

Enhanced TCR with room temperature T_{MI} for potential application in microbolometer

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Abstract—Polycrystalline samples $Nd_{0.5}La_{0.2}Sr_{0.3}MnO_3$ (NL) and $Nd_{0.5}La_{0.2}Sr_{0.3}MnO_3+0.2Ag$ (NL+Ag) are prepared by solid state reaction technique. These compounds are found to be crystallized in orthorhombic structural form. On addition of silver (Ag), the temperature coefficient of resistance (TCR) is significantly improved near the metal-semiconductor/insulator transition (T_{MI}) temperature. The T_{MI} is increased from 288 K (for NL) to 302 K (for NL+Ag). Enhancement in TCR is explained on the basis of the grain growth and their connectivity. The reduction in grain boundaries between grains improved the conduction process. High TCR (5.1%) and room temperature T_{MI} of NL+Ag sample are useful characteristics for MEMS-based uncooled microbolometer for infrared detection.

Index Terms—TCR, T_{MI} , microbolometer, polaron hopping energy and magnetoresistance.

I. INTRODUCTION

Hole doped perovskite manganite oxides $R_{1-x}A_xMnO_3$ have received significant attention due to their ability to switch the conductance between two states at metal-semiconductor/insulator transition temperature (T_{MI}). This switching behavior is a useful property for the development of many electronic devices (e.g. memory devices) [1-5]. In terms of technological application, extremely explored effects are colossal magneto resistance (CMR) and temperature coefficient of resistance (TCR) for spin dependent sensors and infrared detectors, respectively. The CMR is defined as relative change of electrical resistivity in the presence of magnetic field and the TCR is described as $\%TCR = \frac{1}{\rho} \left(\frac{d\rho}{dT} \right) * 100$. High TCR around the vicinity of room temperature T_{MI} is a thrust to realize an uncooled infrared microbolometer with improved sensitivity. The fact that these substituted manganites procure high temperature coefficient of resistance (TCR) in bulk as well as in thin films at room temperature that makes them useful for infrared radiation detectors (i.e. IR detector) for night vision applications [6].

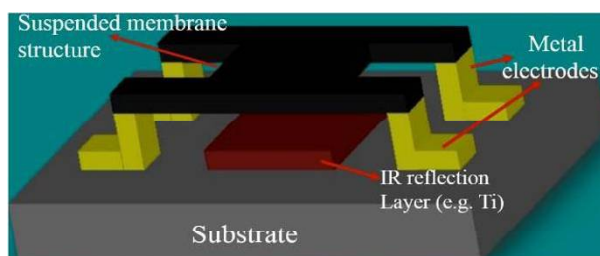


FIG.1. Schematic view of MEMS-based infrared microbolometer

The schematic design of a microelectromechanical system (MEMS) based uncooled microbolometer is illustrated in Fig.1. In this design, suspended membrane should be an IR sensing layer (i.e. thermally sensitive resistive material perovskite manganite). The isolation of this membrane from substrate reduces thermal conductivity between sensing layer and substrate. In this design, membrane structure acts as one pixel and is connected to the substrate by metal electrodes. The speed of infrared detection is improved by design of metal electrodes with smaller dimensional width. This will help to decrease thermal response time and improve the detection speed of infrared radiation. The resistance change of a membrane will be converted to a voltage or current signal by electronic read-out of two dimensional arrays of microbolometers that can be accepted by IR camera circuitry.

This study is focused to develop the manganites with high TCR values and room temperature T_{MI} for uncooled microbolometer.

