

High Magnetoresistance of the Composite of Polyaniline Nanotubes with $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$. Determination of Stiffness Constant and Range Of Interaction of this composite

K.Gupta, P.C. Jana, A.K.Meikap

Abstract— We have synthesized composite of polyaniline nanotubes with Lanthanum strontium manganite ($\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$, LSMO) nanoparticles. A huge increase in magnetoresistance (~73%) is obtained in the nanocomposite containing highest amount of LSMO. This increase in magnetoresistance may be explained by evaluating stiffness constant and average range of interaction of the nanocomposite. Average range of interaction among magnetic ions increases from 5 to 7.736 and value of stiffness constant decreases from 2.75×10^{-5} to $0.74 \times 10^{-5} \text{ eV}(\text{Å}^0)^2$ with increase in LSMO content in the nanocomposites. Increase in average range of interaction and decrease in stiffness constant may be the cause of observed increase in magnetoresistance.

Index Terms— LSMO, Magnetoresistance, Polyaniline, Range of interaction, Stiffness constant

I. INTRODUCTION

Many interesting properties like magnetic, electrical transport, dielectric, and optical properties are obtained in Perovskite structured transitional-metal oxides. Colossal magnetoresistance (CMR) of perovskite manganites is obtained in single crystal[1], thin films[2] and ceramic CMR materials[3]. Whereas manganites can not have wide technological relevance because of their many drawbacks reported by many research groups [4-6]. Importance of inorganic-organic hybrid composite has been grown rapidly [7]. Polyaniline, polypyrrole, polythiophene etc. can be used as an organic counterpart. Among these, polyaniline can be selected for its easy preparation technique, economic importance, good stability and relatively high conductivity. It shows tunable properties like electrical, optical, magnetic and chemical properties [8-12]. These properties can vary with morphologies like nanoparticles, nanotubes, and nanorods etc. of polyaniline [13-15]. Therefore we have synthesized composite of polyaniline nanotubes-LSMO and investigate their different properties. Interestingly, we have obtained a huge increase in magnetoresistance of the composite (73%) as compared to pure LSMO nanoparticles. Hysteresis (M-H)

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loops show that the ferromagnetic behavior of LSMO nanoparticles have been retained in the composite, but the magnetization of composite becomes weaker than pure LSMO nanoparticles. In this paper we have calculated average range of interaction among magnetic ions and value of stiffness constant from magnetization data and tried to explain the reason for high magnetoresistance of the composite in the light of value of stiffness constant and average range of interaction among magnetic ions.

II. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUES

A. Synthesis

Lanthanum oxide (La_2O_3), manganese acetate [$\text{Mn}(\text{CH}_3\text{COO})_2$], and strontium nitrate [$\text{Sr}(\text{NO}_3)_2$], aniline, triethanolamine (TEA), Cetyl triethyl ammonium bromide (CTAB), ammonium peroxodisulphate (APS), acetone, ethanol are collected from the market and purified. Details of synthesis is given in our previous paper[16]. A brief description of preparation is outlined here. LSMO nanoparticles are prepared by standard “pyrophoric reaction process” given in reference [6] using certain amount of aqueous solution of La_2O_3 , $\text{Mn}(\text{CH}_3\text{COO})_2$, and $\text{Sr}(\text{NO}_3)_2$ in stoichiometric proportions. TEA is added to these solutions and are evaporated on a hot plate with constant stirring to get black, fluffy precursor powder which is calcined at 923K to get LSMO nanocrystalline powders. 10 mg of these powders are dissolved in 50 μM CTAB solution which is used as a surfactant and sonicated for 2 hrs to get a homogeneous solution. To this solution, 1mM double distilled aniline is added with constant magnetic stirring at 0 $^\circ\text{C}$ and then ice cooled 0.5(M) aqueous solution of APS is added drop wise for 30 minutes to this solution until color becomes green and kept it in refrigerator at rest for 24 hrs to complete the polymerization. The solid mass obtained is washed with acetone, ethanol and double-distilled water. Two other composites are prepared for comparison by taking 20 and 30 mg of LSMO respectively under similar reaction conditions and pure polyaniline is synthesized under similar reaction condition without using LSMO nanoparticles.

