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Original Research

Giant magneto resistance and temperature coefficient of resistance in $Sm_{0.55}Sr_{0.30}Ag_{0.15}MnO_3$ perovskite☆

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ABSTRACT

Silver ions substituted samarium strontium manganite ($Sm_{0.55}Sr_{0.30}Ag_{0.15}MnO_3$) pervoskite was synthesized by using respective oxides in stoichiometric ratio through solid state reaction. The as-prepared sample was characterized by various analytical techniques to confirm its formation and understand the effect of monovalent silver ions in pervoskite lattice. X-ray diffraction pattern confirms the single phase formation while grain morphology in SEM image indicates good connectivity among the grains. The enhancement in metal to insulator transition temperature shows quenched disorder and magnetoresistance phenomena. The magnetoresistance (MR) and temperature coefficient of resistance (TCR) emerge from grain growth factor and homogeneity induced by Ag^+ ions in the lattice. The reduction in hysteresis loss resulted from antiferromagnetic - ferromagnetic (T_N) and ferromagnetic - paramagnetic (T_c) transitions reveals the removal of disorder in perovskite lattice by Ag^+ ions substitution. This increases the magnetic moment across distinct ions on the applying magnetic field. The rise in MR% (~99%) with silver doping emerging from smooth spin tunneling of the grains across the boundary and suppression of the disordered magnetic fluctuations with increase in magnetic field has been reported. The present compound exhibits the first order nature of magnetism and observed first time the highest value of TCR ~ 95%.

1. Introduction

Rare earth doped manganites ($RE_{1-x}AE_xMnO_3$, where RE: Rare Earth and AE: Alkaline Earth elements respectively) find various promising applications in the field of magnetic recording devices, spintronics, magnetic actuators, bolometric devices and magnetic sensors etc [1–3]. The electronic and magnetic properties of hole doped manganites can be easily tuned by varying composition, electric field, magnetic field strength, pressure and temperature which brings the change in entire system rich properties required for a particular device application. Apart from doping level x, the disorder induced in lattice due to ionic size mismatch of RE and AE metal ions plays a vital role in controlling the electronic and magnetic phase of doped manganites [4].

The disordered samarium strontium manganite ($Sm_{0.55}Sr_{0.45}MnO_3$) (SSMO) perovskite posses a unique system where multiphase competitions give rise to the charge order/orbital order (CO/OO) states and show the most sudden metal – insulator transition (T_{MI}) in comparison to other manganites [5–7]. The metal-insulator transitions (T_{MI}) and Colossal magnetoresistance (CMR) phenomena have been explained on the basis of double exchange and Jahn-Teller mechanism of electron phonon interaction in d–states which concludes that the low temperature phases are in polarized ferromagnetic metallic state and high temperature phases are in polarized paramagnetic insulating state [8]. It is believed that the grain boundaries are also responsible for broadening of resistivity peaks near the T_{MI}, enhancement of low field magnetoresistance (MR) below the T_{MI} [9–11]. The nature of high temperature coefficient of resistance (TCR) depends upon sharp electrical transition and enhancement of grain connectivity [12]. Upto $0.3 \le x \le 0.52$, the behavior of ground states of low bandwidth (W) are ferromagnetic metallic (FMM) and for $x > 0.52$, it is antiferromagnetic insulating (AFMI) in nature [5–7]. In $Sm_{0.55}Sr_{0.45}MnO_3$, a rapid sharp transition from paramagnetic insulating (PMI) to the ferromagnetic metallic (FMM) state is observed. At x ~ 0.5, $Sm_{1-x}Sr_xMnO_3$ system has a natural tendency towards phase separation and hence the occurrence of metamagnetism phenomena. The peculiar properties of SSMO type compounds can be tuned by external conditions e.g. temperature, pressure, magnetic field etc. to give rise

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exotic phenomena.

$Sm_{1-x}Sr_xMnO_3$ exhibits fascinating properties for the composition where x acquires the value in $0.4 \le x \le 0.6$ range. The large mismatch in their ionic radii gives rise to distinct electronic, phonon and magnetic properties as compared to other manganites when the doping level is same [13–17]. The divalent dopents like Sr, Ca have been studied extensively but little attention has been made towards monovalent dopants K^+, Na^+, Ag^+. The monovalency can increase the Mn^{4+} to higher ratio with more charge carrier concentration [12]. In the present investigation, the monovalent silver (Ag^+) ions have been doped to replace Sr^{2+} ions. The distinct difference in ionic radii induces lattice mismatch to change their electronic and magnetic properties. Earlier literature survey on Ag^+ ions substitution shows the enhancement in MR and TCR with Ag^+ ions concentration [12,18,19]. In the present paper, first time reporting the replacement of Sr^{2+} with Ag^+ ions in SSMO system and found that Ag^+ ions favor the double exchange mechanism which is responsible for enhancement of T_{MI} and MR. The sample exhibits first order nature of magnetism. The highest TCR% ~ 95% resulted from sharper transition plays significant role in bolometric devices.

2. Experimental details

The polycrystalline $Sm_{0.55}Sr_{0.30}Ag_{0.15}MnO_3$ sample was synthesized by conventional solid state reaction technique. The high purity fine powders of Sm_2O_3 (99.9%), Sr_2O_3 (99.999+%), AgO and MnO_3 (99.99%) with appropriate stoichiometric ratios were taken for preparation. These powders were ground in an agate mortar for 2 h and calcined at 950 °C for 24 h to ensure homogeneous phase formation. The calcined powder was again ground and compacted into circular pallets of 12 mm diameter with around 2–3 mm thickness. These pallets were first sintered at 1200 °C for 24 h followed by intermediate grindings. The final sintering was done at 1200 °C further for 24 h for homogeneous single phase formation.

