Solution sol–gel processing and investigation of percolation threshold in $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3:x\text{SiO}_2$ nanocomposite

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Abstract

The composites of $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3:x\text{SiO}_2$ ($0 \leq x \leq 0.40$) have been synthesized by sol–gel technique to derive homogeneous nanocomposites. Si^{4+} by virtue of its strong preference for tetrahedral site does not enter the perovskite lattice. The percolation threshold composition has been determined by resistivity measurements at around 90% volume fraction of LCMO. A detailed electrical, magnetic and magneto-transport characterizations have been carried out for composites around the threshold composition ($x = 0.05, 0.10, 0.15$). The magnetoresistance results at 1 T show a sharp peak at T_c and a minimum just below T_c as reported in several polycrystalline LCMO composites.

Keywords: Manganites; Resistivity; Magnetoresistivity; Nanocomposite

1. Introduction

The discovery of colossal magnetoresistance (CMR) in doped manganites [1] triggered increasing attention due to their unusual properties, as well as their potential applications in magnetoresistive transducers and sensors. CMR effect is typically found in perovskite-type oxides with formula $\text{R}_{1-x}^{3+}\text{A}_x^{2+}\text{Mn}_{1-x}^{3+}\text{Mn}_x^{4+}\text{O}_3$, where $\text{R} = \text{La}$

or rare earth ions, like Ce, Nd, Pr, Sm, etc. and $\text{A} = \text{Ca}, \text{Sr}$ or Ba . But the small room temperature magnetoresistance (MR) and its high magnetic field (several Tesla) dependence are the major disadvantages of these materials. So far in several reports, substitutions at A and B sites in perovskite structure have been tried to enhance the MR ratio [2–4].

Recently, some attempts have been made to study this enhancement in MR through the formation of composites of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO) with CeO_2 [5] and of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (LCMO) with SrTiO_3 [6]. The CeO_2 composites

were prepared by solid state reaction method in air where a flash sintering upto 1100°C for 10 min was used followed by cooling at a rate of 500°C/h while in the other case high temperature sintering at 1600°C for 1 h [6] has been used. It was found that below a certain critical concentration x_c of the CeO_2 and SrTiO_3 in LSMO and LCMO, respectively, the increase in the room temperature resistivity ρ_{RT} with x is small. But for $x > x_c$, this rate rises sharply and follows an exponential behavior. This was attributed to the onset of thin metallic percolation routes for charge carriers due to the presence of insulating phases at the grain boundary in the composites. It has been suggested that at the percolation threshold composition, low field MR increases which could have potential for applications [5].

In the present investigation, we have used low temperature sol-gel processing to prepare LCMO/ $x\text{SiO}_2$ ($x = 0.00, 0.05, 0.10$ and 0.15) nanocomposites. We have also synthesized compositions with $x = 0.20, 0.25$ and 0.40 and measured $\rho(T)$ to determine the critical concentration x_c at which percolation process begins in this system. The detailed physical investigations have, however, been carried out only for the compositions, $x \leq 0.15$, which are expected to throw some light on the nature of charge carriers and their transport properties around the percolation threshold composition. The main objective of this investigation is to synthesize a homogeneous composite and to introduce silica as the second phase of the composite outside the LCMO grains since Si^{4+} is unlikely to enter the perovskite structure of LCMO due to its strong preference for tetrahedral coordination. In fact, due to this reason, we could use the sol-gel method in contrast to flash sintering used in LSMO/ CeO_2 and LCMO/ SrTiO_3 composites [5,6]. In those systems, the possibility of Ce^{4+} , Sr^{2+} or Ti^{4+} entering into the LSMO or LCMO lattice could not be ruled out, whereas in the present case, Si^{4+} can either form a chemical compound with other ions retaining the SiO_4 tetrahedra intact or can precipitate as SiO_2 at grain boundaries of LCMO phase. This can have significant effect on the magnetic and transport properties of LCMO. We have used X-ray diffraction (XRD), scanning electron microscopy

(SEM), transmission electron microscopy (TEM), resistivity ($\rho(T)$), magnetoresistivity and thermoelectric power (TEP) measurements for characterizing these composites. The results are presented in this paper.

