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The effect of chemical distribution on the magnetocaloric effect: A case study in second-order phase transition manganites

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ABSTRACT

Ferromagnetic manganites of general formula $ABMnO_3$ (where A is a trivalent rare-earth ion and B is a divalent dopant) are candidates for magnetic cooling applications, since they can present either second- or first-order magnetic phase transitions, and the perovskite structure allows for substantial chemical substitution and tuning of the magnetocaloric properties. The consequent chemical distribution from substitution affects the magnetic and magnetocaloric properties of the compound. The change of relative cooling power with chemical disorder is discussed by the use of the molecular mean-field model. We present experimental results of the ferromagnetic, second-order phase transition $La_{0.70-x}(Er,Eu)_xSr_{0.30}MnO_3$ system.

The magnetocaloric effect of a given magnetic material is characterized by two quantities: the adiabatic temperature variation, ΔT_{ad}, and the isothermal magnetic entropy variation, ΔS_M. Usually, ΔT_{ad} can be directly measured by adiabatic calorimetric methods, while ΔS_M can be obtained from indirect methods either from calorimetric measurements, or magnetic measurements and the use of a Maxwell relation [1]. The search for magnetic materials for magnetic cooling applications covers a wide range of materials [2,3], including first-order magnetic phase transition materials with magneto-structural couplings, and second-order systems like manganites or intermetallic alloys. Our previous work on the study of the magnetocaloric effect in second-order magnetic phase transition manganites of the system $La_{0.70-x}(Er,Eu)_xSr_{0.30}MnO_3$ [4], showed how the substitution of La by the rare-earths Er or Eu sufficiently lowered T_C of the parent composition $La_{0.70}Sr_{0.30}MnO_3$ (~370 K) to values adequate for room-temperature cooling applications. This change of T_C due to cation size change and the increase of cation size disorder is in agreement with previous works [5–7]. In this work, we show how the change of magnetic and magnetocaloric properties, observed with increasing substitution, can be interpreted as an effect of chemical inhomogeneity, consequence of the increasing amount of substitution along the series. With increasing x, the T_C of $La_{0.70-x}Eu_xSr_{0.30}MnO_3$ decreases linearly, with samples not showing any sign of phase separation for the compositions studied, as confirmed by X-ray and SEM/EDS analysis. This result implies that the perovskite structure can withstand this amount of substitution of La with Eu, even though Eu has a considerably lower ionic radius [8]. The magnetic entropy change for an applied field of 1 T is shown in Fig. 1.

The entropy curve widens with increasing x, while the maximum magnetic entropy change value is approximately constant along the series. This widening increases the value of the relative cooling power (RCP), defined as $RCP = \Delta S_M(max) \times \Delta T_{FWHM}$, where ΔT_{FWHM} is the full width at half maximum of the entropy curve. In terms of application, this makes the materials magnetic cooling properties more efficient in a wider temperature range. Also, the curve peak becomes less defined with increasing x, which can be interpreted as an effect of chemical distribution, as will be discussed later. Our earlier results of the $La_{0.70-x}Er_xSr_{0.30}MnO_3$ series [4] showed how a lower limit to solubility appears for $0.035 < x < 0.14$. This has been also reported for the $La_{0.80-x}Er_xSr_{0.20}MnO_3$ system by Ravindranath et al. [9]. For the samples with $x = 0.14$ and 0.21, X-ray diffraction and SEM/EDS analysis determine the formation of a secondary hexagonal (space group $P6_3$ cm) $ErMnO_3$ phase. There is therefore a limit of substitu-

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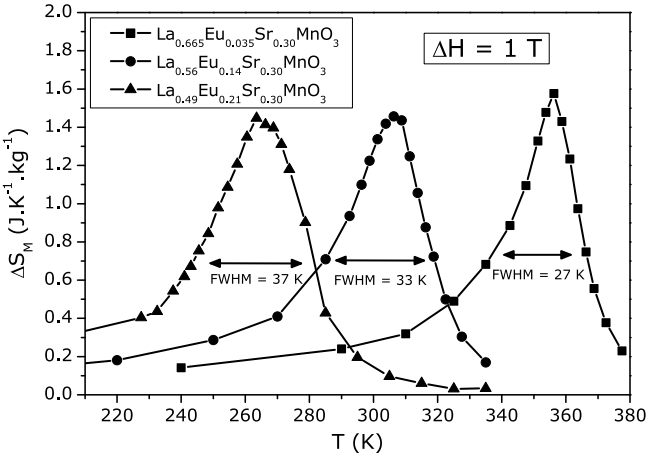

Fig. 1. Magnetic entropy change of the $La_{0.70-x}Eu_xSr_{0.30}MnO_3$ system, for $x = 0.025, 0.14, 0.21$ for an applied field change of 1 T.

