층상구조의 $Na_{1.9}Li_{0.1}Ti_3O_7$과 그 구리 혼입 유도체의 EPR 및 전기적 연구

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EPR and Electrical Studies in Layered $Na_{1.9}Li_{0.1}Ti_3O_7$ and its Copper Doped Derivatives

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요 약. 순수한 또는 미량의 구리(몰 퍼센트(0.0<X<1.0))가 첨가된 세라믹 시료인 층상구조의 sodium litium trititante($Na_{1.9}Li_{0.1}Ti_{3-x}Cu_xO_{7-x}$) 물질을 합성하였다. 상온에서 모든 구리 혼입 유도체와 다양한 낮은 온도에서 0.05 몰 퍼센트 Cu 혼입 유도체의 EPR 특성을 조사하였다. 격자 안의 Ti^{4+}자리에 Cu^{2+}가 치환됨으로 인한 TiO_6 팔면체의 씨그러짐이 나타났다. 또한, $\log(\sigma_{d.c}T)$ 대 1000/T 그래프를 통하여 세개의 특징적인 영역이 관찰되어진다. 가장 낮은 온도 영역은 모든 구리 혼입 유도체의 polaron 과 Li이 치환된 $Na_2Ti_3O_7$의 이온 전도도에 기인한다. 중간 온도영역의 전도 메커니즘은 관련된 층간의 이온 전도도에 기인하며 가장 높은 온도 영역에서는 변형된 층간 이온 전도도에 기인한다.

주제어: 알칼리 타이타네이트, 층상 세라믹, EPR, Polaron, 이온 전도도

ABSTRACT. Sintered ceramic samples of pure and some copper doped layered sodium lithium tri-titanate ($Na_{1.9}Li_{0.1}Ti_{3-x}Cu_xO_{7-x}$) materials with different dopant molar percentages (0.0<X<1.0) have been prepared. The electron paramagnetic resonance (EPR) investigations of all the copper doped derivatives at room temperature (RT) and at various low temperatures for 0.05 molar percentages doped derivative have been carried out. The distortion of TiO_6 octahedra due to the substitution of copper as Cu^{2+} at Ti^{4+} sites in the lattice is proposed in this paper. Furthermore, three distinct regions have been identified in $\log(\sigma_{d.c}T)$ versus 1000/T plots. The lowest temperature region is attributed to electronic hopping conduction (polaron) for all copper doped derivatives and ionic conduction for lithium substituted $Na_2Ti_3O_7$.The mechanism of conduction in the intermediate region is associated interlayer ionic conduction and in the highest temperature region is associated modified interlayer ionic conduction.

Keywords: Alkali Titanate, Layered Ceramic, EPR, Electronic Hopping Conduction (Polaron), Ionic Conduction

INTRODUCTION

The crystal structure of $Na_2Ti_3O_7$ has been determined, using single-crystal methods. The space group is $P2_1/m$, with the unit-cell dimensions $a=8.571$, $b=3.804$, $c=9.135$, $\beta=101.57°$ The structure consists of layers of the composition $(Ti_3O_7)^{2-}$. These are built-up from blocks of six TiO_6 octahedra shearing edges, which are joined by having octahedral corners in common.[1] Recently O.V.Yakubovich and V.V.Kireev have studied the refinement of $Na_2Ti_3O_7$ crystal structure.[2] The structure of $Na_2Ti_3O_7$ has possibility of interlayer ionic conduction and can be used as ion exchangers.[3] Pillaring and photo catalytic properties of partially substituted layered titanates $Na_2Ti_{3-x}M_xO_7$ and $K_2Ti_{4-x}M_xO_9$ (M=Mn,Fe, Co,Ni,Cu) have been studied by M. Machida et al.[4] Electron paramagnetic resonance (EPR) and d.c. conductivity investigations of manganese and iron doped layered polycrystalline $Na_2Ti_3O_7$ and $K_2Ti_4O_9$ have been reported by Shripal et al.[5-8] Furthermore, layered $Li_2Ti_3O_7$ is a good ionic conductor suitable for lithium insertion studies.[9]

