CHAPTER 5
STUDIES IN SOME MANGANESE DOPED 
Na$_{1.89}$Li$_{0.10}$K$_{0.01}$Ti$_3$O$_7$ FINE CERAMICS

Abstract

The polycrystalline sample of Na$_{1.89}$Li$_{0.10}$K$_{0.01}$Ti$_3$O$_7$ and its manganese (0.01, 0.05 and 1.0 molar percentage) doped derivatives have been synthesized through solid-state reaction method. These samples have been characterized through d.c. conductivity studies in the temperature range of 400K-800K. The slopes of log ($\sigma$.T) versus (1000/T) plots are discussed in three distinct regions. The mechanism in Region I involves electronic hopping (polaron) conduction. Region II is attributed to “associated extrinsic ionic conduction through dilated interlayer space” and “Modified interlayer ionic conduction” is in region III. The temperature versus thermo induced (pyro) current by stabilizing the temperature of the sample for about 2 minutes at each desired value in the temperature range of 373-723K for all of the above samples has also been reported in this chapter.
5.1 Introduction

In recent years, there has been much progress in the field of alkali titanate ceramics having layered and tunnel structures [1]. The physico-chemical properties including ionic and electronic conductivity have been extensively investigated because of their potential industrial application as ion exchangers, electrode for secondary batteries, filters, reinforcements, heat insulator, catalysts, etc. [2-10]. The family of alkali titanates crystallizes in about 130 phases [11]. They are also used for (a) intercalate organic guest molecules for fixing radioactive metal ions, (b) prepare non alkali metals compounds in many cutting technologies, and (c) recover radioactive species from liquid waste [12, 13]. Further investigations have been undertaken on the intercalation of alkyl ammonium cations into layered titanate in the presence of macrocyclic [14], visible light induced electron transfer and long lived charge separation in cyaninedye/layered titanate compounds [15], pillaring photocatalytic properties of partially substituted layered titanates: Na$_2$Ti$_{3.3}$M$_x$O$_7$ and K$_2$Ti$_{4.3}$M$_x$O$_9$ (M=Mn, Fe, Co, Ni, Cu) [16].

The powder of varying grain size of layered compounds, namely Na$_2$Ti$_3$O$_7$ and Na$_2$Ti$_6$O$_{13}$ have been prepared by sol-gel process and solid state reaction of Na$_2$CO$_3$ and TiO$_2$ [17-18]. The photochemical properties of Cu$^{2+}$ doped layered hydrogen titanate have been studied by Yanagisawa et al. [19]. Recently, Zhang et al. [20-21] have reported the formation mechanism of H$_2$Ti$_3$O$_7$ nano tubes. Shripal et al. further studied pure Na$_2$Ti$_3$O$_7$, K$_2$Ti$_4$O$_9$ and their manganese-doped derivatives [22-23].

Another series of titanate with composition M$_2$Ti$_6$O$_{13}$ (M=Na, K, Rb) display rectangular tunnel structure and act as good photo catalysts to
decompose water when combined with ruthenium oxide [24]. Recently, Wang et al. [25] have reported synthesis of semi conducting $K_2Ti_6O_{13}$ nanowires with an average diameter of about 10nm by a simple hydrothermal reaction of $Na_2Ti_5O_7$ and KOH. $K_2Ti_6O_{13}$ exhibits a monoclinic structure with lattice parameters $a=15.593$, $b=3.796$, $c=9.108$, and $\beta=99.78$ [26]. Thermodynamic properties of $Na_2Ti_6O_{13}$ have been investigated through electrochemical and calorimetric methods [27]. Recently, our group proposed ferro-electric phase transition in $Na_{2-x}K_xTi_3O_7$ and $Na_{1.9}Li_{0.1}Ti_3O_7$ ceramics [28, 29]. Very recently, Shripal et al. have been reported a.c conductivity investigations in pure and manganese doped layered manganese doped layered $Na_2Ti_3O_7$ ceramics [30]. Dielectric spectroscopic and a.c conductivity studies on layered $Na_{1.9}K_{0.1}Ti_3O_7$ ceramics have further reported by Shripal et al. [31]. Recently, D.Pal et al. have reported preparation and characterization of pure and manganese doped layered $Na_{1.9}Li_{0.1}Ti_3O_7$. Very recently, Geetika et al. [33] have been reported Synthesis and characterization of $Na_{2-x-y}Li_yK_yTi_3O_7$ ceramics.

So far, there is no work available in the literature on manganese-doped derivatives of $Na_{1.89}Li_{0.01}K_{0.01}Ti_3O_7$. It seems interesting to synthesize its manganese-doped derivatives and subsequently characterize them through EPR, d.c. conductivity and pyroelectric investigations. The corresponding results are reported in this chapter.

