CHAPTER VI

STUDIES IN IRON DOPED DERIVATIVES OF $\text{Na}_2\text{Ti}_3\text{O}_7$

Abstract  The results of a.c. electrical conductivity studies in $\text{Na}_2\text{Ti}_3\text{O}_7$ doped with 0.1 and 1.0 molar percentage of iron (named IST-1 and IST-2) have been reported in the temperature range 373-773K. Four distinct regions have been identified in the log ($\sigma T$) versus 1000/T plots for both the samples. Region I with strong frequency but almost temperature independence, region II with less frequency dependence but temperature dependence, anomalous region III with decreased conductivity and region IV with strong temperature dependence but least frequency dependence have been observed in the above plots. Loss tangent ($\tan \delta$) and dielectric constant ($\varepsilon$) versus log $\omega$ plots at different temperatures have also been given in this chapter. Furthermore, the results of $\tan \delta$ and $\varepsilon$ versus temperature at various frequencies have also been reported for both of the samples.
6.1 Introduction

Advanced ceramic materials constitute a technology with a very broad base of current and potential applications and a growing list of material compositions [1]. Some new potential dielectric materials have been made through the cross-substitution of Ba\(^{2+}\) by 1.1 molar combinations of tri (La\(^{3+}\)) and monovalent (Li\(^{+}\), Na\(^{+}\), K\(^{+}\)) at the Ba\(^{2+}\) site in BaTiO\(_3\) [2]. The impedance spectra of Nb doped SrTiO\(_3\) ceramic suggests that under oxidizing condition, the overall electrical behaviour is determined by two microstructural contribution [3]. Synthesis and dielectric characteristic of layered Bi\(_4\).\(_x\)R\(_x\)Ti\(_3\)O\(_{12}\) has been studied by Jose L. Pineda [4]. A series of layered perovskite with general formula A\(_2\)Ln\(_2\)Ti\(_3\)O\(_{10}\) (where A=Na, K, Rb and Ln = La, Nd, Gd, Dy) has been synthesized by many researchers [5,6].

The conductivity generally decreases with increasing lattice contraction. Since their conduction channel is three-dimensionally linked, the lattice contraction resulting from the replacement of the layer ion by the smaller one leads to a decrease of the bottleneck size. Similarly, the application of the external hydrostatic pressure also gives same effect. In such a creation, it is agreeable that Lithium ion conductivities in Ln\(_{0.5}\)Li\(_{0.5}\)TiO\(_3\) are lowered with decreasing the radii of Lanthanide ion (from Ln = La to Pr, Nd and Sn) [7]. On the other hand, the increase of sodium content in La\(_{0.5}\)Li\(_{0.5}\)Na\(_{0.5}\)TiO\(_3\) lowers the ionic conductivity but decreases the available space for the migration of the lithium ion [8].

The synthesis of pillared structures from layered materials has led to the development of a new class of porous catalysts [9]. Several researchers have recently reported the pillaring of layered transition metal oxides such as titanates and niobates [10-17]. The crystal structure of Na\(_2\)Ti\(_3\)O\(_7\) has been first
reported by S. Anderson et al. [18]. The accuracy of this structure determination was low by modern standards. This gave impact to refinement of the crystal structure of the phase. Very recently, refinement of the crystal structure of Na$_2$Ti$_3$O$_7$ has been reported by O.V. Yakubovich et al. [19]. All the calculation in refinement was carried out with the use of the SHELXL program package [20].

The crystal structure of Na$_2$Ti$_3$O$_7$ is characterized by a very high degree of condensation of a polyhedra in layers. Sodium trititanates has a known layered crystal structure and its interlayer cation is exchangeable. Ion exchange reaction interlayer structural unit has been explained by Raymond E. Schaak et al. [21]. The crystal structure of Na$_2$Ti$_3$O$_7$ and K$_2$Ti$_4$O$_9$ do suggest possibility of ionic conduction along the layers and thus application of these materials as ion exchangers [22]. Pillaring and Photocatalytic properties of partially substituted layered titanates Na$_2$Ti$_{3-x}$M$_x$O$_7$ and K$_2$Ti$_{4-x}$M$_x$O$_9$ (M = Mn, Fe, Co, Ni, Cu) have been studied by M. Machida et al. [23]. D.C. conductivity and EPR investigation in iron doped layered Na$_2$Ti$_3$O$_7$ has been reported by Shripal [24].

So far dielectric-spectroscopic and a.c. conductivity investigations of iron doped derivatives of Na$_2$Ti$_3$O$_7$ are concerned, no studies are available in the literature. The corresponding results are reported in this chapter.

6.2 Experimental

The details of preparation of ceramic samples of Na$_2$Ti$_3$O$_7$ have already been given in chapter IV. The iron doped derivatives of Na$_2$Ti$_3$O$_7$ has been synthesized by taking Na$_2$CO$_3$ (99.9% pure AR grade), Fe$_2$O$_3$ (99.7% pure AR grade) and TiO$_2$ (99% pure AR grade) powders in the appropriate molar ratio, method of preparation being similar to that of manganese doped derivatives of
Na$_2$Ti$_3$O$_7$. The details of a.c conductivity and dielectric-spectroscopic measurements have also been described in chapter IV.

