


Chapter 4

X-ray Spectroscopic Study of \( \text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Ti}_x\text{O}_{3+\delta} \).

4.1 Introduction

In the preceding Chapter, it is observed that constant lattice parameters obtained from XRD measurements, shift of Mn\(^{3+}\)-O stretching mode frequencies observed in IR spectra, gradual decrease in Mn\(^{3+}\) content with increasing doping content and substantial reduction in susceptibility of the site-disordered (SD) samples indicate the possibility of Ti\(^{4+}\) ions occupying Mn\(^{3+}\) sites also. To ascertain this fact, we have undertaken further experimental investigations on these materials using EXAFS and XPS techniques.

The X-ray absorption fine-structure (XAFS) technique has proven useful in the determination of interatomic distances, structural disorders through Debye Waller factors (DWF), and type and number of neighboring atoms within the first few co-
ordination shells of the X-ray excited atom. By recording EXAFS at the X-ray K absorption edges of La and Mn ions for the samples of La_{0.67}Sr_{0.33}Mn_{1-x}Ti_xO_{3+y} series, it is possible to study the effect of site-disorder on local structure in these materials. It will be a worthwhile effort to relate the local structure of Mn ions to the transport and magnetic properties of site-disordered materials. It is to be noted that no EXAFS study on Ti doped La_{1-x}Sr_xMnO_3 materials have been reported hitherto.

In this Chapter, we have studied the local structure around La and Mn ions in these site-disordered materials, La_{0.67}Sr_{0.33}Mn_{1-x}Ti_xO_{3+y} for 0 \leq x \leq 0.20. We report herein the room temperature local structure of these materials around Mn and La ions obtained from the analysis of EXAFS data and contents of Mn^{3+} and Mn^{4+} ions obtained from X-ray Photoelectron Spectra. It is interesting to note that the results of iodometric titration measurements, reported in the preceding Chapter agree with those obtained from XPS.

### 4.2 Experimental

XAFS spectra at La and Mn K-edges were recorded at BL01B1 XAFS Beamline at SPring-8 Synchrotron Radiation Facility. Si(111) crystal plane served as the monochromator for Mn K-edge EXAFS and Si(311) for La K-edge EXAFS. The first mirror and the monochromator were fully tuned in order to get optimal
Fig. 4.1: Room temperature Mn K-edge EXAFS of La$_{0.67}$Sr$_{0.33}$Mn$_{1-z}$Ti$_z$O$_{3+\delta}$ samples. (a) Mn Metal, (b) $x = 0.00$, (c) $x = 0.03$, (d) $x = 0.10$, (e) $x = 0.20$. 

109
Fig. 4.2: $\chi(k)$ vs $k$ spectra of room temperature Mn K-edge EXAFS of Mn metal and site-disordered $\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Ti}_x\text{O}_{3+\delta}$ samples.

resolution. For Mn K-edge measurements, fine powder of the sample was brushed onto scotch tape. A number of layers of tape were stacked to obtain absorption lengths $\mu_{\text{Mn}}x \approx 1$ ($\mu_{\text{Mn}}$ is the Mn contribution to the absorption coefficient and $x$ the sample thickness). For La K-edge measurements, the absorbers were made by pressing the samples into pellets of 10 mm diameter with boron nitride as binder. The thickness of the absorber was adjusted such that $\Delta\mu_0x$ was restricted to a value $\geq 1$, where $\Delta\mu_0$ is edge step in the absorption coefficient and $x$ is the sample thickness. XAFS oscillations, $\chi(k) = (\mu - \mu_0)/\mu_0$ ($k$ - photoelectron wavenumber, $\mu_0$ - atomic absorption coefficient), were extracted following standard procedures. FEFFIT program [1] was used to fit Fourier transformed(FT) $k\chi(k)$ data in $q$
space to the theoretical spectra calculated using FEFF6.01 [2]. The Mn and La K-edge EXAFS data was analysed in tandem, to improve the reliability of fits. The room temperature raw data of Mn K-edge EXAFS for Mn metal and samples of the composition, La_{0.67}Sr_{0.33}Mn_{1-z}Ti_{2}O_{3} for 0.00 \leq z \leq 0.20 are presented in Fig. 4.1 and the background subtracted and normalized data are presented in Fig. 4.2. Mn K-edge data were fitted in R-range from 1.8 Å to 3.6 Å and k-range from 3.6 Å^{-1} to 12 Å^{-1}. Raw La K-edge EXAFS spectra of these compounds are shown in Fig. 4.3 and the background subtracted and normalized data are presented in Fig. 4.4. Raw La K-edge EXAFS were fitted in the R-range 1.5 Å to 3.5 Å and k-range 3 Å^{-1} to 16 Å^{-1}. Fourier transforms of the data are presented in Fig. 4.5. The FT spectra are not corrected for phase shift, however, the values of bond lengths reported in the thesis are the corrected values.