5.2 Experimental

Polycrystalline layered samples of $Na_{1.89}Li_{0.01}K_{0.01}Ti_3O_7$ (denoted as S1LPT) have been synthesize by mixing $Na_2CO_3$ (99.9% pure A.R. grade) $TiO_2$ (99.9% pure A.R.grade) powder in stoichiometric ratio and
Manganese doped \( \text{Na}_{1.89} \text{Li}_{0.10} \text{K}_{0.01} \text{Ti}_3 \text{O}_7 \)

Additionally, the manganese doped sodium titanate sample of \( \text{Na}_{1.89} \text{Li}_{0.01} \text{K}_{0.01} \text{Ti}_3 \text{O}_7 \) have been prepared by adding 0.01, 0.05, 1.0 molar percentage of MnO₂ (99.9% pure A.R. grade) powder in the base matrix of \( \text{Na}_{1.89} \text{Li}_{0.01} \text{K}_{0.01} \text{Ti}_3 \text{O}_7 \) and denoted as \( \text{MS}_1 \text{LPT-1, MS}_2 \text{LPT-2, MS}_3 \text{LPT-3} \), respectively. Details of the method of preparation of these ceramics are given in the chapter 3 at section 3.1. XRD-patterns for all the above compositions have been collected on Richseifert Iso-Debyflex 2002 diffractometer using CuKa radiation generated at 30kV and 20 mA. Details of XRD are given in chapter 3 at section 3.2. Details of d.c. conductivity and pyroelectric measurements are given in chapter 3 at section 3.3 and 3.4. The preliminary pyroelectric investigations have also been made in these compounds and explained region wise in the entire temperature range of study. All the measurements were made by stabilizing the temperature of the sample for about 2 minutes at each desired value. The EPR spectra of the manganese-doped samples were recorded on a Varian E-line century series spectrometer model E-109, which operates at X-band frequencies (9.2GHz). Details of EPR are given in chapter 3 at section 3.5.

### 5.3 Results and discussion

XRD patterns of lithium potassium mixed sodium titanate (\( S_1 \text{LPT} \)) and its manganese doped derivatives (\( \text{MS}_1 \text{LPT-1, MS}_2 \text{LPT-2, MS}_3 \text{LPT-3} \)) shows single phase at room temperature and its layered structure has been confirmed [1].

Fig 5.1 shows EPR spectra at room temperature of \( \text{MS}_1 \text{LPT-1, MS}_2 \text{LPT-2, MS}_3 \text{LPT-3} \), manganese doped derivatives of \( S_1 \text{LPT} \). This EPR spectra gives two-peak spectrum, one composite peak ‘A’ with \( g \approx 4.4 \) and
other weak line ‘B’ with $g \approx 2$. The six hyperfine lines have not been seen for MS$_1$LPT-1 & MS$_1$LPT-2 except MS$_1$LPT-3. This indicates that at low doping <1% (molar), very small amount of manganese substitute at interlayer cation sites. It may be possible, hyperfine lines are superimposed due to the presence of bigger K$^+$ ions in interlayer cation sites. For heavily doped MS$_1$LPT-3, these lines can be seen. It seems that in MS$_1$LPT-3, large amounts of Mn$^{2+}$ ions are going at interlayer site. This is reflected well by decreased value of $E_a$, comparable to SLT [32], with the knowledge about the occupancy of manganese ions in S$_1$LPT lattice, it has been easy to discuss the results of conductivity studies in samples with different manganese concentrations. The conductivity plots can be divided into three distinct regions I, II, III and the corresponding results are discussed region wise as in the following.

5.3.1 Region I

Fig 5.2 shows that the region I extend roughly upto 466K, 458K, 460K, 456K for S$_1$LPT, MS$_1$LPT-1, MS$_1$LPT-2 and MS$_1$LPT-3 samples, respectively. The slopes are continuously mounting for all the doped samples. The activation energy of this region for S$_1$LPT is much less than that of SLT reported earlier (0.57eV) [33]. Table 5.1(b) shows less $E_a$ values for manganese doped samples. It means conduction becomes easy for doped samples. It can be seen from the figure, as the impurity contents increases from samples MS$_1$LPT-1 to MS$_1$LPT-3, conductivity also increases.

However, the loose electrons from Ti$_3$O$_7^{2-}$ groups jumping from one Ti-Ti chain to an adjacent one attributed to the hopping process (polaron conduction) has been already proposed by Shripal et al. [34]. For doped
samples (MS₁LPT-1 to MS₁LPT-3) conduction mechanism can be understood by assuming, as manganese ions, which substitute at Ti⁴⁺ sites, are in the tri-positive valance state (Mn³⁺) and their substitution would naturally cause the loose electrons to increase and hence the conductivity in this region 1.