Alkali titanates have also been synthesized by hydrothermal reaction at a relatively low temperature of around $100°C$ and at nano scale.[10] In case of $BaTiO_3$, it is confirmed that copper ions substitute as Cu^{2+} at Ti^{4+} sites.[11]

The structure transformation behavior of $Na_2Ti_3O_7$ by hydrolysis has been investigated in mild and strong acidic aqueous medium.[12] Furthermore, the electrochemical and calorimetric thermodynamical properties of $Na_2Ti_3O_7$ and $Na_2Ti_6O_{13}$ have also been determined by M. Holzinger et al.[13] Zhang et al.[14] have reported the structure and growth of $H_2Ti_3O_7$-type nanotubes by first principal calculation. Recently, Shripal et al.[15] have reported the dielectric- spectroscopic and a.c. conductivity studies on pure and manganese doped layered $K_2Ti_4O_9$ ceramics. They have also reported dielectric-spectroscopic investigation on pure and manganese doped $Na_2Ti_3O_7$[16] Deepam Maurya et al.[17] have further reported the dielectric-spectroscopic and a.c. conductivity studies on layered $Na_{2-x}K_xTi_3O_7$ (X=0.2,0.3,0.4) ceramics. EPR and dielectric-spectroscopic investi-

gations on copper doped $Na_2Ti_3O_7$ have been carried out by Shripal et al.[18]

Safety and recharge ability problems associated to the use of metallic lithium have so for precluded their wide spread marketing that's why we have taken very small amount of lithium There is no published work in the literature on pure and its copper doped lithium substituted layered ceramics $Na_{1.9}Li_{0.1}Ti_3O_7$. The purpose of this study to show the variation of EPR spectra and conductivities of $Na_{1.9}Li_{0.1}Ti_3O_7$ compounds with the variation of Cu^{2+} contents. In the present paper it tries to explain the conductivity behavior based on the structural change of Cu^{2+} sites as observed by EPR. It seems very interesting to investigate these compounds through EPR. d.c.conductivity investigations and corresponding results are given in this paper.

EXPERIMENTAL

The ceramic sample of $Na_{1.9}Li_{0.1}Ti_3O_7$ (denoted as SLT) was prepared by grinding mechanically a mixture of Na_2CO_3 (99.9% pure AR grade Merck Germany). Li_2CO_3 (99.9% pure AR grade Merck Germany) and TiO_2 powders (99% pure AR grade Merck Germany) in the stoichiometric ratio to achieve fine and homogeneous powder. The powder was heated up to 1073 K for 16 hours then cooled to room temperature (RT) and grinded mechanically again for an hour to achieve fine powder. The powder thus obtained was compressed at 15 MPa to get cylindrical pellets (10.25 mm. in diameter and 1.2 mm. in thickness). The pellets so obtained were covered with the remaining powder and heated again at 1073 K for 16 hours. The flat surfaces of these pellets were coated with high purity air-dried silver paste for electrical measurements.

Copper doped derivatives have been prepared by the similar method as above after adding 0.01, 0.02, 0.05,0.10 and1.0 molar percentages of CuO (99.8% pure AR grade Merck Germany) in the base matrix and denoted as CSLT-1, CSLT-2, CSLT-3, CSLT-4 and CSLT-5, respectively.

The XRD patterns of SLT and its all copper doped derivatives were collected on Iso-Debyeflex 2002.

Richscifert & CO. using Cu-Kα radiation generated at 30 KV and 20 mA. The formation of these titanates is confirmed by the XRD patterns obtained at room temperature.

The EPR spectra have been recorded on a Varian E-line Century Series Spectrometer E-109 operating at X-band frequencies (~9.3 GHz). All the spectra were recorded on the sliced pellets of doped derivatives filled in a quartz tube of 6 mm outer diameter. To get the first derivative of EPR signals, 100 KHz field modulation was used. The magnetic field was calibrated accurately with a Varian E-500 digital nuclear magnetic resonance gaussmeter. The Varian temperature controller (E-257/WL-257) was used to maintain the desired sample temperature from 88 K to 573 K for a sustained length of time with an accuracy of about 0.5 K. However, the actual temperature of the sample is measured with help of a potentiometer using a copper constantan thermocouple junction at the sample site.