2. Experimental

Lanthanum oxide, calcium carbonate and manganese carbonate (Aldrich Chem.) were slowly reacted with nitric acid to produce soluble metal nitrates. Stoichiometric amount of the individual metal [i.e., La, Ca and Mn] nitrates were thoroughly mixed in accordance with the composition $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ to form the cationic stock solution. Stoichiometric amount of the cationic stock solution was taken and heated at 70°C for 2 h. Aqueous solution of citric acid (2.5 mole) containing 10% urea was then added to the cationic mixture with thorough stirring. This solution was cooled and mixed with ethyl alcohol and stoichiometric amount of tetraethyl orthosilicate (TEOS). The whole solution was stirred for 1–2 h. The resulting solution was heated at $\sim 200^\circ\text{C}$ to form gel. On further heating, the gel decomposed and produced a fluffy dried mass. The fluffy dried mass was ground to give the precursor powder which resulted in the formation of fine LCMO phase on calcination at 600°C.

Crystallographic structure of the specimen were examined by X-ray diffractometer (Philips PW 1729) using Cu K_α radiation. Scanning Electron Microscopy (Cameca SU 30) and Transmission Electron Microscopy (Philips CM 200) were used to study the microstructure as well as the grain size of the sintered and unsintered pellets of the composites.

The magnetization was measured on a Vibrating Sample Magnetometer (Oxford VSM) in the temperature range 4–300 K. The temperature dependence of resistivity $\rho(T)$ was measured by standard four probe technique in the temperature range 15–300 K. A closed cycle refrigerator and Si-diode sensor have been used for cooling the sample and monitoring the temperature, respectively. Magnetoresistivity measurements have been carried out on the same samples from 300 to 80 K

using a liquid N₂ gas-flow cryostat. An electro-magnet was used to produce the magnetic field of 1.0 T. In the presence of field, the temperature was monitored using a Pt sensor. Seebeck coefficients were measured by a DC differential method [7] in the same temperature range, 15–300 K. The temperature gradient across the sample was measured using two-pairs of copper-constantan thermocouples. The sample was mounted with low temperature epoxy on top of two well separated copper blocks. Strain gauges were attached to these blocks and were used as heater to create the desired temperature gradient. By reversing the current, the thermally generated spurious voltage could be compensated. The temperature gradient between the two copper blocks was kept at 0.5 K. To eliminate the effect of the reference lead, the absolute thermoelectric power of Cu was subtracted from the measured thermoelectric voltage. The entire measurement system, comprising of a 181 Keithley nanovoltmeter, a 1271 Datron multimeter, a 224 Keithley current source and a Lakeshore temperature controller, was interfaced with a PC for automatic data acquisition.

3. Results and discussion

The as prepared precursors powder were X-ray amorphous. Heat treatment of the precursors at 600°C for 2 h resulted in LCMO phase. However, the XRD lines of these powders were broad indicating fine particles. The size of the particle was determined from the (110) line centered at $2\theta = 32.830^\circ$ and had the FWHM of $2\Delta\theta = 0.5^\circ$. Using Scherrer's formula [8] and with $\lambda = 1.54 \text{ \AA}$, the particle size, t is estimated around 17 nm. Increase in the heat-treatment temperature (800°C) resulted in the sharpening of the diffraction lines, reflecting growth in crystallinity in these samples. XRD patterns of pellets sintered at 1200°C are given in Fig. 1. These exhibit lines corresponding to the LCMO phase along with the lines from the insulating phase $\text{Ca}_2\text{La}_8(\text{SiO}_4)_6\text{O}_2$.

