wide temperature interval of operation (from $-40^\circ C$ to $90^\circ C$). These materials can be synthesized by solid-state reaction or by sol-gel techniques, and are relatively cost-effective.

INTRODUCTION

Manganites materials of general formula $ABMnO_3$ (where A is a trivalent rare-earth ion and B is a bivalent transition metal) with a distorted perovskite-type structure were first synthesized by Jonker and van Santen (1950). The authors showed for the first time an oxide with ferromagnetic behaviour and also metallic properties below its Curie temperature – the $La_{1-x}Ca_xMnO_3$ series.

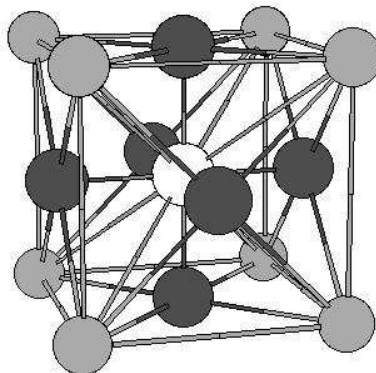


Figure 1 – The cubic Perovskite structure. In this representation, the cubic lattice is formed by the ions of larger radii, while the smaller ions are at the center of the structure. The cubic faces are occupied by the oxygen atoms.

Studies following the discovery of these materials led to the development of the now well-known theory of magnetic coupling between ions – the double-exchange model, by Zener (1951), Anderson and Hasegawa (1955) and de Gennes (1960). A renewed scientific and technological interest in manganites emerged in 1993, when thin films of $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ were found to have an intense magnetoresistive effect, where the electrical resistivity of the material was reduced by $\sim 60\%$ by applying an external magnetic field in the order of a few Tesla, as shown by von Helmolt *et al.* (1993) and Chahara *et al.* (1993). McCormack *et al.* (1994) then found values of 100% decrease in resistivity by applying a 6 T magnetic field to a thin film of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$. This effect was named Colossal Magnetoresistance. This technology is now under development for several types of applications, namely magnetoresistive sensors for digital media storage.

Manganites are now also attracting attention in the field of magnetic refrigeration, after Morelli *et al.* (1996) measured for the first time in 1996 the magnetic entropy variation by applied magnetic field of thick films of $\text{La}_{0.66}(\text{Ca},\text{Sr},\text{Ba})_{0.33}\text{MnO}_3$ deposited by metalorganic decomposition. In applied magnetic fields up to 5 Tesla, those films showed a maximum magnetic entropy change of the order 1.5-2 J/kg.K. This study was followed by Guo *et al.* (1997) who measured the magnetic entropy change of Sol-Gel prepared polycrystalline samples of $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$, under a maximum applied field of 1.5 T, and found values of 5.5 J/kg K, higher than those of pure Gd, 4 J/kg K, for the same field change.

This present work presents a study of the manganite system $\text{La}_{0.70}\text{Sr}_{0.30}\text{MnO}_3$ (LSMO), where we have substituted the La ion by the rare-earth ions Er or Eu. Samples were characterized by X-ray diffraction, electron scanning microscopy techniques and magnetization measurements. While the LSMO system has a T_C (and also maximum of magnetic entropy change) at $\sim 90^\circ\text{C}$, by substituting the rare-earth ions we have tuned the T_C to values near ambient temperature, and below. The ion used for substitution also affects the properties (magnetic, structural) of the system, as will be shown. A preliminary account of the study, with low field measurements, was presented previously (Amaral *et al.*, 2005).

1 EXPERIMENTAL

Polycrystalline samples of the $\text{La}_{0.70-x}(\text{Er},\text{Eu})_x\text{Sr}_{0.30}\text{MnO}_3$ were prepared by solid-state and also sol-gel techniques, as presented in table 1.

Table 1: Nominal composition of prepared samples and synthesis method.

