CHAPTER VII

STUDIES IN IRON DOPED DERIVATIVES OF K₂Ti₄O₉

Abstract  The polycrystalline samples of 0.1 and 1.0 molar percentage Fe₂O₃ doped K₂Ti₄O₉ ceramics (named IPT-1 and IPT-2) have been prepared and characterized through a.c. conductivity and dielectric spectroscopic investigations in the temperature range 373-773K. The log(σₐcT) versus 1000/T plots have been divided into strongly frequency dependent region I, less frequency dependent anomalous region β and almost frequency independent region III. Two peaks named ‘A’ and ‘B’ for sample IPT-1 and three peaks ‘A’, ‘B’ and ‘C’ for IPT-2 sample have been observed in the anomalous region β of the above plots. Furthermore, the results corresponding to the dependence of loss tangent (tanδ) and dielectric constant (ε) on temperature at different frequencies and the frequency at different temperatures for both of the iron doped derivatives IPT-1 and IPT-2 have been reported in this chapter.
7.1 Introduction

A general review of layered compounds is given by Zabel et al. [1,2]. Layered compounds possessing Aurivillius phase also have much attention due to their important role in electro optic devices. These materials are generally described as $M_{n+1}B_nO_{3n+1}$ where $M$ and $B$ are ions with suitable chemical valence and ionic radii e.g. $M = Bi^{3+}, Pb^{2+}, Ba^{2+}, Sr^{2+}, Ca^{2+}, Na^+$, $K^+$ or rare earth elements $B = Ti^{4+}, Nb^{5+}, Ta^{5+}, Fe^{3+}$ or $Ga^{3+}$. Most of the synthesized samples show ferroelectric properties. A series of compositions $B_{1-x}R_xTi_3O_{12}$ where $R_x$ represents a rare earth has been prepared. $R_x = Pr, Nd, Gd$ and $Dy$. $Bi_{4-x}R_xTi_3O_{12}$ has also been studied for dielectric characteristics [3]. Pillaring and photocatalytic property of partially substituted layered titanates $Na_2Ti_{3-x}M_xO_7$ and $K_2Ti_{4-x}Nb_{1+x}O_9$ ($M = Mn, Fe, Co, Ni, Cu$) has been studied by M. Machida et al. [4].

Synthesis of reduced layered titanoniobates $KTi_{1-x}Nb_{1+x}O_5$ is reported by Sugimoto et al. They synthesize polycrystalline samples of $KTi_{1-x}Nb_{1+x}O_5$ ($x = 0.1, 0.2, 0.3$) by solid state reaction [5]. Reduced niobates with layered pervoskite structure show electrical properties ranging from semiconducting, metallic and even superconducting [6-10]. As sufficient $dt_{2g}$-$p\pi$ orbital overlap is crucial for electrical conductivity, it is important to take into consideration the connectivity of the octahedra. In the case of the layered pervoskite structures, corner sharing octahedra spread over two directions. On the other hand, many structures consisting of corner-sharing octahedra in one direction and edge sharing octahedra in another direction are known [11,12]. Potassium Molybdenum oxide, $K_xMO_3$ is one of these oxides and exhibits high conductivity [13-15]. Phase transformation of protonic layered tetra-titanates ($H_2Ti_4O_9$) has been reported by Yin et al. [16]. Synthesis and
photochemical properties of semiconductor pillared layered compounds has been reported by Fujishiro et al. [17].

Recently, photoreduction of $\text{NO}_3^-$ and $\text{NO}_2^-$ under visible light irradiated with layered $\text{H}_4\text{Nb}_6\text{O}_{17}/\text{CdS}$ and $\text{H}_2\text{Ti}_4\text{O}_9/\text{CdS}$ nanocomposites has been investigated by Tawkaew et al. [18]. The crystal structure of $\text{K}_2\text{Ti}_4\text{O}_9$ is similar to other tetra-titanates $\text{M}_2\text{Ti}_4\text{O}_9$ [19]. A.C. conductivity studies on sintered samples of $\text{Na}_2\text{Ti}_3\text{O}_7$, $\text{K}_2\text{Ti}_4\text{O}_9$ and its niobium substituted products were first studied by Kikkawa et al. [20]. Shripal et al. [21-24] investigated $\text{Na}_2\text{Ti}_3\text{O}_7$, $\text{K}_2\text{Ti}_4\text{O}_9$ and $\text{K}_{2-x}\text{Rb}_x\text{Ti}_4\text{O}_9$ and their $(\text{Na}_2\text{Ti}_3\text{O}_7$, $\text{K}_2\text{Ti}_4\text{O}_9)$ manganese and iron doped derivatives through EPR and d.c. conductivity studies Dawar et al. [25] have further reported the results of d.c. electrical conductivity studies on ceramic samples of $\text{Rb}_2\text{Ti}_4\text{O}_9$, $\text{Rb}_2\text{Ti}_5\text{O}_{11}$ and $\text{RbKTi}_4\text{O}_9$.

