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The Magnetocaloric Effect and Electrochemistry Corrosion of La_{0.7-x}Sr_{0.3}Eu_xMnO₃ Manganite

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The structure, magnetic, and the magnetocaloric effect on the La_{0.7-x}Eu_xSr_{0.3}MnO₃ sample prepared by the solid-state reaction method had been investigated. The structure data obtained from X-ray powder diffraction and Rietveld refinement analysis show that all these samples have single-phase and a rhombohedra structure with R-3c space group. With the substitution of the Eu³⁺ content, the volume of unit cells and Mn-O-Mn bond angle increase monotonically as well as the Curie temperature $T_{\rm C}$, which is caused by the weakening of the double exchange interaction. A magnetic entropy change $(-\Delta S_{\rm M})_{\rm max}$ of 2.21 J kg⁻¹K⁻¹ is obtained under a magnetic field change of 20 kOe for La_{0.66}Eu_{0.04}Sr_{0.3}MnO₃ sample. All samples exhibit the FM-PM phase transition with a second-order nature. In the electrochemistry corrosion experiment for the sample, the mass loss rate of the sample is small, so the material possesses optimal anticorrosion performance. The lattice structure and the Curie temperature of the material can be manipulated to some extend with Eu³⁺ substitution, which provides a method for magnetic refrigeration in an electrolyte solution environment.

Keywords: Magnetocaloric effect, Manganite, Curie temperature, Phase transition

1. INTRODUCTION

Perovskite manganite has many novel physical phenomena and potential applications in data storage, colossal magnetoresistance (CMR), and magnetic refrigeration (MR) [1-8]. The MR materials change their temperature with the external magnetic field and have advantages over conventional gas refrigeration, such as high efficiency, environmental friendliness, and small volume [9].

Manganite has several advantages compared with other metallic magnetic refrigeration materials, such as thermodynamic stability, soft toxicity elements, and low production cost [10]. $R_{1-x}M_xMnO_3$ (where R=rare earth elements or A-site element, like La, Nd, Pr; M=alkaline earth elements, such as Sr, Ca, Ba, etc.) is the general formula of perovskite manganite [11-14]. The structure, carrier

density (Mn^{3+}/Mn^{4+}) , and magnetocaloric properties can be easily modified with proper substitution [13, 15-18].

La_{0.7}Sr_{0.3}MnO₃ is one of the widely studied perovskite manganites. It has a second-order magnetic phase transition, and transition temperature (Curie temperature *T*_C) is near room temperature [19]. The magnetic properties are affected by the strength of the double exchange interaction (DE) between Mn³⁺, Mn^{4+,} and oxygen. The substitution of the A-site ions has an essential effect on the double exchange interaction. The other isovalent lanthanide ions substitution of La-site in materials, such as Nd, Yb, Pr and et al., are expected to cause deformation of the MnO₆ octahedron by the smaller size of the substituted cation and result in a change in the double exchange interaction [20, 21]. G. F. Wang et al. studied the crystal structure and magnetic properties when La-site is fully substituted by Nd and Pr [22]. Such substitution can be used to modify the Curie temperature of La_{0.7}Sr_{0.3}MnO₃ from 350 K to room temperature. A.G. Gamzatov et al. reduced La_{0.7}Sr_{0.3}MnO₃ Curie temperature to 260 K with substitution of Pr [23]. Recently, we have found that the Curie and Nell temperature of Pr_{0.5}Sr_{0.5}MnO₃ manganite can be tuned by Eu substitution without losing the MCE. In this work, we explore magnetic and MCE properties of the La_{0.7}Sr_{0.3}MnO₃ perovskite with low content Eu³⁺ substitution and conduct electrochemistry corrosion experiments on the materials to observe the consumption of the materials in the corrosion environment.

2. EXPERIMENTAL

La_{0.7-x}Eu_xSr_{0.3}MnO₃ (x=0.00, 0.02, 0.04 and 0.06) crystals were prepared by using conventional solid-state reaction. The powdered oxides were preliminarily mixed in agate mortar according to the stoichiometric ratio. Then it was put into a ball mill tank, and ball milled for 2 hours, dried and placed in a sintering furnace, heated up to 1273 K in the air for 24 hours. The product was ground into powder, then pressed into a block (13 mm diameter and 2 mm thickness), and sintered at 1373 K for 48 h. Finally, the product was naturally cooled. The electrochemistry station (Parstat 2273) was used to test the AC impedance of the samples. The frequency is ranged from 100 mHz~100 kHz with 10 mV amplitude. Sample with 1×1 cm² size was used as cathode while the platinum with 2×2 cm² size was chosen as anode. Saturated calomel electrode was used as the reference electrode. The powder X-ray diffraction (XRD) test was performed at room temperature with a Cu-K radiometer to determine the purity and uniformity of the material phase. The magnetization measurement was texted in a temperature scope of 290-400 K and a magnetic field of 100 Oe by physical property measurement system (PPMS). Then calculate the ΔS_M from the isothermal magnetization data according to the thermodynamic Maxwell relationship:

$$\Delta S_M = \mu_0 \int_0^{H_{\text{max}}} \left(\frac{\partial \mathbf{M}}{\partial T}\right)_H dH , (1)$$