The stoichiometry of the LCMO phase was preserved in all specimens as is indicated by XRD line positions which essentially remain unchanged. The second phase present mostly in the grain

Fig. 1. X-ray powder diffraction patterns for $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$: $x\text{SiO}_2$ composites with $x = 0, 0.05, 0.10$ and 0.15 . The * indicates the lines corresponding to the insulating $(\text{Ca}_2\text{La}_8(\text{SiO}_4)_6\text{O}_2)$ phase.

boundary is for larger values of x ($= 0.10$ and 0.15) and is assigned to insulating $\text{Ca}_2\text{La}_8(\text{SiO}_4)_6\text{O}_2$. The lattice parameter ' a ' for $x = 0.00$ is $3.854 \text{ \AA}$ which is consistent with that of pure LCMO reported earlier ($a = 3.856 \text{ \AA}$) [9]. As x is increased, the lattice parameter marginally decreases between $0 \leq x \leq 0.1$ and then becomes constant (Table 1).

The particle size of the sample with $x = 0.05$ heat-treated at 600°C for 2 h is estimated from TEM. The average particle diameter is found to be approximately 20 nm. The particle size for the same powder was also estimated from the X-ray line broadening as mentioned above. The mean grain size of the composite was obtained from SEM studies. SEM micrographs of the unsintered pellets showed uniform compaction and corresponding sintered (1200°C for 2 hrs) pellets showed the uniform grain structure with an average grain size of 2–3 μm .

The temperature dependence of magnetization has been measured at 5 kOe for the samples with $x = 0.00, 0.05, 0.10$ and 0.15 and is shown in

Table 1

Different parameters obtained from the magnetic and transport properties of the LCMO: x SiO₂ composites

x	$a = b = c$ (Å)	T_p (K)	ρ_{RT} (Ω cm)	ρ_{T_p} (Ω cm)	$\rho_{T_p}/\rho_{30\text{ K}}$	MR (%) at T_p (K)	S_{RT} (μ V/K)	T_c (K)	$T_{p'}$ (K)
0.00	3.854	260	0.209	0.446	4.46	12.45	-11.12	264	—
0.05	3.844	259	0.189	0.370	4.61	12.80	-11.25	272	231
0.10	3.838	262	0.203	0.372	3.10	13.70	-15.53	271	216
0.15	3.838	265	0.255	0.574	3.13	6.91	-9.63	271	231

Fig. 2. The saturation magnetization M_s at $T = 4\text{ K}$ are 94.0, 85.0, 77.0 and 70.0 emu/g for $x = 0.0, 0.05, 0.10$ and 0.15 , respectively. If all Mn^{3+} and Mn^{4+} spins are aligned parallel due to double exchange the value expected for $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ (assuming spin only moment) is approximately $M_s = 98\text{ emu/gm}$ which is about 4% higher than the value measured in our pure LCMO sample. This observed value agrees with that reported in literature [9]. The value of M_s as a function of x is plotted in the inset of Fig. 2 and shows a linear decrease with x . This decrease in M_s with x is expected due to the decrease in the volume fraction of the LCMO phase and increase of the nonmagnetic phases containing SiO₂ in

Fig. 2. Magnetization (M) vs. temperature for $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3:x\text{SiO}_2$ composite for $x = 0, 0.05, 0.10$ and 0.15 . The inset figure shows the variation of M with x with a linearly fitted solid line.