However, it seems to be interesting to synthesize iron doped polycrystalline layered ceramic samples of $\text{K}_2\text{Ti}_4\text{O}_9$. The results of a.c. conductivity and dielectric-spectroscopic investigations are reported in this chapter.

### 7.2 Experimental

The details of preparation of ceramic samples of $\text{K}_2\text{Ti}_4\text{O}_9$ have already been given in chapter V. However, the iron doped derivatives of $\text{K}_2\text{Ti}_4\text{O}_9$ has been synthesized by mixing the 0.1 and 1.0 molar percentage of $\text{Fe}_2\text{O}_3$ (99.7% pure AR grade) powder in the base matrix and named IPT-1 and IPT-2 respectively. Method of preparation being similar to that of manganese doped derivatives of $\text{K}_2\text{Ti}_4\text{O}_9$. The details of a.c conductivity and
dielectric spectroscopic measurements have also been described in chapter V.

7.3 Results and Discussions

The variation of log ($\sigma_{a.c.}T$) with $1000/T$ for IPT-1 and IPT-2 has been plotted in the temperature range 373-773K. The curves thus obtained are shown in Fig. 7.1. These plots can be divided into four regions named I, II, III and anomalous region $\beta$. The region II is indistinguishable due to the overlapping of anomalous region $\beta$.

**Region I**: This frequency dependent and almost temperature independent region looks up to 498K for both the samples. However, anomalous peak ‘C’ at 423K (ranging from 398-473K) seems to be superimposed in this region for the sample IPT-2. Earlier, this low activation energy region was found [23] up to 440K in d.c. conductivity investigations. The a.c. conductivity in this region is much more higher to the d.c. conductivity values reported earlier [23]. The enhanced conductivity in this region may be attributed to both exchangeable interlayer ionic and electronic conduction together similar to the other layered ceramic compounds undertaken in the previous chapters IV, V and VI.

However, such a.c. frequencies make probably the above a.c. conduction to be responsible for changing the upper limit of this region from 440-498K. The much more frequency dependence of conductivity in IPT-1 than IPT-2 can easily be explained by proposing that the substitution of Fe$^{4+}$ at Ti$^{4+}$ sites [23] increase the number of loose electrons jumping Ti-Ti chains. Further substitution of Fe$^{3+}$ at interlayered K$^+$ sites further reduces the number of such electrons participating in the hopping process.
Furthermore, the existence of anomalous peak 'C' in the IPT-2 can easily be understood by knowing the fact that the trapping of water molecules at two different sites in the interlayered sites in the interlayer space of PT [23]. However, this peak was reported at 490K (in the range 465-520K) in d.c. conductivity investigations [23]. Different nature of working of a.c. signal seems to be responsible for changing of position and range of peak to that reported earlier [23], in d.c. conductivity investigations.

Region II / Anomalous region 'β': Distinct region II mainly responsible for associated interlayer ionic conduction is not seen in both of these plots due to the overlapping of anomalous region 'β' indicating two peaks 'B' at 548K and peak 'A' at 598K. However, these two peaks were found in d.c. conductivity studies [23] for the sample IPT-2 at 548K and 650K respectively. Thus, no change in the position of peak 'B' and lowering of temperature of peak 'C' from 650K to 598K has been obtained in these a.c. conductivity investigations. The origin of occurrence of these two peaks has already been formulated by Shripal et al. [23] and is attributed to the dissociation of water molecules at different temperatures and participation in conduction through protonated species H⁺ or H₃O⁺ and also OH⁻, giving rise in conductivity at two different temperatures [23].