Numerical evaluation of $\Delta S_{\rm M}$ using approximation:

$$\Delta S_{M} = \sum_{i} \frac{M_{i}(T_{i}, H) - M_{i+1}(T_{i+1}, H)}{T_{i+1} - T_{i}} \Delta H_{I}$$

 M_i and M_{i+1} are the magnetization date at the temperature T_i and T_{i+1} .

The block sample is immersed in the prepared NaCl solution with a quality percentage of 3.5, the mass of the sample is measured every 24 hours, and then the mass loss rate is calculated. The surface of the sample is imaged by scanning electron microscope before and after the electric corrosion.

3. RESULTS AND DISCUSSION

We obtain XRD data from the samples at room temperature and use the Rietveld refinement method to analyze the structural parameters [24]. The refinement is carried out on the program GSAS software [25], and the results are shown in Fig. 1.



Figure 1. XRD Rietveld refinement results of $La_{0.7-x}Eu_xSr_{0.3}MnO_3$ (x=0.00 (a), 0.02 (b), 0.04 (c) and 0.06 (d)) samples.

These synthesized La_{0.7}Sr_{0.3}MnO₃ samples are formed in a single phase with an R-3c crystal structure, without any impurities. The lattice parameters of the samples (a, b and c), the lattice volume, the \div^2 , R_{wp}, R_p, and Mn-O-Mn bond angle are listed in Tab. 1.

Parameter	x=0.00	x=0.02	x=0.04	x=0.06
Structure	<i>R-3c</i>	<i>R-3c</i>	<i>R-3c</i>	<i>R-3c</i>
$a(\text{\AA})$	5.493528 (5)	5.493861 (5)	5.495271 (5)	5.496083 (7)
$b(\text{\AA})$	5.493528 (5)	5.493861 (5)	5.495271 (5)	5.496083 (7)
$c(\text{\AA})$	13.338002 (17)	13.341447 (18)	13.344638 (19)	13.34782 (24)
$V(Å^3)$	348.597	348.73	348.992	349.179
<mn-o-< td=""><td>167.8 (5)</td><td>167.8 (5)</td><td>169.3 (5)</td><td>168.2 (6)</td></mn-o-<>	167.8 (5)	167.8 (5)	169.3 (5)	168.2 (6)
<i>Mn></i> (Å)				
χ^2	1.046	1.226	1.104	1.12
R_{wp}	0.1413	0.1585	0.1559	0.1507
R _p	0.1051	0.1207	0.1152	0.1108
P				

Table 1. The samples of lattice parameters (a, b and c), the cell volume (V), the bond angle of Mn-O-Mn, and the deviation $(\div^2, R_{wp} \text{ and } R_p)$

The χ^2 values are 1.046, 1.226, 1.104, and 1.12, which indicates a reliable refinement result. With the increase of Eu³⁺ content, the lattice parameters and lattice volume increase monotonically, and the Mn-O-Mn bond angle increases first and then decreases. A. Bouderbala et al. found a monotonously decrease in Mn-O-Mn's bond angle by increasing content of Eu³⁺ [26]. The reason is attributed to the interstitial doping when the substitution content of Eu³⁺ is less than 0.04, but with further increase the content, the Eu³⁺ enter the lattice and replace the position of La site.



Figure 2. (a) Zero magnetic field cooling (ZFC) and magnetic field cooling (FC) magnetization curves of samples $La_{0.7-x}Eu_xSr_{0.3}MnO_3$ (x = 0.00, 0.02, 0.04 and 0.06) measured at 100 Oe; (b) The reciprocal of magnetic susceptibility (1/ χ) as a function of temperature which is fitted with Curie-Weiss law (dashed lines). The inset shows the dM/dT as a function of temperature and the minimum point is the T_C .

The magnetization corresponds to the function of temperature curves (zero-field cooled (ZFC) and field cooled (FC)) were measured in a constant field of 100 Oe for x=0.00, x=0.02, x=0.04 and x=0.06 samples (Fig. 2(a)). The FC-ZFC curves show a sharp drop in the magnetization curve near 350

K, corresponding to the magnetic state changes from the paramagnetic state (PM) to the ferromagnetic state (FM). The T_C is defined as the peak in the dM/dT curve (the inset of Fig. 2(b)) [27]. The obtained T_C is 350K, 369K, and 365K, respectively. Generally, the change in T_C should follow the change in Mn-O-Mn bond angle [23]. Here, the Mn-O-Mn band angle and T_C as a fuction of the Eu content are shown in Fig 3(a). The change in Curie temperature agrees well with the change in Mn-O-Mn bond angle, which indicates DE interaction dominate the change of magnetic properties in the perovskite manganite during the Eu substitution.