Nominal composition	Method	Sintering
$\text{La}_{0.686}\text{Er}_{0.014}\text{Sr}_{0.30}\text{MnO}_3$	Sol-Gel	1350°C for 68 hours
$\text{La}_{0.665}\text{Er}_{0.035}\text{Sr}_{0.30}\text{MnO}_3$	Solid State	1300°C for 60 hours
$\text{La}_{0.56}\text{Er}_{0.14}\text{Sr}_{0.30}\text{MnO}_3$	Solid State	1300°C for 60 hours
$\text{La}_{0.49}\text{Er}_{0.21}\text{Sr}_{0.30}\text{MnO}_3$	Sol-Gel	1350°C for 68 hours
$\text{La}_{0.665}\text{Er}_{0.035}\text{Sr}_{0.30}\text{MnO}_3$	Sol-Gel	1350°C for 68 hours
$\text{La}_{0.56}\text{Er}_{0.14}\text{Sr}_{0.30}\text{MnO}_3$	Sol-Gel	1350°C for 68 hours
$\text{La}_{0.49}\text{Er}_{0.21}\text{Sr}_{0.30}\text{MnO}_3$	Sol-Gel	1350°C for 68 hours

Solid-state samples were prepared starting from stoichiometric amounts of Er_2O_3 , SrCO_3 and MnO_2 , and heated in air with intermediate crushing/pressing steps. Sol-Gel samples were prepared starting from liquid solutions of the desired metals (in either carbonate, nitrate or oxide forms), and urea, using the method presented by Vazquez *et al.* (1998). In both methods samples are quenched after sintering, in order to minimize the excess oxygen (δ) in the composition. X-ray diffraction patterns were acquired using a Philips X'Pert diffractometer, SEM/EDS analysis were performed on a Philips PHEI Quanta 400 with a Philips EDAX EDS detector and magnetization measurements were taken with a Quantum Design SQUID magnetometer in the temperature range 4-400K in magnetic fields up to 5 Tesla.

2 RESULTS

X-ray diffraction data was taken for all measured samples, showing clean spectra of a LSMO-type single phase. However, the samples with a higher composition of Er, of 14 and 21% show the formation of a secondary phase, structurally equivalent to ErMnO_3 , as obtained from Rietveld refinement (figure 2).

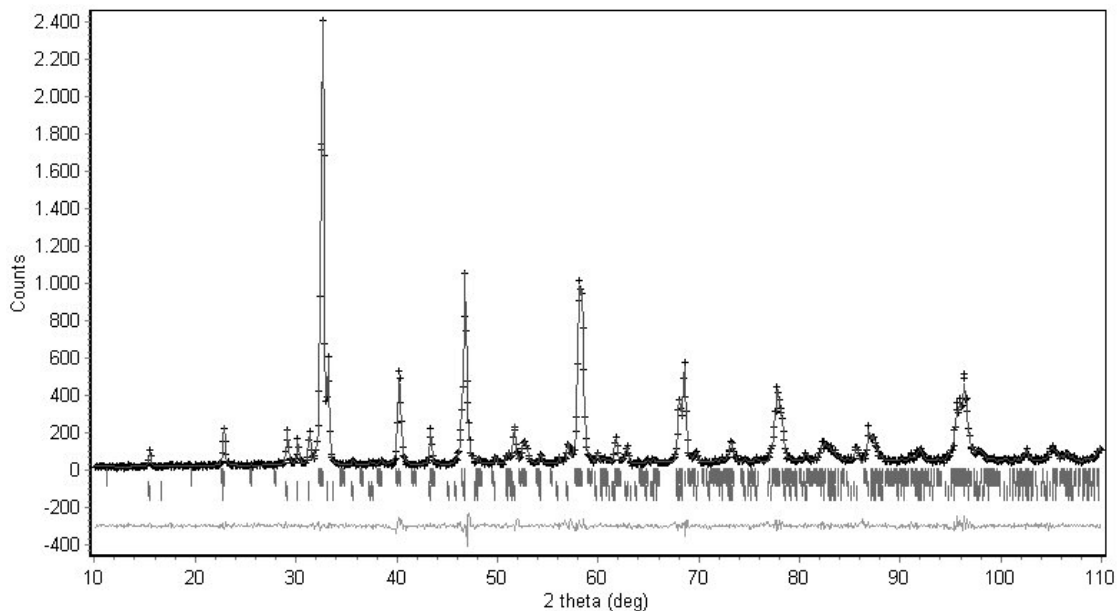


Figure 2 – Rietveld refinement of X-ray diffraction data of the Er = 0.21 sample. First row of identified peaks represent the LSMO-type phase, while the second row identifies a ErMnO -type phase. The lower solid line shows the fit errors.