6.3 Results and Discussion

X-ray powder diffraction patterns obtained for pure sodium tri-titanate (named as ST) and its iron doped derivatives bearing 0.1 and 1.0 molar percentages of Fe$_2$O$_3$ (named IST-1 and IST-2 accordingly) are in single phase at RT and also similar to that reported in the literature [18].

Log ($\sigma$T) versus 1000/T plots for IST-1 and IST-2 in the temperature range 373-898K at 60kHz, 100kHz, 200kHz, 400kHz, 600kHz, 800kHz and 1MHz are shown in Fig. 6.1. These plots can be divided into four distinct regions for both the samples IST-1 (Fig. 6.1.a) and IST-2 (Fig. 6.1.b).

Region I (373-473K) : This nearly temperature independent but strong frequency dependent region may be attributed to the electronic hopping conduction along with the exchangeable interlayer ionic conduction in similar fashion to the other compounds ST and PT undertaken in chapter IV and V. However, the values of a.c. conductivity obtained here in this region for both the compounds are much higher than the d.c. conductivity values reported earlier [24]. Much more increased contribution of electronic hopping conduction may be proposed to explain this fact.

Region II (473-673K) : It is clear from Fig. 6.1.a that this region is still strong frequency dependent with higher slope for IST-1 and less frequency dependent with more higher slope for IST-2 sample. It seems that the substitution of iron as Fe$^{4+}$ at Ti$^{4+}$ [24] sites of sample IST-1 encourages trapping of more electrons responsible for electronic hopping conduction in region II as well. Perhaps, the substitution as Fe$^{3+}$ [24] at interlayer Na$^+$ sites again furnish configuration of atoms in Na$_2$T$_3$O$_7$ lattice in such way that the
jumping electrons involved in hopping process diminishes in IST-2 giving less frequency dependent region (Fig. 6.1.b). Furthermore, the higher a.c. conductivity than d.c. conductivity values reported earlier can further be explained by proposing that the contribution of electronic hopping conduction increases in the sample IST-1. However, the less frequency dependent increased values of conductivity in the IST-2 in which major substitution occur as Fe$^{3+}$ at interlayered sites can easily be explained by proposing that the associated interlayer ionic conduction is dominated here over electronic hopping conduction. The lowering of limit in this region for iron doped derivatives of ST has already been explained in the literature [24].

**Anomalous Region III (from 623-673K)**: The conduction mechanism of such an anomalous region found for different IST samples in which the conductivity decreases with rise in temperature has already been formulated for d.c. conductivity investigations [24]. In this region too, more frequency dependence for IST-1 and less frequency dependence for IST-2 is seen in the conductivity plots. It suggests that the electronic hopping conduction is still strongly contributing up to this higher temperature region for IST-1 which is suppressed in the sample IST-2 probably due to reduction in the population of trapped electrons with the substitution of Fe$^{3+}$ at interlayered Na$^+$ sites.

Probably, the hindered interlayer ionic conduction and electronic hopping conduction co-exist in this anomalous region III.

**Region IV (after 673K)**: The present a.c. conductivity values in this temperature region are comparable to that d.c. conductivity values reported earlier [24] but dependence of conductivity upon frequency still persists (more for IST-1).

Accordingly, the conduction in this region is modified interlayer ionic conduction proposed earlier [24] along with the electronic hopping conduction
(well reflected through frequency dependence of conductivity). Furthermore, the contribution of $\sigma''(\omega)$ starts to dominate in this region for these layered compounds too, as discussed for ST and PT in the previous chapters IV and V respectively.

Fig. 6.2 shows tan$\delta$ versus frequency curves for the sample IST-1 and IST-2 in the temperature range 373-773K. The frequency range of study to obtain such curves is selected from 20kHz to 1MHz. Except for the difference in the numerical values to that of (ST), the trend of variations for both the samples is very similar. Such a trend of variations again reveals that the losses are characteristic of dipole mechanism. The decreased values of tan$\delta$ for the sample IST-1 suggest that the substitution of Fe$^{4+}$ at Ti$^{4+}$ sites (discussed above) results better configuration of the system in terms of losses. Little increase in the values of tan$\delta$ again for the sample IST-2 in which the major amount of substitution occurs as Fe$^{3+}$ at interlayer Na$^+$ sites furnish such a configuration of atoms to give such increased values of tan$\delta$.

