

Effect of paramagnetic manganese ions doping on frequency and high temperature dependence dielectric response of layered $\text{Na}_{1.9}\text{Li}_{0.1}\text{Ti}_3\text{O}_7$ ceramics

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MS received 20 May 2009; revised 23 July 2009

Abstract. The manganese doped layered ceramic samples $(\text{Na}_{1.9}\text{Li}_{0.1})\text{Ti}_3\text{O}_7 : x\text{Mn}$ ($0.01 \leq x \leq 0.1$) have been prepared using high temperature solid state reaction. The room temperature electron paramagnetic resonance (EPR) investigations exhibit that at lower percentage of doping the substitution of manganese ions occur as Mn^{3+} at Ti^{4+} sites, whereas for higher percentage of doping Mn^{2+} ions occupy the two different interlayer sodium/lithium sites. In both cases, the charge compensation mechanism should operate to maintain the overall charge neutrality of the lattice. The manganese doped derivatives of layered $\text{Na}_{1.9}\text{Li}_{0.1}\text{Ti}_3\text{O}_7$ (SLT) ceramics have been investigated through frequency dependence dielectric spectroscopy in this work. The results indicate that the dielectric losses in these ceramics are the collective contribution of electric conduction, dipole orientation and space charge polarization. Smearred peaks in temperature dependence of permittivity plots suggest diffuse nature of high temperature ferroelectric phase transition. The light manganese doping in SLT enhances the dielectric constant. However, manganese doping decreases dielectric loss due to inhibition of domain wall motion, enhances electron-hopping conduction, and impedes the interlayer ionic conduction as well. Manganese doping also gives rise to contraction of interlayer space.

Keywords. Layered ceramics; solid state reaction; frequency dependence dielectric response.

1. Introduction

1.1 Sodium trititanates

Yakubovich and Kireev (2003) have refined the crystal structure of $\text{Na}_2\text{Ti}_3\text{O}_7$. They have reported that the crystals are monoclinic with $a=0.9133(2)\text{nm}$, $b=0.3806(1)\text{nm}$, $c=0.8566(2)\text{nm}$, $\beta=101.57(3)^\circ$ and space group, P_{21}/m . The structure of $\text{Na}_2\text{Ti}_3\text{O}_7$ is built up from the blocks of six TiO_6 octahedra sharing edges joined by octahedral corners in common layers of composition, $\text{Ti}_3\text{O}_7^{2-}$. Its lattice is monoclinic. Projection along (010) plane of $\text{Na}_2\text{Ti}_3\text{O}_7$ structure is shown in figure 1(a). Figure 1(b) shows the structure of $\text{Na}_2\text{Ti}_3\text{O}_7$ in projection down the b -axis. Bonds to oxygen (large circles) from titanium (small circles) are shown, by means of the lighter circles representing atoms at the level $Y=1/4$, the heavier at $Y=3/4$. The bonds from sodium (medium circles) to oxygen are drawn as dotted lines, and the unit cell is shown in the outline. The layers are placed together in such a way as to form two different kinds of positions for the sodium

atoms. Na has a rather usual oxygen arrangement, which to a first approximation has been considered as a cube, but with two oxygens replaced by a single one at the centre of the edge, from which they are missing. Outside the faces opposite to this atom are two additional oxygens, which complete the irregular nine-fold coordination. The second sodium atom $\text{Na}_{(1)}$ is situated in a trigonal prism of oxygens, a seventh oxygen is bounded through the centre of one of the rectangular prism faces. The structure of $\text{Na}_2\text{Ti}_3\text{O}_7$ has the possibility of interlayer ionic conduction and can be used as ion exchangers (Izawa *et al* 1982). Pillaring and photocatalytic properties of partially substituted layered titanates, $\text{Na}_2\text{Ti}_{3-x}\text{M}_x\text{O}_7$ and $\text{K}_2\text{Ti}_{4-x}\text{M}_x\text{O}_9$ ($\text{M}=\text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$), have been studied by Machida *et al* (2000). EPR and mixed electronic ionic conductivity studies of manganese doped and 5% lithium substituted $\text{K}_2\text{Ti}_4\text{O}_9$ have been reported by Pal and Shripal (2007). Correlation between EPR, dielectric spectroscopic and a.c. conductivity studies have been reported by Pal *et al* (2006). EPR and electric conductivity studies of copper doped sodium lithium trititanates have also been reported by Pal *et al* (2005). EPR studies of iron and manganese doped trititanates have been reported by Tangri *et al* (2005).

