Magnetic nanoparticle systems have been the topic of extensive interest, both for their novel features and for their scientific applications \cite{1-3}. Nowadays, a lot of focus is primarily on mixed valence manganites Ln$_{1-x}$A$_{x}$MnO$_3$ (Ln = trivalent rare earth element and A = alkaline earth one) due to their applications in the fields of refrigeration, sensors, magnetic memory devices, catalysts biology and medicine \cite{2-6}. La$_{1-x}$Ca$_{x}$MnO$_3$ manganites (LCMO) exhibit interesting magnetic and transport properties such as canted antiferromagnetic (CAF), charge ordering, ferromagnetic (FM) metallic and paramagnetic (PM) insulating \cite{7-10}. The La$_{0.67}$Ca$_{0.33}$MnO$_3$ manganite is of great interest because of its high colossal magnetoresistive (CMR) effect, which can be utilized in magnetic field sensors, memory devices, and so on \cite{11-13}. It has been demonstrated that mixed valence state of Mn in LCMO leads to double exchange (DE) interactions Mn$^{3+}$–O$^2$–Mn$^{4+}$ which are responsible for ferromagnetic metallic state. The variations of Mn$^{3+}$/Mn$^{4+}$ pairs depend on the doping level and oxygen stoichiometry \cite{14}. These variations would influence the electron hopping and carries localization because of change in the Mn–O–Mn bond length and bond angle.

Since the magnetic and transport properties of manganite nanoparticles are dependent on the strength of DE Mn$^{3+}$–O$^2$–Mn$^{4+}$ interactions, the doping at the A-site as well as sintering temperature are of great interest in altering the double-exchange strength. There are numerous reports on the effect of doping at the A-site as well as sintering temperature on magnetic and transport properties of LCMO perovskites. Siwach et al. reported that unit cell volume of La$_{0.7}$Ca$_{0.3}$MnO$_3$ nanoparticles decrease on lowering the sintering temperature. Lowering of sintering temperature also cause reduction in both ferromagnetic transition temperature ($T_c$) and insulator metal transition temperature ($T_p$) \cite{15}. In case of La$_{0.875}$Sr$_{0.125}$MnO$_3$ nanoparticles, an increase in resistivity and a decrease and broadening of $T_c$ has been observed. This could be associated to the domain status, changes in Mn–O–Mn bond angle and Mn–O bond length \cite{16}. In case of nano-polycrystalline (La$_{1-y}$K$_y$)$_{0.7}$Ba$_{0.3}$MnO$_3$ with $y = 0.0$–0.3, increase in K content increases the value of conductivity and $T_p$ which could be due to increase in the number of holes in the $e_g$ band because of increase in Mn$^{4+}$/Mn$^{3+}$ ratio with K-doping \cite{17}. A structural transition from orthorhombic (Pbnm) to rhombohedral
(R₃C) and increase in unit cell volume has been observed in K-doped manganites La₀.₆₅Ca₀.₃₅₋ₓKₓMnO₃ (0 ≤ x ≤ 0.2) with increasing K. It has been further observed that K doping enhances the strength of the ferromagnetic DE interaction between Mn ions thereby making the system ferromagnetic at room temperature [18]. Though a lot of work has been done on the effect of either A-site doping or sintering temperature on magnetic properties of nano LCMO perovskites, there is hardly any report on the effect of both A-site doping and sintering temperature on magnetic properties of nano LCMO perovskites. Moreover, studies on transport properties of nano LCMO perovskites are limited. In view of this, La₀.₅Nd₀.₂Ca₀.₃₋ₓKₓMnO₃ (x = 0 and 0.05) nanoparticles with different sizes were prepared using sol-gel Pechini method. The effect of both K-doping at A-site and sintering temperature on the structural, magnetic and transport properties has been investigated.