The d.c. 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 Libratherm temperature controller (prc-309) after placing the sample holder in a furnace. The d.c. conductivity have been evaluated by using the through current at different temperature and dimensions of the samples.

RESULTS

Fig. 1 shows the EPR spectrum of pure polycrystalline sample of $Na_{1.9}Li_{0.1}Ti_3O_7$ This spectrum doesn't contain quartet lines (hyperfine structure) of copper(II) ions ($S=1/2,I=3/2$) in the lower field side and on the higher field side but for its copper doped derivatives we have got the spectra as shown in *Fig.* 2.

Figs. 2(a-d) and (e) shows the EPR spectra recorded at RT of CSLT-1, CSLT-2, CSLT-3, CSLT-4 and CSLT-5, respectively at RT. The EPR spectra of all the
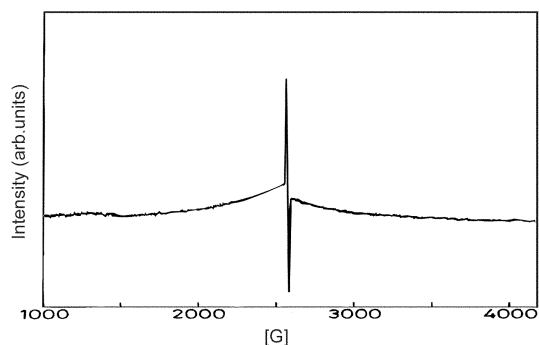

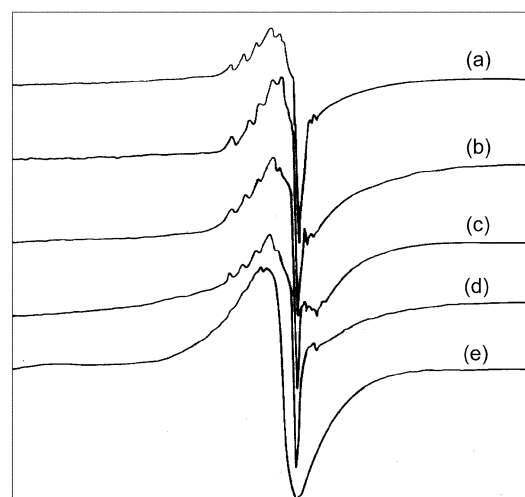*Fig.* 1. EPR spectra of pure polycrystalline samples of $Na_{1.9}Li_{0.1}Ti_3O_7$.

Fig. 2. EPR spectra of different copper-doped polycrystalline samples of $Na_{1.9}Li_{0.1}Ti_3O_7$. (a) CSLT-1, (b) CSLT-2, (c) CSLT-3, (d) CSLT-4, (e) CSLT-5.

above samples except for the sample CSLT-5 have quartet lines (hyperfine structure) of copper(II) ions ($S-1/2,I-3/2$) in the lower field side and on the higher field side one or two broad asymmetric peaks are seen without any hyperfine structure. These spectra are the characteristic pattern of copper doped polycrystalline samples.[19] A well resolved hyperfine spectrum is found in the | part of EPR spectra for the samples CSLT-1 to CSLT-4 containing copper concentration <1%(molar). For CSLT-5 having copper 1% (molar), the hyperfine spectrum gets smeared out [*Fig.* 1(e)]. The symmetry of the crystal field around the copper (II) sites initially (for
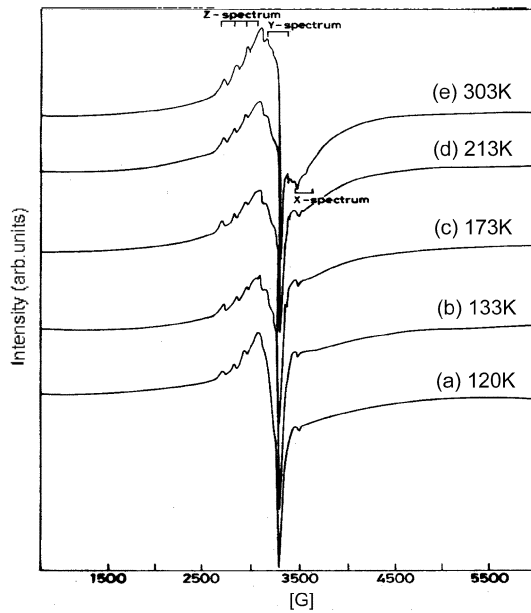
Fig. 3. Temperature variation of EPR spectra of CSLT-3 in temperature range of 120-303 K.