In the present paper, we have reported the influence of manganese doping on frequency dependence dielectric

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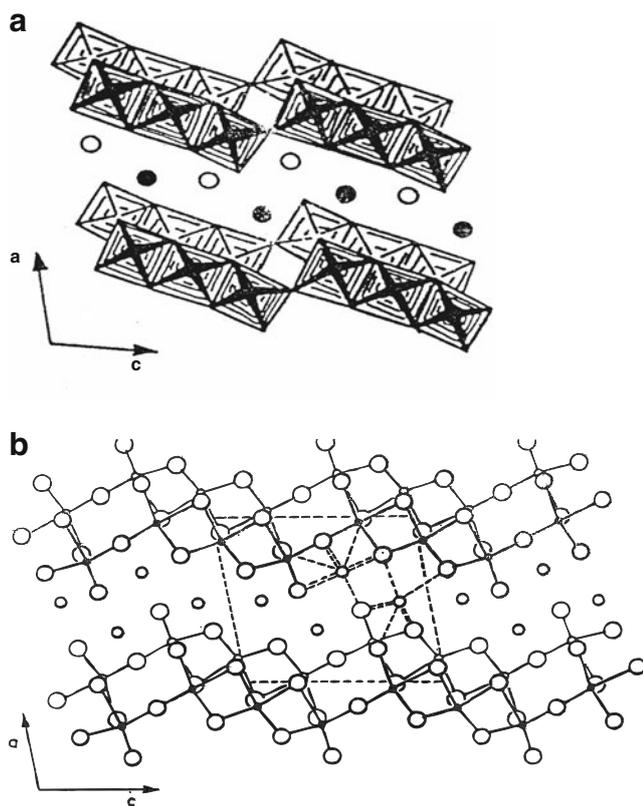


Figure 1. a. Projection along (010) plane of $\text{Na}_2\text{Ti}_3\text{O}_7$ structure and b. structure of $\text{Na}_2\text{Ti}_3\text{O}_7$ seen in projection down the b -axis.

response of layered $\text{Na}_{1.9}\text{Li}_{0.1}\text{Ti}_3\text{O}_7$ ceramics with the help of EPR studies.

2. Experimental

The ceramic sample, $\text{Na}_{1.9}\text{Li}_{0.1}\text{Ti}_3\text{O}_7$ (denoted as SLT), and its manganese-doped derivatives with different molar percentages of MnO_2 (0.01 and 0.1) (denoted as MSLT-1 and MSLT-2) have been synthesized using the sintering process (Pal *et al* 2006). The method of preparation of pelletized doped ceramic samples was similar to that reported earlier in the literature (Pal *et al* 2006). Iso-Debyeflex 2002, Richseifert and Co. diffractometer using $\text{Cu K}\alpha$ radiation was generated at 30 kV and 20 mA, by collecting XRD patterns for all the compositions. The formation of these titanates (MSLT-1 and MSLT-2) was confirmed by the XRD patterns obtained at room temperature (RT). The XRD pattern of these manganese doped derivatives was identical to that reported in literature (Yakubovich and Kireev 2003). The conventional first derivative of X-band (9.447 GHz) EPR absorption spectra was recorded on a Bruker EMX X-band EPR spectrometer. All the spectra were recorded with 100 kHz and 10.0 G modulations. The maximum calibrated power available was 0.201 mW. The high frequency modulation field amplitude ranged typically from 5×10^{-3} mT–0.50 mT with a rectangular TE_{102} cavity (unloaded $Q \sim 7000$) at 100 kHz field modula-

tion. Moreover, the samples for recording of the EPR spectra were kept in a quartz tube (outer diameter, ~ 5 mm), which was then placed at the centre of the resonant cavity. An incident microwave power level of 10 mW had been used for most of the cases to give levels of 10^5 . The magnetic field was calibrated using a central field at 3400 G.