The origin of peak 'C' was reported due to the induced iron substitution partial hydroxylation of oxygen octahedra through very strong hydrogen bonding and the transformation of covalent Ti₄O₉²⁻ sheets from two dimensional to three dimensional [23]. When the compound with a.c. signal of 0.5V applied across its flat faces is heated up the water molecules trapped as above are perhaps disassociated at higher temperatures and participate in conduction H⁺ and OH⁻, giving rise in conductivity at about 598K (earlier at 650K in the d.c. conductivity plot).
Now, the origin of both the anomalous peaks ‘A’ and ‘B’ obtained for both IPT-1 and IPT-2 samples (earlier this peak was not obtained for IPT-1 sample) and peak ‘C’ obtained only for IPT-2 sample was proposed [23] due to iron substitution induced partial hydroxylation of interlayered cations sitting at two different sites resulting additional trapping of water molecules in the lattice.

The observance of peak ‘B’ at the same temperature to that reported earlier for d.c. conductivity investigations by Shripal et al. [23] suggests that the mechanism of dissociation do not change whether the sample is energized by a.c. or d.c. signal. However, both the peaks ‘A’ and ‘C’ obtained in region I in this work but (obtained in region II in the d.c. conductivity plots reported earlier by Shripal et al. [23] ) shift towards lower temperature side when energized by a.c. signal in this work.

Furthermore, these a.c. conductivity values are higher than the d.c. conductivity values reported earlier may be explained by proposing that the role of electronic hopping conduction still persists upto these higher temperatures in these a.c. conductivity investigations.

**Region III (After 648K)**: This region remains more frequency dependent with activation energies 1.15eV at 60kHz and 0.58eV at 1MHz for sample IPT-1 and less frequency dependent with activation energies 1.08eV at 60kHz and 0.86eV at 1MHz for sample IPT-2. It seems that the substitution of Fe$^{4+}$ at Ti$^{4+}$ sites creates enough number of such loose electrons to participate in conduction at the higher temperatures as well reflected through Fig. 7.1.a for IPT-1. Less frequency dependent region III for IPT-2 sample can easily be interpreted by proposing that the major substitution as Fe$^{3+}$ occurs at the two interlayered K$^+$ sites [23] in the sample IPT-2 and reduces the electrons responsible for the hopping process.
Thus, the modified interlayer ionic conduction and electronic hopping conduction (more pronounced for IPT-2) co-exist in this region, the microstructural modification has been created due to the substitution of iron as Fe$^{3+}$ at two different interlayered cation sites and as Fe$^{4+}$ at Ti$^{4+}$ sites and the induced trapping of water molecules at three sites in different manner.

The presence of anomalous peaks in the present a.c. conductivity investigations confirms the iron substitution induced trapping of water molecules resulting in partial hydroxylation of oxygen octahedra and interlayered cations sitting at two different K$^+$ sites in the interlayer pace as has been confirmed, proposed earlier by Shripal et al. [23].

The loss tangent (tanδ) versus log (ω) curves for both the samples (IPT-1 and IPT-2) are shown in Figs. 7.2.a and 7.2.b in the temperature range 523-773K. The analyzed frequency range is 20kHz-1MHz. From these curves it can be seen that the trend of variations for both the samples (IPT-1 and IPT-2) are very similar in nature except for difference in numerical values. These curves can be explained in similar manner to that for other layered compounds undertaken in chapter IV, V and VI.

Figs. 7.3.a and 7.3.b show tanδ versus temperature variation curves plotted in the temperature range 373-773K at 10kHz, 20kHz, 40kHz, 100kHz, 600kHz, 800kHz and 1MHz for both IPT-1 and IPT-2 samples. From these plots it can be seen that the values of tanδ at lower temperature are almost frequency independent upto 523K and then slightly increases upto 573K and further decreases to 623K with the rise in temperature resulting a broad peak for both the samples. After 623K, the values of tanδ increases very rapidly for lower frequencies (10kHz, 20kHz, 40kHz, 100kHz) but remain almost invariant for higher frequencies (600kHz, 800kHz and 1MHz) for both the samples. The increase in the values of tanδ
for IPT-2 than for IPT-1 sample may be attributed to the growth in the population of dipoles due to increase in the inclusion of iron as impurity. Accordingly, the variation of $\tan \delta$ can be explained by assuming that the losses are of mixed type i.e. dipole losses and losses due to electrical conduction.

