Magnetic and electrical transport properties of La$_{0.67}$Ca$_{0.33}$MnO$_3$ (LCMO): xSiCN composites

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The magnetic and electrical transport properties of La$_{0.67}$Ca$_{0.33}$MnO$_3$ (LCMO): xSiCN (x = 0–40 vol %) composites, synthesized by mechanical mixing of citrate gel derived LCMO and polymer derived ceramics SiCN, have been investigated as a function of composition. The ability of SiCN to behave as a sintering additive leads to interesting magnetic and electrical properties. Si$^{4+}$, being strongly favored for tetrahedral coordination, cannot enter the perovskite lattice. Saturation moment, $M_S$ of 68 emu/gm at 5 K and at 5 kOe field of pure LCMO shifts to 79 emu/gm in the sample with x = 0.05 and then decreases monotonically as x increases further. The lower $M_S$, $T_C$ and high electrical resistivity of the sample with x = 0, compared to those which have been reported in the literature, is due to small particle size in nm range. SiCN as a sintering aid increases the particle size of LCMO to 1–2 μm for x = 0.10. Three orders of magnitude change in electrical resistivity (204 Ω cm for x = 0; 0.5 Ω cm for x = 0.05) is explained on the basis of the difference in the mobility of the charge carriers, by fitting the experimental transport data with a correlated polaron hopping model. © 2004 American Institute of Physics. [DOI: 10.1063/1.1667447]

Mixed oxide of rare earth and transition metal elements of the type La$_{1-x}$Ca$_x$MnO$_3$ has spurred considerable interest since the discovery of colossal magnetoresistance (CMR) in these systems in 1993. CMR effect in these compounds is mainly due to the double exchange process as proposed by Zener in 1951. Among the various perovskite manganites, substitutions at the La site (A site) and at the Mn site (B site) have been extensively tried to enhance the CMR effect. Attempts have also been made to increase the MR through the formation of some composites.

In the present work we have incorporated SiCN, a polymer derived ceramics (PDC), as the second phase in La$_{0.67}$Ca$_{0.33}$MnO$_3$ (LCMO) matrix. The main objective of this study is to synthesize a homogeneous composite where SiCN is expected to be present at the grain boundaries of LCMO either as bare SiCN or as any reaction product between LCMO and SiCN. Since Si$^{4+}$ is unlikely to enter the perovskite structure of LCMO owing to its strong preference for tetrahedral coordination, the present investigation intends to demonstrate the effect of a conducting phase (SiCN) on the transport and magnetic properties of LCMO. We have used x-ray diffraction (XRD), scanning electron microscopy (SEM), M vs T, ρ vs T, and MR vs T to characterize these composites. A correlated polaron hopping model has been used to explain the transport properties.

LCMO-SiCN composites containing 5, 10, 20 and 40 vol % of SiCN have been synthesized by solid-state mechanical mixing of citrate gel derived LCMO and polymer derived ceramics (PDC) SiCN followed by sintering at higher temperatures. Conducting SiCN was prepared from commercially available liquid polymer precursor, Ceraset. Composite pellets were sintered at 1100°C for 2 h in static air. The details of structural, electrical and magnetotransport studies have been discussed in this article.

The XRD patterns of the composites show reflections corresponding to the LCMO phase along with the lines from insulating phase Ca$_2$La$_4$(SiO$_4$)$_6$O$_2$. This insulating phase crystallizes gradually as the vol % of SiCN increases in the composites. Cubic symmetry is observed in all the samples. The lattice parameter shows no significant change. This shows that the stoichiometry of the LCMO phase was preserved in all specimens with no Si$^{4+}$ incorporation into the

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LCMO lattice. The lattice parameters of all the composites are given in Table I.

The ESEM micrographs of pure LCMO \((x = 0)\) show the presence of clusters in the matrix. Each cluster contains very fine particles whose diameter is much less than a micron. Addition of SiCN in LCMO matrix acts as a sintering additive. The microstructure of the sample with \(x = 0.10\) shows particles with diameter of the order of 1–2 \(\mu m\). The presence of the insulating phase, silicate, in the LCMO matrix is seen in the micrographs as the black areas.

The temperature dependence of magnetization of the composites, measured at 5 kOe field, is shown in Fig. 1. The saturation magnetization, \(M_S\), at 5 kOe and at 5 K for pure LCMO \((x = 0.0)\) is 67.9 emu/g and a broad \(T_C\) (measured from the minimum of the \(dM/dT\) vs \(T\) curve and given in Table I) is 180 K. The magnetization reaches nearly zero at around 270 K. If all the Mn\(^{3+}\) and Mn\(^{4+}\) spins were aligned parallel due to double exchange, the value expected for pure LCMO (assuming spin only moment) would be approximately 98 emu/g. The reduced value of the saturation moment \(M_S\) and transition temperature \(T_C\) of pure LCMO with wide transition is due to the extremely small particle sizes as well as the presence of FM clusters in the matrix. Addition of 5 vol% SiCN in pure LCMO helps in growth of the LCMO particle and improves the LCMO interparticle contact. Mahesh et al.\(^{10}\) have also observed a suppression of susceptibility as the particle size of LCMO was decreased. The saturation moment for LCMO: xSiCN composites marginally increase for \(x = 0.05\). For \(x > 0.05\), \(M_S\) decreases with \(x\) as would be expected due to the decrease in volume fraction of the LCMO phase and increase of the nonmagnetic phases containing Ca\(_2\)La\(_8\)(SiO\(_4\))\(_6\)O\(_2\) in these composites. All the composites show similar behavior of \(M\) as a function of \(T\) except for a small upturn kink at around 50 K which develops for \(x > 0.05\). Such anomaly has been reported earlier in composites of LCMO with SrTiO\(_3\)\(^6\) and SiO\(_2\)\(^7\) as well as some substituted LCMO samples.\(^{11,12}\) This has been explained on the basis of local microscopic magnetic inhomogeneities\(^{12}\) or due to the presence of the paramagnetic MnO\(_2\) phase in the compound.\(^{11}\) We did not observe MnO\(_2\) phase in XRD but for higher vol% of SiCN \((x \geq 0.10)\) we could observe some Mn rich phase in ESEM microstructure. The variation of, \(M_S\), with composition \((x)\) has been plotted in the inset of Fig. 1. The decrease in \(M_S\) with vol% SiCN added \((x)\) is much more than what can be expected on the basis of the nonmagnetic SiCN phase only. This indicates that SiCN reacts with part of the LCMO to form the insulating Ca\(_2\)La\(_8\)(SiO\(_4\))\(_6\)O\(_2\) phase thereby reducing the magnetic LCMO phase further.