II. EXPERIMENTAL DETAILS

The polycrystalline samples $Nd_{0.5}La_{0.2}Sr_{0.3}MnO_3$ (NL) and $Nd_{0.5}La_{0.2}Sr_{0.3}MnO_3 + 0.2Ag$ (NL+Ag) are synthesized by solid state reaction route, using ingredients Nd_2O_3 , La_2O_3 , $SrCO_3$, Mn_2O_3 and Ag_2O . The stoichiometric amount of mixed powders are grinded several hours and calcined at $1000^\circ C$, $1100^\circ C$ and $1200^\circ C$ for 12 hours with intermediate grinding. Thereafter, freshly prepared poly vinyl alcohol (PVA) binder solution homogeneously mixed with calcined powder to improve the densification of samples. PVA mixed calcined powder is pressed into rectangular pellets by applying a load of 2 tons. These pellets are heated at $500^\circ C$ for one hour to remove PVA and sintered at $1300^\circ C$ for 12 hours in box furnace. The crystalline phase at room temperature is characterized by powder X-ray diffraction (XRD) with $Cu K_\alpha$ radiation at 40 kV and 30 mA. Micro structures of samples are taken by field emission scanning electron microscopy (FE-SEM). Electrical resistivity of samples is measured by using four-probe technique with and without magnetic field of 1Tesla from 10–350 K using a closed cycle refrigerator (CCR) and electromagnet. A Keithley 6221 AC/DC current source is used to supply current (2 mA) to samples. Keithley 2182A Nano voltmeter is used to measure small voltage drop across the samples. Initially, samples are mounted on an oxygen purity copper block located in a vacuum cryostat that is attached to a CCR. The temperature of an oxygen purity copper block is controlled by Cernox sensor.

III. RESULTS & DISCUSSION

The XRD patterns of polycrystalline manganites $\text{Nd}_{0.5}\text{La}_{0.2}\text{Sr}_{0.3}\text{MnO}_3$ (NL) and $\text{Nd}_{0.5}\text{La}_{0.2}\text{Sr}_{0.3}\text{MnO}_3+0.2\text{Ag}$ (NL+Ag) samples prepared by solid state route are shown in Fig.2. From the analysis of XRD results, NL and NL+Ag samples are found to crystallize in orthorhombic (PCPDF Ref No 861534) structure with space group $Pnma$. It can be observed from the XRD patterns, peaks are slightly shifted toward higher angle side in silver added (i.e. NL+Ag) sample. This small shift may be due to generation of internal chemical pressure within the lattice.

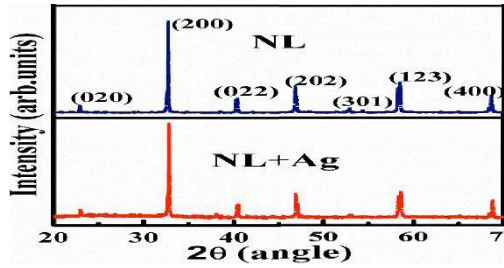


FIG.2. Room temperature XRD patterns of NL and NL+Ag samples

Lattice constants of NL and NL+Ag samples are calculated by least square fitting method. The lattice constants of NL and NL+Ag samples are respectively, $a = 5.455\text{Å}$, $b = 7.727\text{Å}$, $c = 5.454\text{Å}$ & $a = 5.455\text{Å}$, $b = 7.486\text{Å}$, $c = 5.494\text{Å}$. On addition of silver, volume of the lattice is decreasing from 229.96Å^3 (for NL) to 224.39Å^3 (for NL+Ag). The decrease in lattice volume improved the grain growth in Ag-added (i.e. NL+Ag) sample. Density of the samples are measured by using Archimedes principle. On addition of silver, the density of sample is increasing from 6.062 gm/cm^3 (for NL) to 6.303 gm/cm^3 (for NL+Ag). The increase in density will improve better grain growth and connectivity which enhances the conduction process.

The SEM micrographs of NL and NL+Ag sample are shown in Fig.3. The microstructure of silver added (NL+Ag) sample has better grain growth and connectivity as shown in Fig.3. The reduction in grain boundaries between grains improved the conduction process. Average grain size of NL and NL+Ag samples are varies respectively from $\sim 4\mu\text{m}$ to $\sim 8.5\mu\text{m}$ & $\sim 6\mu\text{m}$ to $\sim 14\mu\text{m}$.

