CHAPTER 8
STUDIES IN SOME MANGANESE DOPED LAYERED
$Na_{1.85}Li_{0.10}K_{0.05}Ti_3O_7$ FINE CERAMICS

Abstract

The sintered lithium potassium mixed $Na_{1.85}Li_{0.10}K_{0.05}Ti_3O_7$ and its 0.01, 0.05 and 1.0 % molar percentage MnO$_2$ doped derivatives have been synthesized by high temperature solid-state reaction technique. Electron paramagnetic resonance (EPR) analysis of all manganese doped derivatives at room temperature, d.c conductivity and preliminary Pyroelectric measurements were carried out on the prepared samples. The lithium potassium ions are accommodated with the sodium ions in the interlayer space. The conductivity plots between log ($\sigma$.T) versus 1000/T have been divided into three regions. Region I is attributed to electronic hopping conduction for all the samples, associated interlayer ionic conduction is in intermediate region II and the highest temperature region III to modified interlayer ionic conduction, the modification being affected by oxygen from Ti$_3$O$_7^{2-}$ groups. The observed pyroelectric plots have been discussed regionwise in the temperature range from 373-690 K.
8.1 Introduction

In a series of titanates with the chemical formula \( \text{Na}_2\text{Ti}_n\text{O}_{2n+1} \), to which \( \text{Na}_2\text{Ti}_3\text{O}_7 \) belongs, has zigzag layer structure [1]. Recently the crystal structure is refined [2]. It has been reported that \( \text{Na}_2\text{Ti}_3\text{O}_7 \) has ability to decompose water to hydrogen and oxygen when ruthenium oxide is highly disperse on the titanate [3]. Pillaring and photo catalytic properties of partially substituted layered titanates: \( \text{Na}_2\text{Ti}_{3-x}\text{M}_x\text{O}_7 \) and \( \text{K}_2\text{Ti}_{4-x}\text{M}_x\text{O}_9 \) \((M=\text{Mn, Fe, Co, Ni and Cu}) \) has been studied [4]. In a recent work photochemical properties of \( \text{Cu}^{2+} \) doped layered hydrogen titanates have been reported by Yanagisawa et al. [5]. The formation mechanism of \( \text{H}_2\text{Ti}_3\text{O}_7 \) nanotubes by single-step reaction of crystalline \( \text{TiO}_2 \) and \( \text{NaOH} \) has been investigated via transmission electron microscopy examinations of series specimens with different reaction times and extensive calculation [6]. Kikkawa et al. [7] investigated \( \text{Na}_2\text{Ti}_3\text{O}_7 \), \( \text{K}_2\text{Ti}_4\text{O}_9 \) and its niobium-substituted products through a.c. conductivity studies. \( \text{Na}_2\text{Ti}_3\text{O}_7 \) , \( \text{K}_2\text{Ti}_4\text{O}_9 \), their iron and manganese doped derivatives and \( \text{K}_{2-x}\text{Rb}_x\text{Ti}_4\text{O}_9 \) have been investigated through EPR (electron paramagnetic resonance) and d.c. conductivity measurements by Shripal et al. [8-11]. Recently, Shripal et al. has further reported the dielectric-spectroscopic and a.c. conductivity studies on pure and manganese doped layered \( \text{Na}_2\text{Ti}_3\text{O}_7 \) and \( \text{K}_2\text{Ti}_4\text{O}_9 \) ceramics [12-13].

Furthermore, layered \( \text{Li}_2\text{Ti}_3\text{O}_7 \) is a good ionic conductor suitable for lithium insertion studies [14]. Alkali titanates have also been synthesized by hydrothermal reaction at a relatively low temperature of around 100°C and at nano scale [15]. In case of \( \text{BaTiO}_3 \), it is confirmed that copper ions substitute as \( \text{Cu}^{2+} \) at \( \text{Ti}^{4+} \) sites [16]. The structure transformation behaviour
of Na₂Ti₃O₇ by hydrolysis has been investigated in mild and strong and acidic aqueous medium [17]. Furthermore, electrochemical and calorimetric thermo dynamical properties of Na₂Ti₃O₇ and Na₂Ti₆O₁₃ have also been determined by M.Holzinger et al. [18]. Safety and recharge ability problems associated to the use of metallic lithium have so far precluded their wide spread marketing that’s why we have taken very small amount of lithium.