The flat faces of the sintered pellets were painted with an air-dried high purity silver paste and then mounted in the sample holder evacuated up to 10^{-3} mbar for the electrical measurements. The loss tangent ($\tan\delta$) and parallel capacitance (C_p) of the pelletized samples were directly measured as a function of temperature and frequency by the HP 4194A impedance analyser. The relative permittivity (ϵ') and the bulk a. c. conductivity (σ) of the samples was calculated by using the formula as reported earlier by Pal *et al* (2006).

3. Results and discussion

The $\text{Na}_2\text{Ti}_3\text{O}_7$ crystals are monoclinic with unit cell dimensions $a=9.133(2)\text{\AA}$, $b=3.806(1)\text{\AA}$, $c=8.566(2)\text{\AA}$ and $\beta=101.57(3)^\circ$, space group = $P2_1/m$. The basic framework of $\text{Na}_2\text{Ti}_3\text{O}_7$ is a block of TiO_6 octahedra, three at one level, three at a distance $b/2$ \AA above and below which are joined through common edges (Yakubovich and Kireev 2003). The substitution of lithium ions in the interlayer space does not affect the crystal structure of $\text{Na}_2\text{Ti}_3\text{O}_7$. This confirms the presence of small lithium ions with large sodium ions in interlayer space, which indicates that lithium atoms are accommodated with sodium atoms in a widely opened interlayer space.

Figure 2 shows EPR spectra of all the manganese doped derivatives of $\text{Na}_{1.9}\text{Li}_{0.1}\text{Ti}_3\text{O}_7$. The room temperature EPR spectra have two peaks, peak 'A' with $g \approx 4.22$ and peak B with $g \approx 2.04$. The peak 'A' in EPR spectrum with a large value of g indicates that manganese ion substitutes as Mn^{3+} ($3d^4$ configuration) at Ti^{4+} sites and the surrounding oxygen rearranges to yield a tetrahedral field at the ion site, when an abnormal g value may be possible (Abragam and Bleale 1970). It is seen from figure 2 that the intensity of broad peak 'B' with $g \approx 2.04$ increases continuously from sample MSLT-1 to MSLT-2, indicating that the substituting Mn^{2+} ions in the interlayer space get aggregated and as the doping content of MnO_2 increases from MSLT-1 to MSLT-2, major portion of it acquires interlayer cation sites. The fine structure spectrum although very weak consists of five prominent groups of six hyperfine lines each superimposed on broad peak 'B' with $g \approx 2.04$, is indicated for MSLT-2.

Figures 3(a) and (b) show the variation of $\tan\delta$ with respect to frequency in the temperature range 373–673 K for MSLT-1 and MSLT-2, respectively. The result shows that at lower temperature $\tan\delta$ decreases gradually, when the frequency increases but at higher temperature dielectric loss ($\tan\delta$) decreases exponentially with rise in frequency. This may be an indication of dipole mechanism of losses along with the losses due to motion of loosely bound ions, i. e. losses due to electrical conduction (Mac Chesney *et al* 1963).