Samples are dried in an oven at 300K for overnight. Samples are numbered as S_0, S_1, S_2, S_3, S_4 where S_0, S_1 indicate pure polyaniline and pure LSMO and S_2, S_3, S_4 indicate polyaniline-LSMO composite for 10, 20, 30 mg LSMO, respectively.

B.. Characterization

Morphology of the sample is taken by a Field Emission Scanning Electron Microscope (FESEM) of the model Carl Zeiss Supra 40 vp. Details of the characterizations of the samples are given in reference[16].

III. III. RESULTS AND DISCUSSIONS

A. Morphology

Morphology of composite of polyaniline nanotubes-LSMO (S_2) is represented in Fig.1. This image shows the self-organized nanotubes. CTAB forms a soft template and nanotubes are formed in the template [13-15]. It is observed from the image that LSMO nanoparticles are on the surface and inside the cage like structure. Length of the tube is of about 1 μm and diameters of the tube lies in the range 40-50 nm.

B. Structural characterization

Fig.2 represents the X-ray diffraction pattern (XRD) of S_2 . From this spectrum it is observed that pure polyaniline has no characteristic peaks excluding The peaks that are obtained in XRD spectrum of S_2 at $2\theta = 32, 41, 46, 54, 58, 68, 78$ degree represent the Bragg's reflections from (110), (111), (200), (211), (220), (310) planes. These peaks are indexed on the basis of orthorhombic cell with Pbnm space group symmetry [16]. The average grain size of S_2 calculated from the most intense peak of (110) plane using Scherrer's formula is 30-35 nm. The hump at around $2\theta = 25$ degree for amorphous polyaniline [17-18].

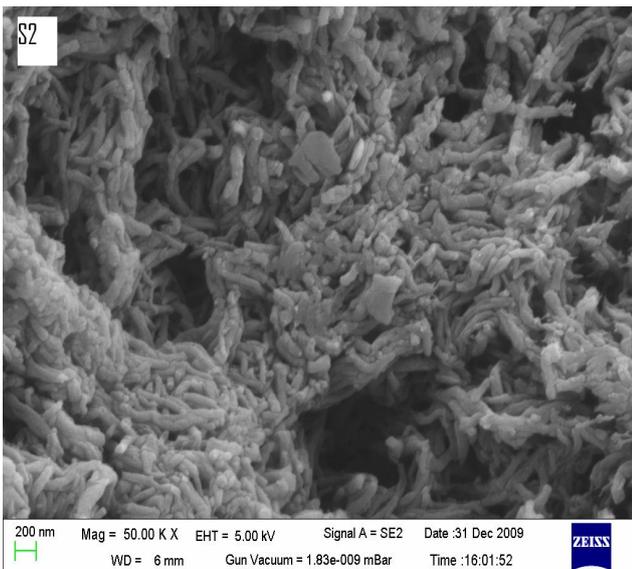


Figure.1 FESEM image of polyaniline (S_0) and polyaniline-LSMO nanotubes (S_2).

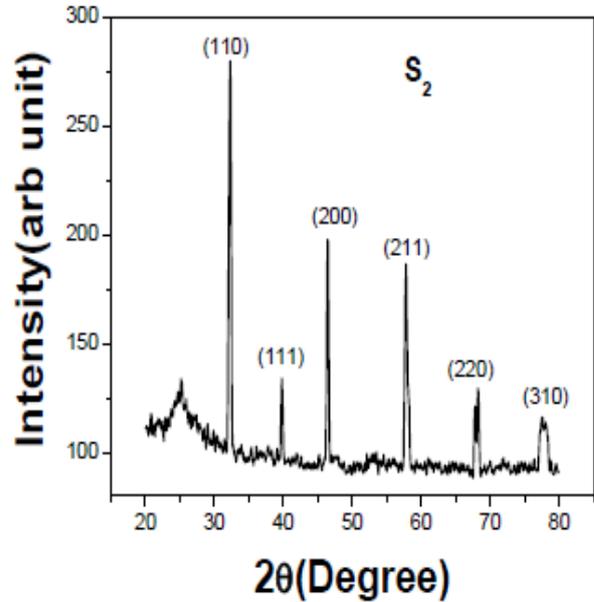


Figure.2 XRD pattern of the composite of polyaniline nanotubes with LSMO (S_2).