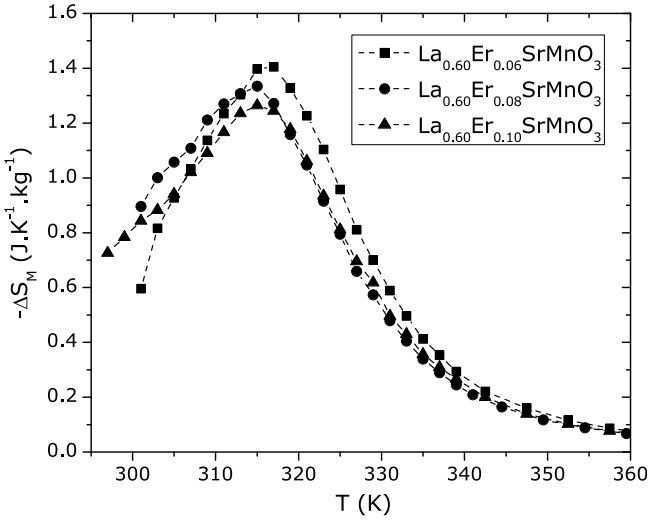

Fig. 3. Magnetic entropy change of the $La_{0.70-x}Er_xSr_{0.30}MnO_3$ system with $x = 0.06, 0.08$ and 0.10, for an applied field change of 1 T.

tion (solubility) of Er in the rhombohedral (space group $R\bar{3}c$) LaSrMnO manganite phase, due to the fact that Er has an ionic radius lower than Eu [8], and the perovskite structure is more unstable with the same x value. To better describe this phenomena, samples of the $La_{0.70-x}Er_xSr_{0.30}MnO_3$ system were prepared with $x = 0.06, 0.08$ and 0.10. Fig. 2 shows the T_C vs. x for the prepared samples, and the solubility limit appears to be between $0.06 < x < 0.08$. X-ray results for these three samples also identifies the presence of the secondary $ErMnO_3$ phase on the $x = 0.08$ and $x = 0.10$ samples, as shown in the inset of Fig. 2.

SEM imaging analysis of the $x = 0.06, 0.08$ and 0.10 samples reveal that there occurs a drastic microstructural change, with EDS analysis identifying some $ErMnO_3$ phase on the $x = 0.08$ and $x = 0.10$ samples, in accordance with the T_C vs. x results. ΔS_M plots, for an applied field change of 1 T, and $x = 0.06, 0.08$ and 0.10 are shown in Fig. 3. Since T_C is approximately the same for the three samples, the difference in ΔS_M is a result of the phase separation phenomenon. Note how the peak broadening appears asymmetrical. This point will be discussed in more detail in the next section.

The effect of inhomogeneity on the magnetocaloric effect has been studied by Romanov et al. [10], by the use of the Landau theory of phase transitions. In this work we present a simplified approach, where the effect of inhomogeneity (chemical distribution) on the magnetocaloric effect is interpreted, in a mean-field perspective, as a distribution of the mean-field exchange parameter λ, and the simplified approach of an exchange field of the type $H_{exch.} = \lambda M$ that describes a second-order magnetic phase transition. The distribution of interactions implies a direct distribution of T_C, since $T_C = \lambda C$ (C is the Curie constant) in this formulation. The spin value used was $J = 2$, saturation magnetization was 100 emu g^{-1}. The maximum value of ΔS_M increases for decreasing λ (and consequently T_C), implying that for a symmetrical distribution, the ΔS_M maximum peak value will shift to a lower temperature, as shown in Fig. 4, for normalized gaussian distributions. The gaussian distribution was chosen to describe a system with random disorder, as consequence of chemical and structural distribution around a mean value. Three variance values were chosen to describe increasingly disordered systems. Note that the magnetic entropy value was calculated for each portion independently, ensuring that thermodynamic relations like the Maxwell relation can be applied. The use of the Maxwell relation presumes an homogeneous system, so applying the relation to the simulated total magnetization data of the distribution would be incorrect.

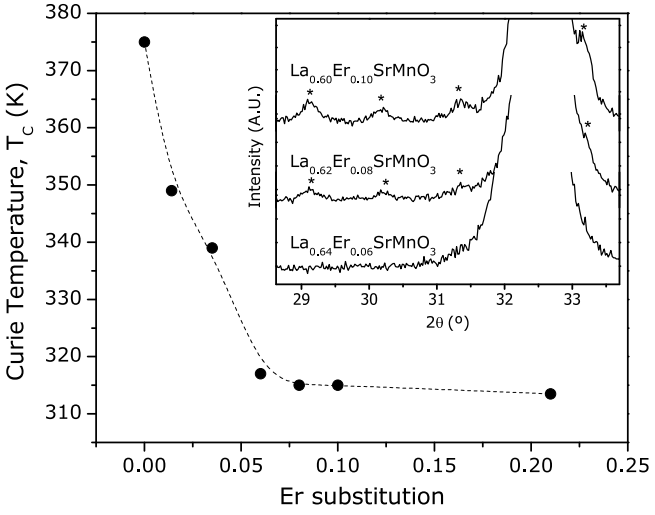

Fig. 2. T_C vs. x for samples of the $La_{0.70-x}Er_xSr_{0.30}MnO_3$ system. Inset: X-ray diffraction data of the samples $x = 0.06, 0.08$ and 0.10, with diffraction peaks of the $ErMnO_3$ phase identified.