low doping) appears to be orthorhombic. The symmetry appears to change to axial as the doping level increases. For CSLT-5 the hyper fine splitting become smeared completely and giving rise to a broad asymmetric EPR signal typical of a heavily doped polycrystalline sample. EPR spectra of CSLT-3 at different temperatures below RT are shown in *Fig.* 3. However, the EPR spectra of copper are analyzed according to the spin Hamiltonian.

$H=g\beta B.S-I.A.S$ With $S=1/2$ and $I=3/2(3d^{9})$ where notations have their usual meaning.

$g_{\parallel}$ and $g_{\perp}$ could be easily determined from EPR at R.T. and at low temperatures. The spin Hamiltonian parameters g (g_{z}) and g $[(g_{x}+g_{y})/2]$ for all EPR spectra of copper doped derivatives at room

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

Derivatives	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$
CSLT-1	2.3321	2.0441	116	26
CSLT-2	2.3567	2.0483	116	22
CSLT-3	2.3853	2.0675	121	30
CSLT-4	2.3674	2.0529	119	28
CSLT-5	2.3825	2.0477	117	31

Table 2. Spin Hamiltonian parameters of copper doped derivative CSLT-3 at various low temperatures.

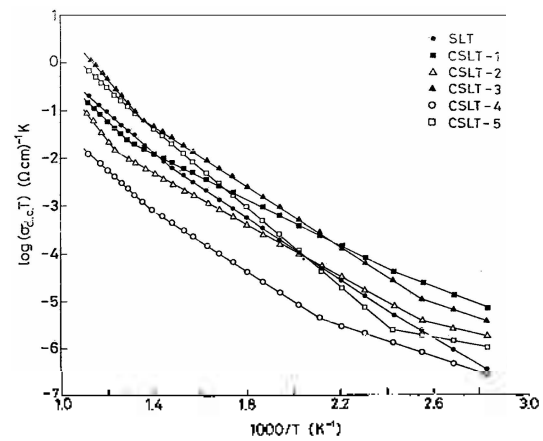| Temperature	$g_{\parallel}$	g	A	A
120 K	2.3872	2.0473	162	30
133 K	2.3538	2.0461	138	33
173 K	2.3420	2.0424	110	39
218 K	2.3218	2.0434	97	41
303 K	2.3853	2.0675	121	30

Fig. 4. log $(\sigma_{dc}T)$ versus 1000/T plots for SLT, CSLT-1, CSLT-2, CSLT-3, CSLT-4 and CSLT-5.

temperature and at low temperatures are tabulated in *Tables* 1 and 2. The calculated g values are given till four decimal place which indicates that the slight variation in g values does effects on the pattern of EPR spectra.[19]

The values of D.C. conductivity for SLT, and its copper doped derivatives were determined in the temperature range 313-833 K. The corresponding $\log(\sigma_{dc}T)$ verses 1000/T plots are shown in *Fig.* 4. For all of the above samples, three regions have been identified over the entire temperature range of study. The activation energies for all the three regions marked I, II, III have been calculated and are given in *Table* 3.

DISCUSSION

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

Table 3. Activation energies obtained from the conductivity plots for all copper doped derivatives.

