



## Investigations on Electrical Studies of Copper Doped Layered HSLT Ceramics

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### ABSTRACT:

Lithium (50%) mixed layered  $\text{Na}_2\text{Ti}_3\text{O}_7$  and its 0.01, 0.05 & 1.0 molar percentage CuO doped derivatives have been prepared through high temperature solid state reaction and characterized through X-ray diffractometer, d.c. conductivity in the temperature range 373-700K and room temperature EPR investigation. Room temperature X-ray diffratograms confirm the phase evolution. Room temperature electron paramagnetic resonance (EPR) data show that  $\text{Cu}^{2+}$  occupies  $\text{Ti}^{4+}$  lattice sites giving rise to electric dipoles which increases electric permittivity. The absorption peak in EPR spectra gets broadened due to increased exchange interaction in heavily doped derivatives. Four distinct regions have been identified in the  $\ln(\sigma T)$  versus  $1000/T$  plots. Various electrical conduction mechanisms have involved during the whole temperature range of study.

**Key words:** Copper, Ceramics, EPR, Conductivity

### 1. INTRODUCTION

The formula of alkali titanates crystallizing in a monoclinic phase is generalized by  $\text{A}_2\text{O} \times n\text{TiO}_2$  ( $3 \leq n \leq 8$ , A is an alkali metal) [1]. Titanate nanotubes and nanowires have many important applications as photocatalysts, gas sensors, high-energy cells and in the field of environmental purification [2, 3]. Alkali metal titanates have been synthesized at nanoscale and studied on account of their robust applicability in biophysics [5]. Papp et al. [6] reported that the tendency of titanates to self-assemble makes them suitable candidates for utilization as efficient photocatalysts. Due to their  $\text{TiO}_2$  derived structural origin, the nanotubes offer a potential in photocatalysis, solar energy conversion, as electrochromic materials, and self-cleaning devices [7]. The photochemical properties of  $\text{Cu}^{2+}$  doped layered hydrogen titanate have been presented elsewhere [8]. Cation exchange property has been studied for protecting environment against lethal radiation of highly radioactive liquid wastes [9]. In this array, Kikkawa et al. [10] reported that  $\text{Nb}^{5+}$  ions doped into  $\text{K}_2\text{Ti}_4\text{O}_9$  naturally occupy  $\text{Ti}^{4+}$  sites and create cation vacancies leading to increased ionic conductivity. Pillaring and photocatalytic properties of  $\text{Na}_2\text{Ti}_{3-x}\text{M}_x\text{O}_7$  and  $\text{K}_2\text{Ti}_{4-x}\text{M}_x\text{O}_9$  ( $\text{M} = \text{Mn, Fe, Co, Ni, and Cu}$ ) have also been reported [11]. Their catalytic and electronic properties are expected to lead to a novel family of

functional porous solids. Actually, it has been already reported by Domen et al. [12, 13] and Sato et al. [14] that pillared materials prepared from layered niobates exhibit the excellent photocatalytic activity for hydrogen evolution reactions. Dharmendra Pal et. al have reported the dielectric properties of light lithium mixed with doping of various impurities (Mn, Cu, Fe)  $\text{Na}_2\text{Ti}_3\text{O}_7$ . [15-20] Now it is very interesting to know about the effect of heavy mixed lithium with Copper paramagnetic doping on crystal structure of  $\text{Na}_2\text{Ti}_3\text{O}_7$  and its dc electrical conduction mechanism.

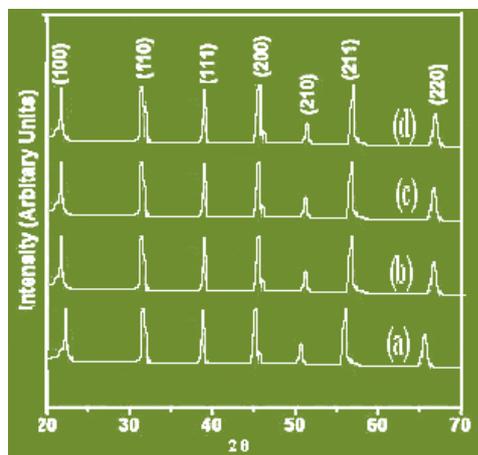
### 2. EXPERIMENTAL

The ceramic sample of  $(\text{NaLi})\text{Ti}_3\text{O}_7$  has been prepared via conventional solid state reaction route as reported earlier [13]. To prepare copper doped derivatives of  $(\text{NaLi})\text{Ti}_3\text{O}_7$  ceramics, the desired molar percentages ( $x = 0.0, 0.01, 0.05$  and  $0.1$ ) hereafter referred to as HSLT,  $\text{C}_1$ -HSLT,  $\text{C}_2$ -HSLT and  $\text{C}_3$ -HSLT of CuO powder (99.9% pure, AR grade) were added to the mixture of alkali carbonates and titanium oxide. The mass so obtained was then calcined at 1173 K for 10 h. After grinding, the powder was compressed using a hydraulic press at 16 MPa to yield pellets, which were covered under the powder of the same composition and then sintered at 1200 K for 1 h,

