

Magnetotransport of $\text{La}_{0.70}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3(\text{Ag})$: A potential room temperature bolometer and magnetic sensor

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Here we report the optimized magnetotransport properties of polycrystalline $\text{La}_{0.70}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3$ and their composites with Ag. The optimization was carried out by varying the Sr and Ag contents simultaneously to achieve large temperature coefficient of resistance (TCR) as well as low field magnetoresistance (MR) at room temperature. Sharpest paramagnetic (PM)-ferromagnetic (FM) and insulator-metal (IM) transition is observed in the vicinity of the room temperature ($T_C \approx 300 \text{ K} \approx T_{\text{IM}}$) for the composition $\text{La}_{0.70}\text{Ca}_{0.20}\text{Sr}_{0.10}\text{MnO}_3:\text{Ag}_{0.20}$. Partial substitution of larger Sr^{2+} ions at the Ca^{2+} ions sites controls the magnitude of the FM and IM transition temperatures, while the Ag induces the desired sharpness in these transitions. For the optimized composition, maximum TCR and MR are tuned to room temperature (300 K) with the former being as high as 9% and the later being $\sim 20\%$ and $\sim 30\%$ at 5 and 10 kOe magnetic fields respectively. Such sharp single peak (TCR $\sim 9\%$) at room temperature can be used for the bolometric and infrared detector applications. The achievement of large TCR and low field MR at $T \sim 300 \text{ K}$ in polycrystalline samples is encouraging and we believe that further improvements can be achieved in thin films which by virtue of their low conduction noise are more suitable for device applications. © 2010 American Institute of Physics. [doi:10.1063/1.3365412]

I. INTRODUCTION

Manganites with general formula $\text{A}_{1-x}\text{A}'_x\text{MnO}_3$ (where A=rare earth element and A' =Alkaline earth metals) are a focal point of research since a long time.¹ These compounds are considered to be promising material for the technological opinion.¹⁻³ Among all fascinating properties, the most outstanding and extensively explored assets are the magnetoresistance (MR) and temperature coefficient of resistance (TCR). MR is the relative change in the electrical resistivity by application of magnetic field and similarly TCR is parametric notation of transition sharpness, defined as, $[1/R*(dR/dT)]$, where R and T are the resistance and temperature, respectively. It is seen that the maximum MR as well as TCR in hole-doped manganites occur near the metal-insulator (MI) transition (T_{MI}) being accompanied with ferromagnetic (FM)-paramagnetic transition. The steep transition about MI crossover determines the sensitivity as well as active zone for these sensors. Practically one desires to have higher TCR and MR near room temperature, i.e., at 300 K.

In this direction there had been various trials before and TCR as high as above 10% and reasonable MR is seen in

$\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3:\text{Ag}_y$ composites.⁴⁻⁶ However the high TCR and optimized reasonable MR, in particular at low fields is always seen at below room temperature ($<265 \text{ K}$) only.⁴⁻⁷ As mentioned before for practical use of manganites as sensors, one aspires for high TCR and MR at room temperature. Though, the working temperature could be enhanced to near room temperature in case of $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{Ba}_x\text{MnO}_3$, the observed values of TCR and MR are reasonably good, but could not improved a lot with silver addition.⁸ In fact our earlier efforts in case of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$, we were not successful.⁹ In view of our consistent approach to improve room temperature TCR and low field MR (LFMR) in the case of pristine⁵ and Ba doped⁸ silver composites, in the present paper we deliberate on Sr doped $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and their Ag added compounds. For optimized composition of $\text{La}_{0.7}\text{Ca}_{0.20}\text{Sr}_{0.10}\text{MnO}_3:\text{Ag}_{0.2}$, the maximum TCR and MR are tuned to 300 K with the former being as high as 9%/K and the later being above 20% at 5 kOe and 30% at 10 kOe field. Although the studied samples are bulk in nature, the thin films fabricated from these bulk targets will serve the ultimate purpose of manganite being used as potential magnetic sensors at room temperature. Further above 9%/K single peak sharp TCR at 300 K can be used for the bolometric and infrared applications. Improved TCR ($>9\%$) and MR ($>20\%$ at 5 kOe) at 300 K is the maximum yet reported for any manganite at room temperature or above.

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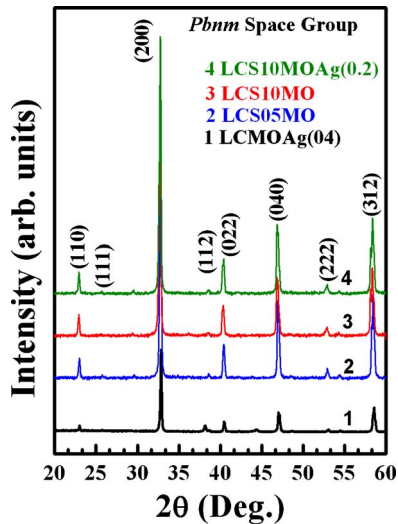


FIG. 1. (Color online) XRD pattern of $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3:\text{Ag}_{0.4}$, $\text{La}_{0.7}\text{Ca}_{0.25}\text{Sr}_{0.05}\text{MnO}_3$, $\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3$, and $\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3:\text{Ag}_{0.2}$.

