Polymer Coated Manganites and Its Magnetic Properties

K. Gupta, P. T. Das, T. K. Nath, P. C. Jana, A. K. Meikap

Abstract*— Synthesis and analysis of magnetic properties of polypyrrole coated $La_{0.9-x}Sm_xSr_{0.1}MnO_3$ (x= 0.2) nanoparticles is the main aim of this investigation. About 60% magneto resistance (MR) is obtained for $La_{0.9-x}Sm_xSr_{0.1}MnO_3$ nanoparticles and it decreases with increasing temperature. Enhanced spin-polarized tunneling between two adjacent grains at the grain boundary may increase the MR. Oscillating type of MR is obtained for polypyrrole coated $La_{0.9-x}Sm_xSr_{0.1}MnO_3$. A core shell type model is attributed to an intermediate exchange coupling between the shell (surrounding) and antiferromagnetic core mainly on the basis of uncompensated surface spins. Samples may be used as multifunctional spintronic devices and magnetic recording medium.

Index Terms*— A. Manganites, B. Polypyrrole, C. Oscillating magneto resistance

I. INTRODUCTION

Transitional-metal oxides (TMO) having perovskite structure are known as materials with a variety of interesting properties like electrical transport, magnetic, dielectric, and optical properties. Manganites having perovskite structure are very interesting for their variety of interesting properties like electrical transport, magnetic, dielectric, and optical properties. From a very long period of time important activities are going intensively on perovskite manganites of the form $Re_xAe_{1-x}MnO_3$ where, Re = La, Nd, Pr, etc. trivalent rare-earth ions and Ae = Sr, Ca etc. divalent alkaline earth ions. Giant negative magnetoresistance, temperature dependent metal-insulator transition, magnetic, spin, orbital and charge ordering phenomena have been the subject of extensive research of these materials. Colossal magnetoresistance (CMR) in single crystals [1], thin films [2] and ceramic CMR materials [3] of perovskite manganites have already been investigated for proper explanation and possible application of their magnetic, electrical, and magnetotransport properties. Metal-insulator transition and its probable causes as well as magnetic properties of different doped manganites have already been investigated by different groups [4,5]. It is the unique electronic structure of these material obtained from hybridized Mn 3d and oxygen 2p orbital under the unique structural and chemical environment that these interesting properties may be obtained. Intra atomic exchange and orbital degrees of freedom of the Mn 3d electrons play an essential role for these observations. Various types of structural distortions also influence electronic properties [6]. Manganites are insulating material due to the Jahn Teller distortion of the conduction band. A scheme of the band diagram [7,8] of manganite to show how Jahn Teller (JT) distortion splits the conduction band is shown in Fig.1. These materials can be metallic by reducing JT distortion with hole doping [4,5]. $LaMnO_3$ becomes antiferromagnetically ordered at low temperatures when a small proportion of Mn^{+4} (~5%) is present, but it becomes ferromagnetic due to the decrease in orthorhombic distortion when La^{+3} is progressively substituted by divalent cations as in $La_xA_{1-x}MnO_3$ (A= Ca, Sr or Ba etc.). Simultaneous existence of electrical and ferromagnetism in manganites can be explained by Zener's double exchange mechanism [9]. According to this mechanism hopping of d-hole occur from Mn^{+4} to Mn^{+3} via oxygen so that Mn^{+4} and Mn^{+3} can change their places. Parallel alignment of the spins on Mn^{+3} and Mn^{+4} increases the rate of hopping of electrons and therefore increases its electrical conductivity. Thus enhanced electrical conductivity requires a ferromagnetic coupling. Double exchange depends on structural parameters like Mn-O-Mn angel, Mn-Mn transfer integral. Observed CMR can be explained in terms of double exchange. This CMR also depends on electron-lattice interaction, antiferromagnetic super exchange interaction between t_{2g} local spins, intersite exchange interaction between the e_g orbitals etc [3]. Inspite of a number of models proposed so far, but details mechanism has not been clearly understood. Nanodimensional magnetic materials have been used in miniaturized magnetic sensor applications, medical diagnostic, magnetic recording media, magnetic refrigeration ferrofluids, catalysis, drug delivery system etc. Giant magneto-resistance, superparamagnetism, small coercivity, low Curie temperature, and low-saturation magnetization are obtained when the size of the magnetic particles is reduced to a few nanometers. Thus we are interested in preparing manganites of having nanodimension. Dey et al [10] had prepared $La_{0.7}Ca_{0.3}MnO_3$ and reported its magneto and electronic properties. 23% MR is obtained for their samples. Dey et al [11] also prepared $La_{0.67}Sr_{0.33}MnO_3$ and almost 20% MR is obtained. We are interested to enhance the MR of the manganites by varying the composition of 'A' site of the manganite and with this aim, we have doped $LaSrMnO_3$ with samarium which is a rare earth element having different peculiarities with respect to magnetic ground state to get increasing MR. As a result huge increase in MR is

