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Phase Separation of $La_{0.70-x}Er_xSr_{0.30}MnO_3$ and its Effect on Magnetic and Magnetocaloric Properties

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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 $T_C \sim 370$ K and magnetic entropy variation comparable to pure Gadolinium. The high value of T_C makes LSMO unsuitable for room-temperature magnetic refrigeration applications, but by substituting La with the high-magnetic moment ion Er, T_C is lowered and total magnetic entropy increases. We have found a limit of solid solubility of Er ions in LSMO, in samples prepared by either solid state or sol-gel techniques in previous works [1], in accordance with other authors [2]. We now present a more detailed study of this limit of solubility, with more samples prepared with Er substitution close to the solubility limit and SEM microscopy clearly showing the changes in microstructure caused by the formation of a secondary $ErMnO_3$ phase, in accordance with x-ray diffraction data and T_C variation along the series. The magnetocaloric properties of the series are also presented, showing the increase of Relative Cooling Power along the series, in applied magnetic fields up to 1 T.

Introduction

The magnetocaloric effect was discovered by E. Warburg in 1881 [3] and is a property of all magnetic materials, since it is related to the variation of magnetic entropy by a change of an applied magnetic field. This effect has been developed since the 30's with the purpose of obtaining very low (<1 K) temperatures [4 and references therein]. More recently there has been a very strong development in magnetic refrigeration for room-temperature applications, with an equally strong research in the search of active magnetic materials used for this purpose [5,6]. Ferromagnetic Manganites of general formula $ABMnO_3$ (where A is a trivalent rare-earth ion and B is a divalent dopant) are candidates for application as materials for active magnetic regenerators, since their ferromagnetic transition (Curie) temperature can be tuned by chemical substitution in large intervals above and below room-temperature. One recent example of this chemical substitution for tuning T_C in manganites is in the $La_{0.70}Sr_{0.30}MnO_3$ (LSMO) system, which is a colossal magnetoresistive ferromagnetic manganite with Tc ~ 370 K, and by substitution of the La ion by the rare-earths Er or Eu, T_C is lowered [1]. In the case of Er substitution, we have shown that a lower limit of T_C is reached, contrary to the case of Eu substitution. This effect is in accordance with the results of other authors in the similar $La_{0.80-x}Er_xSr_{0.20}MO_3$ system and its electronic properties [2]. There is a limit to the solubility of Er in LSMO due to ionic size mismatch, which we will study in more detail in this work.

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Experimental

We have prepared samples of the $La_{0.70-x}Er_xSr_{0.30}MO_3$ (LErSMO) system with x = 0.06, 0.08 and 0.10, close to the estimated solubility limit of $x \sim 0.07$. These were prepared by the sol-gel combustion method described in reference [7], with intermediate grinding steps and sintering temperature of 1350ºC for 68 hours. Structural properties of samples were analyzed by X-ray diffraction using a Phillips X'Pert MPD commercial X-ray diffractometer and microstrutural analysis by scanning electron microscopy with chemical analysis by electron energy dispersive spectroscopy using a Phillips FEI Quanta 400 and EDAX EDS detector. Magnetic properties of the samples were measured using a commercial Oxford vibrating sample magnetometer with maximum applied field of 1 T and temperature range of 300 to 1000 K.

Results

X-ray diffraction data confirms the presence of a hexagonal $ErMnO_3$ phase, for Er substitution above 6%, as shown in Fig. 1, where diffraction peaks around $2\theta \sim 30º$, corresponding to the secondary $ErMnO_3$ phase, appear in the $La_{0.62}Er_{0.08}Sr_{0.30}MnO_3$ sample, and are of increased intensity for $La_{0.60}Er_{0.10}Sr_{0.30}MnO_3$.

