Magnetoresistive behaviour of $\text{La}_{0.67}\text{(Ca}_{0.33}-x\text{Pb}_x)\text{MnO}_3$ nanopowders prepared at lower temperature

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Abstract

We have been able to prepare ultrathin powders of pure and doped $\text{La}_{0.67}\text{Ca}_{0.33-x}\text{Pb}_x\text{MnO}_3$ (LCMO) at a relatively lower temperature of 550°C using a simple, cost-effective and versatile PVA-based chemical route. A maximum magnetoresistance (MR) ratio of $-25\%$ is obtained at 20 K in a magnetic field of 3 kOe. Magnetoresistive behaviour being retained in the nanopowders may have implications for enhancing data storage capacity. The semiconductor-to-metal transition temperature, $T_n$, however, shifts towards the lower temperature as the particle size is reduced. To improve $T_n$ and near-room-temperature MR additives like $\text{NH}_4\text{NO}_3$ and citric acid have been used. In addition, Pb is substituted for Ca.

Keywords: Magnetoresistance; Chemical route; Nanopowders

1. Introduction

The increasing demand for miniaturized high-density magnetic information storage and faster reading devices has driven a significant worldwide effort to improve performance of relevant hardware components. In recent past, giant magnetoresistive (GMR) [1] spin valve structures for magnetic reading heads have come up as a successful alternative to the conventional inductive or anisotropic magnetoresistive (permalloy) reading heads. These GMR sensors promise wide-ranging applications in a variety of other areas as well. Recently, perovskite manganites $\text{A}_{1-x}\text{B}_x\text{MnO}_3$ (A=rare earth, B=Ca, Sr, Ba, etc.) have been widely investigated for their suitability as a next generation MR sensor material. The complex and intimate link among magnetic structure, crystallographic structure and electrical resistivity makes this family of materials more attractive for fundamental scientific study.

$\text{AMnO}_3$ is an antiferromagnetic insulator, but doping of divalent cation $\text{B}^{2+}$ at the rare earth site results in a mixed valence state of $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$. This leads to a quasi-metallic conductivity and ferromagnetic ordering, the latter being developed due to double exchange [2] interaction, which involves electron exchange between neighboring $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$ sites. As a consequence, a field induced temperature-dependent change in electrical resistivity is observed giving rise to a large negative magnetoresistance, i.e., colossal magnetoresistance (CMR) [3]. A generally accepted qualitative explanation of the CMR effect has been given in terms of the magnetic polarons [4]. Above the ferromagnetic ordering temperature ($T_n$) the structural and magnetic interactions lead to the formation of magnetic polarons, composed of an electron (Mn d-state), which ferromagnetically polarizes the surrounding ionic magnetic moment. This quasi particle conducts via thermally assisted hopping. On cooling below $T_n$, the magnetic order destroys the polaron and the resistivity drops with decreasing temperature.

The key to the application suitability of this material system lies in getting a large magnetoresistive response at room temperature and at a low external magnetic field. Some additional important parameters that may have significant role for potential industrial use are the processing temperature and the final grain size. As far as the production of bulk powders for applications is concerned, the common practice is to prepare these by the conventional ceramic (solid state reaction) route. But this route has several limitations [5] in the production of fine powders as it involves sintering at very high temperature (>1400°C) which leads to larger grain size (~200 nm or more). Many
of the limitations of the ceramic technique have been overcome by employing chemical synthesis routes [6]. In this study, we have used a simple, low cost and versatile PVA-based chemical synthesis route to prepare nanopowders of pure and Pb-doped La$_{0.65}$Ca$_{0.35}$MnO$_3$ (LCMO) to investigate their magnetoresistive behavior at a low magnetic field of 3 kOe.

2. Experimental

The chemical route used to obtain the desired metal oxide systems consists of first preparing an aqueous solution of the constituent metal acetates/nitrates in the desired stoichiometric proportion. An aqueous solution of PVA (mol. wt. = 125 000, 10%, w/v) is added to the mixed metal acetates/nitrates solution at a fixed metals ion to vinyl alcohol monomer unit mole ratio (1:2 or 1:4). The resulting homogeneous viscous solution is then gradually heated to ~150°C with constant stirring till a black fluffy dehydrated precursor powder is left behind. This precursor powder is then ground, pelletized and sintered at a temperature ($T_s$) lying in the range 500–900°C. Pure LCMO powders were prepared by the above-mentioned chemical route and the role of NH$_4$NO$_3$ and citric acid as additives to the PVA mixed metal ion solution was also studied. The resulting pure and Pb-substituted powders of different compositions are La$_{0.65}$Ca$_{0.35}$MnO$_3$ (LCMO), La$_{0.65}$Ca$_{0.35}$Pb$_{0.6}$MnO$_3$ (LCPMO1), La$_{0.65}$Ca$_{0.35}$Pb$_{0.5}$MnO$_3$ (LCPMO2) and La$_{0.65}$Pb$_{0.35}$MnO$_3$ (LPMO).