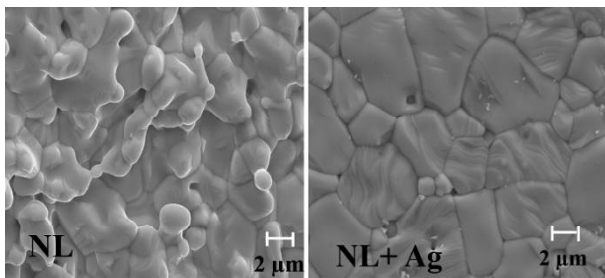


FIG.3. SEM micrograph of NL and NL+Ag sample

The temperature dependent resistivity $\rho(T)$ is measured within the temperature range 10-350 K and shown in Fig.4. $\text{Nd}_{0.5}\text{La}_{0.2}\text{Sr}_{0.3}\text{MnO}_3$ (NL) exhibit T_{MI} at 288 K, while $\text{Nd}_{0.5}\text{La}_{0.2}\text{Sr}_{0.3}\text{MnO}_3+0.2\text{Ag}$ (NL+Ag) at 302K. The T_{MI} is an extrinsic property that depends on synthesis condition and the microstructure of the material [7]. It can be observed that the silver-added sample (i.e. NL+Ag) has sharp T_{MI} around room temperature (i.e. 302 K). Since silver has low melting point, it can act as a catalyst for improving the grain connectivity and grain growth which increase the conduction process between the grains. Due to sharp T_{MI} and grain connectivity, the TCR value of Ag-added sample is enhanced from 2.9% (for NL) to 5.1% as presented in Fig.5. Enhanced TCR with room temperature T_{MI} is inspiring to develop new kind of materials for uncooled infrared microbolometer for the detection of infrared radiation.

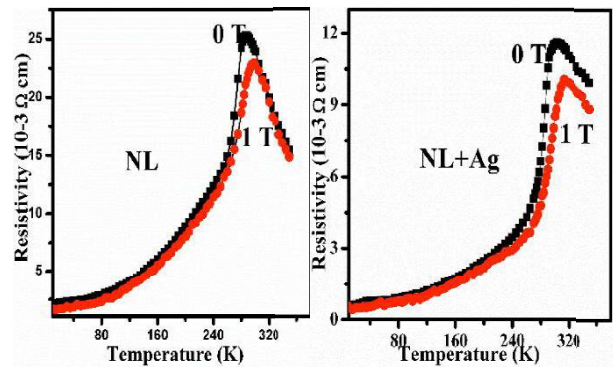


FIG.4. Temperature dependent resistivity with field (1 Tesla) and without field of NL and NL+Ag samples

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

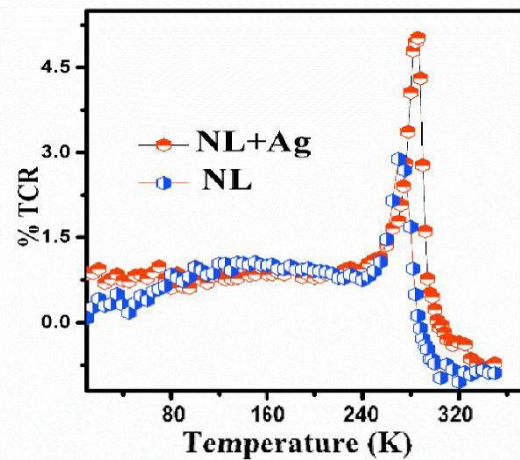


FIG. 5. Temperature dependent %TCR of NL and NL+Ag samples

The temperature dependent resistivity above $T > T_{MI}$ is explained by adiabatic small polaron hopping model $\rho = \rho_0 T \exp\left(\frac{E_p}{k_B T}\right)$. Here ρ_0 residual resistivity and E_p is the polaron hopping energy. Polaron hopping energy (E_p) of the samples has been obtained from the slopes of $\ln(\rho/T)$ vs $1/T$ curves of Fig.6. The measured polaron hopping energies are decreased from 102.55 meV (for NL) to 59.44 meV (for NL+Ag). The decrease in polaron hopping energy enhances the electron hopping between mixed valence manganese ions (Mn^{3+} and Mn^{4+}). These results are clearly supporting an enhanced conduction process in silver added (NL+Ag) sample.