these composites. All the composites show similar behavior of M as a function of T as the pure LCMO sample except for a small upturn kink at around 50 K which develops for $x \neq 0$. This kink is superimposed on the general ferromagnetic type behavior. Such anomaly at around 50 K has been reported earlier in composites of LCMO with SrTiO_3 [6] as well as some substituted LCMO samples [10–12]. Ju and Sohn [13] have explained it on the basis of local microscopic magnetic inhomogeneities arising from the variation in the Mn oxidation state. On the other hand, in Ce doped LSMO composites, this kink has been explained on the basis of the presence of the paramagnetic MnO_2 phase in the compound [10]. In our samples, we did not observe the MnO_2 phase but for higher values of SiO₂ ($x = 0.10, 0.15$) XRD patterns show the presence of the phase $\text{Ca}_2\text{La}_8(\text{SiO}_4)_6\text{O}_2$. The T_c obtained from Fig. 2 are given in Table 1 and is almost independent of the SiO₂ content, x . This indicates that the stoichiometry of LCMO phase within the grains remains essentially unchanged, while SiO₂ and its compounds, which cannot be accommodated within the perovskite structure, precipitate at the grain boundary forming a nonmagnetic insulating layer. However, the decrease in $M_s(0)$ with x shown in the inset of Fig. 2 is much more than what can be expected on the basis of the nonmagnetic SiO₂ phase only. This indicates that SiO₂ reacts with part of the LCMO to form the insulating $\text{Ca}_2\text{La}_8(\text{SiO}_4)_6\text{O}_2$ phase thereby reducing the magnetic LCMO phase further.

The resistivity vs. temperature curves between 30 and 300 K for $x = 0.00$ – 0.15 are given in Fig. 3. All the curves show two peaks, a sharp peak at T_p , close to T_c and the other, a broad one at $T_{p'}$, about 30–40 K below T_c . On the application

Fig. 3. Temperature dependence of resistivity for $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3:x\text{SiO}_2$ composites with $x = 0, 0.05, 0.10$ and 0.15 . In inset ρ_{RT} is plotted as a function of LCMO volume fraction v with a fitted solid line.

of a field of 1.0 T, the sharp peak disappeared in all cases. For $x = 0.05$, T_p is 259 K, $\rho(T_p) = 0.37 \Omega\text{cm}$ and $\rho(T_p)/\rho(30\text{ K})$ is 4.6. These values for other compositions are given in Table 1. The magnitude of resistivity remains unchanged for $x \leq 0.10$, but above this concentration it shoots up sharply. The dependence of room temperature resistivity ρ_{RT} on volume fraction of LCMO, $v[(1 + 0.77x)^{-1} \times 100]$ is shown in the inset of Fig. 3. For $x = 0.10$, ρ_{RT} is $0.203 \Omega\text{cm}$ but for $x = 0.40$ it increases by almost six orders of magnitude. In the percolation model, the exponential rise in resistivity for x greater than 0.10 is usually expressed as $\rho \propto e^{-(v-v_c)}$ where v_c is the percolation threshold. For LCMO/ SrTiO_3 system [6], v_c is around 60% while for LSMO/ CeO_2 composite it is 40% [5]. These are very different from that observed for the present case ($\sim 90\%$) as shown in the inset of Fig. 3.

The double peaks in $\rho(T)$ have been seen in many polycrystalline systems and attributed generally to the structure and thickness of grain boundaries or to the non-magnetic regions between LCMO grains [9–11]. The charge carrier mobility in the absence of an external magnetic field depends on the spin orientation of the

neighboring Mn^{4+} (t_{2g}^3) and Mn^{3+} ($t_{2g}^3 e_g^1$) spin states. In systems where a nonmagnetic phase exists at the grain boundary surrounding the grains comprising of pure magnetic LCMO/LSMO phases, the number of charge carriers and their mobility are expected to be determined by tunneling across the grain boundaries. This would account for the existence of the broad peak at T_p as well as for the exponential growth in resistivity at a critical concentration, v_c , when the transport begins to be controlled by the percolation routes determined by the intergrain spin-polarized tunneling suggested by Hwang et al. [14]. The peak at T_p near T_c in $\rho(T)$ arises from the CMR effect within the grains comprising of the magnetic LCMO/LSMO phases.