The constituent phases and crystallographic structure of the pellets were investigated using an X-ray diffractometer with Cu K$_\alpha$ radiation obtained from a 12 kW rotating anode (model Gigerflex-DR/max-RD-RU200, Rigaku, Japan). Electron microscopic study was carried out in order to confirm the particle size and the polycrystallinity of the powders using a CM20 TEM Philips transmission electron microscope. The electrical resistance of the pellets as a function of temperature was measured by the conventional dc four-probe technique in van der Pauw configuration using a closed cycle He cryostat (APD Cryogenics). A programmable Keithley 224 current source was used to apply a constant current and the resulting voltage was measured with a programmable Keithley 181 nanovoltmeter. In all these cases, for estimation of magnetoresistance, the resistance measurements were carried out at zero as well as at a fixed field of 3 kOe. The magnetoresistance ratio (MR) was calculated as ($R_{3 kOe}$/$R_{0}$) × 100.

3. Results and discussion

The versatile PVA-based chemical synthesis route provided ultra fine powders of the desired perovskite systems. PVA plays dual role [7,8] in the preparation of such fine powders. Firstly, the metal ions get embedded in the long chain polymeric network of the PVA which plays a wrapping and covering role for the cations in the solution so that their mutual contact is avoided and they do not grow in size. This in turn inhibits the segregation and the precipitation of the metal ions in the solution during evaporation. Secondly, the heat liberated during exothermic thermal decomposition of the carbonaceous precursor powder facilitates the solid phase reaction among the constituent metal ions so that the perovskite phase formation takes place at a reduced processing temperature.

The X-ray diffraction patterns obtained for the pure LCMO samples prepared from acetates with metal ion to vinyl alcohol monomer unit mole ratio 1:2 and sintered at different $T_s$ are shown in Fig. 1. It is evident that the samples sintered at and above 550°C crystallize into a single phase perovskite structure of LCMO and have a lattice parameter ~7.7 Å. The average crystallite sizes of the samples are estimated from the classical Scherrer equation [9], i.e., $D_{hkl} = k \lambda / (β/2cosθ)$, where $D_{hkl}$ is the average diameter of the crystal grain, $k$ a constant (shape factor = 0.89), $λ$ the wavelength of X-rays (1.54 Å), $θ$ is the angle of diffraction, $β/2$ the measured full-width at half-maximum (FWHM) of the peak in question and $β$, the FWHM of coincident SiO$_2$ peak used to calibrate the intrinsic width associated with the instrument. The average grain size of a sample sintered at 550°C for 6 h is calculated to be ~25 nm. The same increases to ~40 nm for a sample sintered at 700°C for 12 h and ~89 nm for a sample sintered at 900°C for 24 h. Thus the average grain size is found to be gradually increasing with the sintering temperature. On increasing the metal ion to vinyl alcohol monomer ratio to 1:4 the crystallite size is found to be reduced (~16 nm, sintered at 600°C for 6 h). The crystallite sizes were compared with those obtained from STEM micrographs and were found to be in good agreement.
agreement. The TEM diffraction patterns also confirmed the polycrystalline nature of the powders as observed by XRD.

The electrical resistivity of the samples is observed to decrease substantially with increasing sintering temperature (particle size). When the average particle size increases from 25 to 89 nm the corresponding resistivity value decreases from 230 to 0.15 Ω cm. The measured resistance normalized to that at 300 K for the acetate-based pure LCMO samples is presented in Fig. 2a. The ratio \( \rho(T)/\rho(300) \) increases as the average particle size decreases (Fig. 2a). A semiconductor-to-metal (\(-d\rho/dT \) to \(+d\rho/dT\)) transition is observed in all the samples, and the transition temperature \( T_p \) is observed to shift towards the lower temperature side as the average particle size decreases. This is in agreement with earlier observation [10]. In case of the samples sintered at 600 or 700°C (lower average particle size) the semiconducting behavior reappears at the lower end of the temperature scale, i.e., the resistivity shows an increase again. This observation is more pronounced for smaller particles. This along with the lowering of \( T_p \) can be due to the canting in the manganese sublattice. Since the double exchange [2] between Mn\(^{3+}\) and Mn\(^{4+}\) is strongly dependent on the Mn–O–Mn bond angle, any deviation of the Mn–O–Mn bond angle from the ideal 180° results in the reduction of the hopping probability of the electron between the neighbouring Mn\(^{3+}\)/Mn\(^{4+}\) ions. The reduced hopping probability leads to the increase in the resistivity. The resistivity is lowered on application of an external magnetic field in all samples giving rise to a negative magnetoresistance. A typical MR versus temperature curve for a LCMO sample sintered at 700°C for 3 h is shown in Fig. 2b. A maximum \(|MR|\) of \(-25\%\) was obtained at 20 K for this sample.

The powders prepared from nitrates were found to have better crystallographic structure, i.e., a single-phase perovskite structure without any spurious phase in XRD. In this case also the required perovskite phase formation does not take place at a temperature less than 550°C. The average particle sizes obtained from nitrate-route seem to be lower than those from the acetates. The electrical resistivity of the nitrate-based samples is more than that of the acetate counterpart processed in similar conditions, which further confirms the finer particle nature. A typical normalized resistivity curve of a nitrate-route sample is shown in Fig. 3. The \( T_p \) obtained for a nitrate sample is relatively low in comparison to that of an acetate sample processed at similar conditions.