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followed by furnace cooling to room temperature (RT). Room temperature XRD for  $(\text{NaLi})\text{Ti}_3\text{O}_7$  and DebyeFlex 2002, Richseifert and Co. (Germany) using  $\text{CuK}\alpha$  radiation with the sweep of 3.0 deg/min, range (CPM) = 5 K, time constant = 10.0 s, current = 20 mA, and voltage across the cathode and target 30 kV (figure 1).



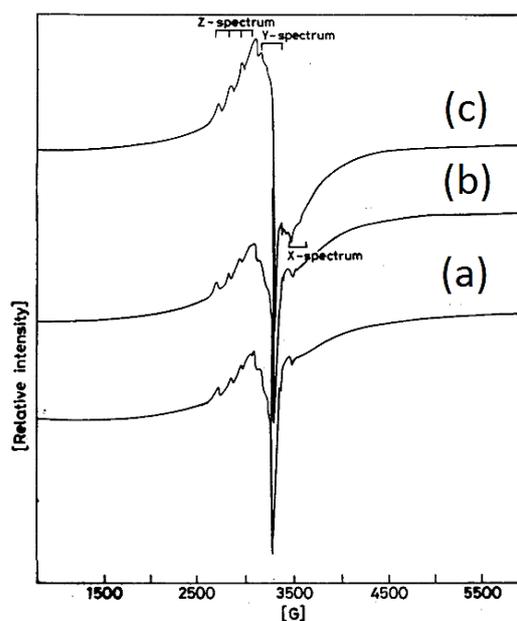
**Figure 1.** X-ray diffraction pattern of Pure and Copper doped Layered Sodium Lithium Titanates (a) HSLT, (b)  $\text{C}_1$ -HSLT, (c)  $\text{C}_2$ -HSLT & (d)  $\text{C}_3$ -HSLT.

The conventional first derivative of X-band (9.447 GHz) EPR absorption spectra were recorded on a Bruker EMX X-band EPR spectrometer 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  $5 \times 10^{-3}$  mT to 0.50 mT with rectangular TE102 cavity (unloaded  $Q \approx 7000$ ) at 100 kHz field modulation. The samples for recording the EPR spectra were kept in a quartz tube (outer diameter ca. 5 mm) which was then placed at the centre of the resonant cavity. An incident microwave power level of 10 mW was used for most of the cases to give levels of 105. The magnetic field was calibrated using a central field at 3400 G.

The conductivity measurements were undertaken in vacuum by applying a potential difference of 3.0 volt across the sample at fixed temperatures and the through current was measured with the electrometer amplifier (Kiethley 614). The temperature of the sample was measured with the help of chromal-alumal thermocouple in contact with the sample site and was controlled with the help of programmable Librathern temperature controller (prc-309) after placing the sample holder in a furnace. The Conductivity has been evaluated by using through current and dimensions of the samples.

for all its copper doped derivatives have been obtained on an X-ray powder diffractometer ISO-3. **RESULTS AND DISCUSSION**

The first derivative of X-band EPR absorption spectra recorded at RT, shown in figures. 2a-c has a peak (with  $g \approx 2.0$ ) at ca. 3300 G (quartets) along with intensive asymmetric lines. Therefore the data represents a superposition of two spectra corresponding to different surroundings of the copper ions. The characteristic spectrum may be explained by an isotropic spin-Hamiltonian, given by  $\mathcal{H} = g\beta$  (B.S.) +  $A$  (I.S.), where notations have their usual meaning. For the fine structure spectrum



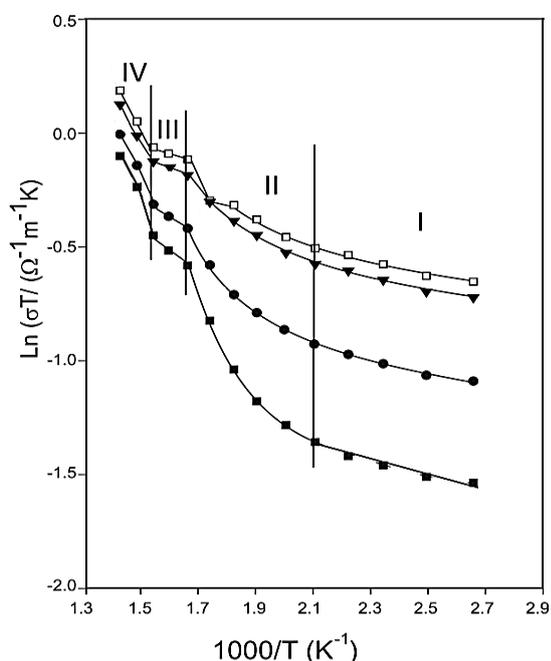
**Figure 2.** EPR spectra of (a)  $\text{C}_1$ -HSLT, (b)  $\text{C}_2$ -HSLT and (c)  $\text{C}_3$ -HSLT.