Thus, the electronic hopping (polaron) conduction is dominant in this region.

5.3.2 Region II

The region II exists roughly up to 671K, 671K, 689K, 671K for S₁LPT, MS₁LPT-1, MS₁LPT-2 and MS₁LPT-3, respectively. The patterns of conductivity are similar for all the doped samples. As the base material used for the preparation of S₁LPT were not ideal pure, some defects (e.g. impurities, interstitials and vacancies) are likely to be present in the interlayer space of the prepared polycrystalline compound. At moderately low temperatures, the cation vacancies present will always form impurity vacancy as well as interstitial vacancy pairs. The large activation energy (Eₐ) in this region is thus naturally attributed to ionic conduction in the presence of such intrinsic defects through interlayer as earlier proposed by shripal et al. [34]. Recently, D.Pal et al. [32] have reported there result of d.c conductivity studies of SLT samples, where lithium plays an important role in conduction.

From fig 5.1, it can be seen that manganese substitute as Mn³⁺ at Ti⁴⁺ sites in doped compounds with 3d⁴ configuration reflect themselves in the composite peak ‘A’ of the EPR spectrum. These substituting Mn³⁺ ions are expected to have smaller ionic radii than Ti⁴⁺ causing to dilate the opposite
Ti-Ti layers. It can be observed from figure 5.2 that conductivity also increases from MS$_1$LPT-1 to MS$_1$LPT-3 as doping content of manganese increases. In the EPR spectrum the weak line 'B' shows that manganese substitute as Mn$^{2+}$ at alkali site in the interlayer space.

The decrease in activation energy can be understood by assuming that in the interlayer space some sodium is replaced by lithium (small radii) and potassium (big radii) causing increase in interlayer space as well as in conductivity. The change in the interlayer space as explained above with the increase in the impurity concentration would cause a corresponding change in the Ea. This is reflected well with the continuous decrease in Ea from S$_1$LPT to MS$_1$LPT-3.

Thus, the ionic conduction in this region may be called as "associated extrinsic ionic conduction through dilated interlayer space".

5.3.3 Region III

From conductivity curves the region III starts from 671K, 671K, 689K, and 671K for S$_1$LPT, MS$_1$LPT-1, MS$_1$LPT-2 and MS$_1$LPT-3 respectively. The activation energy of this region for S$_1$LPT is less than those of region II. This can be understood, as, in this region the I-V pairs break completely up to the lower limit of region III, thus I-V pairs would not affect ionic conduction in region III of pure samples. It may be attributed to free migration of sodium/lithium/potassium ions within the interlayer space, with a lower value of activation energy than that for region II. Shripal et al. [28] have already proposed the conduction mechanism in this region for manganese doped Na$_2$Ti$_3$O$_7$ samples. It seems that the combination of smaller and bigger ion increases the interlayer space. For doped samples,
Table 5.1 shows that Ea values increases as doped quantity increases. For these doped samples, the slope of region III is greater than that of region II which can be understood as, Mn$^{3+}$ substitution at Ti$^{4+}$ sites loosen off some oxygen from Ti$_3$O$_7^2$-groups and then participate in large number for conduction, resulting in the apparent increase in the slope of the conductivity plots as already proposed by Shripal et al. [34].

Thus, the conduction in region III for manganese doped S$_1$LPT derivatives may easily be "Modified interlayer ionic conduction" the modification being affected by loosen oxygen from Ti$_3$O$_7^2$-groups.

Furthermore, Pyroelectricity is the ability of certain materials to generate an electrical potential when they are heated or cooled. As a result of this change in temperature, positive and negative charges move to opposite ends through migration i.e. the material becomes polarised and hence, an electrical potential is established [35].

Fig 5.3 shows the temperature versus thermo induced (probably pyro) current curves for S$_1$LPT, MS$_1$LPT-1, MS$_1$LPT-2 and MS$_1$LPT-3 in the temperature range from 373-690K. To understand the conduction mechanism of this plot for all the samples, three distinct regions have been identified over the entire temperature range of study. Positive current region I exist up to 445K. For S$_1$LPT the conduction mechanism is already explained in the chapter IV. For other ceramics, the existence of dielectric polarization about the polar axis has been proposed in the recent literature [36, 37].

Now, in the present study with low percentage of doping the current decreases first but current increases very rapidly with the increment in
doping. The occurrence of positive region can be understood by assuming that the electronic polarization set up about the polar axis involving electrons. Thus manganese doping plays an important role for the conduction.