One of the crucial observations in the LCMO samples is that the \( T_p \) shifts towards the lower temperature as the

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**Fig. 2.** (a) \( \rho(T)/\rho(300) \) of acetate-route LCMO as a function of temperature at \( H=0 \) and 3 kOe for three different representative samples: (I) metal ion to VA monomer ratio 1:2 and sintered at \( T_s = 600°C \) for 3 h; (II) metal ion to VA monomer ratio 1:1 and sintered at \( T_s = 900°C \) for 24 h; and (III) metal ion to VA monomer ratio 1:4 and sintered at \( T_s = 600°C \) for 6 h. (b) MR (%) of the sample 1 as a function of temperature.

**Fig. 3.** \( \rho(T)/\rho(300) \) of a typical nitrate-route LCMO sample with metal ion-to-VA monomer ratio 1:4 and sintered at 900°C for 24 h, as a function of temperature at \( H=0 \) and 3 kOe.
particle size is reduced. This is a drawback as the maximum magnetoresistance at high fields is usually observed near $T_p$. To make the material suitable for technological applications the $T_p$ should be improved to near room temperature values along with an appreciable near room temperature MR.

$\text{NH}_4\text{NO}_3$ and citric acid were added in order to have better homogenization and liquid state reaction completion. This increased the $T_p$ from $\sim 235$ to $\sim 275^\circ\text{C}$ in a sample prepared by acetate-route and sintered at 900°C for 24 h. Similar samples prepared by nitrate-route with $\text{NH}_4\text{NO}_3$ and citric acid additives, however, resulted in an insulating phase. The most significant result in this study is that a magnetoresistance maximum was observed in all ($\text{NH}_4\text{NO}_3$ + citric acid added) acetate-route samples near the $T_p$ (Fig. 4). The improved MR near $T_p$ ($\sim 275^\circ\text{C}$) along with a metallic state may be due to the partial melting of the grain boundaries [11] leading to better grain connectivity. The grain boundary melting could take place at a lower temperature ($\sim 900^\circ\text{C}$) for such systems with ultra fine particles having a large surface energy.

Since maximum high field MR is usually obtained near $T_p$, we have also attempted to increase $T_p$ near to room temperature by suitable doping. Lead [12,13] was chosen for doping at the Ca site to study its effect on $T_p$ and MR. This is because La$_{1-x}$Pb$_x$MnO$_3$ with 0.26 $< x <$ 0.4 is a ferromagnetic metal at 300 K with a Curie temperature ($T_c$) above 320 K [14] and $T_p$ is usually close to the $T_c$. The XRD studies revealed a cubic structure for all the Pb-doped samples. The lattice parameters of LCPMO1, LCPMO2 and LPMO were calculated to be 3.89, 3.90 and 3.91 Å, respectively. As expected, $T_p$ was observed to increase with the addition of Pb to LCBO (Fig. 5) from $\sim 150$ K to a temperature as high as 290 K. In addition, room temperature magnetoresistance of $\sim -2\%$ (Fig. 6) at a low magnetic field of 3 kOe is observed in nano-grained LPMO, while no room temperature MR was detected in LCMO samples.

4. Conclusion

Nanopowders of pure and doped LCMO have successfully been prepared at a lower processing temperature ($\sim 550$ C) by using a simple, cost-effective and versatile PVA-based chemical route. A semiconductor-to-metal transition is observed in all samples and the transition temperature $T_p$, however, shifts towards the lower temperature as the average particle size decreases. Addition of $\text{NH}_4\text{NO}_3$ and citric acid during the preparation of the powders resulted in an improvement of $T_p$ and a MR maximum was observed near $T_p$. The Pb substitution at Ca site consistently increased $T_p$ to 290 K. The magnetoresistive

![Fig. 4](image-url)  
**Fig. 4.** $\rho(T)/\rho(300)$ and MR (%) of LCMO prepared by acetate-route with $\text{NH}_4\text{NO}_3$ and citric acid additives and sintered at 900°C for 24 h.

![Fig. 5](image-url)  
**Fig. 5.** Effect of Pb concentration on $T_p$. The $T_p$ monotonically increases to near-room temperature.

![Fig. 6](image-url)  
**Fig. 6.** Magnetoresistance ratio (MR) versus temperature for a La$_{0.9}$Pb$_{0.1}$MnO$_3$ (LPMO) sample at $H = 3$ kOe.
behave in these nanopowders can be ascribed to the partial melting of the grain boundaries leading to better grain connectivity. The observation of appreciable low field magnetoresistance in such nanoparticle system may encourage data storage in smaller grains. However, a minimum of one order of magnitude change in $\Delta R/R_{H=0}$ at low field ($\sim 100$ Oe) and at room temperature with a metallic state is required to make it suitable for real applications.

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