The as-prepared sample was characterized for structural details and confirmation of the desired stoichiometry by Bruker AXS- D8 advanced powdered X-ray diffractometer with CuKα radiation operating at 40 kV/100 mA for identifying phase nature. The diffraction pattern was recorded in the 2θ range from 20° to 100° at a step size of 0.02° and a counting time 15 s/steps. The JEOL JSM- 6700 Scanning Electron Microscope (SEM) working at 20 kV was used to observe the microstructure morphology of the compound. The elemental composition of compound is determined by Energy dispersive X-ray (EDX) analysis. The transport measurements of the prepared sample were performed on a rectangular pallet using standard four probe method (PPMS Quantum Design) using a superconducting magnet down to 10 K temperature. The electrical contacts were made by attaching four fine copper wires to the sample using indium soldering.

MR was measured by using the relation $MR\% = (\rho_0 - \rho_H)/\rho_0 \times 100$. TCR is calculated by using the formula $TCR\% = (1/\rho_0)(d\rho_0/dt)*100$. The magnetization measurements were carried out in Zero Field Cooled (ZFC) and Field Cooled (FC) as a function of temperature (T) at 500 Oe and 1 T by using a Quantum Design SQUID magnetometer. The magnetic hysteresis loops were recorded at 5 K and 300 K temperatures from 0 T to 8 T respectively.

3. Results and discussion

The recorded XRD pattern of $Sm_{0.55}Sr_{0.30}Ag_{0.15}MnO_3$ (SSAMO) sample was refined with Rietveld method using the Fullproof program at room temperature. The compound has orthorhombic structure with P*nma* space group having single phase without any impurity. Rietveld analysis shows that the pattern between experimental and calculated values are in close agreement with each other as compared to reported earlier one [20]. The peak symmetry and preferred orientation corrections were appropriately applied. The positional parameters and cation occupancy are also refined by keeping in view the fixed oxygen content. The Rietveld plot indicated in Fig. 1 shows the good fitting and the results derived are summarized in Table 1. The cationic size mismatch due to the difference between ionic radius of Ag^+(1.28 Å) and Sr^{2+}(1.26 Å) strongly influences the degree of electron lattice coupling. This disorder parameter σ^2 increases due to scattering in the electron hopping integral for neighbouring Mn sites. This process encourages the electron localization and tendency toward antiferromagnetism in the phase separated state. When Mn valence values and $< r_A >$ are fixed, an increase in σ^2 causes a weakening of FM and AFM interactions and destabilization of the charge ordering which plays a crucial role in various properties of SSAMO system.

Scanning Electron Microscopy (SEM) has been used to study the microstructure of the pellet which provides a better insight and accuracy of the grain development rather than at the top and bottom surfaces. The grain morphology of the as-prepared sample is presented in Fig. 2(a). In the picture, well defined grains are distributed homogeneously across the system having the sizes in the range of 5 µm. The fine network distribution among the grains is resulted due to silver addition which improves the conductivity of system and sharpens electronic transition. EDX recoded spectrum is shown in Fig. 2(b) and observed the elemental composition in terms of atomic percent of Sm (11.12 at%), Mn (18.09 at%), Sr (7.11 at%), Ag (2.15 at%) and oxygen (61.83%). The compositional analysis confirmed by EDAX shows the elemental composition for Sm, Sr, Ag and Mn close to the stoichiometric value.

The temperature dependent resistivity at different magnetic fields are shown in Fig. 3. The metal to insulator transition temperature (T_{MI}) at 0 T and 5 T are ~ 98 K and ~133 K respectively while it increases in broader sense and T_{MI} ~ 155 K at 8 T is observed. The resistivity in

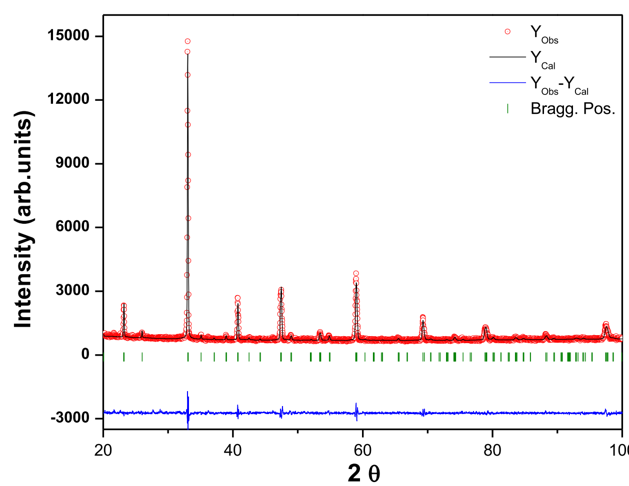

Fig. 1. Rietveld refinement plot of $Sm_{0.55}Sr_{0.30}Ag_{0.15}MnO_3$ system. The measured data (black circles) is shown together with the calculated pattern (red curve) and their difference points are shown below in blue line. The purple small dashes indicate the 2θ position for Bragg's peaks.

Table 1
Values of lattice and structural refined parameters obtained from Rietveld process at room temperature.

Space group	*Pnma*
a (Å)	5.4436
b (Å)	7.6752
c (Å)	5.4363
Volume (Å^3)	227.1327
χ^2	1.641
Bragg's factor	5.47
RF- factor	9.82