II. EXPERIMENTAL DETAILS

The samples of the series $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3:\text{Ag}_y$ ($x = 0.0, 0.05, \text{ and } 0.10$; $y = 0, 0.1, 0.2, 0.3, \text{ and } 0.4$) are synthesized by solid-state reaction route using ingredients La_2O_3 , CaCO_3 , SrCO_3 , MnO_2 , and Ag (powder). The mixed powders were calcined at 1000, 1100, and 1200 °C in air for 24 h and followed by thorough grinding each time. Then the powders were presintered at 1300 °C in air for 24 h. Finally the pelletized ceramics were annealed in air for 24 h at 1400 °C. For loading of oxygen, the pellets were annealed in the flow of oxygen at 1100 °C for 12 h and subsequently slow cooled to room temperature. The structure and phase purity of the samples were analyzed by powder x-ray diffraction (XRD) taken on Rigaku miniflex diffractometer. The $R(T)$ measurements with and without magnetic field (< 14 T) were carried out using four-probe method in the temperature range of 5–400K on a Quantum Design Physical Property Measurement System.

III. RESULTS & DISCUSSION

Figure 1 depicts the room temperature XRD patterns of $\text{La}_{0.7}\text{Ca}_{0.25}\text{Sr}_{0.05}\text{MnO}_3$ (LCS05MO), $\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3$ (LCS10MO), $\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3:\text{Ag}_{0.2}$ [LCS10MOAg(0.2)], along with earlier studied $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3:\text{Ag}_{0.4}$ [(LCMOAg(0.4)).⁵ All the studied samples are crystallized in near single phase along with some silver lines in Ag added compounds. Details of structural refinements along with lattice parameters variations will be reported else where in full paper.¹⁰

The normalized resistance ($R_T/R_{400\text{ K}}$) plots for various Ca/Sr substituted and Ag added LaMnO_3 samples are shown in Fig. 2. As it is well known that $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ has high MI transition temperature (T_{MI}) than $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. This change in the transition temperature with divalent ions (Ca, Sr) substitution is related to the variation in Mn–O–Mn bond angle governs by the ionic size of the dopant. Tilting of Mn–O bond directly affects the electron hopping amplitude from one Mn site to another Mn site in these compounds. So,

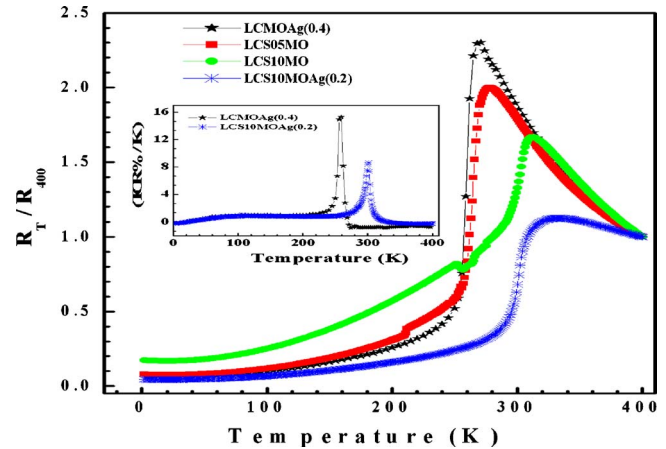


FIG. 2. (Color online) Normalized $R(t)$ plots of $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3:\text{Ag}_{0.4}$, $\text{La}_{0.7}\text{Ca}_{0.25}\text{Sr}_{0.05}\text{MnO}_3$, $\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3$, and $\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3:\text{Ag}_{0.2}$. Inset shows the TCR percent as a function of temperature for $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3:\text{Ag}_{0.4}$ and $\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3:\text{Ag}_{0.2}$.

