Synthesis and properties of nanograined La-Ca-manganite–Ni-ferrite composites

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Abstract

Composites of La_{0.67}Ca_{0.33}MnO_3 (LCMO), a colossal magnetoresistance perovskite and NiFe_2O_4 (NF), an insulating magnetic oxide have been prepared in situ using microwave-refluxing technique. Microstructural studies of the composites show that the two phases are uniformly distributed and the grain size of both the phases is identical, in the range 10–40 nm. The NF appears as a separate phase for concentrations \(x > 0.10\) M, where \(M\) is the molecular weight of NF in the starting precursor solution. For concentrations <0.1 M, the X-ray diffraction studies indicate the presence of only the LCMO phase. Pure LCMO exhibits an insulator–metal transition \(T_{MI}\) at 215 K whereas the magnetic transition \(T_C\) occurs at 250 K. The transition temperatures \(T_C\) of this LCMO phase decreases from 250 to 125 K for the addition of 0.15 M NF while \(T_{MI}\) decreases from 215 to 90 K for the addition of just 0.02 M NF to the precursor solution. The magnetoresistance (MR) magnitude or increase in electrical conductivity of LCMO in the presence of an external magnetic field decreases progressively with the addition of NF. The MR of the composite with 0.01 M NF increases with decreasing temperature to \(\sim 16\%\) at 85 K in the presence of 8.5 kOe external field. The suppression of electrical and magnetic transitions in LCMO is found to be due to substitution of Mn by either or both Ni and Fe. The increasing MR response of the composite is due to the nanocrystalline grain size of the two phases and also partly due to the substitution phenomenon.

Keywords: CMR oxide; Composite

1. Introduction

Perovskite structured manganites, specifically La–Ca–Mn–O, LCMO and La–Sr–Mn–O, LSMO have been studied extensively in the recent past as they exhibit simultaneous magnetic and electrical transitions in certain composition ranges [1,2]. The manganites undergo a paramagnetic, semiconducting to ferromagnetic, metallic transition on cooling which is accompanied by a large conductivity enhancement in the presence of an external magnetic field—negative magnetoresistance. The decrease in magnetoresistance in these oxides becomes extremely large, colossal, near the transition temperature, a phenomenon of great interest to information storage applications. The magnitude of MR which depends on the magnitude of external magnetic field applied becomes colossal only in the presence of large fields at the transition temperature which in turn depends on the composition. Hence in order to enhance the magnitude of MR in the presence of relatively low fields and at high temperatures, substitution doping [2–5], grain size reduction [6,7], distribution of the manganite grains in a non-magnetic insulating matrix and magnetic insulating matrix are used as alternative approaches [8–12]. The paramagnetic, semiconducting state to ferromagnetic, metallic state transition temperatures are found to decrease with substitution doping and grain size reduction. The lowering of transition temperatures is accompanied by an increase in the resistivity and reduced saturation magnetization. The magnetoresistance on the other hand is found to increase with decreasing temperature in the ferromagnetic, metallic state. In the case of composites made using La–Sr manganite and hard magnetic insulators such as Co-ferrite [10], Ba-ferrite [13], it was found that magnetic coupling between the two phases affects the magneto-transport behavior. The composites in these studies however were made by mechanical mixing of the two constituent phases which had very different grain sizes. The process of mechanical mixing together with asymmetric grain size distribution of the two phases lead to problems in percolation related conduction in the composite together with magnetic coupling between the two phases. These composites do not
really provide information about electronic interactions between the two phases present as they are masked by percolation effects.

In the present work therefore composite mixtures of La-Ca-manganite and Ni-ferrite a magnetic insulator, have been made in situ using microwave assisted refluxing technique [13–17]. This technique has the inherent advantage of uniformly distributing the two phases and the two phases will also have a similar grain size distribution as they will be subjected to identical processing conditions. This will overcome the limitations of asymmetric grain sizes for the two phases encountered in earlier investigations and thus facilitate study of possible electronic interactions between the two phases, LCMO and NF. The LCMO–NF nanocomposite studied in the present work has been investigated for the first time in detail although similar composites with different oxides have been studied earlier. The interesting aspect of these nanocomposites is that above the transition temperatures corresponding to LCMO phase, the nanocomposite will be electrically insulating but magnetic due to the presence of NF. Below the transition temperatures of LCMO the composite will be conducting and also magnetic with a CMR behavior. This temperature dependent behavior makes it attractive for innovative applications in magnetic information storage. At the present time however realizing devices from such composites is in development stages as the physical properties are yet to be completely understood. Hence, the present work aims at studying the physical properties such as electrical transport behavior and magnetic transition of these LCMO–NF nanocomposites to understand the effect of Ni-ferrite addition on the electrical transport and magnetic properties of La-Ca-manganite.