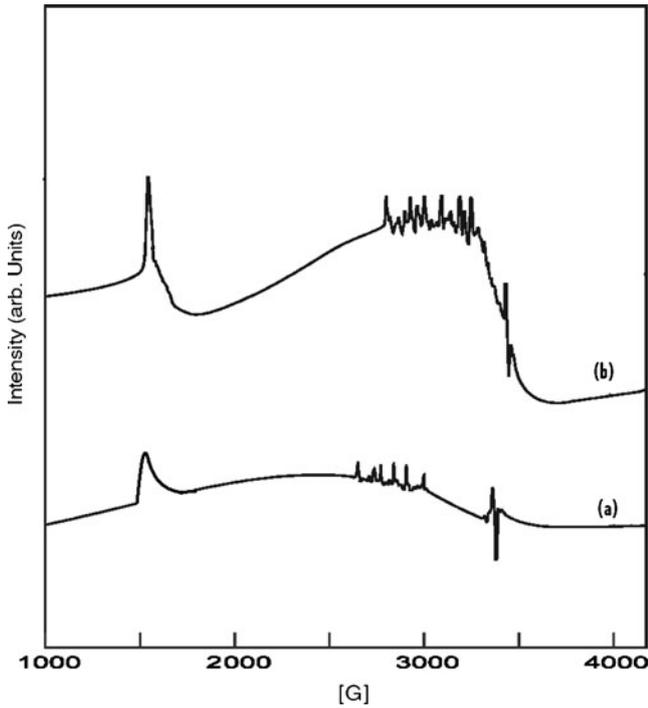


Figure 2. EPR spectra of manganese doped sodium lithium trititanate (a) MSLT-1 and (b) MSLT-2.

Figures 4(a) and (b) show the variation of dielectric constant (ϵ') versus frequency curves for manganese doped derivatives at various temperatures. The curves have the same nature for MSLT-1 and MSLT-2. The value of dielectric constant (ϵ') is lower at higher frequency. Manganese doping increases the value of dielectric constant (ϵ') for MSLT-1 and MSLT-2. All these curves have same nature as for polar dielectrics. It is reported (Mac Chesney *et al* 1963) that when the frequency of alternating voltage increases, the value of dielectric constant of polar dielectric remains invariable, but beginning with a certain frequency (f_0), when polarization fails to settle itself during one half period, dielectric constant (ϵ') begins to drop approaching very high frequencies. Dielectric dispersion is seen for these compounds.

$\text{Ln}\sigma T$ versus frequency curves at different temperatures are shown in figures 5(a') and (b'). From these curves, it is clear that the dependence of a.c. conductivity on frequency decreases with increase in temperature. Thus the electronic hopping conduction is dominant at lower temperature and diminishes with the rise in temperature.

EPR spectra of all the manganese doped derivatives show two distinct peaks 'A' with $g \approx 4.22$ and 'B' with $g \approx 2.04$. Peak A with $g \approx 4.22$ indicates that lower percentage of Mn^{3+} doping ($3d^4$ configuration) substitutes at Ti^{4+} sites. The broad peak 'B' with $g \approx 2.04$ indicates that at higher concentration of doping manganese, ions enter as Mn^{2+} at the interlayer alkali