However, EPR study of doped manganese samples could provide information about its local environment, the crystallographic field and further about the ion-vacancy (I-V) pairs if any exists in the system. As we have already discussed d.c conductivity and pyroelectric studies on Na₁.₈₅Li₀.₁₀K₀.₀₅Ti₃O₇ in previous chapter-4. Therefore it seems interesting to synthesize and characterizes its manganese-doped derivatives through d.c. conductivity, pyroelectric and EPR measurements. The corresponding results are reported in this chapter.

8.2 Experimental

Polycrystalline layered Na₁.₈₅Li₀.₁₀K₀.₀₅Ti₃O₇ (denoted as S₄LPT) has been synthesized by calcining stoichiometric ratio of Na₂CO₃, K₂CO₃, and TiO₂ powders at 1173K for a day. Manganese doped ceramic samples of Na₁.₈₅Li₀.₁₀K₀.₀₅Ti₃O₇ have been prepared by adding 0.01, 0.05, 1.0 molar percentage of MnO₂ powder in the base matrix and denoted as MS₄LPT-1, MS₄LPT-2, MS₄LPT-3, respectively. Details of the method of preparation of these ceramics are given in chapter 3 section 3.1. Detail of XRD pattern for all the above compositions have been given in chapter 3 at section 3.2. Detail 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 details about EPR measurements are also given in chapter 3 section 3.5.

8.3 Results and discussion

XRD patterns obtained for $S_4$LPT, $MS_4$LPT-1, $MS_4$LPT-2 and $MS_4$LPT-3 are in close agreement to that reported in the literature [1]; confirm the formation of these titanates with a monoclinic crystal system.

Fig 8.1 shows the EPR spectra recorded at room temperature of $MS_4$LPT-1, $MS_4$LPT-2 and $MS_4$LPT-3 polycrystalline samples. The sample $MS_4$LPT-2 gives an unresolved peak ‘B’ with $g \approx 2.0$ in the room temperature EPR spectrum. The intensity of this peak increases for $MS_4$LPT-3. Containing enhanced impurity content; peak ‘A’ with $g \approx 4.4$ is obtained for all $MS_4$LPT-1, $MS_4$LPT-2 and $MS_4$LPT-3 samples.

In the room temperature EPR spectrum of $MS_4$LPT-1; observed peak ‘A’ can be ascribed to Mn$^{3+}$ ions sitting at Ti$^{4+}$ sites. The manganese ion also occupy in interlayer sites. The presence of such Mn$^{2+}$ ions is indicated through the weak unresolved structure in the spectrum.

The EPR spectrum observed in sample $MS_4$LPT-2 has peak ‘A’ due to the probably substitution of Mn$^{3+}$ at Ti$^{4+}$ site and some manganese as Mn$^{2+}$ are also in the interlayer site, indicated through a weak unresolved structure in the spectrum.

The fine structure spectrum observed for sample $MS_4$LPT-3, consists very clear two peaks ‘A’ with $g \approx 4.4$ and peak ‘B’ a group of six hyperfine lines with $g \approx 2.0$. 
With this knowledge about the occupancy of manganese ions in S₄LPT lattice, it has been easy to discuss the results of conductivity studies for samples with different manganese concentrations.

The values of d.c. conductivity ($\sigma_{dc}$) for pure S₄LPT and its light blackish manganese doped products have been determined in the temperature range 370K to 750K. Fig. 8.2 shows the corresponding log ($\sigma$ vs T) versus 1000/T plots. For all the samples the three regions I, II, III have been identified over the entire temperature range of study. The activation energies ($E_a$) for all the samples are determined from the slopes of log ($\sigma$ vs T) versus 1000/T plots are summarized in table 8.1(b). These results are accordingly, discussed region wise as in the following,

8.3.1 Region I

Region I extend roughly up to 483K, 471K, 483K, and 500K for the S₄LPT, MS₄LPT-1, MS₄LPT-2 and MS₄LPT-3 samples, respectively. For S₄LPT, the conduction mechanism has already discussed in previous chapter IV. For S₄LPT, the values of activation energies are the least in region I and in region III are intermediate to those in region I and II. However, for doped samples, it is continuously increasing from region I to III.