La and Mn K-edge EXAFS were fitted initially for La_{0.67}Sr_{0.33}MnO_{3} sample. Bond length parameters were varied first, followed by the Debye Waller Factors(DWF). Coordination numbers were initially fixed at the known crystallographic values while fitting Mn K-edge EXAFS and in case of La K-edge EXAFS, 12 La-O bond lengths were divided into three different groups of coordination numbers 3, 6 and 3 respectively on the basis of closeness of their values. Later, coordination numbers had to be varied slightly to improve the quality of fit. The Mn K-edge and La K-edge EXAFS were fitted separately in k-space till equal
Fig. 4.3: Room temperature La K-edge EXAFS of $\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Ti}_x\text{O}_{3+\delta}$ samples.
Fig. 4.4: \( \chi(k) \) vs \( k \) spectra of room temperature La K-edge EXAFS of site disordered \( \text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-z}\text{Ti}_z\text{O}_{3+\delta} \) samples.

La-Mn bond lengths were obtained from both the EXAFS.

EXAFS of the doped samples were fitted later, in the order of increasing doping content. Fitting parameters of the preceding sample were used as starting parameters for fitting the data of the doped samples. DWF parameters were varied first followed by the bond length correlations and, only if required, coordination numbers were varied.

XPS measurements were carried out on an ESCA-3 Mark II spectrometer (VG Scientific Ltd., England) employing Al K\( \alpha \) radiation (1486.6 eV). The powder samples were made into pellets of 8 mm diameter and placed into an UHV chamber housing the analyser at \( 10^{-9} \) Torr. Before the measurements were carried out,
Fig. 4.5: Fourier Transforms of La K-edge EXAFS in site-disordered $\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Ti}_x\text{O}_{3+y}$ samples.

The samples were kept at the preparation chamber for 5 hours for desorption of gases. Binding energies were measured with a precision of $\pm 0.2$ eV. The charging effect was taken care of with respect to the C(1s) peak of adventitious carbon at 285 eV. The data were fitted using Peakfit software programme with gaussian profile.

### 4.3 Results

#### 4.3.1 XPS

Iodometric titration measurements on site-disordered (SD) samples indicate that the doped samples are oxygen-rich. The oxygen content gradually increases
Fig. 4.6: X-ray Photoelectron Spectrum (circles) of La$_{0.67}$Sr$_{0.33}$MnO$_3$ sample along with fitted curves (line). Discontinuous lines represent the deconvoluted $2p_{3/2}$ and $2p_{1/2}$ spectra corresponding to Mn$^{3+}$ and Mn$^{4+}$ ions. * signs indicate the satellite peaks.

from 3.00 for $x = 0.0$ to 3.05 for $x = 0.20$ [Table 3.1]. Excess oxygen (or equivalently cation deficiency) induces extra Mn$^{4+}$ ions in the samples.

