



AC Conductivity Studies of Lithium Mixed Layered Potassium Tetra Titanates ($K_{2-x}Li_xTi_4O_9$) With EPR and XRD Analysis

**Dharmendra Pal^{1*}, Shahanshah Haider Abdi¹, Ghanshyam Tripathi¹,
Virendra Kumar Maurya², Sageer Ahmad Khan³, Kapil Sachan⁴**

¹Department of Physics, BBD National Institute of Technology and Management,
Lucknow, BBD University Campus, Uttar Pradesh, India

²Department of Physics, BBD National Institute of Technology and Management,
Lucknow, BBD University Campus, Uttar Pradesh, India

³Department of Physics, Singhania University, Rajasthan, India

⁴Department of Mechanical Engineering, C. M. J. University, Shillong, Meghalaya, India

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Abstract: Lithium mixed Potassium Tetra Titanates with 0.1, 0.3 and 0.5 molar percentage of Li_2CO_3 (general formula $K_{2-x}Li_xTi_4O_9$) have prepared by a high temperature solid-state reaction route. The XRD results indicate that Lithium ions enter the unit cell maintaining the layered structure of solid solution. The crystals are monoclinic for $x=0.1, 0.3$ and 0.5 . EPR analysis, high temperature range (373-798K) in frequency range 100 kHz-1MHz ac conductivity measurements were carried out on prepared sample. The Lithium ions are accommodated with the Potassium ions in the interlayer space. The EPR spectra of Lithium mixed Potassium Tetra Titanates confirm the partial reduction of Ti^{4+} ions to Ti^{3+} . Four distinct regions have identified in the $Ln\sigma T$ vs $1000/T$ plots. Various conduction mechanisms, which dependence on concentration, frequency and temperature are reported in this paper.

Keyword: Structure and Characterization, Charge transport, AC Conductivity, Mixed conductivity and conductivity transitions.

INTRODUCTION

A family of alkali metal titanates, represented by the general formula $A_2O_nTiO_2$ or $A_2Ti_nO_{2n+1}$ (A=alkali metal and $2 \leq n \leq 9$) is well known to have characterized layered or tunnel type structures depending upon n values [1-5]. These titanates exhibit diverse potential application associated with their high ion exchange ability. Thus, they are used for the host materials to intermediate organic guest molecules. [6] AC conductivity measurements of $Na_2Ti_3O_7$, $K_2Ti_4O_9$ and their niobium- substituted products have been investigated by Kikkawa et al. [7] $Na_2Ti_3O_7$, $K_2Ti_4O_9$, $K_{2-x}Rb_xTi_4O_9$, and their ($Na_2Ti_3O_7$ and $K_2Ti_4O_9$) iron and manganese doped derivatives have been investigated through electron paramagnetic resonance (EPR) and dc conductivity measurements by our group. [8-16] Very recently, Shripal et al. [17, 18] have further reported the dielectric spectroscopic investigations on pure and manganese doped layered $Na_2Ti_3O_7$, and $K_2Ti_4O_9$ ceramics. The crystal structure of $Na_2Ti_3O_7$ consists of layers of composition $Ti_3O_7^{2-}$, like two dimensional sheet centered at the plate (100) plane. The layers are held together by sodium ions, which exist in two different kinds of crystallographic sites. The $Na_2Ti_3O_7$ crystals are monoclinic with unit cell dimensions $a= 0.9133nm$, $b= 0.3806nm$, $c=0.8566nm$ and $\beta=101.57^\circ$ space group = $P_{21/m}$ [4]. O. V. Yakubovich and V. V. Kireev have studied the refinement of this compound [19]. Machida et al. [20] have reported 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). The layered $Na_2Ti_3O_7$ powders of varying grain sizes have been prepared by solid-state reaction of Na_2CO_3 and TiO_2 with average particle sizes [21]. The zigzag layers of $Na_2Ti_3O_7$ have three dipole moments of 5.0, 5.8 and 6.2D (Debye) [22]. EPR and electrical studies in layered $Na_{1.9}Li_{0.1}Ti_3O_7$ and its copper doped derivatives has been reported in my previous research work [23]. EPR and mixed electronic-ionic conductivity studies of pure and manganese doped Layered Potassium Lithium Tetra Titanates ($K_{1.9}Li_{0.1}Ti_4O_9$) have reported in my previous research work [24]. $K_2Ti_4O_9$ has layered lattice of titanium oxygen octahedral, in which the potassium atom occupies the interlayer regions. [25] It also has monoclinic crystal lattice similar to $Na_2Ti_3O_7$ with unit cell dimensions as $a= 1.8255nm$, $b= 0.3790nm$, $c=1.2017nm$ and $\beta=106.43^\circ$. The a. c. conductivity studies in polycrystalline samples of $Na_2Ti_3O_7$ and $K_2Ti_4O_9$ and their Nb containing product were first reported by Kikkawa et al [26]. The ion exchange reactions involving polycrystalline samples of $Na_2Ti_3O_7$ and $K_2Ti_4O_9$ are quite well known [27, 28]. The crystal structure of $Na_2Ti_3O_7$ and $K_2Ti_4O_9$ do suggest possibility of ionic conduction along the layers and thus application of these materials as ion exchanger [28]. The work of Kikkawa et al [26] has opened the new route to study about the various electrical conduction mechanisms involved in mixed compounds of alkali titanates. In this paper we have reported the EPR and dielectric spectroscopic studies of mixed layered Potassium Tetra Titanates with Lithium (molar percentage $0.0 \leq X \leq 0.5$).