Fig. 8.2 shows that the conductivity increases upto MS₄LPT-2. Electronic hopping conduction could take place for such samples similar to the S₁LPT, S₂LPT, S₃LPT derivatives. The electronic hopping conduction has already been proposed to occur for pure and manganese doped sodium trititanate samples [9] through loose electrons from Ti₃O₇, which probably jump from one Ti - Ti chain to adjacent one. However, decrease in conductivity is observed for sample MS₄LPT-3 in comparison to MS₄LPT-2. Sample MS₄LPT-3 does not follow the above behaviour. It
seems that manganese entry at Ti\(^{4+}\) sites become saturated for MS\(_4\)LPT-2. Further addition of impurity leads to the substitution of Mn\(^{2+}\) at the interlayer cation sites, resulted such type of the configuration of I-V pairs is responsible for reducing both electronic hopping and interlayer ionic conduction.

Thus, we get slight increased Ea values and upper limit of this region are MS\(_4\)LPT-2 (483K) and MS\(_4\)LPT-3 (500K). However, upper limit of this region for MS\(_4\)LPT-1(471K) suggests conduction becomes easy.

In region I, the trend of conductivity variation is all most similar to that of S\(_3\)LPT. The conductivity value of MS\(_4\)LPT-2 is lower than MS\(_3\)LPT-1. These results shows, as well as doping of manganese have increased, probably, this substitution reduces the number of loose electrons appreciably suppressing electronic hopping conduction. Thus, the low conductivity of MS\(_4\)LPT-3 can be understood.

Thus, in this region occurred electronic hopping conduction may be extrinsic or otherwise depending on the doping.

**8.3.2 Region II**

The region II extends roughly upto 689K, 689K, 709K, and 689K for S\(_4\)LPT, MS\(_4\)LPT-1, MS\(_4\)LPT-2 and MS\(_4\)LPT-3 samples, respectively. We know that higher value of Ea is naturally attributed to alkali ionic conduction in the presence of extrinsic defects through alkali interlayer [9].

Fig 8.2 shows that conductivity increases for MS\(_4\)LPT-1, after then decreases upto MS\(_4\)LPT-3. The conduction mechanism of S\(_4\)LPT has been already discussed in chapter IV. The conductivity and Ea value decreases for MS\(_4\)LPT-2, MS\(_4\)LPT-3 but increases for MS\(_4\)LPT-1. For MS\(_4\)LPT-1, Mn\(^{3+}\) substitutions at Ti\(^{4+}\) sites causing to dilate the Ti-Ti layers due to their radii
differences. Thus, the increased conductivity of MS₄LPT-I, low Ea value and no any variation to the upper limit of temperature (689K) could be understood. The Mn²⁺ substitution at alkali site (Na, Li, K) causes Ti-Ti layers would become somewhat closer due to the differences of ionic radius similarly to the MS₃LPT-2, MS₃LPT-3 samples, has been already discussed by Shripal et al. [9].

The change in the interlayer space as above with the increase in the impurity concentration would cause a corresponding change in the Ea. The increased Ea values i.e., 0.84eV, .96eV for MS₄LPT-2, MS₄LPT-3, samples respectively and decreased conductivity can thus be understood.

In region II, the patterns of conductivity in S₄LPT and its manganese-doped derivatives are similar to that of S₃LPT and its manganese doped derivatives reported in previous chapter. It seems that the lithium potassium insertion in S₄LPT lattice reduces the number of I-V pairs, evidenced by less Ea comparative to the MS₃LPT derivatives.

Thus, the ionic conduction in this region may be “associated extrinsic ionic conduction through interlayer space.”