Dielectric constant ($\varepsilon$) versus log ($\omega$) plots in the temperature range 373-773K are shown in Figs. 7.4.a (IPT-1) and 7.4.b (IPT-2). The analyzed frequency range is 10kHz-1MHz. The trend of variations for both the curves are similar above 20kHz but different below 20kHz. The values of dielectric constant first increases upto 20kHz for all the temperature except at 773K and then decreases with the increase in frequency resulting a peak for IPT-1 sample while for sample IPT-2 the value of dielectric constant constantly decreases with the increase in frequency.

All these curves show the same nature of variations as for polar dielectrics. It is known [26] that when the frequency of alternating voltage increases the values of $\varepsilon$ of polar dielectric at first remains invariable but beginning with a certain critical frequency $f_0$ when polarization fails to settle itself completely during one half period, $\varepsilon$ begins to drop approaching at very high frequencies the values typical of nonpolar dielectrics. Dielectric dispersion is seen for both of the above compounds.

Fig. 7.5 shows $\varepsilon$ versus temperature curves plotted in the temperature range 373-773K at 80kHz, 100kHz, 200kHz, 400kHz, 600kHz, 800kHz and 1MHz of a.c. signal for both IPT-1 and IPT-2 samples and are very similar to that obtained for iron doped layered Na$_2$Ti$_2$O$_7$ compounds reported in chapter V. It is seen from Fig. 7.5.a that $\varepsilon$ values for IPT-1 sample increases slowly with temperature upto 473K and then decreases upto 523K resulting a broad diminished peak at 448K. The values of $\varepsilon$ further increases
upto 573K and then decreases upto 623K resulting second broad peak at 573K increases then with the rise in temperature.

From Fig. 7.5.b it is clear that the values of $\varepsilon$ for IPT-2 sample first increases then decreases with the rise in temperature resulting a peak at 423K. The $\varepsilon$ values again increases with the temperature and then decrease giving a pronounced peak at 548K. After 623K the values of $\varepsilon$ constantly increases with the rise in temperature. Thus, shifting of both the peaks at lower temperature is seen for IPT-2 sample. The shifting of both the peaks towards lower temperature side by 25K from IPT-1 to IPT-2 sample can easily be explained by assuming that the major iron substitution $\text{Fe}^{3+}$ at interlayered $\text{K}^+$ sites (in IPT-2 sample) results some less stable configuration of electric dipoles present in the interlayer space. Moreover, the major iron substitution as $\text{Fe}^{4+}$ at $\text{Ti}^{4+}$ sites furnish electric dipoles with more stable configuration to break comparatively at higher temperature as observed for IPT-1 sample. The presence of broad peak at lower temperature may be due to microstructural phase change between these temperatures. However, the presence of peak at higher temperature may be attributed to the possible ferroelectric phase transition. The remaining variations in both the curves can be easily understood by proposing that the dipoles are not aligned in the lower temperature region, so when the temperature rises the orientation of dipoles is facilitated and this increases the dielectric constant. As the temperature grows the chaotic thermal oscillation intensifies and the degree of orderliness of their orientation is diminished. This causes the curve of dependence $\varepsilon(T)$ to pass through the maximum and drop.
7.4 Conclusions

The outcome of the present investigations are:

1) For the first time, iron doped derivatives of layered $\text{K}_2\text{Ti}_4\text{O}_9$ have been characterized through, a.c. conductivity coupled with dielectric-spectroscopic investigations. The prominent role of electronic hopping conduction up to very high temperatures has been seen in these layered compounds.

2) The peaks named ‘C’, ‘B’ and ‘A’ in the anomalous region for heavily iron doped $\text{K}_2\text{Ti}_4\text{O}_9$ have been obtained to confirm iron substitution induced partial hydroxylation of interlayered cations sitting at two different sites along with the partial hydroxylation of oxygen octahedra through very strong hydrogen bonding.

3) The modified interlayer ionic conduction and electronic hopping conduction (more pronounced for IPT-2) co-exist in the higher temperature region III.

4) Dipole losses and the losses due to electrical conduction have been proposed in both IPT-1 and IPT-2 samples.

5) Dielectric dispersion has also been seen in both the iron doped layered ceramics.

6) Through dielectric spectroscopic investigations, the presence of electric dipoles in the interlayer space has been identified. As the temperature rises dipoles tend to align in the direction of the electric field applied.