6.2 Experimental

The nano-polycrystalline samples La₀.₅Nd₀.₂Ca₀.₃₋ₓKₓMnO₃ (x = 0 and 0.05) were prepared using sol-gel Pechini method. The analytical grade reagents with 99.9% purity were used as starting materials. La₂O₃ and Nd₂O₃ were preheated at 1000°C for 6h to remove the moisture and other gases. The stoichiometric amounts of reactant materials La₂O₃, Nd₂O₃, CaCO₃, K₂CO₃ and Mn(CH₃COO)₂·4H₂O were dissolved in dilute nitric acid by heating at 80°C for the conversion of corresponding oxides/carbonates/acetates to nitrates. Nitrates were chosen as the metal precursors in sol-gel method because they are fundamental for the method, the NO₃⁻ groups being the oxidizing agents, as well as their high solubility in water allows a proper homogenization [19]. The solutions were then placed on a heating plate in order to evaporate water. The residues containing metal nitrates were dissolved in 100ml of distilled water to get a clear solution. Citric acid (CA), in the molar ratio of nitrates to citric acid as 1:3, was then added. The solutions were stirred on magnetic stirrer for about 1h followed by the addition of ethylene glycol (EG) which was used as a surfactant as well as polymerization agent (EG:CA molar ratio of 4:1). The resulting solutions were again stirred for about 1h and then heated on hot plate to promote solvent removal and allow polymerization of metal cations. A viscous gel was finally obtained which was then transferred to electrical oven with a subsequent
raising of temperature up to 200°C to affirm the propagation of a combustion which transforms the gel into a fluffy mass. This mass was then grinded in a mortar to fine powder. The powders were divided into four parts and heated at 700°C, 800°C, 900°C and 1100°C for 4h in each case to obtain samples of different particle sizes. La$_{0.5}$Nd$_{0.2}$Ca$_{0.3}$MnO$_3$ samples heated at 700°C, 800°C, 900°C and 1100°C were named as LCM7, LCM8, LCM9, and LCM11 respectively, while K-doped samples La$_{0.5}$Nd$_{0.2}$Ca$_{0.25}$K$_{0.05}$MnO$_3$ as LCKM7, LCKM8, LCKM9, and LCKM11.

The phase purity and structure of polycrystalline samples were recorded by X-ray diffraction (XRD) technique at room temperature using a Rigaku SmartLab 9kW rotating anode X-ray diffractometer with monochromatized CuK$_\alpha$ radiation (\(\lambda = 1.54056\) Å) in the 2\(\theta\) range 10°–100°. The structure refinements were carried out by Rietveld analysis using GSAS program. The oxygen stoichiometry of all the materials was determined by the iodometric method within experimental error of ±0.002, the details have been reported elsewhere [20, 21]. The morphology and elemental analysis of the samples were obtained by using FE-SEM Quanta 200 FEG scanning electron microscope (SEM) linked with energy dispersive X-ray spectroscopy (EDX). Transmission electron microscopy (TEM) observation of the samples was performed on a FP 5022/22-Tecnai G2 20 S-TWIN USA. Faradays method provided with Polytronic made electromagnet was used for carrying out magnetic measurements in the zero-field cooled (ZFC) modes in the temperature range 80–300K. Resistivity measurements were done using conventional four probe method in the temperature range of 80–300K. For resistivity measurements, electrical contacts were made on smooth surface of circular pellets by using Silver epoxy.

### 6.3 Results and discussion

#### 6.3.1 Structural analysis

X-ray diffraction (XRD) patterns of the LCM and LCKM samples sintered at different temperatures are displayed in Figs.6.1 and 6.2 while data are given in Tables 6.1–6.8 respectively. The patterns have indicated that all the samples are single phase without any impurity of reactant oxide or of any biproduct. At 700°C, the XRD peaks show a broad distribution due to nanocrystalline character of samples. With the rise in
Fig. 6.1: Typical Miller-indexed XRD patterns for $\text{La}_{0.85}\text{Nd}_{0.2}\text{Ca}_{0.3}\text{MnO}_3$. 
Fig. 6.2: Typical Miller-indexed XRD patterns for $\text{La}_{0.5}\text{Nd}_{0.2}\text{Ca}_{0.25}\text{K}_{0.05}\text{MnO}_3$. 
### Table 6.1: Powder X-ray diffraction data of LCM7

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\(a = 5.4638\); \(b = 5.4382\); \(c = 7.6810\); space group = \textit{Pbnm}
Table 6.2: Powder X-ray diffraction data of LCM8

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\(a = 5.4530; b = 5.4402; c = 7.6896; \) space group = \(Pbnm\)
Table 6.3: Powder X-ray diffraction data of LCM9

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\(a = 5.4509; \ b = 5.4520; \ c = 7.7009; \) space group = \(Pbnm\)
Table 6.4: Powder X-ray diffraction data of LCM11

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\[ a = 5.4611; \ b = 5.4589; \ c = 7.7070; \text{ space group } = \text{Pbnm} \]
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\(a = 5.4637\); \(b = 5.4392\); \(c = 7.6966\); space group = \(Pbnm\)
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$a = 5.4642; b = 5.4447; c = 7.6926; \text{space group} = Pbnm$
Table 6.7: Powder X-ray diffraction data of LCMK9

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<th>d_{cal} (Å)</th>
<th>I_{obs}</th>
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<th>k</th>
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<td>1</td>
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\(a = 5.4537;\ b = 5.4615;\ c = 7.7324;\) space group = \(Pbnm\)
Table 6.8: Powder X-ray diffraction data of LCMK11