EXPERIMENTAL PROCEDURES

Sample Preparation: The ceramic sample of $K_{2-x}Li_xTi_4O_9$ (with $0.1 \leq X \leq 0.5$) were prepared by grinding mechanically a mixture of K_2CO_3 (99.9% pure AR grade Merck Germany), Li_2CO_3 (99.9% pure AR grade Merck Germany) and TiO_2 powder (99% pure AR grade Merck Germany) to achieve fine powder and heated up to 1100K for 16 hrs. The heated products were cooled to room temperature (RT) and mixed in acetone for grinding up to one hour to achieve fine powder. This fine powder is again heated up to 1100K for 14 hrs and cooled to room temperature (RT) at the rate of 3.0K per minute. This powder was compressed at 15Mpa to yield the pellets. The Palletized samples (10.25mm. in diameter and 1.25mm. in thickness) were wrapped in platinum foils, heated again up to 1073K for 14 hrs and cooled to room temperature (RT) at the rate of 3.0K per minute.

XRD analysis: The crystal structure and phase identification of sintered pellets was carried out by Iso-Debye flex 2002 Richseifert and Co. X-ray diffractometer using Cu-K α radiation generated at 30 kV and 20 mA.

EPR Analysis: The EPR spectra were recorded on a Varian E-line Century Series spectrometer E-109, which operates at X-band frequencies (~9.3 GHz). All the spectra were recorded with a 100 KHz field modulation. The magnetic field was calibrated accurately with a Varian E-500 digital nuclear magnetic resonance gauss meter.

AC Conductivity Measurements: Sintered pellets were polished and flat surface were coated with high purity silver paste and then dried before taking electrical measurements. The pellets were then mounted in the sample holder evacuated up to 10⁻³ mbar for the electrical measurements. The loss tangent (tan δ) and parallel capacitance (C_p) of the palletized samples were directly measured as a function of temperature and frequency by the HP 4194A impedance analyzer. The bulk a. c. conductivity (σ) of the samples were calculated by using expressions-

$$\text{Conductivity} \quad \sigma = G(t/A) \quad (i)$$

Where f is the frequency of a. c. signal, t is the thickness and A is the area of cross-section of the pellet.

RESULTS AND DISCUSSION

XRD Analysis:

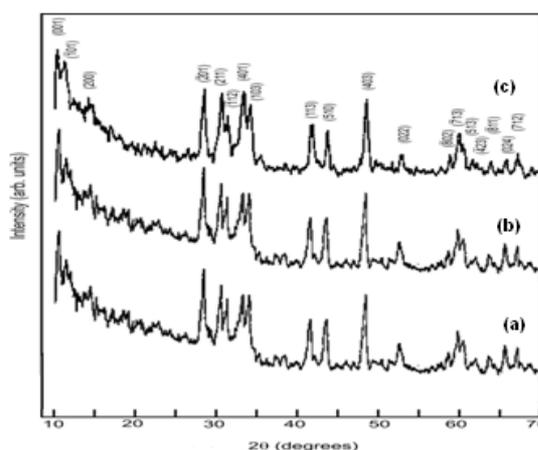


Fig. 1(a) XRD of K_{2-x}Li_xTi₄O₉, with X= 0.1(a), 0.3(b) and 0.5(c)