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obtained for our samples. Importance in the inorganic-organic nanocomposite is growing rapidly because of their wide range of use. Conducting polymers has emerged as one of the thrust areas in experimental research [12-14]. Polypyrrole (PPy), polythiophene, polyaniline, etc. can be

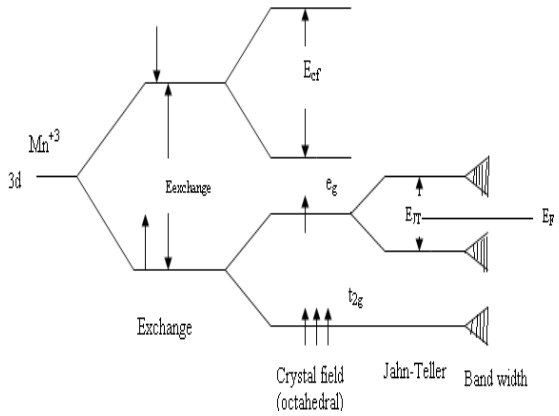

Figure.1 Jahn Teller (JT) distortion in the conduction band

used as the conducting organic part in this inorganic-organic nanocomposite. We have especially selected polypyrrole for our investigation because of its easy synthesis, good atmospheric stability, high conductivity and also tunable electrical, optical, magnetic and chemical properties along with large variety of applications. Beside this, surface modification has also been done by using polypyrrole [15,16]. We have previously synthesized polyaniline coated $La_{0.67}Sr_{0.33}MnO_3$ and a huge increase (73%) in MR is obtained. We [17] are thus interested to synthesize polypyrrole-$La_{0.9-x}Sm_xSr_{0.1}MnO_3$ nanocomposite and compare their magnetoresistance with uncoated $La_{0.9-x}Sm_xSr_{0.1}MnO_3$. We have started our investigation with the aim to increase in magnetoresistance because it is necessary to increase magneto-resistance for a good Giant Magnetoresistance sensing device. Interestingly, oscillating magnetoresistance has been observed in polypyrrole coated $La_{0.9-x}Sm_xSr_{0.1}MnO_3$ which has not been reported earlier. This type of observation is rare and more interesting with respect to application. Chang et al [18] had proposed theoretically an oscillating MR in diluted magnetic semiconductor barrier structures. Mamani et al [19] had reported experimentally and theoretically the nonlinear transport and oscillating MR in double quantum wells in the region of magnetic fields below 1 T. These type of materials are thus of great importance as they may be used in multifunctional spintronic devices and as magnetic recording media.

II. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUES

High-purity Samarium oxide (Sm_2O_3), Lanthanum oxide (La_2O_3), Manganese acetate $Mn(CH_3COO)_2$, and Strontium nitrate $Sr(NO_3)_2$ were used in this investigation. Pyrrole, triethanolamine (TEA), Cetyltrimethyl ammonium bromide (CTAB, a surfactant), ammonium peroxodisulphate (APS), acetone, ethanol were used as received from the market and purified as required for the investigation. Polypyrrole-$La_{0.9-x}Sm_xSr_{0.1}MnO_3$ nanocomposite (PLSSMO) was prepared by two-step method. In the first step, we had prepared $La_{0.9-x}Sm_xSr_{0.1}MnO_3$ (LSSMO) nanoparticles by "pyrophoric reaction process" similar to Dey et al [10]. In the second step, coating of these LSSMO samples was done by a typical in situ chemical oxidative polymerization of polypyrrole. LSSMO powders were dispersed in CTAB (a surfactant) by sonication for 2 hours. Pyrrole was added to this solution at room temperature (300C) and then aqueous solution of APS (an oxidant) was added drop wise for 30 minutes to this solution. The color of the solution became black. The solution kept in refrigerator at rest for 24 hours to complete the polymerization process. The solid mass obtained was washed with acetone, ethanol and double-distilled water.

The phase identification of the fine powdered composite and polymer was performed using X 'Pert pro X-ray diffractometer with nickel filter and Cu kα radiation (λ=1.5414 Å) with 2θ ranging from 20 to 700. Field-emission scanning electron microscope (FESEM) image of the samples were recorded at room temperature to investigate the particle size and microstructure of the samples. The temperature-dependent dc resistivity and magnetoresistance were measured using a pellet of individual sample by four-probe method at 3 mA sample current in the temperature range of 2 to 300K employing a closed cycle helium refrigeration cryostat.