2. Experimental methods

Nanograin sized composites of (1 − x)M La$_{0.67}$Ca$_{0.33}$MnO$_3$ (LCMO)$_x$M NiFe$_2$O$_4$ (NF) where x = 0, 0.01, 0.02, 0.05, 0.10, 0.15, 0.50 and 1 M represents molecular weight, were prepared by precipitation using microwave refluxing. Simultaneously decreasing the concentration of LCMO from 1 M and increasing the concentration of NF in solution increases the quantity of NF in the composites. Stoichiometric amounts of La-acetate, Ca-acetate, Mn-acetate, NiCl$_2$·6H$_2$O and FeCl$_3$ salts were partially dissolved in ethylene glycol to obtain a precursor solution. The pH of this solution was ∼5.8 for all compositions, except for the case of x = 1 where the pH was 0.9. Initially the salts were not completely soluble in ethylene glycol. Addition of KOH to this solution at ∼80°C converts the acetate to hydroxides and the solution becomes clear at a pH of 10.5. Increasing the pH to ∼11.5 leads to a gel formation in all the cases except for x = 1 where it forms a gel at a pH of ∼2.5. The gel solution was refluxed at ∼200°C, boiling point of ethylene glycol, using a microwave heat source (250 MHz, 980 W) for a period of 1.0 h. The precipitate obtained after refluxing was centrifuged and washed with distilled water several times (20). The centrifuged powder was finally dried using an IR lamp. Thermogravimetric analysis was done up to 900°C at a rate of 10°C min$^{-1}$ to determine the calcination and sintering temperatures. The thermogravimetric analysis shows that in all the cases ∼30–35% weight loss occurs below 250°C corresponding to evaporation of ethylene glycol. The weight loss decreases with increasing temperature and becomes nearly 0 for T > 700°C. Hence, calcination of the powders was done at 700°C for 1 h and sintering at 850°C. The calcined powder was cold pressed without any binders into a pellet before sintering at 850°C for 30 min.

Microstructural characterization of the composite was done using a combination of X-ray diffraction and transmission electron microscopy. Cu K$_\alpha$ radiation, λ = 0.1541 nm, was used for X-ray diffraction and the X-ray diffraction patterns were recorded at slow scanning speeds of 0.08° min$^{-1}$ for an accurate phase identification by Rietveld refinement. The electrical transport in the temperature range 20–300 K was studied using the standard dc four-probe technique in the presence and absence of a magnetic field. The magnetic transition was studied using a Faraday balance in an external field of 0.3 T and also a vibrating sample magnetometer at high temperatures to determine the Curie temperature.

3. Results and discussion

The results of phase identification by powder X-ray diffraction are shown in Fig. 1. The diffraction patterns do not show any clear peaks in the as-prepared condition indicating the absence of

![Fig. 1. The X-ray diffraction patterns of (1 − x)M La$_{0.67}$Ca$_{0.33}$MnO$_3$ (LCMO)$_x$M NiFe$_2$O$_4$ (NF) composites exhibit clear crystalline peaks. The NF phase is observed only in composites with x > 0.10 M. All the peaks could be identified with either LCMO or NF phases. The development of NF phase in the composites is marked by an asterisk for 0.10 M NF.](image-url)
Table 1
The unit cell parameters obtained by Reitveld refinement of the X-ray diffraction pattern for the two components, La–Ca–Mn–O and Ni-ferrite in the composite mixtures as a function of increasing Ni-ferrite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameter (Å)</th>
<th>Space group</th>
<th>Cell volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
</tr>
<tr>
<td>L</td>
<td>5.507(8)</td>
<td>7.766(9)</td>
<td>5.465(3)</td>
</tr>
<tr>
<td>0.01 M NF</td>
<td>5.515(3)</td>
<td>7.769(3)</td>
<td>5.469(5)</td>
</tr>
<tr>
<td>0.0 M NF</td>
<td>5.520(6)</td>
<td>7.774(1)</td>
<td>5.471(2)</td>
</tr>
<tr>
<td>0.05 M NF</td>
<td>5.521(6)</td>
<td>7.776(3)</td>
<td>5.472(8)</td>
</tr>
<tr>
<td>0.10 M NF</td>
<td>5.522(8)</td>
<td>7.785(8)</td>
<td>5.476(1)</td>
</tr>
<tr>
<td>0.15 M NF</td>
<td>5.523(2)</td>
<td>7.781(8)</td>
<td>5.473(2)</td>
</tr>
<tr>
<td>0.50 M NF</td>
<td>5.524(0)</td>
<td>7.799(7)</td>
<td>5.497(6)</td>
</tr>
<tr>
<td>NF</td>
<td>8.352(8)</td>
<td>8.352(8)</td>
<td>8.352(8)</td>
</tr>
</tbody>
</table>