Mn$^{4+}$ and Mn$^{3+}$ contents in the samples were also determined using their Mn 2p core level X-ray photoelectron spectra. Figs. [4.6 and 4.7] show the Mn 2p X-ray photoelectron spectra of the samples in the range $0.0 \leq x \leq 0.20$. The Mn 2p spectra exhibit two main peaks around 642.5 eV and 654 eV. The two main peaks correspond to the spin-orbit split $2p_{3/2}$ and $2p_{1/2}$ levels, whereas the weak structure at around 24 eV from the main peak is the satellite of the $2p_{3/2}$ peak. The satellite
Fig. 4.7: XPS spectra (circles) for site-disordered La$_{0.67}$Sr$_{0.33}$Mn$_{1-x}$Ti$_x$O$_{3+\delta}$ samples along with the fitted curve (line).

of the $2p_{3/2}$ peak is not visible because it overlaps with the $2p_{1/2}$ peaks. The two main peak features were deconvoluted, using a curve fitting 'Peakfit' programme, into those corresponding to $2p_{1/2}$ and $2p_{3/2}$ states of Mn$^{3+}$, Mn$^{4+}$ ions and their satellites. The peaks for $2p_{3/2}$ states are higher in binding energy than those for $2p_{1/2}$ states by about 11.6 eV. The Mn$^{4+}$ and Mn$^{3+}$ contents are calculated from areas under the curves corresponding to Mn$^{4+}$ and Mn$^{3+}$ ions. Results obtained through iodometric and XPS methods closely match with each other and clearly indicate the greater Mn$^{4+}$ content in the samples in relation to the stoichiometric samples. This is possible if Ti$^{4+}$ ions occupy both Mn$^{4+}$ and Mn$^{3+}$ sites. For the undoped sample, the Mn$^{4+}$:Mn$^{3+}$ ratio is found to be 33:67. XPS data and its
Table 4.1: Mn$^{4+}$ and Mn$^{3+}$ contents obtained from XPS data (Experimental values) are compared with the values calculated with the assumption that Ti$^{4+}$ ions occupy Mn$^{4+}$ sites alone. Effect of oxygen non-stoichiometry is considered in obtaining calculated values. Numbers in the parenthesis indicate estimated errors.

<table>
<thead>
<tr>
<th>Doping content (x)</th>
<th>Calculated value (%)</th>
<th>Experimental values (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mn$^{4+}$ : Mn$^{3+}$ : Ti$^{4+}$</td>
<td>Mn$^{4+}$ : Mn$^{3+}$ : Ti$^{4+}$</td>
</tr>
<tr>
<td>0.03</td>
<td>32.0(±1.8) : 65.0(±1.8) : 3</td>
<td>32.2(±0.9) : 64.8(±0.9) : 3</td>
</tr>
<tr>
<td>0.05</td>
<td>32.0(±2.0) : 63.0(±2.0) : 5</td>
<td>31.3(±0.7) : 63.7(±0.7) : 5</td>
</tr>
<tr>
<td>0.10</td>
<td>29.0(±1.6) : 61.0(±1.6) : 10</td>
<td>27.7(±0.8) : 62.3(±0.8) : 10</td>
</tr>
<tr>
<td>0.20</td>
<td>23.0(±1.4) : 57.0(±1.4) : 20</td>
<td>23.7(±0.8) : 56.3(±0.8) : 20</td>
</tr>
</tbody>
</table>

fit for x = 0.00 sample are shown in Fig. 4.6.

### 4.3.2 XANES

Normalized Mn K-edge XANES spectra, recorded at room temperature, for site disordered La$_{0.67}$Sr$_{0.33}$Mn$_{1-x}$Ti$_2$O$_{3+d}$ samples are shown in Fig. 4.8 recorded for EXAFS studies with a step of 1eV. However, the chemical shift of the inflection point of the main absorption edge is reported to be about 4.2 eV for Mn$^{3+}$ and Mn$^{4+}$ ions in LaMnO$_3$ and CaMnO$_3$ respectively [3, 4]. If Ti$^{4+}$ ions occupy Mn$^{4+}$ sites alone, the effective valence of the Mn ion will come close to +3 and shift of the main absorption edge should be seen in XANES spectra. Such a shift has been reported in Ti doped La$_{0.7}$Ca$_{0.3}$Mn$_{1-x}$Ti$_x$O$_3$ samples [5]. The main peak arising due to 1s-4p electronic transition and a prepeak at about 15 eV below the main peak are clearly visible in all the spectra. Positions of the main peak and
Fig. 4.8: Normalised XANES spectra of La$_{0.67}$Sr$_{0.33}$Mn$_{1-x}$Ti$_x$O$_{3+δ}$ samples.
the prepeak are almost the same over the entire doping range \((0.00 \leq x \leq 0.20)\). All peak profiles are very similar to each other. Surprisingly, chemical shift of the main absorption edge is not observed over the entire doping range. The absence of such a chemical shift indicates that average valence of Mn ion is nearly the same in these samples. In other words, \(\text{Mn}^{4+}/\text{Mn}^{3+}\) ratio is nearly constant in these samples and which can be seen as the effect of Ti\(^{4+}\) ions occupying both the Mn sites.