the  $g_{\parallel}$  ( $g_z$ , quartet lines or hyperfine structures) and  $g_{\perp}$  ( $(g_x + g_y)/2$ , intensive asymmetric lines) components of the  $g$  tensor correspond to the quartet lines and intensive asymmetric lines pertaining to this peak. The observed EPR spectra show that the symmetry of the copper complex is orthorhombic ( $g_x \neq g_y \neq g_z$ ) at low doping <1% being characteristic of distorted octahedral copper (II) complexes ( $3d^9$  configuration). The hyperfine spectra have not been resolved in these materials. Also on heavy doping, the characteristic peak in the higher field side gets broadened due to increased exchange interaction (dipole-dipole). As anticipated, analysis of the calculated  $g$  values ( $g_{\parallel}$  and  $g_{\perp}$ ) listed in Table 1 indicates that the splitting occurs in the octahedral symmetry, and the copper site attains  $\text{Cu}^{2+}$  ( $3d^9$ ,  $S = 1/2$ , and  $I = 3/2$ ) state at the host site of  $\text{Ti}^{4+}$  ion. Furthermore,  $\text{Cu}^{2+}$  inclusion at the  $\text{Ti}^{4+}$  site modifies the crystal field around it into an orthorhombic one, which eventually attains axial symmetry on heavy doping.

As doping increases due to the saturation on  $Ti^{4+}$  site  $Cu^{2+}$  ions enters in to the interlayer alkali site. Moreover, this acceptor doping activates a charge compensation mechanism, dependent upon the evolution of oxygen vacancies in the lattice, producing electric dipoles consisting of a  $Cu^{2+}$  ion (effectively negative charge) and an oxygen vacancy site (effectively positive charge).

**Table 1.** Spin Hamiltonian parameters of all copper doped derivatives.

Derivatives	$g_{\parallel}$	$g_{\perp}$
C <sub>1</sub> -HSLT	2.4321	2.0322
C <sub>2</sub> -HSLT	2.3754	2.0461
C <sub>3</sub> -HSLT	2.4328	2.0438



**Figure 3.**  $\ln(\sigma T)$  ( $\Omega^{-1}m^{-1}K$ ) vs  $1000/T$  ( $K^{-1}$ ) plots for Copper doped heavy mixed lithium Sodium Titanate (HSLT).

With this knowledge about the occupancy of copper ions in  $(LiNa)Ti_3O_7$  lattice, it becomes easy to discuss the results of conductivity studies as above. A broad categorization of conductivity plots into three regions is quite evident and the corresponding results are accordingly discussed region wise.

The values of D.C. conductivity for HSLT, C<sub>1</sub>-HSLT, C<sub>2</sub>-HSLT and C<sub>3</sub>-HSLT were determined in the temperature range 373-700K. The corresponding  $\log\sigma T$  versus  $1000/T$  plots are shown for all samples three regions I, II, III, have been identified

over the entire temperature range of study (figure 3).

### 3.1 Region I

Region I exist up to 373-473K for HSLT, C<sub>1</sub>-HSLT, C<sub>2</sub>-HSLT and C<sub>3</sub>-HSLT respectively. In this region conduction seems to be characteristic of the host and is attributed to the hopping process involving loose electrons from  $Ti_3O_7^{2-}$  groups, which jump from one Ti-Ti chain to an adjacent one. Such process would involve low activation energy. Thus the lower slope in this region can be understood. The small slope for HSLT in this region indicates that such type of configuration has been formed which reduces the number of loose electrons appreciably suppressing electronic hopping conduction. It seems that the exchangeable interlayer ionic conduction is prominent in this region for HSLT. However for C<sub>1</sub>-HSLT, C<sub>2</sub>-HSLT and C<sub>3</sub>-HSLT samples this interlayer ionic conduction disappears.