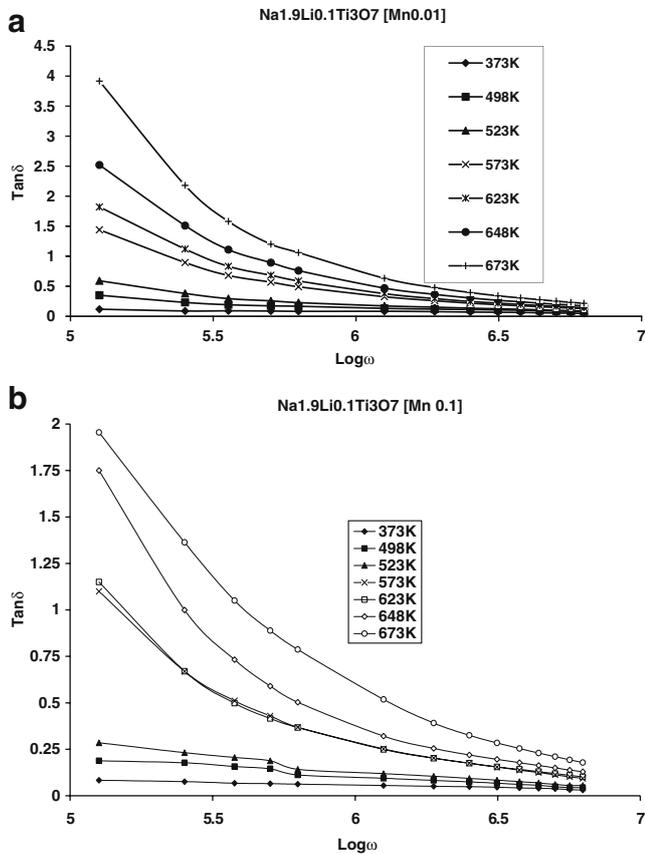


Figure 3. a-b. Loss tangent ($\tan\delta$) versus frequency for MSLT-1 and MSLT-2.

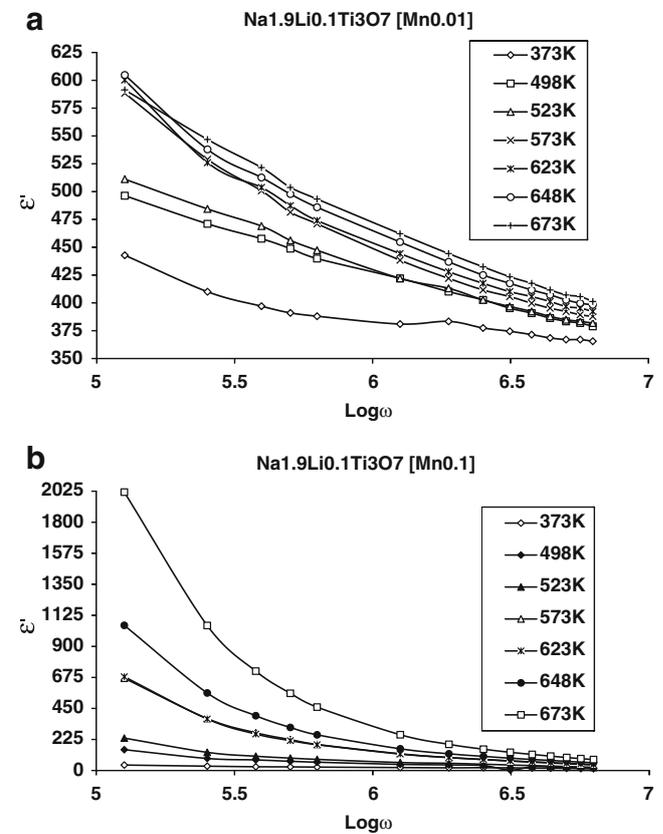


Figure 4. a-b. Relative permittivity versus frequency for MSLT-1 and MSLT-2.