Sample's Name	Region-I eV	Region-II eV	Region-III eV
SLT	0.57	0.64	0.90
CSLT-1	0.37	0.45	0.89
CSLT-2	0.23	0.53	1.17
CSLT-3	0.32	0.57	1.08
CSLT-4	0.32	0.59	0.85
CSLT-5	0.17	0.78	0.85

octahedral copper(II) complexes (3d^{9}configuration).[11,19,20]

The analysis of g values (g and g) shows that g >g > 2. This shows that the copper (II) ions occupy the distorted octahedral sites.[11,19,20] Since the Cu^{2-} spectra observed in Na$_{1.9}$Li$_{0.1}$Ti$_3$O$_7$ can be obtained only if the Cu^{2-} ions are in a distorted octahedral environment compressed along one of the axes leaving the ground state d$_{z}^2$ orbitally non degenerate.[11] The Cu^{2-} ions are very likely to occupy Ti^{4-} sites in the Na$_{1.9}$Li$_{0.1}$Ti$_3$O$_7$ lattice. Such incorporation of divalent metal ions in Na$_2$Ti$_{3-x}$M$_x$O$_7$ has been suggested by Machida *et al*.[4] Since Ti^{4-} and Cu^{2-} are hetrovalent ions therefore some charge compensation mechanism is required to maintain the overall charge neutrality of the lattice.

Furthermore, the smearing out of the hyperfine structure in the EPR spectrum of CSLT-5 with high copper (II) concentration may be attributed due to the excessive exchange interaction.

With this knowledge about the occupancy of copper ions in Na$_{1.9}$Li$_{0.1}$Ti$_3$O$_7$ 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.

Region-1 The conductivity curves show that the region I exists up to 413 K, 413 K, 393 K, 393 K, 473 K and 413 K for CSLT-1, CSLT-2, CSLT-3, CSLT-4 and CSLT-5, respectively. The activation energy of this region for SLT is much greater than that of pure Na$_2$Ti$_3$O$_7$ reported earlier (0.27 ev).[6] At lower temperature smaller Li$^-$ having high mobility and bigger Na$^-$ having relatively low mobility will probably come together forming cluster in the inter-

layer and hence making conduction difficult resulting increase in activation energy. It seems that the presence of smaller Li$^-$ ions with high mobility along with the Na$^-$ ions in the interlayer space are responsible for such a high activation energy. An appreciable fall in the conductivity values towards the lower temperature side of SLT relative to pure Na$_2$Ti$_3$O$_7$[6] is reflected well in *Fig. 3*.

It seems that the presence of Li$^-$ and Na$^-$ in 1:20 ratio in the interlayer space results such type of Na-Li-Ti configuration. which appreciably reduces the number of loose electrons form Ti$_3$O$_7^{2-}$ groups and subsequently suppresses the electronic hopping (polaron) conduction.

For copper doped derivatives, the activation energy first decreases up to CSLT-2. The EPR spectra of CSLT-1, CSLT-2 also confirms the compression of TiO$_6$ octahedra. Accordingly, the dilation of interlayer space seems to be responsible for such a change in activation energies up to CSLT-2 and therefore conduction becomes easy. As the copper concentration increases, the interlayer space now contracted up to CSLT-4, therefore the activation energy increases and conduction becomes difficult. The lower activation energy of CSLT-5 can be explained by looking the EPR spectrum of CSLT-5 which confirm the regular octahedral axial symmetry. It seems that the height and width of potential wells along the Ti-Ti chains become shallower for loose electrons form Ti$_3$O$_7^{2-}$ groups participating in conduction.

Thus, SLT and its all the copper doped derivatives may have interlayer ionic conduction and electronic hopping (polaron) conduction respectively.

Region-II From the conductivity curves, it is clear that the region II exists up to 673 K, 733K, 773 K, 713 K, 713 K and 733 K of CSLT-1, CSLT-2, CSLT-3, CSLT-4 and CSLT-5, respectively. The conductivity values of SLT are comparable to that of pure Na$_2$Ti$_3$O$_7$[6] but activation energy is comparatively lower (0.64 ev for SLT and 0.73 ev for pure Na$_2$Ti$_3$O$_7$). The decrease in activation energy in high temperature region tells that probably clusters of Li$^-$ and Na$^-$ get broken subjected to high temperature. The mechanism of conduction for SLT can

thus be understood as associated interlayer ionic conduction.