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<th>(d_{\text{cal}}) (Å)</th>
<th>(I_{\text{obs}})</th>
<th>(h)</th>
<th>(k)</th>
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\(a = 5.4658; b = 5.600; c = 7.7110;\) space group = \(Pbnm\)
calcinations temperature, the peaks became sharper and sharper indicating the increase in crystalline nature of the phases. Rietveld profile refinements were performed using the GSAS-EXPGUI software packages [22]. XRD patterns can indexed in the orthorhombic system with Pbnm space group. Pseudo-Voigt function and a sixth order Chebychev polynomial were used in the refinement. Atomic occupations were set according to the stoichiometry of the phases and not refined in this work. Finally, individual isotropic and positional parameters were refined. A relatively good fit between the experimental and theoretical patterns (Figs. 6.3 and 6.4) is obtained thus confirming the formation of phases. The refined parameters along with goodness-of-fit parameters ($R_{wp}$, $R_p$ and $\chi^2$) are summarized in Tables 6.9 and 6.10. It can be seen that in both the LCM and LCKM samples, the unit cell volume increases with increase in sintering temperature. This increment can be attributed to increase of grain size with increase in temperature. Also at same calcinations temperature, the unit cell volume of LCKM samples was found to be higher than those of LCM samples, which is consistent with larger ionic radius of K than Ca.

The crystallite size ($D$) was estimated by eliminating instrumental broadening effect using the Scherrer equation from the XRD peak (112) of highest intensity and its values are given in Table 6.11. The results show that crystallite size in case of both LCM and LCKM samples increased with increasing calcinations temperature which could be credited to the grain growth of the particles and rise in density [23].

6.3.2 Elemental and microstructural analysis

The chemical composition for the constituent elements of the synthesized samples has been analysed by Energy Dispersive X-ray Spectroscopy (EDX). EDX spectra of LCM and LCKM samples heated at 700°C and 1100°C are displayed in Fig. 6.5. The results show that all the samples are formed with no trace of any foreign elements within the detection limits. Measurements were done on two distinct regions and the averages of mass percentage of these two regions are given in Tables 6.12 and 6.13. Since oxygen element (light element) can hardly be identified exactly by EDX, we present the chemical composition of all elements except oxygen. It can be observed from Tables 6.12 and 6.13.
Fig. 6.3: Rietveld profile fitting for the XRD patterns of La$_{0.5}$Nd$_{0.2}$Ca$_{0.3}$MnO$_3$. 
Fig. 6.4: Rietveld profile fitting for the XRD patterns of $\text{La}_{0.5}\text{Nd}_{0.2}\text{Ca}_{0.25}\text{K}_{0.05}\text{MnO}_3$. 
Table 6.9: Structural parameters obtained from the Rietveld refinement of X-ray diffraction pattern for La$_{0.5}$Nd$_{0.2}$Ca$_{0.3}$MnO$_3$ samples heated at different temperatures. The atomic sites are: La/Nd/Ca 4c\([x, y, 0.25]\); Mn 4b \([0.5, 0, 0]\); O(1) 4c\([x, y, 0.25]\); O(2) 8d\([x, y, z]\) in the space group \(Pbnm\)

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<th>Temperature</th>
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<th>(800^\circ C)</th>
<th>(900^\circ C)</th>
<th>(1100^\circ C)</th>
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<td>(a (\text{Å}))</td>
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<td>5.4530(10)</td>
<td>5.4509(15)</td>
<td>5.4611(6)</td>
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<tr>
<td>(b (\text{Å}))</td>
<td>5.4382(9)</td>
<td>5.4402(10)</td>
<td>5.4520(11)</td>
<td>5.4589(6)</td>
</tr>
<tr>
<td>(c (\text{Å}))</td>
<td>7.6810(10)</td>
<td>7.6896(15)</td>
<td>7.7009(16)</td>
<td>7.7070(4)</td>
</tr>
<tr>
<td>(V (\text{Å}^3))</td>
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<td>228.1151</td>
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<td>O(1)</td>
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<td>0.0652(21)</td>
<td>0.0622(23)</td>
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<td>(Y)</td>
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<td>(Z)</td>
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<td>(R(F^2))</td>
<td>0.1211</td>
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<td>0.0831</td>
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Table 6.10: Structural parameters obtained from the Rietveld refinement of X-ray diffraction pattern for La$_{0.5}$Nd$_{0.2}$Ca$_{0.25}$K$_{0.05}$MnO$_3$ samples heated at different temperatures. The atomic sites are: La/Nd/Ca/K 4c[x, y, 0.25]; Mn 4b [0.5, 0, 0]; O(1) 4c[x, y, 0.25]; O(2) 8d[x, y, z] in the space group Pbnm.