Figure 3(b) shows the lattice parameters a, b, c, and V changes monotonically as a function of Eu content. But there is a maximum in the $T_{\rm C}$ vs. x (Eu) curve, as shown in Fig. 3(a). In general, the substitution of La³⁺ ions with a smaller ionic radius of Eu³⁺ ions should reduce the average ionic radius of the A-site ($R_{\rm A}$). The reduction of the $R_{\rm A}$ will weaken the double exchange reaction as well as the $T_{\rm C}$ [27]. The reason is that the Eu³⁺ does not enter the lattice with a small amount of Eu³⁺ substation but enters the interstitial void, as discussed by A. Bouderbala [23].



Figure 3. (a) The T_C and the bond angle of Mn-O-Mn as a function of Eu content; (b) The lattice parameters a, b, c and V as a function of Eu content

The M-T curve also shows the magnetization of the Eu substituted samples in the FM state is more significant than that of the parent sample, and the maximum value of the magnetization changes the same as the Eu content increases decreases with further substitution. When the temperature is below $T_{\rm C}$, the divergence between FC and ZFC curve depends on the magnetic field's uniformity and strength. Here, the divergence has not become more extensive, so there is no significant number of ferromagnetic clusters in the long-range ferromagnetic order of the samples [28].

The temperature dependence of the inverse susceptibility (χ^{-1}) is calculated, and the PM part (above $T_{\rm C}$) is fitted with the Curie-Wise law:

 $1/\chi = (T - \theta_p)/C, (3)$

According to the relevant result of Fig. 2(b), the magnetic susceptibility of the paramagnetic phase is fitted well with the Curie-Weiss law, and corresponding paramagnetic Curie temperature θ_p is obtained.



Figure 4. The isothermal magnetization curves (M-H curves) of samples $La_{0.7}Eu_xSr_{0.3}MnO_3$ (x=0.00 (a) and 0.02 (b)); the H/M and M² curves calculated from the M-H curve (x=0.00 (c) and x=0.02 (d)).



Figure 5. Magnetic entropy change curves of samples La_{0.7-x}Eu_xSr_{0.3}MnO₃, (x=0.00, 0.02, 0.04 and 0.06). The inset shows the RCP as a function of Eu content.

The typical isothermal magnetization curves for samples with x=0.00 and x=0.02 (Fig. 4(a) and 4(b)). The magnetization increases sharply below $T_{\rm C}$ and under the five kOe, then quick saturates. Above $T_{\rm C}$, the sample's state is paramagnetic, so the magnetization curve shows a linear change. The isothermal magnetization curve does not show any S-shape like the magnetization curve, indicating second-order phase transition material. To further confirm the nature of phase transition, the plot of M² as a function of H/M around $T_{\rm C}$ (Arrott plot) is shown in Fig. 4(c) and 4(d). According to Banerjee's law, when the Arrott curve slope is positive, the nature of phase transition is second-order. When the Arrott curve has a negative slope, it is a first-order phase transition [29]. Our data show that the slopes of all the curves are positive, which gives a provision that these samples have a second-order nature of phase transition.

Using the thermodynamic Maxwell equation Eq. 2, the calculated $-\Delta S_M$ curves of the samples is plotted in Fig. 5. The obtained ΔS_M value are 2.16 J kg⁻¹K⁻¹, 2.07 J kg⁻¹K⁻¹, 2.21 J kg⁻¹K⁻¹ and 2.04 J kg⁻¹K⁻¹ under the magnetic field change of 20 kOe, for x=0, 0.02, 0.04 and 0.06 respectively, and these values are listed in Tab. 2.

