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Study of structural effect on Eu-substituted LSMO manganite for high temperature coefficient of resistance

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Abstract: In this work, Eu substituted $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) is studied to achieve high temperature coefficient of resistance (TCR). The compounds $La_{0.7-x}Eu_xSr_{0.3}MnO_3$ with $x = 0$, 0.1 0.2 and 0.3 are prepared by solid state reaction route and their structural and transport properties are examined by different characterization techniques. The metal-semiconductor/insulator transition temperature (T_{MI}) decreases from 390 K (for $x = 0$) to 240 K (for $x = 0.3$) with decrease in average ionic radius $< r_A >$ of A-site. The maximum TCR percentage of $La_{0.7-x}Eu_xSr_{0.3}MnO_3$ compound is found to be increased for $x = 0.2$ (1.9 %) and for $x = 0.3$ (3.36 %) compared to its parent compound $La_{0.7}Sr_{0.3}MnO_3$ (1.1%). The substitution of Eu increases the lattice distortion, which enhances

the TCR value from 1.1% to 3.36%. The robustness of distortion increases with decreasing $<r_A>$ is well correlated with the high magneto-resistance, high TCR findings.

Keywords: Manganite, TCR, T_{MI}, polaron hopping energy, magnetoresistance

1. Introduction

The physical properties of hole doped manganites $R_{1-x}A_xMnO_3$, where R is a rare earth element (e.g. La, Pr, Nd, etc.) and A is a divalent element (e.g. Sr, Ca, Ba, etc.), have been extensively studied. The existence of intriguing characteristics such as charge-ordering and its melting, electronic phase separation, have been addressed in terms of the presence of Mn ion in mixed valence states, leading to competing magnetic exchange interactions [1, 2]. The colossal magnetoresistance (CMR) and the temperature coefficient of resistance (TCR) are useful for magnetic data storage, read-write heads and infrared detectors (bolometer) [3-5]. The temperature coefficient of resistance (TCR) is a useful parameter to determine the resolution of infrared detector (IR). The fact that the substituted manganites with high temperature coefficient of resistance $(TCR\% = \frac{1}{\rho}\left(\frac{d\rho}{dT}\right)*100)$ at room temperature make them potential candidates for IR detectors for night vision applications [6, 7].

In perovskite based manganites, the d-orbitals (e_g-orbitals) are strongly hybridized with oxygen p-orbitals and form an electrically active band gap [8]. This hybridization can be influenced by variation in internal chemical pressure within the lattice introduced by substitution. This generates structural disorder in the lattice due to local oxygen displacements, which in turn affects Mn-O-Mn bond angle and the bond length [9, 10]. Goldschmidt tolerance factor τ is defined as $\tau = <r_A> + r_0 / \sqrt{2}(r_B + r_0)$ where $<r_A>$ and r_B are the radii of the average A-site and B-site ions and r_0 is the radius of oxygen ion. For $\tau < 1$, Mn-O-Mn bond angle decreases from $180°$ which increases carrier localization in the lattice. Internal chemical pressure induced localization decreases charge carrier hopping integral t $(= \cos(\theta/2),$ where $'\theta'$ is angle between the spins on neighbouring sites) between Mn^{3+} and Mn^{4+} ions. In general, disorder is quantified by means of the variance of the A-site cation radius distribution (σ^2) defined as $\sum y_i r_i^2 - <r_A>^2$ where y_i and r_i are the fractional occupancies and effective ionic radii of rare earth and divalent ions, respectively. Thus, the variation in ionic radii at A-site leads to competing electronic phases at a particular temperature, hence influencing the electrical transport properties of the perovskite manganites [11].

In this paper, the effect of systematic variation of the A-site ionic radii in Type I-manganites has been studied in order to tune TCR % and T_{MI} for applications in IR cameras. The shift in T_{MI} towards lower temperatures with enhanced TCR % as well as maximum MR % at T_{MI} have been investigated. The present study is focussed to control the TCR % through internal chemical pressure induced effects for applications in night vision infrared detectors.

2. Experimental details

The polycrystalline compounds of $La_{0.7-x}Eu_xSr_{0.3}MnO_3$, where $x = 0$ (LESMO 0), 0.1 (LESMO 1), 0.2 (LESMO 2) and 0.3 (LESMO 3), are synthesized by solid state reaction route using ingredients La_2O_3, Eu_2O_3, $SrCO_3$ and Mn_2O_3. Stoichiometric amount of starting compounds are ground several hours and calcined at 1000 °C, 1100 °C and 1200°C for 12 hours with intermediate grinding steps. The polyvinyl alcohol (PVA) is mixed with the calcined powder and pressed into rectangular pellets by applying a load of 2 tons. These pellets are heated at 500 °C for one hour to remove PVA and finally, sintered at 1300 °C for 12 hours. The phase analysis at room temperature is characterized by powder X-ray diffraction (XRD) with Cu K_α radiation at 40 kV and 30 mA (PANanalytic X'pert pro). Microstructural examination is performed by using field emission scanning electron microscopy (FE-SEM, Carl ZEISS SUPRA 40). The cationic stoichiometry ratios are confirmed by energy dispersive X-ray spectrometer (EDS) measurements. Electrical resistivity is measured by indigenously designed four-probe measurement set-

up with and without a magnetic field of 1 tesla (T) over the temperature range from 10-400 K using a closed cycle refrigerator (CCR) and electromagnet.