The resistivity versus temperature curves in the range 5–375 K are given in Fig. 2. All the compositions show a distinct metal-insulator transition, \(T_{MI}\) at a temperature close to their ferromagnetic transition temperature, \(T_C\) (Table I). The peak resistivity, \(\rho_{MI}\), drastically drops from 204 \(\Omega\) cm for pure LCMO \((x = 0.0)\) to 0.15 \(\Omega\) cm for \(x = 0.05\) which is about three orders of magnitude less. The metal-insulator transition temperature also shifts to 265 K for the sample with \(x = 0.05\) from 169 K for pure LCMO \((x = 0.0)\) and then decreases marginally as \(x\) increases further. The increase in \(T_{MI}\) and decrease in resistivity with the addition of SiCN in LCMO are due to the particle size effect discussed earlier. The lower \(T_{MI}\) of the pure LCMO is observed earlier\(^{13}\) and has been ascribed to the presence of the nonstochiometric defects.

The resistivity has been examined using the dc hopping resistivity based on the correlated small-polaron hopping model discussed in details elsewhere.\(^{14}\) To fit our resistivity data we have used \(S_\sigma^2 = 1, \sigma_\sigma^2 = (1 - 0.95S_\sigma^2)^{1/2}\) and \((1 - S_m)^2 = (1 - m^k)\), where \(k\) is a variable dependent on the

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<th>(M_S) (emu/g)</th>
<th>(T_{MI}) (K)</th>
<th>(\rho_{MI}) (Ω cm)</th>
<th>%MR</th>
<th>(n) ((10^{17}\text{ cm}^{-3}))</th>
<th>(U_0) (K)</th>
<th>(T_{ca}) (K)</th>
<th>(\epsilon_p) (K)</th>
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**FIG. 1.** Magnetization behavior of the composites LCMO: xSiCN \((0 \leq x \leq 0.40)\) with temperature at 5 kOe field. Inset shows the variation of saturation magnetization (measured at 5 kOe field) with composition, \(x\).
compositions ($x$). The $\theta$ added to $T$ in the cosh term, compared to the original equation discussed in Ref. 9, is to take care of the zero point vibration of the atoms which prevent the complete localization of the polarons as $T \to 0$ and is taken as 50 K to fit the experimental data. The coefficient “$c$” and “$c'$” has been taken as 0.35 and 0.05, respectively, for pure LCMO ($x=0$). These coefficients for the other composites ($0.05 < x < 0.40$) have been taken as 0.33 and 0.78, respectively, to fit the resistivity data. The other parameters used to fit the resistivity data have been given in Table I and the fit to the experimental resistivity data for the composites is shown in Fig. 2 as solid lines. In each case there is a good fit with theory for $\rho(T)$ in the range 20 K–$T_C$. Using Eqs. (1) and (2) described in Ref. 14 and the parameters given in Table I, the charge carrier density $n$ has been calculated and is found to increase from $2.1 \times 10^{17}$ cm$^{-3}$ for $x=0$ to $82.2 \times 10^{17}$ cm$^{-3}$ for $x=0.05$ and then gradually decreased to $1.5 \times 10^{17}$ cm$^{-3}$ up to $x=0.40$. The activation energy for polaron hopping also decreases from 755 K for $x=0$ to 415 K for $x=0.05$ and then monotonically increases to 575 K up to $x=0.40$.

The MR results with 5 T field for all the composites are shown in Fig. 3. These results show a peak near $T_C$ followed by a large temperature independent MR and a low temperature rising part at the end. While $\rho_{MT}$, $T_{MT}$, $T_C$ and long range ferromagnetic order are greatly affected by the particle size, the value of MR near the peak does not show a significant change. But the MR shows a sharp peak near $T_C$ for the composites with bigger particle size against a broad plateau for pure LCMO. MR is not affected much by the particle size as also suggested by Mahesh et al.\textsuperscript{10} The magnetic field dependence of MR is shown in the inset of Fig. 3 for the composition $x=0.05$ and 0.10. The low field MR behavior supports the grain boundary scattering of the polarized electrons. Mahendiran et al.\textsuperscript{15} have observed a similar effect of low field MR behavior for their pure LCMO and have explained the low field region to arise from the motion of the domain walls and the high field region to arise from the gradual increase of the spontaneous magnetization on application of the magnetic field.

Therefore, the magnetic and electrical transport properties of LCMO:SiCN composites are greatly affected by the particle size.

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