The dilation of interlayer space due to substitution of Cu^{2+} at Ti^{4+} sites has also been reported by Machida et al.[4]Furthermore, the copper(II) ions occupy Ti^{4+} sites as evident from EPR spectra of all copper doped derivatives (*Fig. 2*). Accourdingly, the interlayer space get dilated due to compression of TiO_6 octahedra and make easier conduction. The results of EPR spectra as discussed above further suggest that the distortion of TiO_6 octahedra due to increased substitution of Cu^{2+} at Ti^{4+} sites occur in such a way that the distance between the opposite Ti-Ti chains starts to decrease after CSLT-1. The continuously increasing values of activation energies can thus be understood. It may also be noticed that the much-increased copper concentration in CSLT-5, the interlayer space gets contracted much more than that of SLT. Thus, the activation energy suddenly increases for CSLT-5 in this region.

Accordingly, the associated interlayer ionic conduction for SLT, associated ionic conduction through dilated interlayer space for CSLT-1, CSLT-2, CSLT-3 and CSLT-4 and interlayer ionic conduction through contracted interlayer space for CSLT-5 can thus be understood.

Region III From conductivity curves, it is clear that the region III starts from 673 K, 733 K, 773 K, 713 K, 713 K and 733 K for CSLT-1, CSLT-2, CSLT-3, CSLT-4 and CSLT-5, respectively. The activation energies of this region for SLT and all the copper doped derivatives are greater than those of region II. It seems that Cu^{2+} substitution at Ti^{4+} sites (as reflected well from EPR spectra) loosen off few oxygens, from $Ti_3O_7^{2-}$ groups and then participate in conduction in this region. It seems that oxygens making dipoles with Ti^{4+}/Cu^{2+}, start to break at the lower limit of this region and then loosen off oxygens to participate in conduction. Thus, the conduction mechanism in this region may be understood as associated modified interlayer ionic conduction. The activation energy is comparable for SLT and CSLT-1 which indicates that the loosen oxygens as above are very less in number. As the copper concentration increases for CSLT-2 to CSLT-3 electro-

static self energy of dipoles (Ti-O/Cu-O) increases and breaking of oxygens become difficult to participate in conduction therefore the activation energies are higher in CSLT-2 and CSLT-3.

For further increase of copper concentration in CSLT-4 and CSLT-5 it seems that the electrostatic self-energy of dipoles further decreases, participation of loosen oxygens become easy and the activation energy decreases simultaneously.

Accordingly, the conduction mechanism in this region may be associated modified interlayer ionic conduction in which the loosen oxygens from $Ti_3O_7^{2-}$ groups take part in conduction along with the associated interlayer alkali ions.

CONCLUSIONS

The analysis of EPR spectra shows that the distortions of octahedra occur due to the substitution of Cu^{2+} at Ti^{4+} sites.

The smearing out of the hyperfine structure in the EPR spectrum of the highly copper doped CSLT-5 sample is attributed to excessive exchange interaction.

In the lower temperature region I, the mechanism of conduction can be attributed to interlayer ionic conduction for SLT and electronic hopping (polaron) conduction for all the copper doped derivatives of SLT.

In the mid temperature region II, the mechanism of conduction can be attributed to associated interlayer ionic conduction" for SLT associated ionic conduction through dilated interlayer space for CSLT-1, CSLT-2, CSLT-3 and CSLT-4 while contracted interlayer ionic conduction for CSLT-5 takes place.

The conduction mechanism in higher temperature region III may be proposed as "associated modified interlayer ionic conduction" in which the loosen oxygens from $Ti_3O_7^{2-}$ groups take part in conduction.

These copper doped $Na_{1.7}Li_{0.3}Ti_3O_7$ layered ceramic compounds can be put in the class of mixed ionic-electronic materials.

The layered compound CSLT-1 may be very suitable for intercalation and ion exchange application materials. Ion exchange investigations of CSLT-1

may be proposed for further studies.

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