In region II, the current changes its sign from positive to negative, very sharply in a very short range of temperature. It means a phase transition occurs in region II. For MS₁LPT-3, phase transitions takes place at higher temperature comparative to others and get maximum current in region III. This can be understood by assuming that the ionic polarization (orientational or migrational) takes place in this region. Recently it is discovered that the shape and the position of pyroelectric peak are dependent on the type and the temperature of the phase transition [38]. In region III, it is seen that the current increases for MS₁LPT-1 than decreases for MS₁LPT-2 and again increases for MS₁LPT-3. The mechanism of positive current region can be understood by assuming the electronic polarization set up about the polar axis involving hoping electrons. The appearance of negative current region can easily be interpreted due to the ionic polarization set up about the polar axis involving various ionic dipoles present in the lattice. However, the phase transition region in the mid temperature range reflect that the dominance of electronic polarization in the lower temperature range starts to disappear with the rise in temperature and the dominance of ionic polarization starts towards the higher temperature range.
5.4 Conclusions

The present study reveals the following points:

1. For the first time Li (x=0.10) and K content (y=0.01) has been inserted into the interlayer space of Na$_2$Ti$_3$O$_7$ lattice and also its manganese-doped derivatives are synthesized and studied.

2. Electron hopping (Polaron) conduction takes place in region I.

3. The conductivity results of region II reflected that substituting Mn$^{3+}$ ions at Ti$^{4+}$ sites causes to dilate space between opposite Ti-Ti layer. The ionic conduction in this region may be “associated extrinsic ionic conduction through dilated interlayer space”.

4. The conductivity and activation energies in region III are increasing from S$_1$LPT to MS$_1$LPT-3. This gives a signature of the role of loose oxygen’s from Ti$_3$O$_7^{2-}$ groups. Such behavior is expected so long as Mn$^{3+}$ substitutes at the Ti$^{4+}$ sites as in the case for the samples up to MS$_1$LPT-3. Thus, the conduction in region III for manganese doped S$_1$LPT derivatives may easily be understood as “Modified interlayer ionic conduction”.

5. The preliminary pyro / thermo induced investigations have been tried and reported for the first time in these layered alkali titanates.
Table 5.1(a) Nomenclature for Na$_{1.89}$Li$_{0.10}$K$_{0.01}$Ti$_3$O$_7$ doped with different concentration of manganese ions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molar parentage of doped ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>S$_1$LPT</td>
<td>0.00</td>
</tr>
<tr>
<td>MS$_1$LPT-1</td>
<td>0.01</td>
</tr>
<tr>
<td>MS$_1$LPT-2</td>
<td>0.05</td>
</tr>
<tr>
<td>MS$_1$LPT-3</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Table 5.1(b) Values of Activation energies (eV), determined from the slopes of log (σt) vs 1000/T plots for different pure Na_{1.89}Li_{0.10}K_{0.01}Ti_{3}O_{7} and their manganese doped derivatives

<table>
<thead>
<tr>
<th>Samples</th>
<th>Activation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Region I</td>
</tr>
<tr>
<td>S_{1}LPT</td>
<td>0.41</td>
</tr>
<tr>
<td>MS_{1}LPT-1</td>
<td>0.36</td>
</tr>
<tr>
<td>MS_{1}LPT-2</td>
<td>0.33</td>
</tr>
<tr>
<td>MS_{1}LPT-3</td>
<td>0.36</td>
</tr>
</tbody>
</table>
Fig. 5.1 EPR spectra of different manganese doped samples of $S_1$LPT at room temperature. Central field: 3370G.

(a) MS$_1$LPT-1  (b) MS$_1$LPT-2  (c) MS$_1$LPT-3
Fig. 5.2 Log (σ T) versus 1000/T plots of pure S₁LPT and different manganese doped samples.

〇 S₁LPT  ● MS₁LPT-1  △ MS₁LPT-2  ▲ MS₁LPT-3
Fig. 5.3 Thermo induced current versus temperature for pure and different manganese doped samples

△ S_{1}LPT ▲ MS_{1}LPT-1 ○ MS_{1}LPT-2 ● MS_{1}LPT-3
REFERENCES

32. D. Pal, P. Chand, R.P.Tandon and Shripal, Preparation and Characterization of pure and manganese doped Layered Na1.85Li0.10K0.01Ti3O7, Proceeding of the National Seminar on Ferroelectric and Dielectrics, Allied Publishers (2004), 39
35. Wikipedia, the free encyclopedia
38. F. Yujun, X. Zhuo, Y. Tongquing and Yaoxi, Chinese Science bull. 13,(2000), 45