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<th>800°C</th>
<th>900°C</th>
<th>1100°C</th>
</tr>
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<td>5.4537(8)</td>
<td>5.4658(4)</td>
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<tr>
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</tr>
<tr>
<td>c (Å)</td>
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<td>7.7324(7)</td>
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<tr>
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<td>0.0157(18)</td>
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that the experimental values of mass percentages of all elements (except K) are in good
agreement with the theoretical values. The results further confirm that in LCKM samples,
vaporization of K occurs during sintering, which becomes more vigorous at 1100°C. Since the experimental and theoretical values of mass percentages of all elements (except K) are in good agreement, so we had presented only the atomic fractions of K of LCKM samples in Table 6.11. The results of iodometric titrations (Table 6.11) suggest that increase in sintering temperature leads to a decrease in oxygen content of the perovskite ceramics thereby resulting in the formation of oxygen vacancies which become dominant at 1100°C. Increase in oxygen vacancies with sintering temperature in such perovskite manganites has also been reported by Ju et al and Li et al [14, 24]. Smaller oxygen content in LCKM ceramics compared to LCM at same sintering temperature could be due to vaporization of K as evident from EDX results. The iodometric and EDX results further suggest that Mn in all the phases is present in mixed valence state of +3 and +4. The fractions of Mn$^{3+}$ and Mn$^{4+}$, calculated on the basis of charge compensation, are given in Table 6.11.

Scanning electron microscope (SEM) technique was done to investigate the morphology of the samples. The SEM micrographs of the LCM and LCKM samples calcined at 1100°C are represented in Fig.6.6. Both samples have spherical, oval and

<table>
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<th>Sample</th>
<th>LCM7</th>
<th>LCM8</th>
<th>LCM9</th>
<th>LCM11</th>
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<td>2.997</td>
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<tr>
<td>$f$</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>0.044</td>
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<tr>
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Fig. 6.5: EDX spectrum of La$_{0.5}$Nd$_{0.2}$Ca$_{0.3}$MnO$_3$ and La$_{0.5}$Nd$_{0.2}$Ca$_{0.25}$K$_{0.05}$MnO$_3$. 
Table 6.12: EDX results of $\text{La}_{0.5}\text{Nd}_{0.2}\text{Ca}_{0.3}\text{MnO}_3$

<table>
<thead>
<tr>
<th>Compound</th>
<th>LCM7</th>
<th>LCM8</th>
<th>LCM9</th>
<th>LCM11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Cal. Mass%</td>
<td>Exp. Mass%</td>
<td>Exp. Mass%</td>
<td>Exp. Mass%</td>
</tr>
<tr>
<td>La</td>
<td>32.57</td>
<td>32.73</td>
<td>32.65</td>
<td>32.64</td>
</tr>
<tr>
<td>Nd</td>
<td>13.53</td>
<td>13.43</td>
<td>13.46</td>
<td>13.50</td>
</tr>
<tr>
<td>Ca</td>
<td>5.64</td>
<td>5.65</td>
<td>5.61</td>
<td>5.62</td>
</tr>
<tr>
<td>Mn</td>
<td>25.76</td>
<td>25.79</td>
<td>25.83</td>
<td>25.81</td>
</tr>
</tbody>
</table>

Table 6.13: EDX results of $\text{La}_{0.5}\text{Nd}_{0.2}\text{Ca}_{0.25}\text{K}_{0.05}\text{MnO}_3$

<table>
<thead>
<tr>
<th>Compound</th>
<th>LCMK7</th>
<th>LCMK8</th>
<th>LCMK9</th>
<th>LCMK11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Cal. Mass%</td>
<td>Exp. Mass%</td>
<td>Exp. Mass%</td>
<td>Exp. Mass%</td>
</tr>
<tr>
<td>La</td>
<td>32.57</td>
<td>32.62</td>
<td>32.64</td>
<td>32.63</td>
</tr>
<tr>
<td>Ca</td>
<td>4.70</td>
<td>4.57</td>
<td>4.59</td>
<td>4.65</td>
</tr>
<tr>
<td>K</td>
<td>0.92</td>
<td>0.88</td>
<td>0.81</td>
<td>0.71</td>
</tr>
<tr>
<td>Mn</td>
<td>25.77</td>
<td>25.69</td>
<td>25.67</td>
<td>25.72</td>
</tr>
</tbody>
</table>
Fig. 6.6: SEM micrographs of $\text{La}_{0.5}\text{Nd}_{0.2}\text{Ca}_{0.3}\text{MnO}_3$ and $\text{La}_{0.5}\text{Nd}_{0.2}\text{Ca}_{0.25}\text{K}_{0.05}\text{MnO}_3$