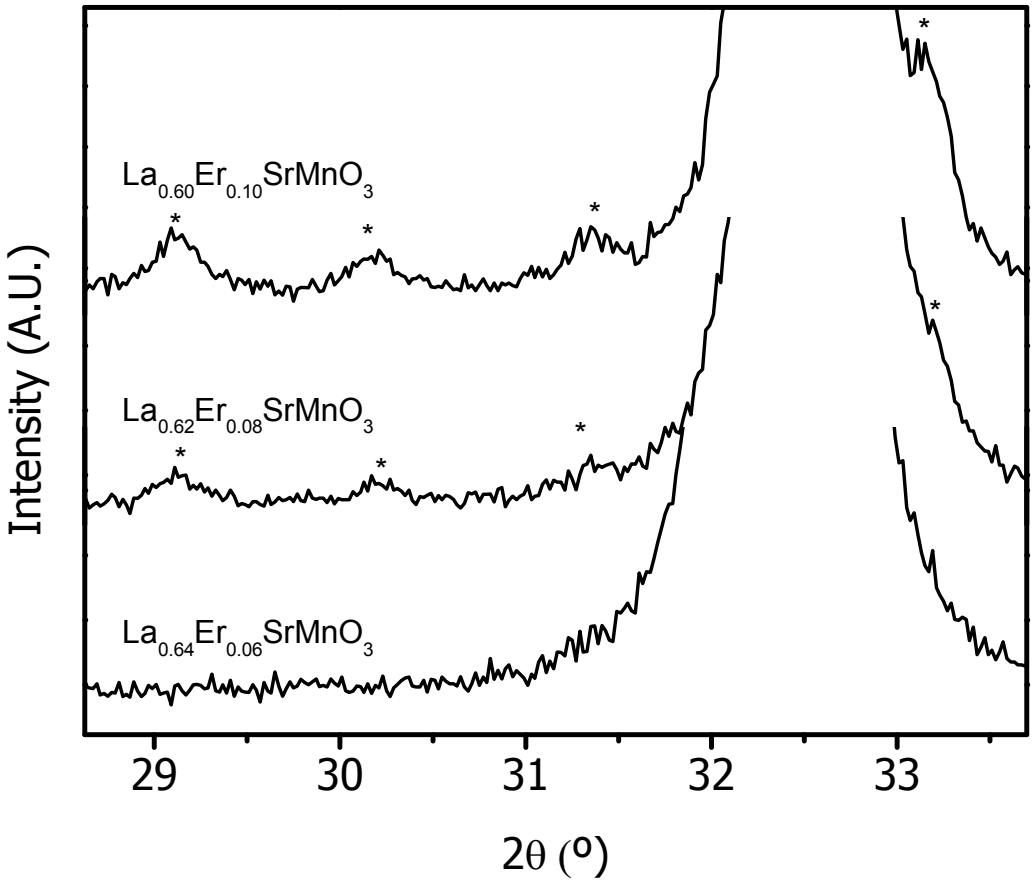

Figure 1: X-ray diffraction data of $La_{0.70-x}Er_xSr_{0.30}MO_3$ with x=6, 8 and 10. Symbol (*) indicates $ErMnO_3$ phase diffraction peaks.

The analysis of the dependence of T_C with Er substitution reflects this limit of solid solubility between the 6% and 8% sample, as shown in Fig. 2, together with results from a previous study [8].