3. Results and discussion

3.1 XRD results

The crystal structure has been studied by analyzing XRD data using Rietveld method and FULLPROF software [12]. The quality of refinement is evaluated through the goodness of the fit parameter χ^2 as given in Table 1. Rietveld analysis indicates that crystal structure of LESMO 0 is in rhombohedral structure with $R\overline{3}c$ space group. With the substitution of Eu, the structure changes from rhombohedral (for $x = 0$) to orthorhombic (for $x = 0.1$ to 0.3) with *Pnma* space group. Neila Dhahri et al. [13] observed that the crystal structure of $La_{0.67-x}Eu_xSr_{0.33}MnO_3$ compound exhibits rhombohedral structure with $R\overline{3}c$ space group up to $x = 0.3$. Further, it is reported that crystal structures of $La_{0.5}Eu_{0.2}Sr_{0.3}MnO_3$ [14] and $La_{0.4}Eu_{0.3}Sr_{0.3}MnO_3$ [15] are in orthorhombic structure with *Pnma* space group. However, our Rietveld refinement indicates that crystal structure of $La_{0.7-x}Eu_xSr_{0.3}MnO_3$ changes to orthorhombic structure with *Pnma* space group with $x \geq 0.1$. The refined lattice parameters are given in Table 1. Smaller ionic size of Eu^{3+} substitution in place of La^{3+} decreases the tolerance factor from 0.9601(for LESMO 0) to 0.9519 (for LESMO 3) which in turn increases lattice distortion leading to oxygen ion displacement along [110] in pseudocubic pervoskite [10]. Oxygen ion displacement along [110], to release the developed strain decreases Mn-O-Mn bond angle from ideal 180°, which is consistent with our refinement. A distortive structure promotes the charge localization mechanism and suppresses the carrier hopping between Mn^{3+} and Mn^{4+} sites which in turn leads to increase in resistivity.

The SEM micrographs of polycrystalline compounds $La_{0.7-x}Eu_xSr_{0.3}MnO_3$ with $x = 0, 0.1\ 0.2$ and 0.3 are shown in Fig. 2(a). All compounds show very good grain connectivity. Furthermore, it can be observed from the microstructures of SEM images that the grain boundaries are increasing with the substitution of Eu. The increase in grain boundaries decreases the inter-grain conduction process which is consistent with electrical resistivity observations. A typical EDS spectrum of LESMO 2 compound to confirm the cationic stoichiometry ratios is presented in Fig. 2.

3.2 Transport properties

The temperature dependent resistivity of different compounds is shown in Fig. 3 within the temperature range 10-400 K. All compounds exhibit metal-semiconductor/insulator (T_{MI}) transition at different temperatures. The T_{MI} decreasing from 390 K (for $x = 0$) to 240 K (for $x = 0.3$) with substitution of Eu. This is attributed to the fact that the average radius $<r_A>$ of A-site decreases from 1.384 Å (for $x = 0$) to 1.360 Å (for $x = 0.3$) with the substitution of Eu. In perovskite manganites, as $<r_A>$ decreases the effective A-site cation radius distribution (σ^2) increases, that results in an enhanced disorder in the lattice. The lattice disorder decreases the Mn-O-Mn bond angle and the Mn-O bond distances as confirmed from structural study. The decrease in Mn-O-Mn bond angle suppresses the charge carrier hopping, which in turn favors the e_g electrons to be in the localized states. Therefore, the hopping amplitude of carriers from Mn^{3+} to Mn^{4+} decreases due to the suppression of delocalized hopping sites. In the case of 30% Eu substituted (LSEMO 3), the increase in resistivity with sharp T_{MI} is observed which is caused by suppression of delocalized hopping sites.

As discussed earlier, TCR is one of the important parameters to improve the sensitivity of uncooled infrared microbolometer. In this study, with the substitution of Eu, TCR percentage value increases from 1.1(for LESMO 0) to 3.36 (for LESMO 3), as shown in Fig. 4. Enhanced TCR in comparison to parent compound (LESMO 0) is attributed to the decreasing of average A-site ionic radius. It can be observed in Fig. 5 that the T_{MI} is shifting to lower temperature as $<r_A>$ is decreasing, but TCR% values are increasing. These values are comparable to

vanadium oxide (-2 to-4 %) [16] and amorphous silicon (-2.1%)[17], which are commonly used for infrared detectors.