sintered at 1100°C.
some irregular particle shapes, present non-uniform morphologies with few voids and holes randomly scattered among them. The creation of these characteristics is attributed to the large volume of gases released during combustion. Moreover, images confirm the formation of cluster and agglomeration of particles and the grain boundaries are sharply visible. To know the morphology and microstructure of nano-crystalline samples, transmission electron microscopy (TEM) measurements of LCM7 and LCKM7 powders calcined at 700°C have been carried out. It can be seen from TEM micrographs (Fig.6.7) that both the powders are composed of nearly spherical nanoparticles with almost irregular granular shape. The average grain sizes of LCM7 and LCKM7 were found to be 30.3 nm and 31.2 nm respectively, which are close to the crystallite size (Table 6.11) obtained from XRD using Scherrer equation.

6.3.3 Magnetic properties

We have examined the effect of sintering temperature as well as size of doped element K on the magnetic as well as transport properties of all the samples. Magnetization measurements have been undertaken as a function of temperature in a zero magnetic field and the behavior of magnetization versus temperature curve is shown in Figs.6.8 and 6.9.

The results show that all the compounds undergo a transition from paramagnetic to ferromagnetic state with decreasing temperature. The Curie temperature $T_c$ was determined from the inflection point of $d\chi/dT$ versus $T$ curves as shown in Figs.6.10 and 6.11 and its values are listed in Tables 6.14 and 6.15. It can be seen that the doping of K in LCM samples leads to the increment in $T_c$. It is observed that the factors like the average A-cation radius as well as Mn$^{4+}$/Mn$^{3+}$ ion ratio plays key role in magnetic nature of these samples. The introduction of monovalent K$^+$ for divalent cation Ca$^{2+}$ in LCM leads to oxidation of Mn$^{3+}$ to Mn$^{4+}$ thereby causing an increase in the number of Mn$^{4+}$ ions. All these Mn$^{4+}$ ions are coupled ferromagnetically with an equal proportion of Mn$^{3+}$ ions leading to formation of Mn$^{4+}$–Mn$^{3+}$ pairs. This results in the increment of the ferromagnetic double exchange (DE) interactions Mn$^{3+}$–O$^{2-}$–Mn$^{4+}$ which are responsible for larger magnetization and higher $T_c$ of K-doped samples [25].
Fig. 6.7: TEM micrographs of \( \text{La}_{0.5}\text{Nd}_{0.2}\text{Ca}_{0.3}\text{MnO}_3 \) and \( \text{La}_{0.5}\text{Nd}_{0.2}\text{Ca}_{0.25}\text{K}_{0.05}\text{MnO}_3 \) sintered at 700°C.
Fig. 6.8: Temperature Dependence of the molar magnetic susceptibility ($\chi_m$) for $\text{La}_{0.5}\text{Nd}_{0.2}\text{Ca}_{0.3}\text{MnO}_3$.

Fig. 6.9: Temperature Dependence of the molar magnetic susceptibility ($\chi_m$) for $\text{La}_{0.5}\text{Nd}_{0.2}\text{Ca}_{0.25}\text{K}_{0.05}\text{MnO}_3$. 
Fig. 6.10: $d(\chi_m)/dT$ versus $T$ plot for La$_{0.5}$Nd$_{0.2}$Ca$_{0.3}$MnO$_3$.

Fig. 6.11: $d(\chi_m)/dT$ versus $T$ plot for La$_{0.5}$Nd$_{0.2}$Ca$_{0.25}$K$_{0.05}$MnO$_3$. 
### Table 6.14: Magnetic and electrical parameters of La$_{0.5}$Nd$_{0.2}$Ca$_{0.3}$MnO$_3$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Theta$ (K)</th>
<th>$T_c$ (K)</th>
<th>$C$ (Kemu/mol)</th>
<th>$\mu_{\text{obs}}$ (B.M.)</th>
<th>$\mu_{\text{cal}}$ (B.M.)</th>
<th>$T_{MS}$ (K)</th>
<th>$E_p$ (meV)</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCM7</td>
<td>141</td>
<td>168</td>
<td>0.370</td>
<td>4.649</td>
<td>4.887</td>
<td>164</td>
<td>180.0</td>
<td>0.9988</td>
</tr>
<tr>
<td>LCM8</td>
<td>147</td>
<td>190</td>
<td>0.226</td>
<td>5.949</td>
<td>4.893</td>
<td>194</td>
<td>170.1</td>
<td>0.9993</td>
</tr>
<tr>
<td>LCM9</td>
<td>158</td>
<td>193</td>
<td>0.198</td>
<td>6.355</td>
<td>4.898</td>
<td>200</td>
<td>147.4</td>
<td>0.9979</td>
</tr>
<tr>
<td>LCM11</td>
<td>154</td>
<td>180</td>
<td>0.230</td>
<td>5.897</td>
<td>4.920</td>
<td>184</td>
<td>148.7</td>
<td>0.9970</td>
</tr>
</tbody>
</table>