8.3.3 Region III

It seems from the plots that region III roughly starts from 689K, 689K, 709K, and 689K for the samples S₄LPT, MS₄LPT-1, MS₄LPT-2 and MS₄LPT-3, respectively. As from the previous discussion in chapter VII, we know that at the upper limit of region II associated (I-V) pairs are completely dissociated. Here the conduction would not be affected by (I-V) pairs and may be attributed to free migration of alkali ions within the interlayer space.
It seems that substitution of Mn$^{3+}$ at the Ti$^{4+}$ site loosen oxygen from the Ti$_3$O$_7^{2-}$ groups and then participate in large number for conduction resulting apparent increases in conductivity. Furthermore doping of manganese, as in MS$_4$LPT-2 and MS$_4$LPT-3 occurs as Mn$^{2+}$ in the interlayer space, evidenced by peak 'B' and six hyperfine lines. However, the dissociated (I-V) pairs obtained from upper limit of region II, would than perhaps pull some of the loose oxygen. This process reduces the number of participating loose oxygen in the conduction in this region. The activation energy in this region is increasing with the increase of doping but this is not too much as observed for S$_1$LPT S$_2$LPT and S$_3$LPT. The Ea values are decreasing continuously from S$_1$LPT to S$_4$LPT. It seems that decrease in Ea value is due to the reduction of loose oxygen (participating in conduction) and bigger potassium insertion in interlayer space.

In region III, the conductivity value of MS$_4$LPT-1 and MS$_4$LPT-2 are approximating similar but comparatively very much low than MS$_3$LPT-1 and S$_3$LPT. It can be clearly seen that the slope of S$_4$LPT is much lower than S$_3$LPT. It seems that reduced conductivity value is due to the reduced participating ions.

Finally, the conduction in this region III for a manganese doped S$_4$LPT derivatives may be "modified interlayer ionic conduction" the conduction being affected by loosen oxygen from Ti$_3$O$_7^{2-}$ groups.

Furthermore, pyroelectricity is the property presented by certain materials that exhibit an electric polarization $P_i$ when a temperature variation $\delta\Theta$ is applied uniformly: $P_i = p_i^T \delta\Theta$. Where $p_i^T$ is the pyroelectric coefficient at constant stress. Pyroelectric crystals actually have a spontaneous polarization, but the pyroelectric effect can only be observed during a
temperature change. If the polarisation can be reversed by the application of an electric field, the crystal is ferroelectric.

If the crystal is also piezoelectric, the polarization due to an applied temperature variation is also partly due to the piezoelectric effect. The coefficient describing the pure pyroelectric effect is the pyroelectric coefficient at constant strain, \( p_i^S \). The two coefficients are related by: 
\[
p_i^T = c_{ijkl}d_{klm}\alpha_{ijn} + p_i^S
\]
where the \( c_{ijkl} \) are the elastic stiffnesses, the \( d_{klm} \) the piezoelectric coefficients and the \( \alpha_{ijn} \) the linear thermal expansion coefficients. The converse effect is the electrocaloric effect. If a pyroelectric crystal is submitted to an electric field, it will undergo a change of entropy \( \Delta\sigma: \Delta\sigma = p_i E \) and will release or absorb a quantity of heat given by \( \Theta V \Delta\sigma \) where \( \Theta \) is the temperature of the specimen and \( V \) its volume [19].

Fig 8.3 shows the temperature versus thermo induced (probably pyro) current curves for the samples \( S_4\text{LPT} \), \( MS_4\text{LPT}-1 \), \( MS_4\text{LPT}-2 \) and \( MS_4\text{LPT}-3 \) in the temperature range from 373-690K. Three distinct regions have been identified over the entire temperature range of study.

Positive current region I exist upto 445K. For \( S_4\text{LPT} \) the mechanism has already been explained in chapter IV. For other ceramics, the existence of dielectric polarization about the polar axis has been proposed in the recent literature (20, 21). Now in the present experiment region I have positive current approximate above than 1\( \mu \)A and this increases upto \( MS_4\text{LPT}-2 \) except \( MS_4\text{LPT}-3 \). For \( MS_4\text{LPT}-3 \) decreased current is observed. The mechanism of positive current region can be understood by assuming the electronic polarization set up about the polar axis involving hoping electrons. As well as doping content increases current also increases.
In the region II, the current changes its sign from positive to negative very sharply in a very short range of temperature. It means the phase transition occurs in region II. For $S_4$LPT phase transitions occur at 480K than 475K for $MS_4$LPT-1 and $MS_4$LPT-2 and 470K for $MS_4$LPT-3. 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.