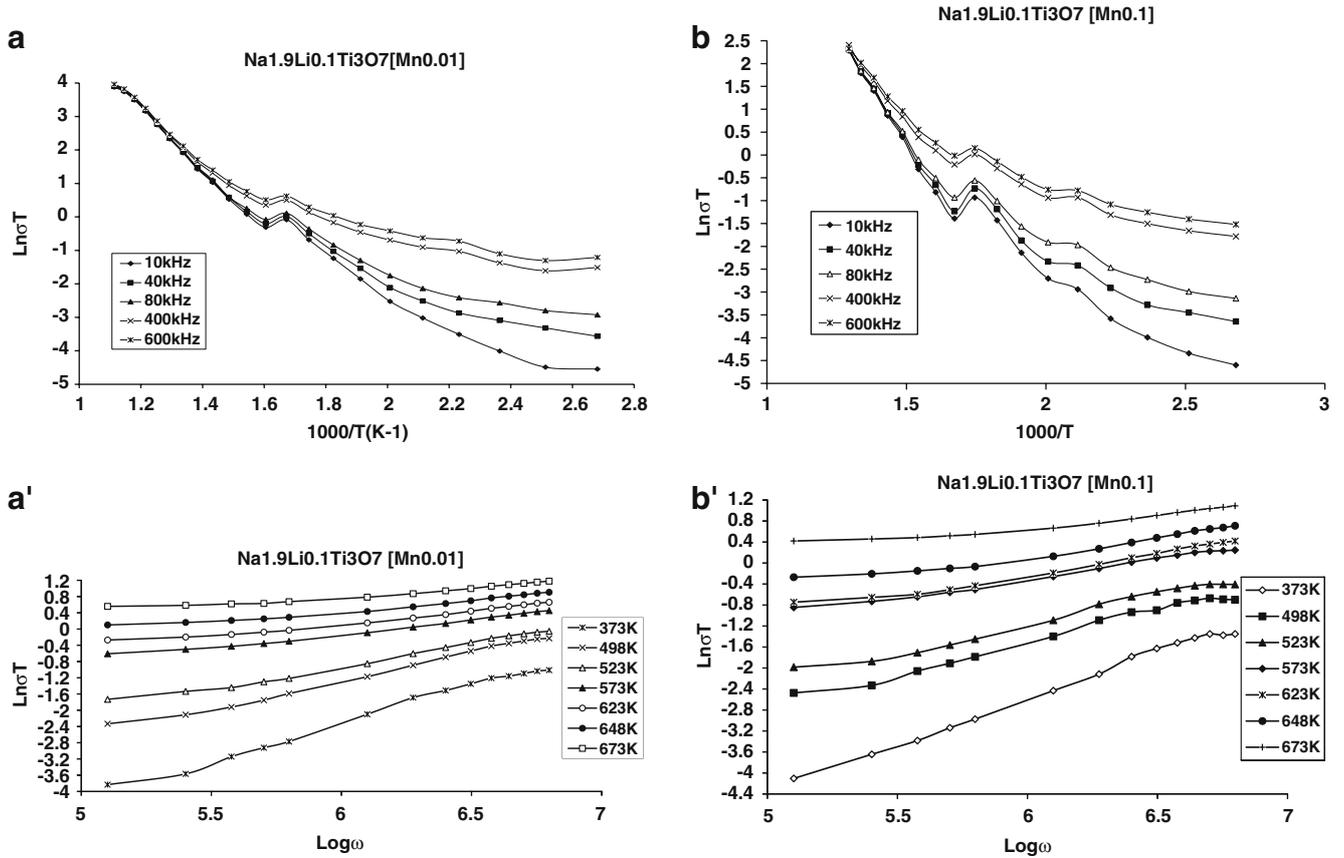


Figure 5. (a) and (a') $\text{Ln}\sigma T$ versus $1000/T$ and $\text{Ln}\sigma T$ versus frequency and (b) and (b') $\text{Ln}\sigma T$ versus $1000/T$ and $\text{Ln}\sigma T$ versus frequency.

sites, and create the necessary vacancy at the nearby alkali sites. The ion vacancy ($I-V$) pairs, so obtained would furnish an EPR spectrum consisting of five groups of six lines each. Since the present system is polycrystalline, so the observed EPR spectrum would be averaged as one corresponding to all possible orientations of $I-V$ pairs with respect to the magnetic field. Since we observe only one broad peak at $g \approx 2.04$, therefore, an aggregation of Mn^{2+} ions is proposed, which produces an exchange narrowed EPR signal here.

The dependence of dielectric loss ($\tan\delta$) on frequency can be explained with the help of equation given below

$$\text{Tan}\delta = \frac{\omega^2 \tau^2 (G_{\text{in}} + S) + G_{\text{in}}}{\omega [S\tau + C_g(\omega^2 \tau^2 + 1)]},$$

where the symbols have their usual meanings (Tareev 1979). One can easily explain from this equation

$$\begin{aligned} \text{Lim}_{\omega \rightarrow 0} \tan\delta &= \infty, \\ \text{Lim}_{\omega \rightarrow \infty} \tan\delta &= 0. \end{aligned}$$

The observed appreciable decrease in $\tan\delta$ with rise in frequency at higher temperatures may be due to the accumulation of charges at interfaces in a multiphase material hence interfacial polarization (space charge polarization) takes place (Cook and Tennery 1961; Mac Chesney *et al* 1963).