### Table 6.15: Magnetic and electrical parameters of La$_{0.5}$Nd$_{0.2}$Ca$_{0.25}$K$_{0.05}$MnO$_3$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Theta$ (K)</th>
<th>$T_c$ (K)</th>
<th>$C$ (Kemu/mol)</th>
<th>$\mu_{\text{obs}}$ (B.M.)</th>
<th>$\mu_{\text{cal}}$ (B.M.)</th>
<th>$T_{MS}$ (K)</th>
<th>$E_p$ (meV)</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCKM7</td>
<td>170</td>
<td>173</td>
<td>0.279</td>
<td>5.354</td>
<td>4.848</td>
<td>173</td>
<td>163.8</td>
<td>0.9988</td>
</tr>
<tr>
<td>LCKM8</td>
<td>195</td>
<td>204</td>
<td>0.267</td>
<td>5.473</td>
<td>4.858</td>
<td>202</td>
<td>156.5</td>
<td>0.9981</td>
</tr>
<tr>
<td>LCKM9</td>
<td>199</td>
<td>210</td>
<td>0.247</td>
<td>5.689</td>
<td>4.869</td>
<td>207</td>
<td>146.8</td>
<td>0.9973</td>
</tr>
<tr>
<td>LCKM11</td>
<td>183</td>
<td>195</td>
<td>0.262</td>
<td>5.525</td>
<td>4.894</td>
<td>192</td>
<td>139.8</td>
<td>0.9983</td>
</tr>
</tbody>
</table>
Generally, average A-cation radius <\(r_A\)> also plays an important role to bring a change in \(T_c\) values. The substitution of larger K\(^+\) (1.64 nm) for smaller Ca\(^{2+}\) (1.34 nm) ion results an increase in the value <\(r_A\)>. As a result, Mn–O–Mn angle in perovskites straightens thereby enhancing the alignment of Mn\(^{3+}/\text{Mn}^{4+}\) pairs. These changes leads to strengthening of the hopping integral of \(e_g\) electrons, which consequently enhances the force of DE Mn\(^{3+}–\text{O}^{2−}–\text{Mn}^{4+}\) interactions and ferromagnetism. As a result, an increase in magnetization and higher value of \(T_c\) of K-doped samples is observed compared to their undoped counterparts [26]. Moreover, different behavior of the dc susceptibility of LCM and LCKM samples can be seen by increasing the sintering temperature from 700°C to 1100°C. The Curie temperature and magnetization occur to rise sharply with increasing sintering temperature showing the onset of ferromagnetic ordering except for samples at 1100°C (Tables 6.14 and 6.15). The increase in charge-ordering with sintering temperature has also been reported with the other manganite systems [14, 24, 27-31]. It is well known that the noncrystalline material forms a nonmagnetic surface layer which is the main cause of the decrease in magnetization in small grain size samples. Heavier strain is generated at the grain boundaries due to smaller size grains which leads to rise of more nonferromagnetic or weak antiferromagnetic regions which can disturb the long-range ferromagnetic order. The atomic disordered surface per volume ratio therefore decreases with increase in size thus leading to increase in magnetization and \(T_c\) [31, 32]. However, in case of samples heated at 1100°C, anomalous behaviour is predicted as \(T_c\) is decreased with sintering temperature [33-36]. The most probable reason is the increase in oxygen vacancies with sintering temperature, which becomes dominant at 1100°C (as evident from iodometric results (Table 6.11)). The higher oxygen vacancy in samples sintered at 1100°C therefore leads to a decrease in the number of \(\text{Mn}^{4+}\) ions and consequently Mn\(^{3+}/\text{Mn}^{4+}\) pairs, which are responsible for ferromagnetism thereby causing smaller magnetization and lower value of \(T_c\). The decrease in magnetization and \(T_c\) at higher temperature on the basis of oxygen vacancies in perovskite manganites has also been reported by Ju et al and Li et al [37, 38].