This result can be attributed to the ionic size mismatch between La and Er ions. While the lattice can accommodate the Eu ions, the greater difference of radius between La and Er means that there is a definite limit of solid state solubility of Er ions in the LSMO structure. This effect was recently observed by Ravindranath *et al.* (2003). This secondary phase formation will affect the magnetic properties of the systems, so to better analyse this occurrence, detailed SEM/EDS measurements were performed to chemically analyse both phases, since the amount of Er in the main phase has decreased from its nominal value. Small particles of the ErMnO_3 -type phase were found, with size of the order 2-5 μm and composition given in table 2.

Table 2: EDS composition measurements of samples with secondary phase.

Sample	Phase	EDS analysis
$\text{La}_{0.56}\text{Er}_{0.14}\text{Sr}_{0.30}\text{MnO}_3$	LSMO-type	$\text{La}_{0.66}\text{Er}_{0.066}\text{Sr}_{0.45}\text{MnO}_{3+\delta}$
	ErMnO_3 -type	$\text{La}_{0.10}\text{Er}_{0.97}\text{Sr}_{0.19}\text{MnO}_{3+\delta}$
$\text{La}_{0.49}\text{Er}_{0.21}\text{Sr}_{0.30}\text{MnO}_3$	LSMO-type	$\text{La}_{0.59}\text{Er}_{0.10}\text{Sr}_{0.47}\text{MnO}_{3+\delta}$
	ErMnO_3 -type	$\text{La}_{0.10}\text{Er}_{0.95}\text{Sr}_{0.16}\text{MnO}_{3+\delta}$

To characterize the magnetocaloric properties of samples with a secondary phase, measurements that are normalized to mass (or mol) are re-normalized to the amount of primary phase percentage present on the sample. The presence of an ErMnO_3 -type phase will not contribute to the magnetocaloric measurements near room temperature, since its T_C is below 100 K. In accordance with X-ray diffraction measurements, SEM/EDS measurements of La-Eu and La-Er with low % of Er show no secondary phase, as well as presenting near nominal composition. Typical magnetization $M(T,H)$ isotherms in the measurement interval are shown in figure 3.

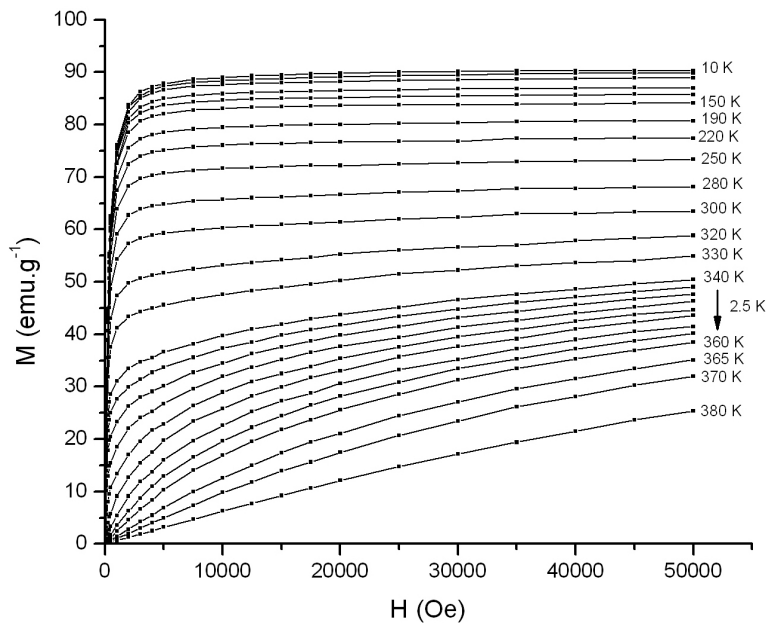


Figure 3 – Magnetization versus applied magnetic field isotherms measured for $\text{La}_{0.686}\text{Er}_{0.014}\text{Sr}_{0.30}\text{MnO}_3$ sample.

The T_C of studied compositions were determined by Magnetization versus Temperature measurements, at an applied field of ~ 50 Oe. The results are summarized in figure 4. There is an approximately linear decrease in T_C with substitution of Er or Eu. Note that the considered values of Er/Eu composition are those measured by EDS analysis, which affects the results of samples with secondary ErMnO_3 -type phase.