The low value of $\tan\delta$ at higher frequencies is the outcome of the low reactance offered by the ceramic sample.

The higher rate of increase of $\tan\delta$ for low frequencies is attributed to the space charge polarization. At higher frequency, samples offer low reactance to the sinusoidal signal and hence minimize the conduction losses, therefore, the amount of dielectric losses are the characteristic of dipole mechanism and electrical conduction.

As the temperature increases from 523 K, $\tan\delta$ increases sharply, this may be due to its molecular structure with large losses due to the dipole relaxation polarization as the relaxation peaks indicated in the high region. The decreased values of $\tan\delta$ for the samples MSLT-1 and MSLT-2 suggest that the substitution of Mn^{3+} at Ti^{4+} site results in better configuration of the system in terms of losses. Moreover, from these plots it can be seen that there is very little frequency dispersion of dielectric loss. The low value of dielectric loss at high frequency is the outcome of the low reactance offered by the ceramic samples (Lingwal *et al* 2003). The trend of variation of dielectric loss with frequency is a feature of dielectric loss due to dipole orientation and space charge polarization (Tareev 1979).

The dependence of dielectric constant (ϵ_r) for MSLT-1 and MSLT-2 on frequency at a certain fixed temperature is shown in figures 4(a) and (b). The dependence of ϵ_r on frequency has approximately similar nature for samples MSLT-1 and MSLT-2. The values of ϵ_r remains invariant up to the temperature 423 K for MSLT-1 and MSLT-2. The

existence of three types of dipoles may be due to different roles of three types of dipoles generated due to the substitution of manganese ions Mn^{3+} at Ti^{4+} site and Mn^{2+} at two interlayer alkali sites. It can also be seen that ϵ_r continuously decreases as the frequency increases in higher temperature region. The nature of dependence of relative permittivity may be different in solid ionic (linear i.e. not ferroelectric) dielectric. In most of the cases, an ionic mechanism of polarization increases ϵ_r when temperature grows. However, in some cases, the values of ϵ_r may diminish when temperature rises, particularly in those substances in which the ionic displacement intensifies the internal field and thereby the electronic polarization (Mac Chesney *et al* 1963). The molecules cannot orient themselves in the polar dielectric in the low temperature region and when temperature raises the orientation of the dipoles is facilitated which increases the dielectric constant. As the temperature grows the chaotic thermal oscillation of the molecules intensifies and degree of orderliness of their orientation diminishes. This causes the curves of dependence ϵ_r to pass through the maximum and then drop. The observed dispersion in ϵ_r frequency relation can be explained on the basis of Maxwell Wagner model, in which the solid is assumed to be composed of well conducting grains separated by poorly conducting grain boundary. The decrease in dielectric constant with divalent ion doping addition, according to Mac Chesney *et al* (1963) and Cook and Tennery (1961) was attributed to the formation of weak layers at the grain boundaries of the base matrix, $Na_{1.9}Li_{0.1}Ti_3O_7$. These boundary layers are assumed to be compositionally different from the interior of the grain and may arise because of reaction between Mn ions and $Na_{1.9}Li_{0.1}Ti_3O_7$ or may originate from (Mn–Na/Li–Ti) complex oxide segregation at the grain boundaries. On manganese doping, dielectric constant increases, the increase in the dielectric constant value is accompanied by the simultaneous rapid decrease in dielectric loss, which may be ascribed to the pinning of domain wall motion due to oxygen vacancies. The acceptor doping activates charge compensation mechanism consequent upon the evolution of oxygen vacancies in the lattice, producing electric dipole constituted by a Mn^{2+} ion {effectively negative charge} and an oxygen vacancy site {effectively positive charge}.