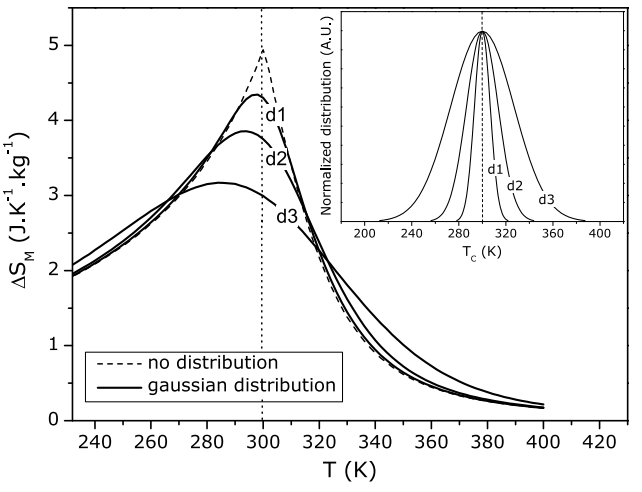

Fig. 4. Magnetic entropy change for an applied field of 5 T, for mean-field theory, and gaussian distributions centered at $T_C = 300$ K with several widths, shown in inset.

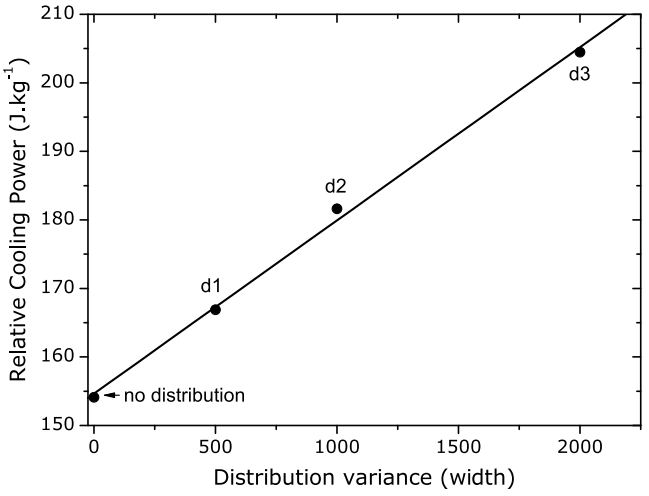

Fig. 5. Relative cooling power for an applied field of 5 T, for distributions centered in 300 K with different widths. Line represents a linear fit of the data.

The result shown in Fig. 4 implies that the maximum ΔS_M value for a distribution does not directly indicate the T_C value of the majority phase, as one would presume. The resulting RCP increases in an approximately linear way with the width of the distribution, for the used distributions, as shown in Fig. 5.

The mean-field results adequately describe the change in the magnetocaloric curves of the $La_{0.70-x}Eu_xSr_{0.30}MnO_3$ system, for the studied samples (Fig. 1) The peak broadening effect cancels out the expected increase of the peak ΔS_M value from lower T_C values, and in general terms, the peak change can be attributed to a symmetric chemical distribution.

In the $La_{0.70-x}Er_xSr_{0.30}MnO_3$ system, the broadening of the entropy curves for concentration of Er around the solubility limit (Fig. 3) is clearly asymmetrical. In the paramagnetic phase the shape is quite similar for the three samples, but in the ferromagnetic phase there is a clear increase in width for higher Er concentration. So the λ or T_C distribution cannot be taken as symmetrical. There is a considerable amount of sample with a lower T_C than the value corresponding to the LaErSrMnO phase at the solubility limit of $0.06 < x < 0.07$. This can be attributed to the presence of the LaErSrMnO phase with Er concentration higher than the solubility limit, which would indicate that chemical equilibrium may have not been reached during sample synthesis.

In conclusion, the structure, phase purity, magnetization and magnetocaloric study of the $La_{0.70-x}(Er,Eu)_xSr_{0.30}MnO_3$ system allowed us to show how the magnetic entropy change curves of a second-order phase transition system, with various samples of the same family, can be described in terms of a distribution of magnetic interactions (and corresponding T_C value). This analysis allows an interpretation that can distinguish a symmetrical chemical broadening around a mean concentration (the $La_{0.70-x}Eu_xSr_{0.30}MnO_3$ system), and an asymmetrical chemical distribution, which can be due to a phase separation phenomena (the $La_{0.70-x}Er_xSr_{0.30}MnO_3$ system).

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