C. Magnetic properties

Fig. 3 shows the variation of magnetization with magnetic field at 300K for S_2 . Magnetization increases with increase in

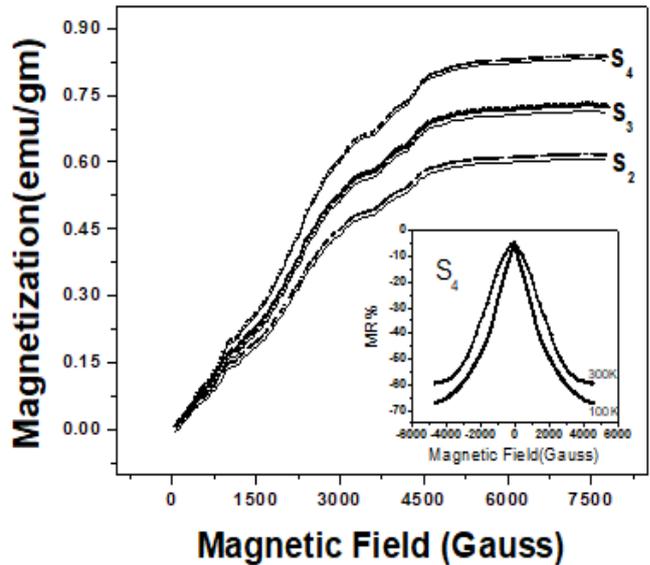


Figure.3 Dependence of magnetization with the applied magnetic field at room temperature polyaniline-LSMO nanocomposites (S_2, S_3, S_4). The solid lines represent theoretical fit with Eq.(2). Inset shows the variation of percentage Magnetoresistance of S_4 with magnetic field.

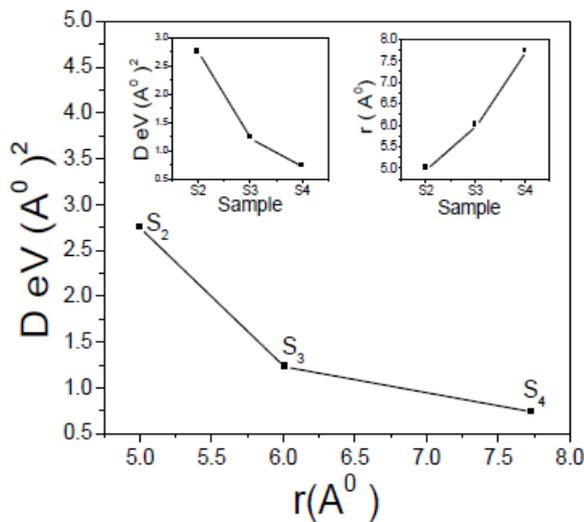


Figure.4 Variation of Stiffness constant(D) with range of interaction(r). Inset shows variation of Stiffness constant(D) and range of interaction(r) with variation of sample.

ferromagnetic LSMO content in the composite. This indicates the interaction between polarized spin of Mn⁺³ ions via indirect exchange through conducting electrons of polyaniline. Ferromagnetic behavior of the composite (S₂, S₃ and S₄) is indicated by Hysteresis loops (not shown in manuscript). Saturation magnetizations of the composites (S₂, S₃ and S₄) are 0.61, 0.73 and 0.84 emu/gm respectively, but it is reported in literature that saturation magnetization (M_s) of LSMO nanoparticles is 40-50 emu/gm[19]. This decrease in saturation magnetization (M_s) of the composite is due to presence of nonmagnetic polyaniline [20]. Measurements of transverse magnetoresistance (MR) of the composite are done in the temperature range 77-300K and at magnetic field –5 to 5 KGauss. For this purposes we have used the equation

$$MR = \frac{\rho(H, T) - \rho(0, T)}{\rho(0, T)} \quad (1)$$

Field dependence of MR of S₄ is given in the inset of Fig.3 at temperatures 100 and 300K. It shows the usual behavior of polycrystalline materials. MR of other composites (S₂ and S₃) at various temperatures also behave in a similar manner [16] and values of MR of S₂, S₃ and S₄ at various temperature are given in Table 1. It is observed that MR of polyaniline coated LSMO nanoparticle is much higher than uncoated LSMO nanoparticles as reported in the literature [6].

Table 1 Magnetoresistance(MR) at H=3 KGauss at several temperatures, for polyaniline-LSMO nanocomposite samples (S₂, S₃ and S₄).