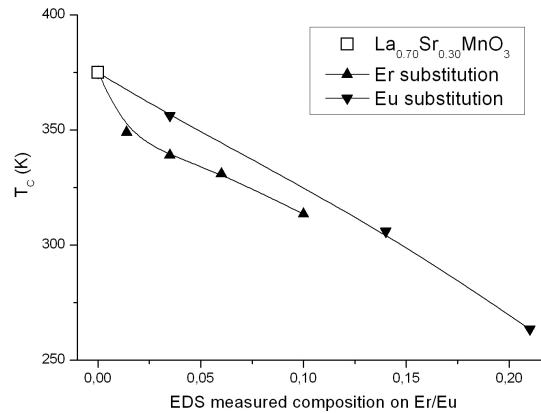


Figure 4 – Evolution of T_C with Er/Eu substitution. For samples that show a secondary ErMnO_3 -type phase, the considered Er concentration was measured by EDS chemical analysis.

Besides the difference in size, Eu^{3+} and Er^{3+} also have a considerable distinction in magnetic properties. While Eu^{3+} has a non-magnetic 7F_0 ground state with zero magnetic moment, Er^{3+} with a ${}^4I_{15/2}$ ground state has a magnetic moment of $9 \mu_B$. Using a high field extrapolation, we studied the saturation magnetization of the samples at low temperatures, to confirm these features and determine the way the Er ions align their magnetic moment with respect to the Mn ions. Results are shown in figure 5.

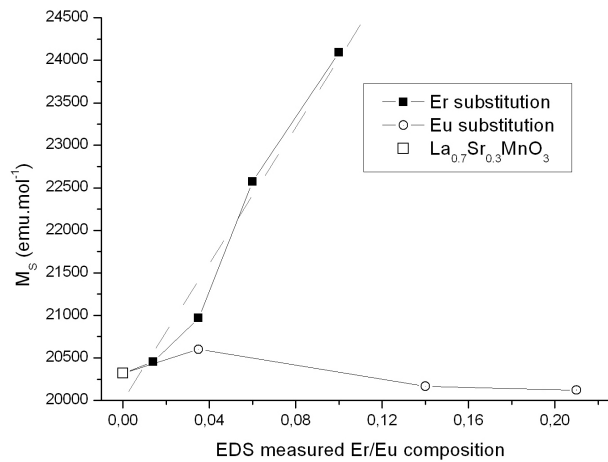


Figure 5 – Saturation magnetization as function of Er/Eu composition. Dashed line shows linear fit to Er-substituted M_S values.

The introduction of Er ions produces a noticeable increase of M_S , compared to the approximately constant values of the Eu-series. The linear fit allows us to estimate that for each Er ion present in the sample, a net moment of $\sim 7 \mu_B$ contributes to the overall magnetization. This value is near the net magnetic moment of an Er ion, $9 \mu_B$.

The magnetocaloric properties of samples were estimated indirectly via magnetization measurements, using the integration of the Maxwell relation (1). The derivative and integral were performed numerically from the measured $M(T, H)$ data points.

$$\Delta S_M(T, \Delta H) = \int_{H_i}^{H_f} dS_M(T, H)_T = \int_{H_i}^{H_f} \left(\frac{\partial M(T, H)}{\partial T} \right) dH \quad (1)$$

The magnetic entropy change results for a magnetic field change from 0 to 1 Tesla are presented in figure 6.