Fig. 6.3 shows the tan$\delta$ versus temperature curves for both IST-1 (Fig. 6.3.a) and IST-2 (Fig. 6.3.b) samples in the temperature range 373-773K. It is clear that the curves obtained for these samples are again very similar. The first relaxation peak observed for both the samples at 423K and the second relaxation peak is observed at 623K being more prominent for the sample IST-2. The existence of these two relaxation peaks in tan$\delta$ versus temperature curves can be explained by proposing that the presence of two types of dipoles generated in the interlayer space because of two types of iron substitutions. It can be proposed that the substitution of Fe$^{4+}$ at Ti$^{4+}$ sites seems to be responsible for creation of the first type dipoles in the interlayer space giving peak at 623K and the second type of dipoles are present in the
interlayer space of both the doped derivatives giving peak at 423K in these plots.

Figs. 6.4 shows dielectric constant ($\varepsilon$) versus frequency curves for IST-1 and IST-2 in the temperature range 373-773K. The analyzed frequency range is 10kHz to 1MHz. Both of the curves possess similar trend of variations as for polar dielectrics and it is clear that the frequency independent portion has least value of dielectric constant for ST. The dielectric dispersion is seen for both the compounds. Furthermore, the increase in the inclusion of iron as impurity increases the number of electric dipoles for charge neutrality present in the interlayer space. Thereby increase in the values of dielectric constant is seen for IST-1 and IST-2 samples.

Fig. 6.5 shows $\varepsilon$ versus temperature curves for IST-1 and IST-2 samples in the temperature range 373-773K at 200 kHz, 600kHz and 1MHz. It can be seen from these plots that $\varepsilon$ first increases slowly with the temperature upto 473K then a broad peak appears more pronounced for the sample IST-2 at 598K and finally increases with the rise in temperature.

These results can now be explained similar to that for ST and different MST compounds discussed in chapter IV by assuming again that a microstructural phase change exist between these temperatures. Peaks in the higher temperature region may be due to the possible ferroelectric phase transition. The remaining variations in all the curves can be easily understood by proposing that the dipoles are not aligned in the low temperature region so when the temperature rises the orientation of dipoles is facilitated and this increases dielectric constant. As the temperature grows the chaotic thermal oscillation of molecules are intensified and the degree of orderliness of their orientation is diminished. This causes the curves of dependence $\varepsilon(T)$ to pass through the maximum and then drop.
6.4 Conclusions

The outcome of the present investigations are:

1) For the first time iron doped derivatives of sodium trititanate (IST-1 and IST-2) have been characterized through a.c. conductivity and dielectric-spectroscopic investigations.

2) In the lower temperature region I, electronic hopping conduction co-exist with the exchangeable interlayer ionic conduction, in region II associated interlayer ionic conduction is dominated over electron hopping conduction. Conduction in region III is due to co-existence of hindered interlayer ionic and suppressed electronic hopping conduction, while conduction in region IV is modified interlayer ionic conduction.

3) The substitution of iron as Fe$^{4+}$ at Ti$^{4+}$ sites in IST-1 sample seems to be responsible for trapping of more electrons. The substitution of iron as Fe$^{3+}$ at interlayer Na$^+$ sites furnish configuration of atoms in Na$_2$Ti$_3$O$_7$ lattice in such a way that the numbers of jumping electrons involved in hopping process again reduces giving less frequency dependent region II of IST-2 sample.

4) The losses are the characteristic of dipole mechanism for both the iron doped samples and showing two types of dipoles present in the interlayer space.

5) Increased number of dipoles in the interlayer space due to iron substitution and the possibility of ferroelectric phase transition both are reflected through dielectric-spectroscopic investigations.
REFERENCES

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Fig. 6.1 (a) Na$_2$Ti$_2$O$_7$(Fe 0.1%) AT DIFFERENT FREQUENCIES

Fig. 6.1 (b) Na$_2$Ti$_2$O$_7$(Fe 1.0%) AT DIFFERENT FREQUENCIES
Fig. 6.2 (a) \( \text{Na}_2\text{Ti}_3\text{O}_7(\text{Fe } 0.1\%) \) AT DIFFERENT TEMPERATURES

Fig. 6.2 (b) \( \text{Na}_2\text{Ti}_3\text{O}_7(\text{Fe } 1.0\%) \) AT DIFFERENT TEMPERATURES
Fig. 6.3 (a) Na$_2$Ti$_3$O$_7$(Fe 0.1%) at different frequencies

Fig. 6.3 (b) Na$_2$Ti$_3$O$_7$(Fe 1.0%) at different frequencies
Fig. 6.4 (a) Na$_2$Ti$_3$O$_7$(Fe 0.1%) AT DIFFERENT TEMPERATURES

Fig. 6.4 (b) Na$_2$Ti$_3$O$_7$(Fe 1.0%) AT DIFFERENT TEMPERATURES
Fig. 6.5 (a) \( \text{Na}_2\text{Ti}_3\text{O}_7 \text{(Fe 0.1\%)} \) at different frequencies.

Fig. 6.5 (b) \( \text{Na}_2\text{Ti}_3\text{O}_7 \text{(Fe 1.0\%)} \) at different frequencies.