The phase formation of the sintered K_{2-x}Li_xTi₄O₉ where X= 0.1, 0.3 and 0.5 molar % of Li₂CO₃ ceramics is revealed by X-ray diffraction (XRD), shown in figure 1(a). All the XRD peaks of three different mixed K₂Ti₄O₉ (PT) compounds are similar to results already reported in literature. [23, 29,] It can be explained the mixed Li⁺ [(0.076nm)] ions occupy the alkali K⁺(ionic radii 0.102nm).sites in PLT lattice structure. Ceramic has layered lattice of Titanium octahedral in which the Potassium atoms occupy the interlayer regions. It also has mono clinic crystal lattice similar to K₂Ti₄O₉ with unit cell a=1.8255nm, b=0.3790nm, c=1.2017nm and $\beta=106.43^\circ$.

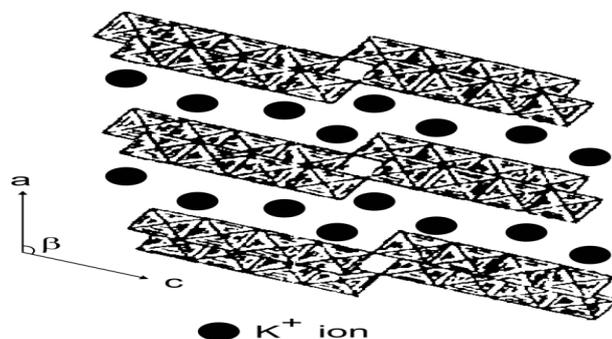


Fig. 1(b) Schematic crystal structure of $K_2Ti_4O_9$

The basic frame work of $K_2Ti_4O_9$ is given by four TiO_6 octahedra sharing edges at one level. These units are joined by similar blocks above and below by additional edge sharing. The zig-zag strings so formed extending in the direction of b-axis, are combined by sharing corners of octahedral. There are two kinds of interlayer spacing in $K_2Ti_4O_9$ due to shift of neighboring layers relative to each other in amount of b-spacing. Potassium ions are accommodated in the widely opened interlayer space. Half of them are located at the level $Y=1/4$ in one interlayer region and the rest are at the level $Y=3/4$ in the other interlayer region. Schematic crystal structure of $K_2Ti_4O_9$ and $K_{2-x}Li_xTi_4O_9$ are shown in fig. 1(b) and 1(c)

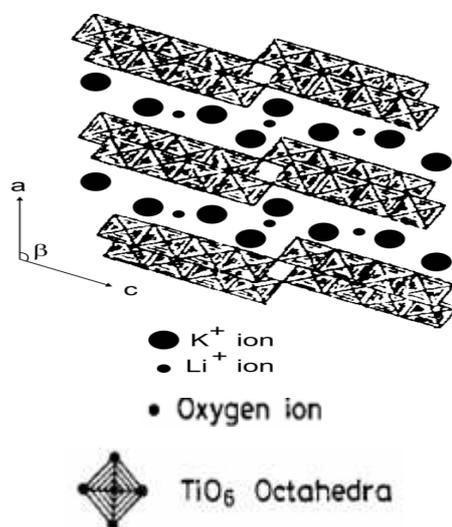


Fig. 1(c) Schematic crystal structure of $K_{2-x}Li_xTi_4O_9$

which shows the presence of small Lithium ions with large Potassium ions in the interlayer space

EPR Spectra analysis:

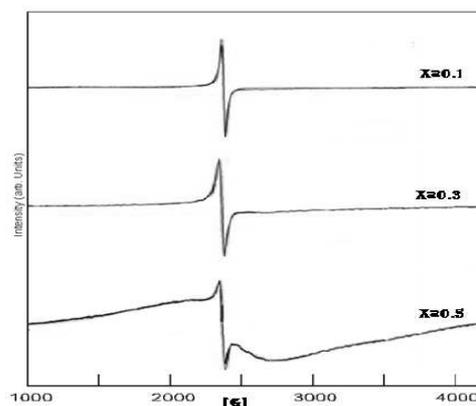


Fig. 2- EPR spectra of Lithium mixed Potassium Tetra Titanates $K_{2-x}Li_xTi_4O_9$
[X= 0.1(a), 0.3 (b) and 0.5(c)]