The spontaneous magnetization in a ferromagnetic material can occur only below \(T_c\) and above this temperature, such a material acts like a paramagnetic material and obeys Curie-Weiss (CW) law, which is defined by the equation [39].
Figs. 6.12 and 6.13 display the variation of inverse molar susceptibility as a function of temperature. The linearity of plots in high temperature region indicates a Curie-Weiss behavior for the phases well above $T_c$. The value of Curie constant $C$ has been calculated from the slope of $\chi_m^{-1} - T$ plot and by knowing the value of $C$, the effective magnetic moment has been measured by the relation:

$$\mu_{\text{eff}} = 2.828\sqrt{C}$$

The value of theoretical magnetic moment ($\mu_{\text{cal}}$) can be calculated from the given relationship [40, 41]:

$$\mu_{\text{cal}} = \sqrt{0.2\mu_{\text{Nd}^{3+}}^2 + x\mu_{\text{Mn}^{4+}}^2 + y\mu_{\text{Mn}^{3+}}^2}$$

where $x$ and $y$ are the fractions of Mn$^{4+}$ and Mn$^{3+}$ ions (Table 3) in the samples and $\mu_{\text{Nd}^{3+}}$ (3.62 B.M.), $\mu_{\text{Mn}^{4+}}$ (4.90 B.M.) and $\mu_{\text{Mn}^{3+}}$ (3.87 B.M.) are the spin only magnetic moments of Nd$^{3+}$, Mn$^{3+}$ and Mn$^{4+}$ respectively. The values of $C$, $\mu_{\text{eff}}$ and $\mu_{\text{cal}}$ are listed in Tables 6.14 and 6.15. The higher value of $\mu_{\text{eff}}$ than $\mu_{\text{cal}}$ shows that ferromagnetic interactions are dominant in the phases. The paramagnetic Curie temperature ($\Theta$) was determined from $\chi_m^{-1} - T$ plots and its values are also mentioned in Tables 6.14 and 6.15. It has been observed that the value of $\Theta$ is positive for all the samples, suggesting dominant ferromagnetic interactions in them. Further, the values of $\Theta$ are found to be slightly lower than $T_c$, which could be associated with the presence of short-range order slightly above $T_c$ due to magnetic inhomogeneity.

6.3.4 Transport properties

The temperature dependence of resistivity $\rho(T)$ of polycrystalline LCM and LCKM samples was measured in zero magnetic field in the temperature range 80-300K and the resistivity versus temperature ($\rho - T$) behaviour is shown in Figs. 6.14 and 6.15. In the high temperature region, $\rho - T$ plot displays a continuous increase in resistivity with decreasing temperature, indicating semiconducting behavior of samples. Semiconducting behavior of perovskite manganites has already been reported by many research groups [33, 42]. However, as the temperature drops, the temperature coefficient of resistivity
Fig. 6.12: Plot of temperature dependent inverse molar magnetic susceptibility ($\chi_m^{-1}$) for the $La_{0.5}Nd_{0.2}Ca_{0.3}MnO_3$.

Fig. 6.13: Plot of temperature dependent inverse molar magnetic susceptibility ($\chi_m^{-1}$) for the $La_{0.5}Nd_{0.2}Ca_{0.25}K_{0.05}MnO_3$. 
Fig. 6.14: Resistivity ($\rho$) dependence on temperature ($T$) for La$_{0.5}$Nd$_{0.2}$Ca$_{0.3}$MnO$_3$ sintered at 800°C, 900°C and 1100°C (Inset shows $\rho$ versus $T$ plot for sample sintered at 700°C)