Nominal composition	$T_{\rm C}({\rm K})$	<i>H</i> (kOe)	$ \Delta S_M/_{max}(J\cdot/kg\cdot K) $	Reference
$Pr_{0.7}Ca_{0.3}Mn_{0.98}Co_{0.02}O_3$	106	50	2.18	31
$La_{0.67}Pb_{0.33}Mn_{0.85}Co_{0.15}O_3$	297	10	2.73	18
$La_{0.2}Pr_{0.5}Sr_{0.3}MnO_3$	299	18	1.95	23
$Pr_{0.7}Sr_{0.3}MnO_3$	262	18	3.15	23
$La_{0.67}Ca_{0.13}Ba_{0.2}Mn_{0.96}Co_{0.04}O_3$	272	16	2.68	14
$Pr_{0.7}Sr_{0.3}CoO_3$	158	40	0.93	32
$Pr_{0.6}Sr_{0.4}MnO_3$	320	25	2.3	33
$Pr_{0.7}Ca_{0.3}Mn_{0.95}Co_{0.05}O_3$	104.97	50	2.96	34
$La_{0.7}Sr_{0.3}Mn_{0.95}Co_{0.05}O_3$	300	15	1.17	19
$La_{0.7}Sr_{0.3}MnO_3$	350	20	2.16	This work
$La_{0.68}Eu_{0.02}Sr_{0.3}MnO_3$	350	20	2.07	This work
$La_{0.66}Eu_{0.04}Sr_{0.3}MnO_3$	369	20	2.21	This work
$La_{0.64}Eu_{0.06}Sr_{0.3}MnO_3$	365	20	2.04	This work

Table 2. Magnetic Entropy Change ($|\Delta S_M|_{max}$) of Several Manganese Ore in the low magnetic field

The results show that the magnetic entropy curves have a pleasing symmetry, and the maximum value of $|\Delta S_M|_{\text{max}}$ is obtained for x=0.04. The inset in Fig. 5 shows the relative cooling power (*RCP*) of samples. The *RCP* can be expressed as $RCP=|\Delta S_M|_{\text{max}} \times \Delta T_{\text{FWHM}}$, ΔT_{FWHM} is the full width at half maximum of ΔS_M versus T curve. A relatively large *RCP* value is obtained, which indicates that the refrigeration performance of the sample is relatively stable.

The $-\Delta S_{\rm M}$ curve will collapse into a master curve at T<T_C in second-order phase transition materials when the temperature is rescaled, but it does not happen in first-order phase transition materials [30]. We calculated the $\Delta S_{\rm M}$ under four applied magnetic fields (5, 10, 15, and 20 kOe) at different temperatures to analyze field dependence of the sample The maximum value $|\Delta S_{\rm M}|_{\rm max}$ is used to normalize the $\Delta S_{\rm M}$ data. The Eq. 5 is used to rescale the temperature axis:

$$\Theta = \begin{cases}
-\frac{(T - T_{c})}{(T_{1} - T_{c})} & T \leq T \\
\frac{(T - T_{c})}{(T_{2} - T_{c})} & T > T
\end{cases}$$
(5)

Here, θ is rescaled temperature, T_1 and T_2 are reference temperatures, it determined by the formula: $\Delta S_M(T_1)/\Delta S_M(max) = \Delta S_M(T_2)/\Delta S_M(max) = 1/2$. The function between normalized entropy change and θ in x = 0.00 and x = 0.04(Fig. 6(a) and (b)). These points are almost folded into one curve, with good coincidence. It shows independence from the external magnetic field. The second-order phase transition can be proved by the observation of the normalized curve.



Figure 6. The normalized entropy changes change with the rescaling temperature θ of the La_{0.7-} $_xEu_xSr_{0.3}MnO_3$ (x = 0.00 (a) and 0.04 (b)) samples.

The corrosion of ceramic materials usually causes changes in the mass of the materials, and the mass-loss rate (L_m) can reflect the degree of pollution. In this experiment, the sample's mass loss rate was measured by immersing in a 3.5% NaCl solution. The measurement results of the material mass loss rate after soaking are shown in Table 3.

Table 3. Changes of mass loss with time

Immerse time /	0	24	48	72	96
hours					
Mass loss rate (L _m)	0.00	0.05	0.03	0.04	0.05
/ %					



Figure 7. The SEM images of the sample before and after the electrochemistry corrosion experiment.

Table 3 shows that after being immersed, the mass loss rate of the sample is low, and it changes irregularly within the error range of the weighing. The SEM image of the material (Figure 7) shows no change in the sample's appearance. All these indicate that the sample has optimal anticorrosion performance. Moreover, the sample was also immersed into the 3.5 wt.% NaCl solution to test the AC impedance. According to the Figure 8, it was obvious that corrosion resistance of the sample was about 32 kohm which contributed directly to better anticorrosion performance.



Figure 8. AC impedance of samples

4. CONCLUSIONS

The structure, magnetic, and MCE of the $La_{0.7-x}Eu_xSr_{0.3}MnO_3$ samples reached the following conclusions. The samples have the R-3c crystal structure, and the lattice volume increases with Eu substitution. The substitution of Eu slightly changes the Curie temperature, of the sample and the maximum ΔS_M value is 2.21 J kg⁻¹K⁻¹ for x = 0.04. All samples have second-order phase transition

properties. The sample has better corrosion resistance so that it can work in a harsh environment. The good MCE performance of the samples indicates its potential application in room-temperature magnetic refrigeration.

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