### 4.3.3 EXAFS

Results of various experimental techniques, that are discussed in the previous Chapter, indicate that Ti\(^{4+}\) ions occupy both, \(\text{Mn}^{3+}\) as well as \(\text{Mn}^{4+}\), sites in \(\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Ti}_x\text{O}_{3+d}\) \((0.00 \leq x \leq 0.20)\) samples. To ascertain this fact, we have undertaken the EXAFS investigations of the SD samples. Our interest lies mainly in \(\text{La}-(\text{Mn/Ti})\), and \(\text{Mn}-(\text{Mn/Ti})\) bond lengths, as these correlations can reveal whether Ti\(^{4+}\) ions occupy \(\text{Mn}^{3+}\) sites or not. \(\text{La}-(\text{Mn/Ti})\) bond length obtained from La K-edge EXAFS and \(\text{Mn}-(\text{La/Sr})\) bond length obtained from Mn K-edge EXAFS are expected to be the same.

#### La K-edge EXAFS

Fits of inverse Fourier transforms of La K-edge EXAFS of \(x = 0.00, 0.05, 0.10\) and 0.20 samples are presented in Fig. 4.9. \(\text{La}-(\text{Mn/Ti})\) and \(\text{La}-(\text{La/Sr})\) bond lengths,
obtained by fitting La K-edge EXAFS, remain nearly the same for the samples in the range 0.00 ≤ x ≤ 0.20. In case of La-O bond lengths, the maximum difference is 0.04 Å for La-O₁ bond [Table 4.2]. Nearly constant bond lengths in these materials is in tune with the almost similar lattice parameters obtained by the analysis of X-ray Diffraction patterns of these materials [Table 3.1]. As La-(Mn/Ti) correlation in La K-edge EXAFS includes scattering from Mn³⁺/⁴⁺ and Ti⁴⁺ ions, DWF for La-(Mn/Ti) bond length is observed to increase systematically with doping content x. However, the changes in La-O bond lengths and their Debye Waller Factors are small and non-systematic and can be understood in terms of random distribution of Ti⁴⁺, Mn³⁺ and Mn⁴⁺ ions in the sample and
Table 4.2: Structural parameters obtained from La K-edge EXAFS for site disordered La_{0.67}Sr_{0.33}Mn_{1-x}Ti_xO_{3+y} samples. Figures in brackets indicate uncertainties in the last digit.