The MR results with 1 Tesla field for $x \leq 0.15$ are shown in Fig. 4. As noted by many others [11,15–17] these results show two components—a peak near T_c and a linear increase in MR at low temperature which is almost independent of the SiO_2 concentration. As discussed by Li et al. [17], the peak at T_c arises from the CMR effect amongst charge carriers inside the grain. The nearly concentration-independent, linear increase in low temperature MR as $T \rightarrow 0$ has been attributed to

Fig. 4. $\text{MR}(\rho(0) - \rho(H))/\rho(0)$ plotted against temperature for 1 T field for $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3:x\text{SiO}_2$ composites with $x = 0, 0.05, 0.10$ and 0.15 .

arise from strong scattering due to magnetic inhomogeneity at grain boundaries. On the other hand, Hwang et al. [14] attribute the low temperature MR to arise from their tunneling model across the grain boundaries. Between the two models we believe that the spin-dependent scattering of the polarized electrons at the grain boundaries accounts satisfactorily for the composition-independence of the MR effect observed by us.

The results of the thermopower, S , as a function of temperature are summarized in Fig. 5. We have accounted for the resistivity data on the charge carriers hopping between nearest-neighbor sites without any activation energy, $E_a = 0$, $\text{Mn}^{3+} \rightleftharpoons \text{Mn}^{4+}$. The transport is thus dependent on the number of charge carriers and their mobility. These quantities, as discussed above, are difficult to disentangle as both depends on the spin-disorder scattering. It is, therefore, instructive to consider the Seebeck coefficient that contains a transport term and a statistical term and is given by

$$S = \frac{k}{e} \left[\frac{Q}{k} + \frac{\varepsilon_F}{kT} \right]. \quad (1)$$

Fig. 5. Temperature dependent Seebeck co-efficient (S) for $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3:x\text{SiO}_2$ composites with $x = 0, 0.05, 0.10$ and 0.15 . In inset figure both M and S are plotted on the same temperature scale.

Here Q is the lattice entropy transported by the charge carriers and ε_F is the Fermi energy. The lattice entropy, Q , transported by the electrons, involves both the charge and the spin and is generally small in oxides [18]. The statistical term containing ε_F , in a mixed valence system having a concentration c of mobile charge carriers on energetically equivalent sites is given by [18]

$$S \sim -\frac{k}{e} \ln \left[\gamma \frac{(1-c)}{c} \right], \quad (2)$$

where γ is the spin degeneracy. For T greater than T_c , $\gamma = 2$ can be used but well below T_c , $\gamma = 1$. If this is the dominant mechanism, taking $\gamma = 2$, $S = -10 \mu\text{V/K}$, we get $c = 0.7$ at $T = 300 \text{ K}$ which agrees well for the LCM phase within the grain. For $T = 50 \text{ K}$ with $\gamma = 1$ and $S = -0.5 \mu\text{V/K}$, we obtain $c = 0.5$, irrespective of the SiO_2 concentration. As shown in the inset of Fig. 5, S vs. T varies in a manner similar to M vs. T . This shows that as T varies from 300 to 50 K the spins get aligned and c changes gradually from 0.7 to 0.5.

4. Conclusions

$\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3:x\text{SiO}_2$ nano-composites were prepared by a solution sol-gel process. These composite powders were characterized for their structural, microstructural, magnetic and transport properties. These studies show that SiO_2 does not enter the LCMO lattice due to strong preference of Si^{4+} ion for tetrahedral co-ordination. SiO_2 , on the other hand, is found to remain at grain boundary region forming insulating phases without disturbing the stoichiometry of LCMO phase within the grain. Resistivity increases by several orders of magnitude for a critical concentration of SiO_2 , a behavior observed for the percolating systems. The peak in ρ vs. T near T_c is attributed to the CMR effect inside the grains while the broad peak below T_c is attributed to scattering at the grain boundary, which also accounts for the low temperature MR observed in $\text{LCM}:x\text{SiO}_2$ nanocomposites.

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