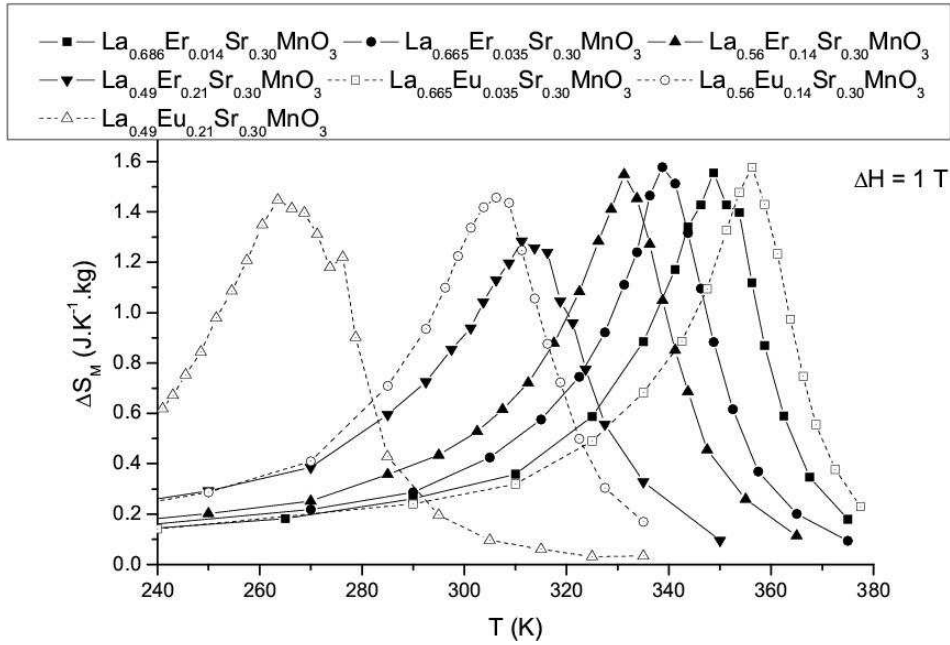


Figure 6 – Magnetic entropy change for a ΔH of 1 T, as function of temperature.

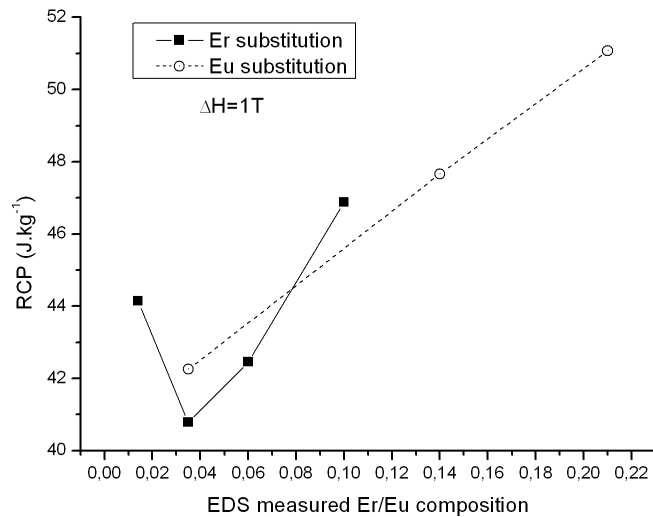


Figure 7 – Relative Cooling Power as function of Er/Eu composition.

While the maximum magnetic entropy variation remains approximately constant, the ΔS_M curves broaden by Er/Eu substitution, increasing their operating temperature range, as quantified by their relative cooling power, defined by the following expression (2),

$$RCP(S) = -\Delta S_M (\max) \times \Delta T_{FWHM} \quad (2)$$

where ΔT_{FWHM} represents the width at half maximum of the ΔS_M curve.

As shown in figure 7, while the Eu series shows a steady increase of RCP, the Er series presents a sharper increase. In previous works, (Reis *et al.*, 2004a, 2004b), (Amaral *et al.*, 2004), we have analysed the contribution of magnetoelastic and magneto-electronic contributions to the magnetic free energy. Using the framework of the Landau theory of phase transitions it was shown that an enhanced magnetic entropy change is related to an enhancement of those contributions, with respect to simple ferromagnets. A similar analysis reveals that this is also the case in the present series.

CONCLUSION

We show that by substituting the La ions of LaSrMnO₃ by Er or Eu ions, there is a decrease of T_C , with an approximately linear dependence. For a composition of Er ions between 3.5 and 14% there is a formation of a secondary ErMnO₃-type phase, in both solid-state and sol-gel prepared samples. Magnetocaloric properties of the Eu-series evolve with Eu concentration by a linear increase of RCP values, implying an increase of the operating temperature interval, since maximum ΔS_M are approximately constant through the series. In the Er-series, the RCP values show a higher increase of RCP, associated with the cooperative behaviour of the Er ions' magnetic moments. The formation of a secondary phase in the Er series limits the application of this material, since a considerable proportion of material of the secondary phase does not contribute to magnetic refrigeration near room temperature. The studied compositions show considerable magnetocaloric properties in a wide range of operating temperatures, from -40°C to 90°C. These results permit the creation of composites or thermal cascades of chemically similar compounds to produce an active magnetic element with a wide temperature interval of operation, using a relatively inexpensive material, synthesised by either solid state reaction or sol-gel techniques.

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