<table>
<thead>
<tr>
<th></th>
<th>x=0.00</th>
<th>x=0.05</th>
<th>x=0.10</th>
<th>x=0.20</th>
</tr>
</thead>
<tbody>
<tr>
<td>La-O_1</td>
<td>R(Å)</td>
<td>2.48(1)</td>
<td>2.43(1)</td>
<td>2.45(1)</td>
</tr>
<tr>
<td></td>
<td>DWF(Å^2)</td>
<td>0.008(2)</td>
<td>0.007(2)</td>
<td>0.006(1)</td>
</tr>
<tr>
<td>n</td>
<td>3.3(5)</td>
<td>3.3(5)</td>
<td>3.3(3)</td>
<td>3.3(2)</td>
</tr>
<tr>
<td>La-O_2</td>
<td>R(Å)</td>
<td>2.64(1)</td>
<td>2.63(1)</td>
<td>2.63(1)</td>
</tr>
<tr>
<td></td>
<td>DWF(Å^2)</td>
<td>0.010(2)</td>
<td>0.008(3)</td>
<td>0.008(1)</td>
</tr>
<tr>
<td>n</td>
<td>6.2(7)</td>
<td>6.2(6)</td>
<td>6.2(4)</td>
<td>6.2(3)</td>
</tr>
<tr>
<td>La-O_3</td>
<td>R(Å)</td>
<td>2.84(2)</td>
<td>2.85(3)</td>
<td>2.86(1)</td>
</tr>
<tr>
<td></td>
<td>DWF(Å^2)</td>
<td>0.005(2)</td>
<td>0.006(3)</td>
<td>0.006(6)</td>
</tr>
<tr>
<td>n</td>
<td>2.7(6)</td>
<td>2.7(7)</td>
<td>2.7(3)</td>
<td>2.7(5)</td>
</tr>
<tr>
<td>La-Mn/Ti</td>
<td>R(Å)</td>
<td>3.39(1)</td>
<td>3.39(1)</td>
<td>3.39(1)</td>
</tr>
<tr>
<td></td>
<td>DWF(Å^2)</td>
<td>0.005(1)</td>
<td>0.006(1)</td>
<td>0.006(1)</td>
</tr>
<tr>
<td>n</td>
<td>8.1(4)</td>
<td>8.1(4)</td>
<td>8.1(2)</td>
<td>8.1(2)</td>
</tr>
</tbody>
</table>

resulting oxygen displacement that is permissible in rhombohedral (R̅3C) structure. In this structure, effect of oxygen displacements will be evident, more on La-O_1 and La-O_3 bonds compared to that on La-O_2 as well as Mn-O bonds as observed in our samples [Table 4.2].

**Mn K-edge EXAFS**

Mn K-edge EXAFS were fitted with k-weighting, in R-range 1.8 Å to 3.6 Å and k-range 3.6 Å⁻¹ to 12 Å⁻¹. Fits of the inverse Fourier transforms of Mn K-edge EXAFS for x = 0.00, 0.03, 0.10 and 0.20 are presented in Fig. 4.10 and the results of the Mn K-edge analysis are presented in Table 4.3. Mn-O, Mn-Mn
Fig. 4.10: $k$-weighted backtransformed Mn K-edge EXAFS spectra (circles) along with fitted curves (line) in $La_{0.67}Sr_{0.33}Mn_{1-x}Ti_xO_{3+\delta}$ samples.

as well as Mn-La bond lengths for the samples, obtained by fitting Mn K-edge EXAFS, are almost the same over the entire doping range $0.00 \leq x \leq 0.20$. The constant La/Sr ratio at the scattering site reflects in the almost constant DWF associated with Mn-(La/Sr) bond length whereas increasing disorder with doping at (Mn/Ti) scattering site reflects in increasing DWF associated with La-(Mn/Ti) bond lengths.

Both La and Mn K-edge EXAFS were fitted initially for $La_{0.67}Sr_{0.33}MnO_3$ sample. Bond lengths were varied first, followed by their Debye Waller Factors. Coordi-
Table 4.3: Structural parameters obtained from Mn K-edge EXAFS for site-disordered \( \text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Ti}_x\text{O}_{3+x/6} \) samples. Figures in brackets indicate uncertainties in the last digit.