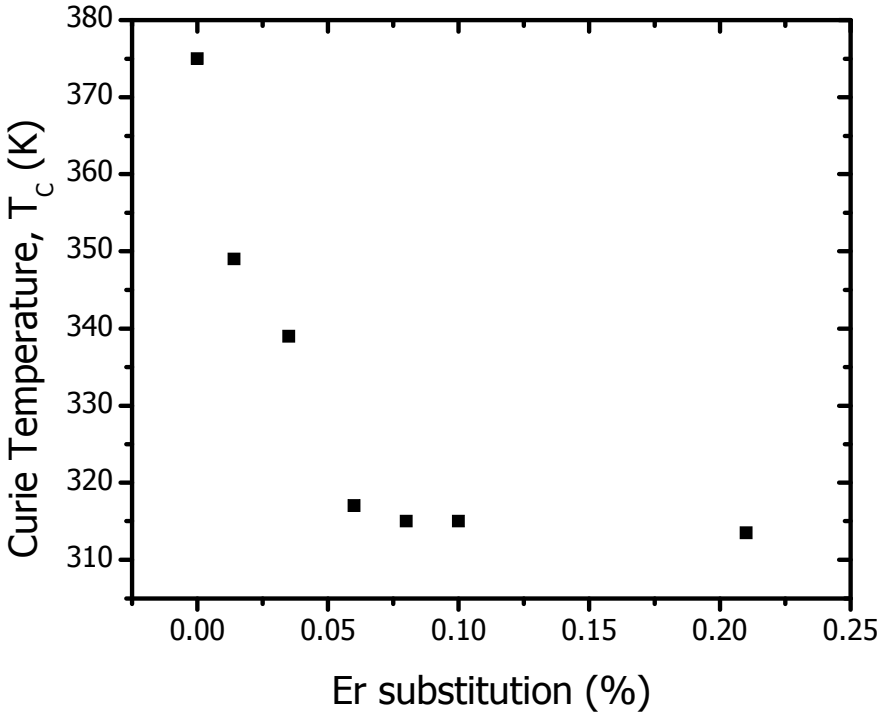

Figure 2: Dependence of Curie temperature T_C with Er substitution.

SEM microstructural analysis of the samples with Er content near the solubility limit show the drastic changes in microstructure due to the formation of the secondary phase. Well defined grain boundaries gradually loose their sharp faces and deform. $ErMnO_3$ secondary phase was identified by chemical EDS analysis.

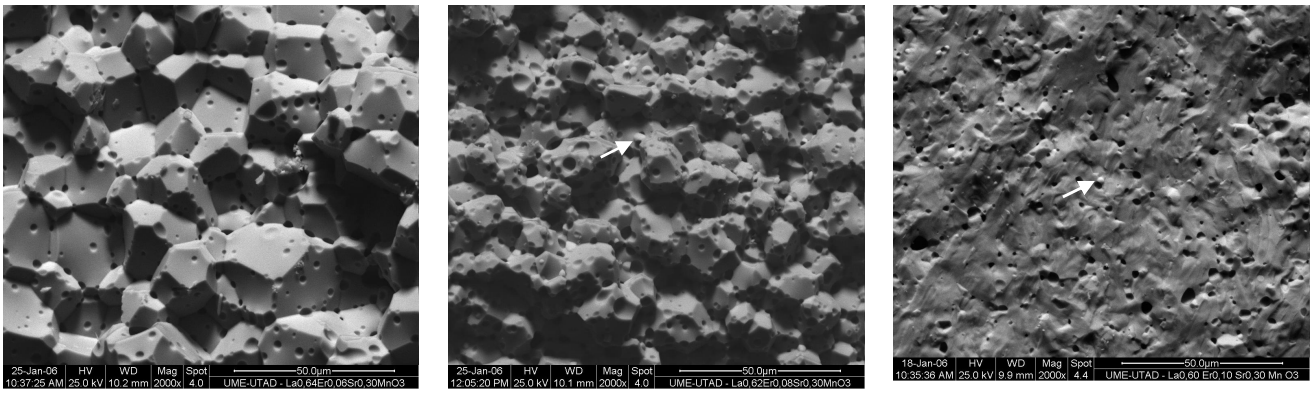

Figure 3: SEM imaging of fracture surface of $La_{0.70-x}Er_xSr_{0.30}MO_3$ samples with x = 6, 8 and 10 at 2000× magnifying factor. White arrows indicate secondary $ErMnO_3$ phase.

Variation of magnetic entropy with a change of applied magnetic field (magnetocaloric effect) up to 1T was estimated indirectly from isothermal magnetization measurements [9] and is shown in Fig. 4, for temperatures near T_C.