L represents La–Ca–Mn–O, NF represents Ni-ferrite and a, b, c are the three unit cell lengths.

either of the crystalline phases—LCMO or Ni-ferrite. The crystalline phase formation takes place on calcining at 700 °C and sintering at 850 °C, as seen clearly in Fig. 1, which shows several peaks. In the case of composites with x < 0.05 M NF, the diffraction pattern indicates the presence of only the LCMO phase. Increasing the NF content to 0.10 M results in the appearance of separate NF phase and this grows with increasing concentration. A Reitveld structural refinement procedure was used to analyze the diffraction patterns and it was found that for x < 0.10 M, the NF phase is not detectable. All the peaks in the X-ray diffraction pattern could be identified with either the LCMO phase or NF phase. This clearly shows that the two phases LCMO and NF, form separately with no detectable third phase. The LCMO phase has an orthorhombic crystal structure corresponding to the Pnma space group while NF is cubic, Fd3m. The unit cell parameters and unit cell volume obtained from Reitveld refinement are given in Table 1.

The size of the LCMO and NF grains in the composites was determined from the half width of the diffraction peaks using Scherer relation and is given in Table 2. The grain size of both the phases is found to be in the 10–40 nm range showing that no significant grain growth takes place during sintering and that it is independent of composition. The grain size was also determined independently using bright field transmission electron microscopy and the typical micrographs from LCMO, NF and composite mixture of the two phases are shown in Fig. 2. The selected area diffraction patterns from pure LCMO, NF, LCMO:0.50 M NF are also shown in Fig. 2. The grains are polyhedral in nature and agglomerate into large particles of size ≈70 nm. The average grain size is found to be ~25 nm, in agreement with the X-ray results. The selected area diffraction pattern from the composite with 0.50 M NF shows several rings which were found to be a superposition of the diffraction patterns from pure LCMO and NF. This clearly shows that the two phases, LCMO and NF are present as individual components in the composite with different grain sizes without intermixing.

The electrical resistivity of LCMO, NF and the composites in the absence of external magnetic field was studied in the temperature range 20–300 K and is shown in Fig. 3. Pure LCMO phase exhibits an insulator–metal transition at TMI on cooling at ∼215 K, in agreement with earlier results [6]. Addition of NF to LCMO is found to decrease this transition temperature and finally lead to complete suppression for x as low as ∼0.05 M NF. The composites exhibit a typical semiconducting or insulating resistivity behavior for x ≥ 0.05 M. The absolute resistivity

Table 2
The structural, electrical and magnetic transition parameters of La–Ca–Mn–O and Ni-ferrite composites

<table>
<thead>
<tr>
<th>x M NF</th>
<th>Crystallite size (XRD) (nm)</th>
<th>Particle size (TEM) (nm)</th>
<th>TMI (K)</th>
<th>TC (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LCMO phase</td>
<td>NiFe₂O₄ phase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>13.8</td>
<td>*</td>
<td>20–60</td>
<td>215</td>
</tr>
<tr>
<td>0.01</td>
<td>14.2</td>
<td>*</td>
<td>20–60</td>
<td>210</td>
</tr>
<tr>
<td>0.02</td>
<td>14.8</td>
<td>*</td>
<td>20–80</td>
<td>90</td>
</tr>
<tr>
<td>0.05</td>
<td>15.6</td>
<td>*</td>
<td>20–80</td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>17.5</td>
<td>10.8</td>
<td>20–80</td>
<td></td>
</tr>
<tr>
<td>0.15</td>
<td>18.4</td>
<td>19.5</td>
<td>20–100</td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>24.8</td>
<td>35.2</td>
<td>20–120</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td></td>
<td>38.5</td>
<td>70–120</td>
<td></td>
</tr>
</tbody>
</table>

TMI and TC represent the insulator–metal and magnetic transition temperatures respectively. *Phase not detected. **Transition not detected.
Fig. 2. Diffraction pattern of composite with $x = 0.50$ M NF shows several rings which were found to be a superposition of the diffraction patterns from pure LCMO ($x = 0$ M) and NF ($x = 1.0$ M). The bright field micrographs corresponding to the three cases are shown below the selected area diffraction patterns. The scale bar corresponds to 100 nm in all the cases.