<table>
<thead>
<tr>
<th></th>
<th>x=0.00</th>
<th>x=0.03</th>
<th>x=0.10</th>
<th>x=0.20</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mn-O</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R(Å)</td>
<td>1.92(1)</td>
<td>1.92(1)</td>
<td>1.92(1)</td>
<td>1.92(1)</td>
</tr>
<tr>
<td>DWF(Å²)</td>
<td>0.007(2)</td>
<td>0.007(1)</td>
<td>0.007(2)</td>
<td>0.009(1)</td>
</tr>
<tr>
<td>n</td>
<td>5.5(6)</td>
<td>5.5(3)</td>
<td>5.5(4)</td>
<td>5.7(5)</td>
</tr>
<tr>
<td><strong>Mn-(La/Sr)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R(Å)</td>
<td>3.39(1)</td>
<td>3.39(1)</td>
<td>3.39(1)</td>
<td>3.39(1)</td>
</tr>
<tr>
<td>DWF(Å²)</td>
<td>0.009(1)</td>
<td>0.010(1)</td>
<td>0.010(1)</td>
<td>0.010(1)</td>
</tr>
<tr>
<td>n</td>
<td>8.4(7)</td>
<td>8.4(5)</td>
<td>8.4(5)</td>
<td>8.6(5)</td>
</tr>
<tr>
<td><strong>Mn-(Mn/Ti)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R(Å)</td>
<td>3.81(1)</td>
<td>3.82(1)</td>
<td>3.81(1)</td>
<td>3.82(1)</td>
</tr>
<tr>
<td>DWF</td>
<td>0.004(1)</td>
<td>0.002(1)</td>
<td>0.003(1)</td>
<td>0.002(1)</td>
</tr>
<tr>
<td>n</td>
<td>5.6(5)</td>
<td>5.6(2)</td>
<td>5.6(2)</td>
<td>5.6(2)</td>
</tr>
<tr>
<td><strong>Mn-O-(Mn/Ti)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R(Å)</td>
<td>3.83(1)</td>
<td>3.83(1)</td>
<td>3.83(1)</td>
<td>3.83(1)</td>
</tr>
<tr>
<td>DWF(Å²)</td>
<td>0.007(5)</td>
<td>0.007(1)</td>
<td>0.007(1)</td>
<td>0.007(1)</td>
</tr>
<tr>
<td>n</td>
<td>12.4(6)</td>
<td>12.4(3)</td>
<td>12.4(3)</td>
<td>12.3(4)</td>
</tr>
</tbody>
</table>

Coordination numbers were initially fixed at the known crystallographic values while fitting Mn K-edge EXAFS and in case of La K-edge EXAFS, twelve La-O bond lengths were divided into three different groups of coordination numbers 3, 6 and 3 respectively on the basis of closeness of their values. Later, coordination numbers had to be varied slightly to improve the quality of fit. The Mn K-edge and La K-edge EXAFS were fitted in tandem so that equal La-Mn bond lengths were obtained from both the EXAFS.

It is surprising that Mn-(Mn/Ti) distance obtained from Mn K-edge EXAFS and La-(Mn/Ti) distance obtained from Mn K-edge as well as La K-edge EXAFS remains almost the same in all the samples. All earlier studies on Ti doped
lanthanum manganites [6, 7, 8, 9, 10, 11, 12, 13, 14, 15] have shown that Ti$^{4+}$ ions (Ionic radius 0.74 Å) occupy Mn$^{4+}$ ionic sites (Ionic radius 0.67 Å) alone and hence lattice parameters of the doped material increase with doping content [6, 7, 8, 9, 10, 11]. Therefore, in case of such a substitution, Mn-Mn and Mn-La distances are expected to increase with the increasing amount of Ti doping.