Temperature (K)	S ₂	S ₃	S ₄
77	56.7	66.7	73.0
150	47.2	57.5	66.4

250	37.9	48.9	57.9
320	29.5	43.8	52.5

Table 2 Range of interaction $\langle r \rangle$ and stiffness constant (D) value of polyaniline-LSMO nanocomposite

Sample no	$\langle r \rangle$ (Å)	D eV (Å) ⁰ ²
S ₂	5	2.75 × 10 ⁻⁵
S ₃	6.01	1.23 × 10 ⁻⁵
S ₄	7.736	0.74 × 10 ⁻⁵

In multidomain system, the magnetization process is determined by the domain wall movement or rotation. This movement depends on the anisotropy which is sensitive to structure like defects, anisotropic distribution of atoms and defects. Hence the field dependent magnetization is a structure sensitive property.

At temperature less than transition temperature (T<T_C) in ferromagnetic materials, the field dependence magnetization is given by[21]

$$M(T, H) = M_s(T) \left[1 - \frac{a(T)}{H} - \frac{b(T)}{H^2} \right] + c(T)H^n \quad (2)$$

where $n = 1$ for crystalline materials and $n = \frac{1}{2}$ for amorphous materials. M_s(T) is spontaneous magnetization at temperature T, a(T), b(T) and c(T) is constant at a given temperature T. The last term of the above equation is due to the paraprocess. The contribution of paraprocess become small at low fields and the contributions of microstructure is dominant. On other hand at large fields the paraprocess dominates and the terms resulting from the macrostructure vanishes.

At low field, magnetization can be written as

$$M(T, H) = M_s(T) \left[1 - \frac{a(T)}{H} - \frac{b(T)}{H^2} \right] \quad (3)$$

The term $\frac{a}{H}$ and $\frac{b}{H^2}$ are attributed to stress field around dislocations and voids for nonmagnetic inclusions [22-23]. Eq.(2) can be analyzed by nonlinear regression method as follows for the determination of temperature dependent constant a and b

$$\begin{pmatrix} \sum_i I & \sum_i I/H_i & -\sum_i I/H_i^2 \\ \sum_i I/H_i & -\sum_i I/H_i^2 & -\sum_i I/H_i^3 \\ \sum_i I/H_i^2 & -\sum_i I/H_i^3 & -\sum_i I/H_i^4 \end{pmatrix} \times \begin{pmatrix} M_s(T) \\ M_s a(T) \\ M_s b(T) \end{pmatrix} = \begin{pmatrix} \sum_i M_i \\ \sum_i M_i/H_i \\ \sum_i M_i/H_i^2 \end{pmatrix}$$

Where $a = \left(\frac{3k_B}{4\pi D}\right)^{\frac{3}{2}} \times 2.612$

$$b = \left(\frac{3k_B}{4\pi D}\right)^{\frac{5}{2}} \times 1.341 \times 3 \frac{\pi}{4} \langle r^2 \rangle$$

$$\langle r^2 \rangle = \frac{\int r^4 J(r) d^3 r}{\int r^2 J(r) d^3 r}$$

$$D = 2S \int r^2 J(r) \rho(r) d^3 r$$

and ρ is the pair distribution function, D is the stiffness constant and $\langle r^2 \rangle$ gives average value of square of range of interaction for first nearest neighbors. Values of stiffness constant (D) and square of range of interaction for first nearest neighbors $\langle r^2 \rangle$ of the composite are given in Table

2. It is observed that the range of interaction increases with increase in LSMO content in polyaniline matrix and the value of stiffness constant decreases with increase in LSMO content in polyaniline matrix. Fig.4 shows the variation of both range of interaction and stiffness constant with LSMO content in the sample. A reciprocal variation of D with r is found for these samples. It is observed when the value of stiffness constant of the sample decreases, the range of interaction increases. Therefore decrease in stiffness constant and increase in range of interaction may be probable cause of enhancement in magnetoresistance.

IV. CONCLUSION

We have prepared composite of polyaniline nanotubes with Lanthanum strontium manganite by chemical oxidative reaction. This composite exhibits a remarkable increase in magneto-resistance upto 73 % (for S_4 at 77K) and increases with the increase in LSMO content. The average range of interaction is increased and the value of stiffness constant is decreased by the increase in LSMO content in polyaniline

matrix. Giant magneto resistance observed in polyaniline-LSMO nanocomposite may be due to decrease in the value of stiffness constant.

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