III. RESULTS AND DISCUSSION

To verify the nanodimension of the each individual constituent particle of LSSMO powders the structural characterization was done through x-ray diffraction (Fig.2) and

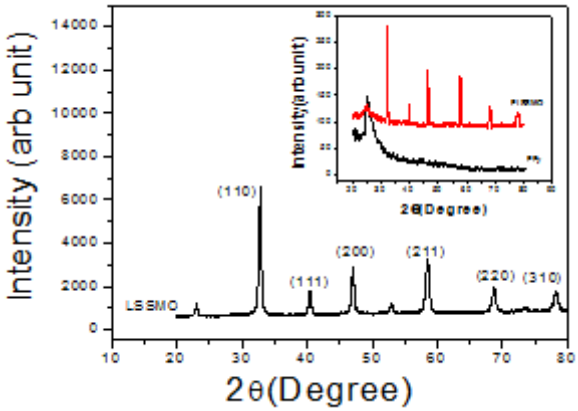

Figure.2 XRD spectrum of PPy, LSSMO, PLSSMO

field emission scanning electron microscopy (FESEM, Fig.3). The as-prepared precursor powders were amorphous but single phase LSSMO nanocrystalline powders were obtained after heating at 750°C. Peaks were indexed on the basis of orthorhombic cell with Pbnm space group symmetry.

Dey et al [10] had obtained a similar type of indexing of the crystalline phase of $La_{0.7}Ca_{0.3}MnO_3$. These peaks were arised from the finite number of diffracting planes present inside the samples.

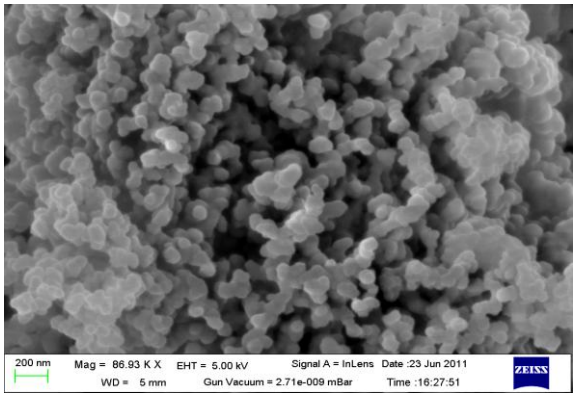

Figure.3 FESEM of PLSSMO

Average grain size calculated by the Scherrer's formula lies in the range 30-35 nm for LSSMO. Inset of Fig.2 shows XRD pattern of pure polypyrrole (PPy) and polypyrrole coated LSSMO nanoparticles (PLSSMO). PPy is amorphous in nature
but peaks obtained in the composite are due to the presence of LSSMO nanoparticles. Grain sizes in PLSSMO samples lie in between 40-50 nm and this increase in grain size may be due to PPy coating. Fig.3 shows the morphology of the PLSSMO. FESEM image shows granular morphology of PLSSMO. Grain size of PLSSMO is 40-50 nm.

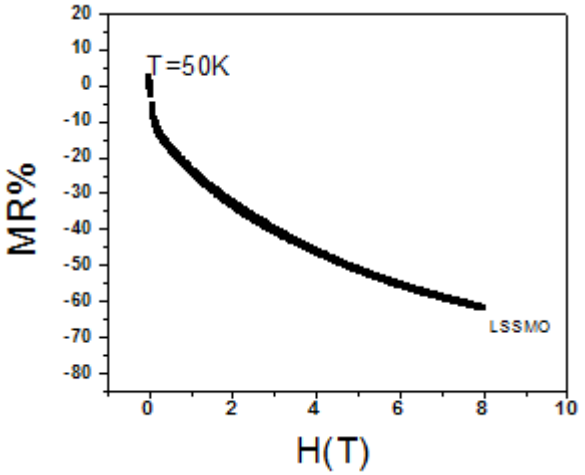

Figure.4 MR% of LSSMO

MR measurement is done by a disc shaped nanocrystalline LSSMO and PLSSMO samples. In Fig.4 we have plotted the field dependent MR of different LSSMO nanoparticles, at 50K.
About 60% MR is obtained for $La_{0.9-x}Sm_xSr_{0.1}MnO_3$. This exhibits the usual behavior of polycrystalline samples with a large negative MR at very low-field regime, followed by a slower varying of MR at comparatively high field regime. It is observed that MR decreases with increase in temperature. Dey et al (10,11) obtained 18-20 and 23% MR for $La_{0.67}Sr_{0.33}MnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ respectively. Xie et al [20] obtained 44-52% MR for $La_{2/3-x}Eu_xCa_{1/3-y}Sr_yMnO_3$. To obtain the temperature dependence of MR for LSSMO nanoparticles, we have separated the part of MR originating from the spin-polarized tunneling (MRSPT) from the part of the MR identified by the suppression of spin fluctuation (MRINT) by a model as proposed by Raychaudhuri et al [21,22]. It is based on spin-polarized transport of conduction electrons at the grain boundaries for the motion of magnetic domain-wall at grain boundaries in presence of magnetic field. It is the proposal of Helman and Abeles [23] which extends the idea about