The EPR spectra shown in fig. 2 of Li substituted $K_2Ti_4O_9$ [$K_{2-X}Li_XTi_4O_9$ with $X=0.2, 0.4$ and 0.6] confirm the presence of Ti^{3+} ions, which result by the reduction of Ti^{4+} ions upon lithium. The g factor is 2.008 and falls in the range characteristic of d^1 ions in the distorted octahedral site. The absence of resolved hyperfine structure expected for the two titanium isotopes Ti (7.75% abundant, $I = 5/2$) and Ti (5.5% abundant, $I=7/2$) with the nuclear magnetic moment suggests that the unpaired spin is shared by several Ti nuclei. The substitution of Lithium ions in the interlayer space does not affect the crystal structure of $K_2Ti_4O_9$. This confirms the presence of small Lithium ions with large Potassium ions in the interlayer space. With the knowledge of about occupancy of Lithium ions in $K_2Ti_4O_9$ lattice, the ionic ac conductivity results can be discussed region wise.

AC conductivity

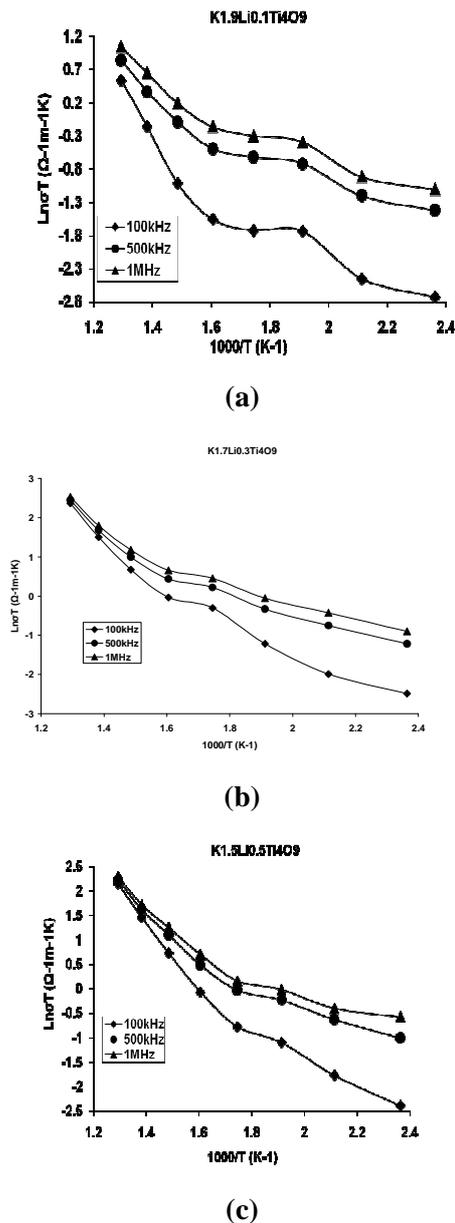


Fig. 7 Temperature dependence ac conductivity plots for (a) PLT-1, (b) PLT-2 & (c) PLT-3

Fig.2 (a), (b), and (c) show the variation of conductivity curves $\text{Ln}\sigma T$ versus $1000/T$. The obtained conductivity curves are divided into three regions. The region wise discussion is given below.

Region-I: The almost frequency dependent and temperature independent region-I exists up to 473K for PLT-1, 473K for PLT-2 and 523K for PLT-3. The nature of a.c.conductivity can be interpreted by proposing that electronic hopping conduction plays major role in this region with lowest activation energy as already proposed.[Pal D. 2005] Many research groups have been interpreting such results by proposing that a.c. conductivity due to electronic hopping conduction increases with the frequency (ω) and is proportional to ω^s , where s is a parameter having value less than unity. Such a frequency dependence, which has been attributed to a wide distribution of relaxation times due to distribution of jump distance and the barrier heights has been observed in a wide variety of low mobility materials. Higher value of a. c. conductivity than d. c. conductivity reported by may be explained by proposing that the exchangeable interlayer ionic and electronic hopping conduction co-exist in this temperature region. The appearance of peak at 473K in conductivity curve for PLT may be due to the presence of Li^+ in the interlayer space results such type of K-Li-Ti configuration, which appreciably reduces the number of loose electrons from $\text{Ti}_3\text{O}_7^{2-}$ groups and subsequently suppresses the electronic hopping (polaron) conduction. However, for copper doped derivatives this interlayer ionic conduction disappears.