The continuous increase in the conductivity from C<sub>1</sub>-HSLT to C<sub>3</sub>-HSLT can be explained by assuming that the manganese ions, which substitute at  $Ti^{4+}$  sites, are in valance state ( $Cu^{2+}$ ) their substitution would naturally cause the number of loose electrons to increase appreciably to jump through Ti-Ti chains in conduction. However observed decreased for conductivity in sample C<sub>3</sub>-HSLT suggest that the copper entry at  $Ti^{4+}$  sites become saturated for C<sub>3</sub>-HSLT and further addition of impurity leads to the substitution of  $Cu^{2+}$  at the interlayer cation sites resulting such type of the configuration of I-V pairs responsible for reducing both electronic hopping and interlayer ionic conduction. Thus the electronic hopping conduction in this region may be extrinsic or otherwise depending on the doping.

### 3.2 Region II

It is seems from conductivity curves that region II exists up to 473-598K for HSLT, C<sub>1</sub>-HSLT, C<sub>2</sub>-HSLT and C<sub>3</sub>-HSLT respectively. The higher slope in this region is naturally attributed to alkali ionic conduction in presence of extrinsic defects through alkali interlayer. The activation energy decreases and conductivity increases for HSLT. This can be explained by assuming that Lithium ion plays an important role in the conduction mechanism. The change in the interlayer space with the increase in the impurity decreases up to C<sub>1</sub>-HSLT. This is due to copper ions as  $Cu^{2+}$  occupying  $Ti^{4+}$  sites. The continuous increase in activation energies up to can be understood by knowing the fact that interlayer distance contract due to substitution of  $Cu^{2+}$  at interlayer alkali sites. This fact is reflected well through EPR spectra of these samples. Thus the ionic conduction in this region may be attributed to

“Associated extrinsic ionic conduction” through contracted interlayer space.

### 3.3 Region III

This region exists up to 598-648K for all pure and copper doped derivatives. This region may be due to dissociation of aggregation of  $\text{Na}^+$  and  $\text{Li}^+$  ions in the interlayer space, which then take part in conduction.

### 3.4 Region IV

From the conductivity curves it is clear that region III starts from 648K up to temperature range of study for HSLT,  $\text{C}_1$ -HSLT,  $\text{C}_2$ -HSLT and  $\text{C}_3$ -HSLT, respectively. It seems the transformation of  $\text{TiO}_6$  octahedral into  $\text{CuO}_4$  tetrahedral arrangement due to  $\text{Cu}^{2+}$  substitution at  $\text{Ti}^{4+}$  sites. For HSLT and its copper doped derivatives the slope of region III is greater than that of region II. This can easily be understood that some of the reduction as oxygen loosen off from  $\text{Ti}_3\text{O}_7^{2-}$  groups, which than participate large number in conduction. The observed increase in slope up to  $\text{C}_1$ -HSLT in region III can be explained by assuming that  $\text{Cu}^{2+}$  substitution at  $\text{Ti}^{4+}$  sites becomes saturated. Further doping of copper as in sample  $\text{C}_2$ -HSLT and  $\text{C}_3$ -HSLT occurs, as  $\text{Cu}^{2+}$  interlayer alkali sites reduces the no. of participating loose oxygens in the conduction of this region. The conduction of this region may easily be understood Modified interlayer ionic conduction the modification been affected by loosen oxygens from  $\text{Ti}_3\text{O}_7^{2-}$  groups.

## 4. CONCLUSION

The outcomes of present investigations: The analysis of EPR spectra shows that the distortions of octahedral occur due to the substitution of  $\text{Cu}^{2+}$  at  $\text{Ti}^{4+}$  sites. As doping percentage increases due to saturation on  $\text{Ti}^{4+}$  site copper ions as  $\text{Cu}^{2+}$  enters into the interlayer alkali (NaLi) site.

The smearing out of the hyperfine structure in the EPR spectrum of the highly copper doped  $\text{C}_3$ -HSLT sample is attributed to excessive exchange interaction.

The reduction of number of loose electrons from  $\text{Ti}_3\text{O}_7^{2-}$  groups due to substitution of smaller lithium ions at interlayer  $\text{Na}^+$  sites is seen through conductivity plots of HSLT however, copper substitution as  $\text{Cu}^{2+}$  at  $\text{Ti}^{4+}$  sites and  $\text{Cu}^{2+}$  at interlayer alkali (NaLi) ion sites both further loosen electrons form  $\text{Ti}_3\text{O}_7^{2-}$  groups to participate in conduction through hopping process.

In region III observed increase in conductivity for HSLT indicates that Li inclusion at interlayer  $\text{Na}^+$  sites increases the conductivity and lithium ionic conduction starts relatively at lower temperatures.

In samples  $\text{C}_1$ -HSLT to  $\text{C}_3$ -HSLT the conduction at higher temperature is strongly affected due to participation of loose oxygen from  $\text{Ti}_3\text{O}_7^{2-}$  groups.

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