was also found to increase by orders of magnitude below room temperature as the NF content increases in the composites. The resistivity below 90 K for $x = 0.05$, 0.10 and 0.15 M composites and below 180 K for $x = 0.50$ M composite could not be measured accurately as it was $>10^6 \Omega \text{cm}$. The resistivity of pure NF also could not be measured as it was highly insulating in nature. Huang et al. [12] studied the electrical behavior of LSMO/Ba-ferrite composites with increasing ferrite content and found that the absolute resistivity increases with increasing insulating ferrite content, in agreement with the present results. The magnetoresistance measured in an external magnetic field of 8.5 kOe is shown in Fig. 3 inset for $x < 0.02$ M NF. For $x > 0.02$ M NF the composites exhibit a semiconducting behavior which does not have any negative magnetoresistance and hence they were not studied. The MR in general increases continuously with decreasing temperature in both the cases and reaches about 16% at 85 K. The MR in the temperature range between $T_C$ and $T_{MI}$ in both the cases however shows a slight saturating behavior, possibly due to the presence of non-metallic ferromagnetic state in this range.
The magnetic transition temperature $T_C$ of the composites determined in an external field of $0.3\, T$ is shown in Fig. 4. The paramagnetic to ferromagnetic transition on cooling is progressively decreased to lower temperatures with increasing addition of NF to LCMO (see Table 2). The transition temperature $T_C$ decreases from $\approx 250\, K$ for pure LCMO to $\approx 125\, K$ when $x = 0.15\, M$. For composites with $>0.15\, M$ NF the magnetic behavior is dominated by NF which has a $T_C$ of 858 K, well above the room temperature. For $T < 300\, K$ however both pure NF and 0.50 M NF composite exhibit a nearly temperature independent susceptibility behavior consistent with the transition temperature of pure NF. The lowering of $T_C$ with increasing NF is in qualitative agreement with the electrical and magnetic transitions shows that the grain boundaries play a significant role in magnetotransport behavior of the composites. In order to determine the magnetic transition behavior of NF rich composites, the magnetization of these electrically insulating composites was studied in an external field of 0.3 T in the range 80–300 K and the results are shown in Fig. 5 and Table 2. The $T_C$ of NF decreases from 860 to 475 K for $x = 0.10\, M$ composite. The absolute magnetization of the composites at 85 K in an external magnetic field of 20 kOe is shown in the inset of Fig. 5 and it shows a sharp drop till $x = 0.15\, M$ before reaching a saturation behavior for NF dominated composites. A combination of low temperature and high temperature magnetization studies clearly show that NF rich composites exhibit a single magnetic transition temperature corresponding to that of NF while low NF composites exhibit both NF and LCMO magnetic transitions above and below room temperature as shown in the inset of Fig. 5.

The phenomenon of colossal magnetoresistance in manganites is due to a combination of magnetic and electrical transition occurring simultaneously. The double exchange process, which mediates these transitions, depends on external factors and is highly susceptible to processing conditions and the chemical composition. In the case of pure LCMO ($x = 0\, M$) the double exchange process is due to electron transport via $\mathrm{Mn}^{3+}–\mathrm{O}^2–\mathrm{Mn}^{4+}$. Addition of transition metal ions which substitute either the $\mathrm{Mn}^{3+}$ or $\mathrm{Mn}^{4+}$ are known to suppress the double exchange process and promote insulating, antiferromagnetic behavior. The lowering of electrical and magnetic transition temperatures coupled with an increase in absolute resistivity with the addition of NF to LCMO observed in the present work clearly shows that the double exchange process in LCMO is severely affected. Ahn et al. [18] and Sun et al. [19] find that systematic doping of $\mathrm{Mn}^{3+}$ by $\mathrm{Fe}^{3+}$ induces insulating, antiferromagnetic behavior. A substitutional doping with 0.18 Fe for Mn results in complete suppression of the transitions and an insulating behavior. In the case of Ni doping a similar behavior, promoting insulating, antiferromagnetic state at the expense of metallic, ferromagnetic state is observed [20,21]. At relatively low doping levels the ferromagnetic interactions such as $\mathrm{Mn}^{3+}-\mathrm{O}^2–\mathrm{Ni}^{2+}(\mathrm{Fe}^{3+})$ and $\mathrm{Mn}^{3+}-\mathrm{O}^2–\mathrm{Mn}^{4+}$ account for the weak transitions. At high doping levels however the antiferromagnetic super-exchange interactions, $\mathrm{Mn}^{4+}–\mathrm{O}^2–\mathrm{Mn}^{4+}$, $\mathrm{Ni}^{2+}–\mathrm{O}^2–\mathrm{Ni}^{2+}$ and $\mathrm{Fe}^{3+}–\mathrm{O}^2–\mathrm{Fe}^{3+}$ dominate resulting in an insulating, non-magnetic state for the LCMO phase. The presence of Ni- and Fe-salts in the precursor solution acts as a source of Ni- and Fe-ions for substituting Mn in LCMO in the present work. The volume of LCMO unit cell is found to increase with the addition of NF as seen from the data given in Table 1, which has not been observed earlier. This is probably due to the large size of $\mathrm{Ni}^{2+}$ and $\mathrm{Fe}^{3+}$ compared to $\mathrm{Mn}^{3+}$ and $\mathrm{Mn}^{4+}$ where the substitutions take place. The volume of pure LCMO unit cell in the present work is found to be $\approx 233.8\, \text{Å}^3$ which has an average grain size of $\approx 14\, \text{nm}$, determined from X-ray diffraction results. This unit cell value is close to that observed...
for bulk LCMO wherein the grain size is of the order of several microns. The reduction of $T_C$ and $T_M$ observed for this nanometer grain LCMO is due to the increased surface effect that has been observed earlier but contrary to the enhancement in transition temperatures reported recently [22].