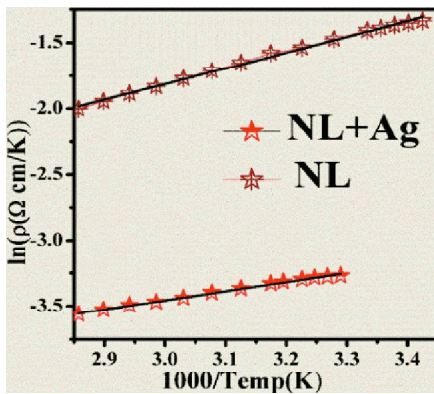


FIG. 6. Fitted curves of the $\ln(\rho/T)$ vs $1/T$ for adiabatic small polaron hopping model $\rho = \rho_0 T \exp\left(\frac{E_p}{k_B T}\right)$ above T_{MI} of NL and NL+Ag samples

Magnetoresistance is defined as $\%MR = 100 * ([\rho(0,T) - \rho(H,T)] / \rho(0,T))$ where $\rho(H,T)$ and $(0,T)$ are measured resistivities with (1Tesla) and without field is shown in Fig 7. Resistivity of the samples is decreasing with the presence of magnetic field and the transition T_{MI} is shifting to higher temperature. High magnetoresistance is observed at vicinity of transition temperature. Near to transition temperature T_{MI} , an external magnetic field can reduce the spin disorder which enhances the electron hopping between the mixed valence manganese ions (Mn^{3+} and Mn^{4+})[8]. This results in a large resistivity drop called as colossal magnetoresistance. In this study silver added sample NL+Ag has high MR value 40% and NL with 23% at near T_{MI} is shown in Fig.7. An enhancement of magnetoresistance (MR) at low magnetic field is the requirement for magnetic recording devices [9]. Low electrical resistivity (good electrical conductivity) will ensure the better connectivity of the device with external circuitry.

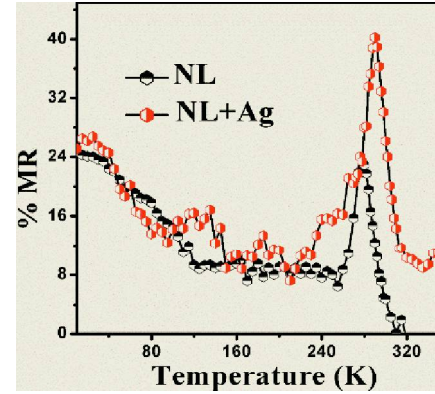


FIG. 7. Magnetoresistance vs Temperature with in the field of 1 Tesla

IV. CONCLUSIONS

In this work, polycrystalline samples $Nd_{0.5}La_{0.2}Sr_{0.3}MnO_3$ (NL) and $Nd_{0.5}La_{0.2}Sr_{0.3}MnO_3 + 0.2Ag$ (NL+Ag) are synthesized by solid state reaction route. The transition temperature T_{MI} found increasing from 288K to 302 K when 20% silver is added to $Nd_{0.5}La_{0.2}Sr_{0.3}MnO_3$. On addition of silver, TCR is increased from 2.9% to 5.1%. Since the sensitivity of bolometer depend on TCR values, high TCR with room temperature T_{MI} will be very helpful for the development of microbolometer with enhanced sensitivity. The improvement in low field magnetoresistance (40% at 1 Tesla) is observed at room temperature in silver addition sample.

V. REFERENCES

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