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 [22].

In the region III, it is seen that the current increases for $MS_4$LPT-1 to $MS_1$LPT-3. This can be understood as the ionic dipoles probably break and detached cations move which produce thermal induced probably pyrocurrent. On impurity substitution the numbers of detached cations increases resulting apparent increase in the current as observed.
8.4 Conclusions

The outcome of the present investigations can be summarized as-

1. For the first time Na\textsubscript{1.85}Li\textsubscript{0.10}K\textsubscript{0.05}Ti\textsubscript{0.05}O\textsubscript{7} and its (0.01, 0.05 and 1.0) molar percent manganese doped samples have been synthesized and characterized.

2. In region I, electronic hopping conduction (Polaron conduction), though Ti-Ti chains could take place.

3. In region II, the ionic conduction may be "associated extrinsic ionic conduction through interlayer space.”

4. In Region III, increment in conductivity is due to the participation of loosening oxygen from the Ti\textsubscript{3}O\textsubscript{7\textsuperscript{-2}} groups. The conduction in this region III for manganese doped S\textsubscript{4}LPT derivatives may be “modified interlayer ionic conduction” the conduction being affected by loose oxygen from Ti\textsubscript{3}O\textsubscript{7\textsuperscript{-2}} groups

5. The preliminary pyro / thermo induced investigations have been tried and reported for the first time in these layered alkali titanates.

6. These manganese doped Na\textsubscript{1.85}Li\textsubscript{0.10}K\textsubscript{0.05}Ti\textsubscript{0.05}O\textsubscript{7} compounds can be put in the class of mixed ionic- electronic materials.
Table 8.1 (a) Nomenclature for Na$_{1.85}$Li$_{0.10}$K$_{0.05}$Ti$_3$O$_7$ doped with different concentrations of manganese ions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molar parentage of doped ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>S$_4$LPT</td>
<td>0.00</td>
</tr>
<tr>
<td>MS$_4$LPT-1</td>
<td>0.01</td>
</tr>
<tr>
<td>MS$_4$LPT-2</td>
<td>0.05</td>
</tr>
<tr>
<td>MS$_4$LPT-3</td>
<td>1.0</td>
</tr>
</tbody>
</table>
8.1(b) Values of Activation energies (eV), determined from the slopes of log (σT) vs 1000/T plots for different pure Na$_{1.85}$Li$_{0.10}$K$_{0.05}$Ti$_3$O$_7$ and their manganese doped derivatives

<table>
<thead>
<tr>
<th>Samples</th>
<th>Activation energy (eV)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Region I</td>
<td>Region II</td>
<td>Region III</td>
</tr>
<tr>
<td>S$_4$LPT</td>
<td>0.36</td>
<td>0.69</td>
<td>0.42</td>
</tr>
<tr>
<td>MS$_4$LPT-1</td>
<td>0.32</td>
<td>0.66</td>
<td>0.72</td>
</tr>
<tr>
<td>MS$_4$LPT-2</td>
<td>0.32</td>
<td>0.61</td>
<td>0.84</td>
</tr>
<tr>
<td>MS$_4$LPT-3</td>
<td>0.33</td>
<td>0.61</td>
<td>0.96</td>
</tr>
</tbody>
</table>
Fig. 8.1 EPR spectra of different manganese doped samples of $S_4LPT$ at room temperature. Central field: 3370G.

(a) $MS_4LPT$-1    (b) $MS_4LPT$-2    (c) $MS_4LPT$-3
Fig. 8.2 Log (σ T) versus 1000/T plots of pure S₄LPT and different manganese doped samples.

△ S₄LPT  ▲ MS₄LPT-1  ○ MS₄LPT-2  ● MS₄LPT-3
Fig. 8.3 Thermo induced current versus temperature for pure and different manganese doped samples

○ S₄LPT  ● MS₄LPT-1  △ MS₄LPT-2  ▲ MS₄LPT-3
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