The composite synthesized with 0.5 M NF in the precursor solution exhibits peaks in the X-ray diffraction pattern (Fig. 1), corresponding to both the phases, LCMO and NF. This composite however does not exhibit either electrical or magnetic transitions at low temperatures, <300 K except for the high temperature magnetic transition at 745 K. The Mn-ions in the LCMO phase in this composite get heavily substituted with Ni or Fe, leading to large lattice expansion as seen by Reitveld analysis of the X-ray diffraction data (Table 1). This changes the electronic behavior completely to semi-conducting, non-magnetic nature. The Ni-ferrite phase on the other hand which is ferromagnetic and insulating, undergoes a magnetic transition as seen in Fig. 5. The transition temperature in this case is reduced compared to that of pure Ni-ferrite, $x = 1.0$, because of loss of Ni and or Fe to the LCMO phase in the composite. Hence in the present work compositions beyond $x = 0.5$ M were not investigated in detail as they will not be of importance for magnetoresistance based applications.

Yan et al. [10] and Huang et al. [12] have studied the effect of insulating, ferromagnetic (FM) phase on the magnetotransport and magnetic behavior of La–Sr–Mn–O, a colossal magnetoresistive oxide similar to LCMO. They find that the presence and magnetic behavior of La–Sr–Mn–O, a colossal magnetoresistive, ferromagnetic (FM) phase on the magnetotransport behavior observed by Yan et al. [10] and Huang et al. [12].

The MR for the 0.01 M NF composite shows an increasing behavior with decreasing temperature, similar to the behavior observed by Yan et al. [10] and Huang et al. [12]. The MR is found to be 16% at 85 K in a field of 8.5 kOe, shown in the inset of Fig. 3.

4. Conclusions

The electrical and magnetic properties of magnetic La–Ca–Mn–O and insulating magnetic Ni-ferrite composites prepared by an in situ technique have been studied in detail. The in situ preparation technique results in the formation of uniformly distributed nanograin composite mixture of the two phases. The La–Ca–Mn–O phase however loses its negative magnetoresistive behavior due to a substitution of Mn with either or both Ni and Fe. The electrical transition is suppressed for $x > 0.02$ M NF while the magnetic transition is observed till $x = 0.15$ M NF. The nanograin size of the LCMO phase has a significantly high grain boundary scattering, which leads to enhanced resistivity and a reduction in the metallic behavior. This results in a lower critical value of Ni-ferrite for insulator–metal transition compared to the magnetic transition. These results clearly show that Mn substitution by Ni and Fe is more favored compared to the formation of pure La–Ca–Mn–O when all the cations are present. Above $x = 0.10$ M however the Ni-ferrite phase forms separately together with substituted La–Ca–Mn–O phase which is insulating and antiferromagnetic. The suppression of electrical transition in composites with $x > 0.02$ M NF but the presence of a magnetic transition in these composites indicates that although the classical double exchange is effective in the ferromagnetic phase, lack of a percolative conduction path leads to the absence of a macroscopic metallic state.

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References