by proper optimization of Sr and Ca concentration one can easily tune the T_{MI} to room temperature. As shown is Fig. 2, the T_{MI} increases with Sr concentration in $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3$. But the sharpness of transition decreases that could be recovered by reducing the intergrain tunnel resistance. As in FM/metallic region the intergrain barrier in granular perovskite behaves as nonmagnetic as well as nonconducting. So the double-exchange interaction, which is often used to explain the conductive behavior of manganite, becomes weaker on the surfaces of grains. However with the help of external field or by producing a conducting channel between the grains the tunnel resistance can be reduced. It is believed that if it may possible than granular perovskite can have large value of TCR and can behave like tunnel-GMR. In order to enhance the sharpness/intergrain conductivity, silver has been added to the pristine samples. Metallic silver having low melting point will help during sintering process (liquid phase sintering) and also segregates at the grain boundaries creating conducting channels. The SEM micrograph of pure and Ag-doped sample of LCS10MO are shown on Figs. 3(a) and 3(b). These figures clearly indicate that sample with silver as additives have better grain growth and connectivity. The T_{MI} remains nearly constant with silver addition^{5,8} though sharpness improves. Inset is showing the TCR (measure of sharpness) as a function of temperature for LCMOAg(0.4) and LCS10MOAg(0.2) composition. The maximum TCR ($\sim 15\%/K$) is obtained for LCMOAg(0.4) but below room temperature. For uncooled operations, room temperature high TCR is required. A $\sim 9\%/K$ value of TCR above room temperature is obtained for LCS10MOAg(02), which is the optimum value of TCR achieved in the case of $\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3:\text{Ag}_y$ compounds. In polycrystalline bulk samples, a $\sim 9\%/K$ value above room temperature is quite reasonable. Moreover, further optimization of samples as a thin film can yield good and encouraging results for application purposes.

As far as magnetic measurements are concerned, in $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3:\text{Ag}$ system, the para-FM transition temperature (T_C) remains almost constant for all compositions.⁵ But

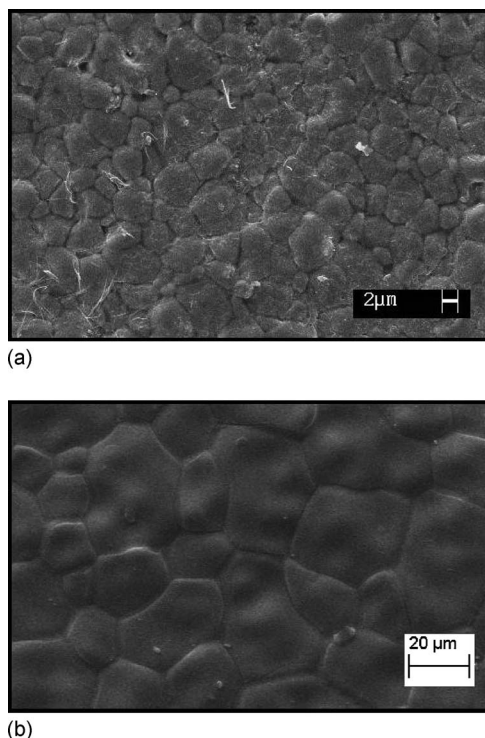


FIG. 3. SEM micrograph of (a) $\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3$ and (b) $\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3:\text{Ag}_{0.2}$.

T_C varies slightly for $\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3+\text{Ag}_y$ ($y=0, 0.2, 0.3,$ and 0.4) compounds. The variation in T_C can be correlated with slight substitution of Ag into the main matrix (Sr being larger) or to the concept of mixed phase in manganites.¹¹ As shown in Fig. 4, there is large change in the resistivity values of $\text{LCS10MO}(\text{Ag}0.2)$ with applied field. The change in the resistivity with applied field has been calculated in terms of MR (inset Fig. 3). For application point of view, LFMR is required since high magnetic fields are not easily accessible. In our samples, high MR at low field has been observed for LCS10MO silver samples. For $\text{LCS10MOAg}(0.2)$ samples, the observed MR is about $\sim 30\%$ at room temperature under applied field of 10 kOe which is quite high at room temperature under low field. The maximum MR value for pristine $\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3$ is nearly 16% (10 kOe) and that of $\text{LCMOAg}(0.4)$ is 10% (10 kOe) at 300 K. With such a high LFMR values for

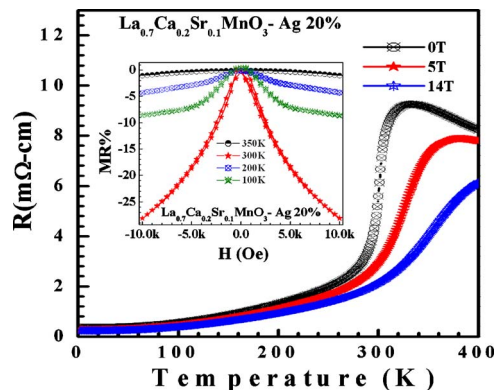


FIG. 4. (Color online) Resistivity plots of $\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3:\text{Ag}_{0.2}$ under applied field of 0, 7, and 14 T. Inset shows MR percent of $\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3:\text{Ag}_{0.2}$ at fixed temperatures of 100, 200, 300, and 350 K.

$\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3:\text{Ag}_y$, with optimum value at $\text{Ag}(0.2)$, can be explored and further optimized for industrial purposes.

In summary we have optimized both high TCR ($\sim 9\%/K$) and LFMR ($\sim 30\%$ at 10 kOe) at room temperature for $\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3+\text{Ag}(0.2)$ compound. The studied materials could be the potential candidates for room temperature bolometer (high TCR) and magnetic sensor (high MR).

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