4.4 Discussion

Mn$^{4+}$ contents in the samples were determined using X-ray photoelectron spectra from areas under deconvoluted curves corresponding to Mn$^{4+}$ and Mn$^{3+}$ ions. The Mn$^{4+}$ contents obtained from XPS closely match with those obtained from iodometric titration method within the limits of experimental errors. It is clear from these results that the doped samples are oxygen-rich (cation deficient) and hence the Mn$^{4+}$ content is higher than that expected in stoichiometric samples. Absence of any significant chemical shift in the Mn K-edge in the X-ray absorption spectra and in biding energies of Mn 2p core levels in X-ray photoelectron spectra, is in tune with the nearly same average valence of the Mn ions. It is well known that the binding energies of Mn 2p core levels in X-ray photoelectron spectra [3, 16] and the Mn K-edge peak position in X-ray absorption spectra [5, 18, 19] are sensitive to the amount of hole doping (Mn$^{4+}$ content) in the samples. Generally, the higher Mn$^{4+}$ content is attributed to the presence of cation vacancies (or
oxygen excess) in the samples [20, 21, 22]. However, in our $x = 0.10$ site — disordered sample, higher magnetoresistance at low temperatures can not be explained on the basis of cation vacancies alone. Moreover, as discussed in the previous Chapter, the nearly constant lattice parameters of these samples point towards the possibility of a fraction of Ti$^{4+}$ ions occupying Mn$^{3+}$ as well as Mn$^{4+}$ sites. In fact, ionic radius of a Ti$^{4+}$ ion is closer to that of a Mn$^{3+}$ ion, rather than that of Mn$^{4+}$ ion. Although, the reported literature on Ti doped lanthanum manganites [6, 7, 8, 9, 10, 11, 12, 13, 14, 15] has invariably shown that Ti$^{4+}$ ion occupies Mn$^{4+}$ sites alone, there is a distinct possibility, on the basis of size considerations, that a fraction of the Ti$^{4+}$ ions can occupy Mn$^{3+}$ sites. Furthermore, transport and magnetic properties of these site — disordered materials suggest that Ti$^{4+}$ ions occupy Mn$^{4+}$ as well as Mn$^{3+}$ sites and the local structural investigations around La and Mn ions in these samples provide the evidence for it.

Analysis of the room temperature La and Mn K-edge EXAFS [Tables 4.2 and 4.3] shows that La-Mn, Mn-Mn and Mn-O distances are almost the same in all the samples. This augurs well with the nearly constant lattice parameters obtained from analysis of X-ray diffraction measurements of these materials [Table 3.1]. Nearly constant Mn-O and Mn-Mn bond lengths and increased number of Mn$^{3+}$-O-Mn$^{4+}$ Zener pairs are responsible for the room temperature ferromag-
netic transition for $x = 0.10$ and $x = 0.20$ samples. To understand the effect of Ti
doping on local structure of Mn ion, we consider the two possibilities. First one is
of all Ti$^{4+}$ ions occupying Mn$^{4+}$ sites alone and the second is of a fraction of Ti$^{4+}$
ions occupying Mn$^{3+}$ sites in addition to Mn$^{4+}$ sites. With the first possibility, it
is difficult to explain the reasons for the observed systematic increase in oxygen-
excess ($\delta$) with $x$, having employed the identical synthesis procedures for all of
them. If it is still assumed that all the doped Ti ions (10%) enter into Mn$^{4+}$
sites, then 5% of Mn$^{3+}$ ions should have converted into Mn$^{4+}$ state to give the
experimentally observed 28% Mn$^{4+}$ content [Table 4.1] in the site – disordered
$x = 0.10$ sample. Therefore, for every two Ti$^{4+}$ ions occupying Mn$^{4+}$ site, one
Mn$^{3+}$ ion is converted into Mn$^{4+}$ ion, in this sample. Conversion of Mn$^{3+}$ ion
into Mn$^{4+}$ ion reduces its ionic radius by 0.115 Å while Ti$^{4+}$ ion occupying Mn$^{4+}$
site increases the ionic radius of the ion at doped site by 0.07 Å, ionic radii of
Mn$^{3+}$, Mn$^{4+}$ and Ti$^{4+}$ being 0.79 Å, 0.67 Å and 0.74 Å respectively [23]. In
such a case, crystal structure being the same and lattice parameters remaining
nearly constant, average La-(Mn/Ti) as well as Mn-(Mn/Ti) bond lengths are
expected to increase. This increase is expected to be higher at doping content
$x = 0.20$. However, La-(Mn/Ti) and Mn-(Mn/Ti) bond lengths obtained from
La as well as Mn K-edge EXAFS do not exhibit any such increase [Tables 4.2
and 4.3]. In the case of the second possibility, Ti$^{4+}$ ions can occupy both Mn$^{4+}$
and Mn$^{3+}$ sites. In this case, a fraction of Ti$^{4+}$ ions that occupies Mn$^{3+}$ sites will decrease La-(Mn/Ti) and Mn-(Mn/Ti) distances, while the other fraction occupying Mn$^{4+}$ sites will increase these distances. Hence, it is possible to obtain the average values of La-(Mn/Ti) and Mn-(Mn/Ti) distances to be nearly constant. Such almost equal La-(Mn/Ti) and Mn-(Mn/Ti) bond lengths are observed in our site – disordered samples [Tables 4.2 and 4.3] and therefore, we believe that Ti$^{4+}$ ions occupy both the Mn sites in these samples.