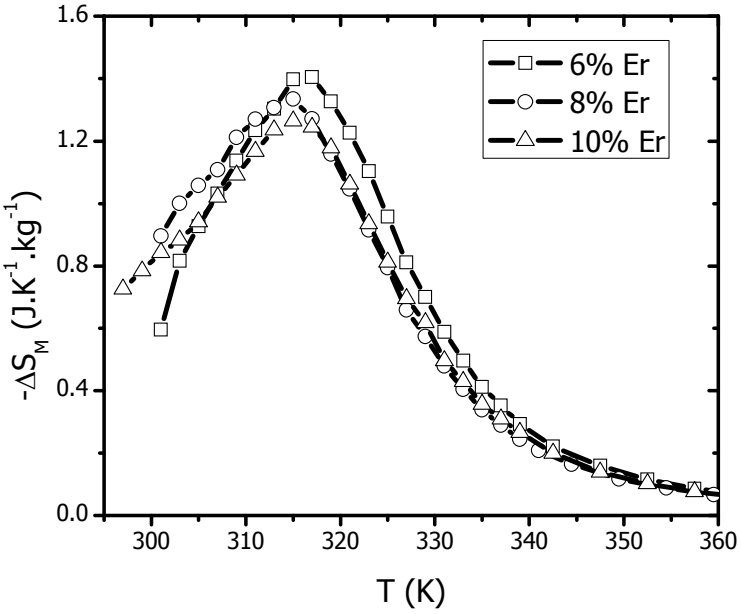

Figure 4: Magnetic entropy variation with an applied magnetic field change of 1 T for 6, 8 and 10% Er-substituted samples.

The formation of the secondary phase negatively affects the maximum value of ΔS_M, since the value is normalized to mass of sample, and $ErMnO_3$ is an antiferromagnet with T_N ~80 K, not contributing to entropy variation in this temperature range. The shape of the ΔS_M curve also changes, gradually widening with increasing substitution of Er. This effect is positive in terms of the applicability of this material in magnetic cooling devices, taking into account the rise in the relative cooling power, which is defined as:

$$RCP = \Delta S_M \times \Delta T_{FWHM} , \qquad (1)$$

where ΔT_{FWHM} represents the full width at half maximum of the magnetic entropy variation curve. Fi. 5 shows the increase of RCP with substitution.

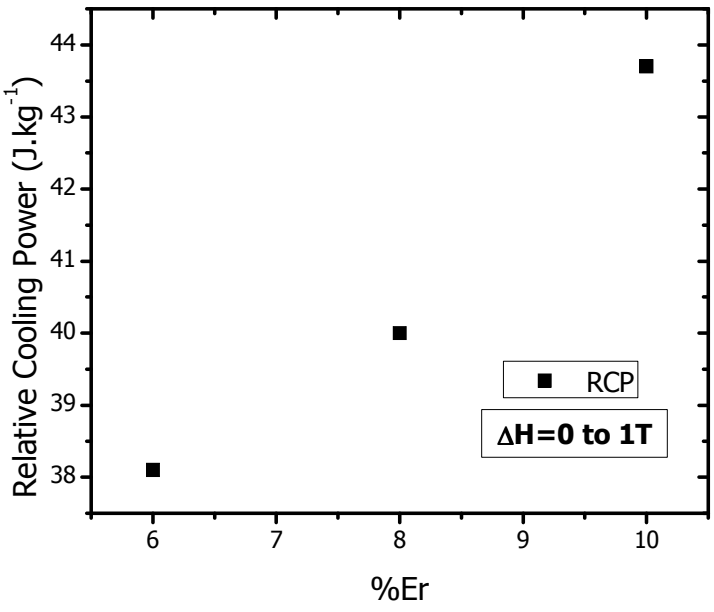

Figure 5: Relative cooling power versus Er-substitution, for 6, 8 and 10%.

This widening of the ΔS_M curve to temperatures below T_C, compared to samples with Er content below the limit of solid state solubility suggests that some of the main LErSMO manganite phase still has Er content above the solubility limit, with lower T_C. This suggests that the process of $ErMnO_3$ separation does not reach its thermodynamic limit in 68 hours of sintering time.

Conclusions

We have shown in this work how ionic size mismatch between La and Er ions in $La_{0.70}Sr_{0.30}MnO_3$ induces a phase separation of $La_{0.70-x}Er_xSr_{0.30}MO_3$ and $ErMnO_3$ for Er content over 6%. This phase separation phenomena decreases maximum value of magnetic entropy change for a maximum applied field of 1T, but the broadening of the transition increases the relative cooling power. The broadening of the transition indicates a distribution of Er content along the main manganite phase and also that preparation methods can be further controlled to improve applicability of this material in magnetic cooling.

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