Temperature dependent resistivity can be classified into two regimes: low temperature $T < T_{MI}$ and high temperature $T > T_{MI}$. In the case of $T < T_{MI}$, TCR is positive (i.e. $\frac{d\rho}{dT} > 0$ metallic like behaviour), while for $T > T_{MI}$, it is negative (i.e. $\frac{d\rho}{dT} < 0$ semiconductor/insulator like behaviour).

The temperature dependent resistivity (semiconductor/Insulator region) above $T > T_{MI}$ is explained by adiabatic small polaron hopping model $\rho = \rho_0 T \exp(\frac{E_P}{k_\beta T})$, where ρ_0 is residual resistivity and E_P is the polaron hopping energy. Polaron hopping energy (E_P) of the compound has been determined from the slopes of $\ln(\rho/T) \, vs \, 1/T$ curves presented in Fig. 6. The measured polaron hopping energies for LESMO 1, LESMO 2 & LESMO 3 are 72.88 meV, 74.60 meV and 139.14 meV, respectively. In this model, we did not apply polaron hopping model to LESMO 0, because it has less resistivity measurement data after T_{MI}. The increase in polaron hopping energy decreases the electron hopping between mixed valence manganese ions (Mn^{3+} and Mn^{4+}). It can be concluded that the estimated polaron hopping energy values increase with substitution, which can be attributed to the increase in the internal chemical pressure induced lattice disorder.

3.3 Magnetoresistance

Magnetoresistance is defined as $\%MR = 100*(\{\rho(0,T) - \rho(H,T)\}/\rho(0,T))$, where $\rho(H,T)$ and $\rho(0,T)$ are the resistivities with and without a magnetic field H, respectively. The application of external magnetic field strongly supresses the resistivity and shift the T_{MI} to higher temperatures. This can be due to fact that applied magnetic field induces delocalization of charge carriers, which in turn reduces the resistivity and also causes the local ordering of the magnetic spins. The ferromagnetic metallic state may evolve at the expense of the paramagnetic semiconductor/insulating state due to the establishment of long range magnetic ordering. As a result, the hopping electrons (e_g) completely polarized inside the magnetic domains and are easily hop between Mn^{3+} and Mn^{4+} via oxygen which will influence the MR behaviour. It is shown in Fig. 7 with the substitution of Eu, the maximum magnetoresistance enhanced from 17% (for LESMO 0) to 42% (for LESMO 3). T_{MI} shift towards higher temperatures and enhanced magnetoresistance are well correlated with variation in internal chemical pressure [18, 19]. The enhanced magnetoresistance in the presence of small magnetic field is useful for magnetic information storage devices [20].

4. Conclusions

The polycrystalline compounds $La_{0.7-x}Eu_xSr_{0.3}MnO_3$ with $x = 0$, 0.1, 0.2 and 0.3 are prepared by solid state reaction route. Substitution of Eu shifts T_{MI} from 390 K (for LESMO 0) to 240 K (for LESMO 3). With the decrease of $<r_A>$, the TCR % value increases from 1.1% (for LESMO 0) to 3.36 % (for LESMO 3). Small polaron hopping energies, low field magnetoresistance and TCR% values are increased which are attributed to the increase in lattice distortion with the substitution of Eu. It can be concluded that the physical properties of the manganites can be tuned by variation in internal chemical pressure for desired applications such as infrared detectors, memory devices, etc.

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Figure Captions

Fig. 1. XRD patterns of $La_{0.7-x}Eu_xSr_{0.3}MnO_3$ compounds where $x = 0, 0.1, 0.2$ & 0.3.

Fig. 2. (a) SEM micrographs of $La_{0.7-x}Eu_xSr_{0.3}MnO_3$ where $x = 0, 0.1, 0.2$ & 0.3, 2(b) (magnification at 10 KX) the energy dispersive X-ray spectrum of LESMO 2 compound.

Fig. 3. Temperature dependent resistivity without and with magnetic field (1 tesla).

Fig. 4. Temperature variation of TCR % for the $La_{0.7-x}Eu_xSr_{0.3}MnO_3$ ($x = 0, 0.1, 0.2$ & 0.3) compounds.

Fig. 5. Maximum TCR% and T_{MI} with respect to A-site ionic radius.

Fig. 6. Fitted curves of $\ln(\rho/T)\, vs\; 1/T$ for adiabatic small polaron hopping model above T_{MI}.

Fig. 7. Magnetoresistance vs Temperature with in the field of 1 tesla.

Table Captions
Table 1
Lattice parameters, bond angles, A-site cation radius distribution (σ^2), A-site average radius $<r_A>$, and Tolerance factor (τ) of $La_{0.7-x}Eu_xSr_{0.3}MnO_3$ where $x = 0, 0.1\; 0.2$ & 0.3.