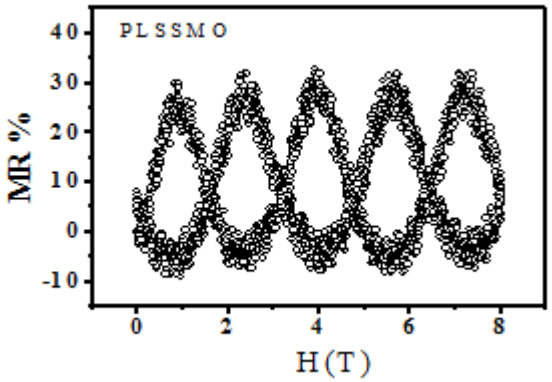

Figure.5 MR% of PLSSMO

spin-polarized tunneling. This model describes the magnetic-field dependence of MR taking gradual slippage of domain walls across the grain-boundary pinning centers at applied magnetic field. According to this model

$$MR = -A\int_0^H f(k)dk - JH - kH^3 \quad (1)$$

where k is the pinning strength of the domain boundaries pinned at the grain-boundary pinning centers in zero field. Grain boundaries have a distribution of pinning strengths (defined as the minimum field needed to overcome a particular pinning barrier) given by f (k) expressed as

$$f(k) = A\exp\left(-Bk^2\right) + Ck^2\exp\left(-Dk^2\right) \quad (2)$$

A, B, C, D, J, and k are fitting parameters .MRSPT can be calculated from

$$MR_{SPT} = -\int_0^H f(k)dk \quad (3)$$

We have fitted Eq.(1) to MR curves of LSSMO nanoparticles in a similar way as Raychaudhuri et al have done. Differentiating Eq. (1) with respect to H and putting Eq.(2) we get

$$\frac{d(MR)}{dH} = A\exp\left(-BH^2\right) + CH^2\exp\left(-DH^2\right) - J - 3kH^2 \quad (4)$$

Experimental (MR-H) curves are differentiated and fitted to Eq. (4) for finding out the best-fit parameters at several temperatures. Using these best-fit parameters we have fitted Eq.(1) with experimental MR vs. H curves of LSSMO and an excellent fit is obtained. The values of experimental MR, MR_{SPT} [calculated using Eq.(3)] and MR_{INT} are 60.0 , 51.6 and 8.4 at 50K.

Fig.5 shows the variation of MR of the PLSSMO nanocomposite with magnetic field at different temperatures. A typical oscillating type of magnetoresistance is obtained in PLSSMO. Fig.5 shows variation of MR with magnetic field for PLSSMO. It is observed that MR oscillates with varying magnetic field in these temperatures. This oscillating type of behavior can be accounted from the proposed phenomenological core-shell type of model based on the disordered surface obtained due to polypyrrole coating in the nanograin. Core region is ordered and does not take part in oscillation, but oscillation takes place in between shell and the disordered surface. Oscillation occurs due to intermediate localization (competition between weak localization and delocalization) i.e. deviation of antiferromagnetic ordering in presence of polypyrrole. At very low temperature polypyrrole behaves as dielectric material and at this low temperature spin state remain ordered. A negligible deviation from antiferromagnetic ordering occurs. At high temperature deviation of spin from antiferromagnetic ordering occurs more in presence of polypyrrole.

IV. CONCLUSION

Polypyrrole coated manganite nanocomposite shows oscillating MR. Uncoated manganite shows usual behavior of polycrystalline materials. MR increases to 60 at 50K for LSSMO. Contribution of MR_{SPT} is more than MR_{INT} in total MR of the uncoated sample. Enhancement of spin-polarized tunneling of conduction electrons between two adjacent grains at the grain boundary may increase MR. MR varies with temperature for uncoated samples. A core shell type model is attributed to an intermediate exchange coupling between the core and the shell of PLSSMO mainly on the basis of uncompensated surface spins. Polypyrrole coated manganites will be more economic than pure manganites. These types of materials may be used in spintronic devices. The synthesis procedure may be extended with different polymer and ferrites for tailored materials.

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