Anomalous region: This region exists from 473K to 648K for PLT-1, from 473K to 573K for PLT-2 and from 523K to 623K for PLT-3. The existence of first peak at 523K for PLT-1, PLT-2 and PLT-3 in conductivity curves may be due to micro structural phase change such a peak also appears in dielectric constant versus temperature plots at 523K for all copper doped derivatives. Furthermore, the observed peak at 598K in conductivity curve for PLT-1, PLT-2 and PLT-3 may be due to substitution of Li^+ at K^+ sites. Their substitution would naturally cause the number of loose electrons to increase appreciably to jump through Ti-Ti chains in conduction.

Region II: The almost temperature dependent and less frequency dependent region exist up to 648K for SLT, up to the temperature range of study for PLT-1, from 573K to 698K for PLT-2 and from 623K to 698K for PLT-3. This can be explained by assuming that the interlayer ionic conduction dominates over electronic hopping conduction The slope of conductivity plots is higher then region I so the mechanism of conduction may be attributed due to associated interlayer ionic conduction.

Region III: The almost temperature dependent and frequency independent region III exists from 648K for SLT, from 698K for PLT-2 and PLT-3. The slope of conductivity curves for PLT, PLT-2 and PLT-3 are greater than those of region II. It seems that Li^+ at K^+ sites loosen off few oxygens, from $\text{Ti}_3\text{O}_7^{2-}$ groups and then participate in conduction in this region. It seems that oxygens making dipoles with Li^+ / K^+ 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.

Accordingly, the conduction mechanism in this region may be associated modified interlayer ionic conduction in which the loosen oxygens from $\text{Ti}_4\text{O}_9^{2-}$ groups take part in conduction along with the associated interlayer alkali ions.

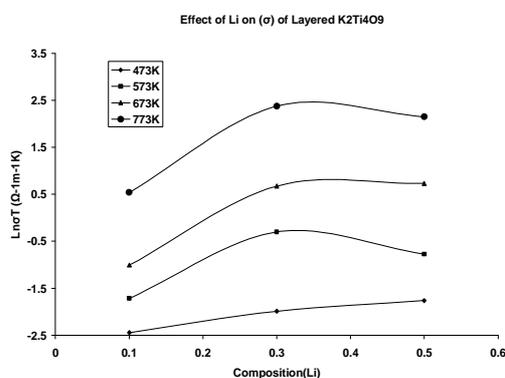


Fig. 8- Effect of Li on ac conductivity ($\text{Ln}\sigma T$ ($\Omega^{-1}\text{m}^{-1}\text{K}$) of Layered $\text{K}_2\text{Ti}_4\text{O}_9$

Fig.3 shows the variation of $\ln\sigma T$ vs. composition (X). The conductivity increases as the lithium concentration increases. The electrical conductivity increases as the lithium concentration increases in all layered titanates, this is due to increase of ionic conduction in interlayer space.

CONCLUSIONS

* The outcomes of the present investigations may be summarized as: For the first time-layered polycrystalline $K_{2-x}Li_xTi_4O_9$ (with X=0.1, 0.3 and 0.5) titanates have been synthesized and characterized through EPR and ac conductivity investigations.

* The EPR spectra of Lithium mixed Sodium Tri Titanates confirm the partial reduction of Ti^{4+} ions to Ti^{3+} .

* AC electrical conductivity studies show that the electronic hopping conduction exists in the entire temperature range of study and diminishes with rise in temperature.

- (a) In region I the proposed conduction mechanism is electronic hopping conduction or polaronic conduction.
- (b) The ionic conduction as 'Hindered interlayer ionic conduction' is proposed in region II.
- (c) The conduction mechanism in region III is associated interlayer ionic conduction with a part of electronic hopping conduction towards the lower temperature end of this region.
- (d) The unassociated interlayer ionic conduction exists in region IV.

* The dilation of zigzag interlayer space of $K_2Ti_4O_9$ (with X=0.1, 0.3 and 0.5) at the inclusion of Lithium ions has been identified in this work. Layered $K_{2-x}Li_xTi_4O_9$ (with X=0.1, 0.3 and 0.5) ceramics can be put in the class of mixed ionic-electronic materials.

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***Correspondence Author: Dr. Dharmendra Pal**, Department of Physics,
BBD National Institute of Technology and Management,
BBD University Campus, Lucknow, Uttar Pradesh, India, 227105