Figure 5 shows the $\ln\sigma T(\Omega^{-1}m^{-1}K)$ versus $1000/T$ and $\ln\sigma T(\Omega^{-1}m^{-1}K)$ versus $\log \omega$ plots for MSLT-1 and MSLT-2, respectively. These curves are divided into three regions viz. regions I, II and III.

3.1 Region I (lower temperature region)

The strongly frequency dependent and almost temperature independent region exists up to 598 K for MSLT-1 and 573 K for MSLT-2. In ionic host lattices, where the interaction between orbital of neighbouring ions, there is polarization of lattice associated with the presence of electronic carriers, and its polarization field is referred to as polaron. Two types of polarons play a major role in the conduction process at relatively lower temperature region.

When the association is weak (large polarons), conductivity is similar to quasi-free electrons which results with the small effective mass. When the electronic carrier plus the lattice distortion has the linear dimension smaller than the lattice parameter, it is referred to as a small polaron, and the mobility is strongly affected by the lattice distortion which must move along with the electronic carrier. The loosened electrons from the negative ions and from the impurities in the crystal transported through the solid would contribute to the conduction. The polaron is an electron that always moves around together with the associated lattice polarization that minimizes its energy. The nature of a. c. conductivity can be interpreted by proposing that the electronic hopping conduction, in which the hopping of electrons through shallow barrier along Ti–Ti chain takes part in conduction. These electrons play a major role in this region. Such a frequency dependence of conductivity is attributed to a wide distribution of relaxation times due to barrier height. The conduction mechanism for the low temperature region can be expressed by the equation

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/4}].$$

3.2 Region II (mid temperature region)

This region exists from 598 K to 623 K for MSLT-1 and 573 K to 598 K for MSLT-2. It is seen that in this temperature region the conductivity value decreased with increasing temperature. The conduction mechanism in this region has been formulated by proposing that the loose oxygens produced by the substitution of Mn^{3+} at Ti^{4+} will be trapped by cation vacancies present in the interlayer space leading to decrease in the conductivity. It suggests that the electronic hopping conduction is still strongly contributing up to this higher temperature region for MSLT-1 and MSLT-2.

So the conduction mechanism for MSLT-1 and MSLT-2 may be hindered by interlayer ionic conduction and electronic hopping conduction.

3.3 Region III (higher temperature region)

Almost temperature dependent and very less frequency dependent regions exist from 623 K for MSLT-1 and from 598 K for MSLT-2 up to the temperature range of study. The dependence of conductivity upon the frequency persists for manganese-doped derivatives for MSLT-1 and MSLT-2. The electronic contribution is less than the total conduction in the higher temperature region showing that at higher temperatures the conduction is mainly ionic. Accordingly, the conduction mechanism in this region may modify interlayer ionic conduction along with the polaronic conduction for MSLT-1 and MSLT-2. From these curves, it is clear that the dependence of a.c. conductivity decreases with increase in temperature. The frequency dependence of conductivity is the characteristic of electron hopping conduction, which decreases with rise in

temperature, indicating a decrease in electron hopping conduction and an increase in interlayer ionic conduction.

4. Conclusions

(I) Manganese doped layered sodium lithium trititanates, $\text{Na}_{1.9}\text{Li}_{0.1}\text{Ti}_3\text{O}_7$ ceramics, can be put in the class of mixed ionic–electronic materials.

(II) Manganese doping is found to increase the dielectric constant along with the decrease in dielectric loss in lightly doped composition.

(III) Two types of manganese substitutions and dipoles in the interlayer space as well have been identified through $\tan \delta$ versus temperature plots for doped derivatives of sodium lithium trititanates ($\text{Na}_{1.9}\text{Li}_{0.1}\text{Ti}_3\text{O}_7$) ceramic.

(IV) Dielectric-spectroscopic investigations show the presence of dipole mechanism of losses along with the losses due to the motion of loosely bound ions and space charge polarization at higher temperature.

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