Fig. 6.15: Resistivity ($\rho$) dependence on temperature ($T$) for La$_{0.5}$Nd$_{0.2}$Ca$_{0.25}$K$_{0.05}$O$_3$ sintered at 800°C, 900°C and 1100°C (Inset shows $\rho$ versus $T$ plot for sample sintered at 700°C)
abruptly becomes positive and the phases display metallic nature. The metal-semiconductor transition temperatures ($T_{MS}$) for the phases are listed in *Tables 6.14 and 6.15*. These results indicate that the materials are ferromagnetic-metallic at low temperature ($T < T_{MS}$) and become paramagnetic-semiconductor at high temperature ($T > T_{MS}$). Also, the values of $T_{MS}$ are found to be close to $T_c$ indicating a strong correlation between electrical and magnetic properties of the samples. It can be seen from *Tables 6.14 and 6.15* that at same sintering temperature, K-doped samples have lower resistivity and higher $T_{MS}$ than their undoped counterparts. This variation could be explained on the basis of A-site cation radius $\langle r_A \rangle$. The hopping of electrons from the occupied sites, Mn$^{3+}$ ions, to the unoccupied sites Mn$^{4+}$ ions (holes) leads to electronic conduction in these materials. The increase in $\langle r_A \rangle$ with K doping, because of its larger size, increases the Mn–O–Mn angle. This may result an increase in the tendency of hopping of $e_g$ electrons from Mn$^{3+}$ to Mn$^{4+}$ sites thereby causing a decrease in resistivity and increment in $T_{MS}$. Moreover, substitution of monovalent K for divalent Ca in such manganites oxidises Mn$^{3+}$ to Mn$^{4+}$. This results an increase in the number of Mn$^{4+}$ ions (holes) making hopping of $e_g$ electrons from Mn$^{3+}$ to Mn$^{4+}$ sites more easy. It can be seen from *Tables 6.14 and 6.15* that resistivity decreases with sintering temperature while there is increase in $T_{MS}$. This could be due to the fact that the grain growth of the samples occurs with rise in sintering temperature which provides a better intergrain connection. The magnetic disorder and grain boundary effect are therefore significantly decreased, which are creating the scattering effect on the grain boundary. As a consequence, the grain boundaries become small and hence the charge carriers encounter less restriction which leads to decrease in resistivity and increase in $T_{MS}$ because of enhancement in double exchange effect [43, 44]. However, a reverse trend in resistivity and $T_{MS}$ is observed in samples sintered at 1100°C. This could be due to presence of higher oxygen vacancies in the samples sintered at 1100°C (as can be seen from iodometric results, *Table 6.11*). Increase in oxygen vacancies decreases the concentration of Mn$^{4+}$ ions (holes) which in turn decreases the tendency of hopping of $e_g$ electrons from Mn$^{3+}$ to Mn$^{4+}$ sites thereby causing an increase in resistivity and reduction in $T_{MS}$ with sintering temperature. The increase in resistivity and reduction in $T_{MS}$ with sintering temperature on the basis of
With a view to get information about the type of conduction mechanism in perovskite manganites, different models for conduction such as Arrhenius model, Small polaron hopping (SPH) model and Mott’s variable range hopping (VRH) model were applied to the resistivity data. In the high temperature region, it was observed that the resistivity data was best fitted by SPH model with best agreement factors $R$ (Tables 6.14 and 6.15). The resistivity according to SPH model is given by where $E_p$ is the polaron hopping energy,

$$\rho = \rho_o T \exp \left( \frac{E_p}{k_B T} \right)$$

hopping energy, $T$ is the absolute temperature, $k_B$ is Boltzmann constant, and $\rho_o$ is pre exponential factor. The polaron hopping energy was estimated from the slope of $\log(\rho/T)$ versus $1/T$ plots (Figs. 6.16 and 6.17) and its values are given in Tables 6.14 and 6.15.

The values of $E_p$ are found to be in good agreement with the reported ones [33, 46]. It can be seen that at same sintering temperature, undoped samples have higher $E_p$ than their K-doped counterparts. This is due to reason that lower value of $<r_A>$ in undoped samples reduces the Mn–O–Mn bond angle which results narrowing of bandwidth. As a result, the effective band gap increases and hence the charge carriers need more polaron hopping energy to overcome this band gap [46, 47]. The results further suggest that $E_p$ decreases with sintering temperature. This could be due to fact that the grain growth of the samples with sintering temperature provides a better intergrain connection thereby significantly decreasing the magnetic disorder and grain boundary effect. Consequently, the grain boundaries become small and hence the charge carriers encounter less restriction thereby causing enhancement in double exchange effect, which leads to decrease in $E_p$ with sintering temperature.

### 6.4. Conclusions

The effect of sintering temperature and A-site cation radius on the structural, magnetic and transport properties of $La_{0.5}Nd_{0.2}Ca_{0.3-x}K_x MnO_3$ ($x = 0.0$ and $0.05$) manganites has been investigated. The following conclusions can be mentioned:
Fig. 6.16: Plots of $\log (\rho/T)$ versus $1/T$ for $\text{La}_{0.5}\text{Nd}_{0.2}\text{Ca}_{0.3}\text{MnO}_3$.

Fig. 6.17: Plots of $\log (\rho/T)$ versus $1/T$ for $\text{La}_{0.5}\text{Nd}_{0.2}\text{Ca}_{0.25}\text{K}_{0.05}\text{MnO}_3$. 
La$_{0.5}$Nd$_{0.2}$Ca$_{0.3-x}$K$_x$MnO$_3$ (x = 0.0 and 0.05) manganites were prepared by sol-gel method.

Rietveld refinements confirmed the orthorhombic symmetry of samples corresponding to the $Pbnm$ space group.

The unit cell volume rises with K-doping as well sintering temperature.

All the phases show paramagnetic to ferromagnetic transition at low temperature.

The materials show ferromagnetic-metallic behaviour at low temperature ($T < T_{MS}$) and paramagnetic-semiconductor at high temperature ($T > T_{MS}$).

The metal-semiconductor transition temperatures ($T_{MS}$) are found to be close to $T_c$ indicating a strong correlation between transport and magnetic properties of the samples.

The electrical properties are dominated by SPH model with polaron hopping energy declines with K-doping as well as sintering temperature.
REFERENCES


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