It is also possible to estimate the percentage of Ti ions that occupy Mn$^{3+}$ sites and Mn$^{4+}$ sites so as to give nearly equal La-(Mn-Ti) and Mn-(Mn/Ti) distances. If 60% of Ti ions occupy Mn$^{3+}$ sites, it is possible to obtain the nearly constant Mn-Mn distances. The percentage of Mn$^{3+}$ and Mn$^{4+}$ ions in $x = 0.10$ sample is expected to be 61% and 29% respectively, in such a case. These values closely match with those obtained from XPS and iodometric techniques [Table 4.1]. Even for $x = 0.20$ sample, with the above mentioned pattern of substitution, expected percentages of Mn$^{3+}$ and Mn$^{4+}$ ions are 55% and 25% respectively which closely match with those obtained by XPS and iodometric techniques. The close resemblance between experimentally observed Mn$^{4+}$ and Mn$^{3+}$ contents and those calculated with the assumption that 60% of Ti$^{4+}$ ions occupy Mn$^{3+}$ sites establishes the fact that in site – disordered La$_{0.67}$Sr$_{0.33}$Mn$_{1-x}$Ti$_x$O$_{3+y}$ samples Ti ions can occupy both the Mn sites. The charge imbalance caused by Ti$^{4+}$
ions occupying Mn$^{3+}$ sites is neutralised by producing cation vacancies in these samples. Therefore, as the doping content $x$ increases, number of Ti$^{4+}$ ions occupying Mn$^{3+}$ sites will also increase and result in more cation vacancies (oxygen excess $\delta$). It explains the reason for observed systematic increase of oxygen excess $\delta$ with increasing doping content $x$, in spite of employing identical synthesis procedures for all the samples. Hence, the EXAFS study of the \textit{site – disordered} La$_{0.67}$Sr$_{0.33}$Mn$_{1-x}$Ti$_x$O$_{3+\delta}$ samples firmly establish the fact that Ti$^{4+}$ can occupy both the Mn sites in the samples. It is to be noted that these samples were synthesized with a low annealing temperature and lesser grinding. The modified synthesis procedure is responsible for the observed site-disorder in these samples.

Effect of synthesis procedure on structural, transport and magnetic properties of rare-earth manganites has been reported in other rare-earth mangnite systems earlier [24, 25]. A \textit{site – ordered} sample with $x = 0.10$ was also prepared by employing higher annealing temperature and greater grinding. The transport, magnetic and structural properties of these samples are significantly different from those of the \textit{site – disordered} sample of the same composition. These properties were discussed in the previous Chapter.

Although, various types of cation disorders have been reported lately [21, 26, 27, 28, 29, 30, 31, 32, 33, 34], this work has identified a new type of site-disorder that has not been reported earlier. In contrast to the earlier reported work on
Ti doped lanthanum manganites, we have been able to show that, with modified synthesis procedure, Ti$^{4+}$ ions can occupy both Mn$^{3+}$ as well as Mn$^{4+}$ sites.

4.5 Conclusion

Nearly constant La-Mn and Mn-Mn bond lengths, obtained from La and Mn K-edge EXAFS analysis, clearly indicate that Ti$^{4+}$ ions can occupy both Mn$^{4+}$ and Mn$^{3+}$ sites, in site-disordered La$_{0.67}$Sr$_{0.33}$Mn$_{1-x}$Ti$_x$O$_{3+y}$ samples. Constant binding energy in XPS measurements for the doped as well as undoped samples and absence of chemical shift of Mn K-edge absorption features lend support to these observations.
Bibliography