7) Although both IPT-1 and IPT-2 do not show any prominent frequency dispersion but these compounds may have non relaxor ferroelectric property.
8) The presence of dielectric constant peak towards higher temperature may be due to any microstructural phase change (not known) / possible ferroelectric phase change.
REFERENCES

Fig. 7.1 (a) $K_2TiO_3(Fe \, 0.1\%)$ AT DIFFERENT FREQUENCIES

Fig. 7.1 (b) $K_2TiO_3(Fe \, 1.0\%)$ AT DIFFERENT FREQUENCIES
Fig. 7.2 (a) $K_2TiO_4(Fe 0.1\%)$ AT DIFFERENT TEMPERATURES

Fig. 7.2 (b) $K_2TiO_4(Fe 1.0\%)$ AT DIFFERENT TEMPERATURES
Fig. 7.3 (a) $K_2Ti_4O_9(Fe \ 0.1\%)$ AT DIFFERENT FREQUENCIES

Fig. 7.3 (b) $K_2Ti_4O_9(Fe \ 1.0\%)$ AT DIFFERENT FREQUENCIES
Fig. 7.4 (a) $K_2TiO_3$(Fe 0.1%) at different temperatures

Fig. 7.4 (b) $K_2TiO_3$(Fe 1.0%) at different temperatures
Fig. 7.5 (a) $K_2Ti_4O_9(Fe \ 0.1\%)$ AT DIFFERENT FREQUENCIES

Fig. 7.5 (b) $K_2Ti_4O_9(Fe \ 1.0\%)$ AT DIFFERENT FREQUENCIES
EPILOGUE

The dielectric-spectroscopic and a.c. conductivity measurements are used first time as basic tools to characterize the manganese and iron doped polycrystalline layered \( \text{Na}_2\text{Ti}_3\text{O}_7 \) and \( \text{K}_2\text{Ti}_4\text{O}_9 \) prepared by ceramic method. Preliminary pyroelectric investigations on pure and manganese doped \( \text{Na}_2\text{Ti}_3\text{O}_7 \) are also given.

This work has given a better understanding of dielectric polarization and factors involved in a.c. conduction occurring in these layered compounds from RT to 898K. The creation of three types of electric dipoles (I-V pairs) to maintain the charge neutrality in the interlayer space of above layered ceramics has been identified due to substitution of manganese/iron as \( \text{Mn}^{3+}/\text{Fe}^{4+} \) at octahedral Ti\(^{4+}\) sites and as \( \text{Mn}^{2+}/\text{Fe}^{3+} \) at two different cation sites in the interlayer space. These dipoles tend to align in the direction of the electric field with the rise in temperature and subsequently participate in conduction causing associated interlayer ionic conduction in the mid temperature region. For further rise in temperature, the dipoles are broken and cause to unassociated interlayer ionic conduction towards the higher temperature region.

In all the above compounds electronic hopping conduction plays significant role with the interlayer ionic conduction up to high temperatures (500-600K). One extraordinary result confirmed through a.c. conductivity investigations is the three types of trapping of water molecules through iron induced partial hydroxylation in
accordance with the iron substitution at three sites in $K_2Ti_4O_9$ lattice without involving hydrolysis work.

A wonderful achievement in this work is the significant appearance of the so called pyrocurrent in the external circuit after heating pure and manganese doped $Na_2Ti_3O_7$ ceramic samples without applying any potential difference across their flat faces. It may be proposed on the basis of present work that if all the above materials with nanosize particles will be synthesized and characterized through all the investigations done, so far, the most interesting and encouraging properties suitable for industrial applications are expected. Thin film fabrication and characterization is also needed to acquire more knowledge about the so called layered alkali titanates and to exploit these materials for numerous industrial applications.
**Research Publications arising out of the present work**

1. Dielectric-spectroscopic and a.c. conductivity investigations on pure and manganese doped Na$_2$Ti$_3$O$_7$ ceramics (to be sent very shortly).

2. Dielectric-spectroscopic and a.c. conductivity investigations on pure and manganese doped K$_2$Ti$_4$O$_9$ ceramics (to be sent shortly).

3. Dielectric-spectroscopic and a.c. conductivity investigations on iron doped Na$_2$Ti$_3$O$_7$ ceramics (to be sent shortly).

4. Dielectric-spectroscopic and a.c. conductivity investigations on iron doped K$_2$Ti$_4$O$_9$ ceramics (to be sent shortly).